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Verres et céramiques de chalcogénures pour applications en optiques actives

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### Résumé

# Partie I Nouvelle technique de synthèse des verres et vitrocéramiques de chalcogénure

Les verres de chalcogénure ont été étudiés pendant des années pour leur excellente transmission allant de 0,4  $\mu$ m à plus de 20  $\mu$ m suivant leur composition. Ces verres sont stables face à la cristallisation et possèdent de faibles énergies de phonon par rapport aux verres d'oxydes et aux verres de fluorures. Par conséquent, ce sont des matrices idéales pour le dopage des ions de transitions ou de terre-rares. Les verres de chalcogénures présentent un haut indice de réfraction linéaire (2<n<4), ce qui fait d'eux de bons matériaux candidats pour la génération de signal non-linéaire. Aussi, des vitrocéramiques possédant des cristaux non centro-symétriques peuvent réaliser ce but. Cependant, puisque les matériaux de départ sont sensibles à l'oxydation, les verres de chalcogénure doivent être synthétisés dans des tubes de silice scellés sous vide. De manière générale, les vitrocéramiques sont obtenues par un recuit isotherme des verres effectués à  $T_g$ +30°C pendant plusieurs heures. Malheureusement, le procédé de cristallisation contrôlé est difficile à maîtriser du fait de la thermodynamique entre le verre et le cristal.

La mécano-sythèse est récemment apparu comme une nouvelle voie de synthèse de verres et vitrocéramiques à base de chalcogénures. Cette méthode innovante est présentée dans cette étude. Ainsi des vitrocéramiques  $GeS_2+\beta GeS_2$ ,  $Ge_{20}Sb_{12}S_{68}+CdS$  ou encore la composition  $Ge_{15}Ga_{20}S_{65}$ , qui se situe en dehors du domaine de formation des verres ont été synthétisées suivant cette nouvelle technique.

#### 1. Non-linéarité des vitrocéramiques à base de GeS<sub>2</sub>

Dans cette partie, des verres et des vitrocéramiques de  $GeS_2$  ont été synthétisés en utilisant deux procédés différents: la méthode traditionnelle de fusion et trempe et une seconde méthode associant la mécano-synthèse au frittage par Spark Plasma Sintering. Les propriétés de transmission optique, de génération de signal non linéaire de second ordre ainsi que les effets photo-induits et de morphologies ont été étudiées.



Figure 1. Courbes de transmission des échantillons traités et non-traités (photos) (a); photos d'échantillon GS1 (vitrocéramique préparé par le recuit du verre GeS<sub>2</sub> à 490°C pendant 96 h) pris par microscope électronique à balayage (b)

Le procédé de cristallisation habituel consiste à recuire le verre de base au dessus de sa température de transition vitreuse dans un four ventilé. Dans une grande majorité des cas, cela conduit à une cristallisation non-homogène avec des cristaux qui se situent sur la surface du verre, ce qui est le cas de la vitrocéramique GS1 (vitrocéramique préparé par le recuit du verre GeS<sub>2</sub> à 490°C pendant 96 h). Une couche de cristaux non homogène d'environ 3 à 10  $\mu$ m a été générée sur la surface du verre, les cristaux ayant une taille inférieure au micron. Ainsi, une forte dispersion est observée aux courtes longueurs d'onde tandis que les échantillons présentent une transparence nettement améliorée dans le domaine infrarouge (Figure 1 (a)). Ainsi, générer des cristaux de  $\beta$ -GeS<sub>2</sub> de manière homogène dans un verre GeS<sub>2</sub> par la méthode traditionnelle est un processus incontrôlable. Mais en raison d'une transmission suffisament élevée à 0,9  $\mu$ m et 1,8  $\mu$ m, la génération de signal non-linéaire de second ordre peut être mesurée sur la vitrocéramique GS1 (la Figure 2). Comme prévu en raison de l'isotropie du verre, aucun signal non-linéaire n'a été observé sur le verre de base.



Figure 2. Frange de Maker de la vitrocéramique GS1 recuit à 490°C pendant 96 h. Le signal a été comparé avec celui de référence du quartz

Par ailleurs, la génération de phénomènes photoinduits a été observé sur les échantillons de GeS<sub>2</sub> (verre sans recuit) et GS1 (verre GeS<sub>2</sub> recuit à 490°C) en utilisant un laser CO<sub>2</sub> microseconde pulsé et un laser continu vert. Le changement d'absorption est très sensible à la présence ou non de cristallisation dans la matrice du verre GeS<sub>2</sub>. Au cours de l'irradiation par laser vert (532 nm), le phénomène d'effets photo-induits est certainement lié à une transition électronique intra l'énergie de bande interdite, alors que pour le laser IR, le phénomène d'effets photo-induits est lié à l'interaction avec les phonons.

D'autre part, les vitrocéramiques GC1 et GC2 sont synthétisées par mécano-synthèse avec frittage. Les paramètres de synthèse sont affichés dans le Tableau 1.

| Nom | T /°C | Pression<br>/MPa | Durée<br>/min | Diamètre<br>/mm | $\rho$ /g·cm <sup>-3</sup> | Couche | Broyage<br>atmosphère | épaisseur<br>(mm) |
|-----|-------|------------------|---------------|-----------------|----------------------------|--------|-----------------------|-------------------|
| GC1 | 450   | 50               | 10            | 8               | 2,80                       | Та     | Boîte à gant          | 0,57              |
| GC2 | 450   | 50               | 15            | 8               | 2,75                       | Та     | Air                   | 0,57              |

Tableau 1 Paramètres des essais de frittage SPS et caractéristiques des vitrocéramiques

Cette nouvelle technique permet d'incorporer les cristaux de nature souhaitée dans la matrice vitreuse. En comparant les deux échantillons, la vitrocéramique préparée à partir de poudres broyées sous air présente une forte porosité après le frittage (voir la Figure 3 (b)); par contre la vitrocéramique obtenue à partir de poudres broyées dans la boîte à gants présente un taux de densification supérieure à 99% (voir la Figure 3 (a)). Contrairement à la vitrocéramique GC2, la GC1 présente une transmission relativement bonne dans le domaine

infrarouge (voir la Figure 3). Les pertes des signaux optiques par diffusion sont principalement liées à la présence de cristaux d'environ 500 nm mais peuvent aussi être dû au changement d'indice de réfraction entre les grains et joints des grains où l'oxygène peut être accumulé. Néanmoins, il a été prouvé que le broyage en boîte à gants est un moyen efficace pour réduire la pollution de l'eau et de l'oxygène. Par conséquent, la possibilité de synthétiser une vitrocéramique de chalcogénure transparente en utilisant le processus de mécano-synthèse combiné au frittage par Spark Plasma Sintering a été démontrée. Mais, selon la courbe de transmission et les clichés MEB de la vitrocéramique GC1 (la Figure 3), il est encore loin à accomplir pour réaliser des échantillons parfaitement transparents dans l'infrarouge en utilisant cette technique innovante.



Figure 3 Transmission infrarouge des vitrocéramiques préparées par SPS, polies sur les deux faces (les encarts sont les photos des échantillons); Photos MEB des tranches de vitrocéramiques du GC1 (a) et GC2 (b) préparées par SPS

# 2. Préparation et propriété non-linéaire étudiée sur la vitrocéramique $Ge_{20}Sb_{12}S_{68}+CdS$

Le CdS est considéré comme un matériau idéal pour réaliser des phénomènes nonlinéaires de second ordre. En raison de sa structure non centro-symétrique, il présente un haut coefficient non-linéaire de second ordre,  $+44\pm12,6$  pm/V, tandis que celle de  $\beta$ GeS<sub>2</sub> est 7,3 pm/V. Le verre Ge<sub>20</sub>Sb<sub>12</sub>S<sub>68</sub> a été choisi comme matrice hôte pour être dopée par des cristaux de CdS puisque ces deux matériaux présentent des indices de réfraction et des densités relativement proches.

Les cristaux de CdS ont été synthétisé de deux manières différentes, l'une avec réaction statique (cristal CdS-1), l'autre a réagi dans un pH = 9,55 solution sous agitation et précipité avec centrifugation pour éviter une croissance cristalline (cristal CdS-2). Selon les photos

MEB (la Figure 4 (a)), la taille des cristaux CdS-1 n'est pas homogène variant de quelques dizaines de nanomètres à quelques micromètres. Différentes structures sont aussi présentes, les cristaux pouvant former de gros agrégats au cours du processus de réaction. Les cristaux de CdS obtenus par la deuxième méthode présentent une plus faible agrégation (voir la Figure 4 (b)), une morphologie est plus uniforme proche de la centaine de nanomètres, ainsi qu'une simple structure hexagonale. Le cristal CdS-1, sulfuré à 600°C sous flux de H<sub>2</sub>S, a été mélangé avec la poudre de verre par broyage mécanique pendant une heure avec une vitesse de rotation faible pour éviter l'amorphisation du cristal. Cependant, cette technique ne permet pas de diminuer la taille des agrégats de CdS (voir la Figure 4 (c)). Le cristal CdS-2 (avant séchage) a été mélangé avec la poudre amorphe avec un faible ajout de solvant (éthanol) par agitation. On peut observer une absorption des cristaux par la poudre de verre sur la Figure 4 (d).



Figure 4 Photos MEB de la poudre CdS-1 (a) après sulfuration, de la poudre CdS-2 (b), d'un mélange de poudre CdS-1 avec la poudre de verre (c) et un mélange de poudre CdS-2 avec la poudre de verre (d)

Les échantillons CC369, CC370 et CC371 sont frittés par SPS à partir des mélanges de poudre CdS-1 avec la poudre de verre. Les dénominations des échantillons sont listées dans le Tableau 2 ci-dessous. Les matériaux composites obtenus présentent une faible transmission (Figure 5 (a)). Les agrégats de grande dimension et la possible présence de carbone après frittage dans les vitrocéramiques provoquent de fortes diffusions. Malheureusement, ces trois échantillons étaient trop opaques dans le domaine du visible et du proche IR pour réaliser des mesures de non linéarité de second ordre. Les échantillons CD213 et CD214, frittés par Hot-Pressing (voir les conditions sur le Tableau 2) présentent une transmission pouvant atteindre 60% à 10,5 µm. Par contre, leur transmission est relativement faible aux plus courtes longueurs d'ondes, proche de 30% à 6 µm (voir la Figure 5 (b)) tandis qu'aucun signal n'est observé avant 1 µm. Les pertes de transparence peuvent être causées par différents facteurs : porosités formées entre les grains des vitreux et les cristaux CdS, contamination lors du frittage. Par ailleurs, les contaminations inévitables de l'éthanol résiduel et de l'air affectent fortement la transmission causant de grandes bandes d'absorption de CO<sub>2</sub>, O-H, et H<sub>2</sub>O. Alors que la température de frittage de 380°C ne semble pas assez haute pour densifier parfaitement le matériau, le frittage effectué à 385°C permet d'obtenir un échantillon plus dense mais la matrice, instable, forme des cristaux de Cd<sub>4</sub>GeS<sub>6</sub>. Il est donc fortement difficile de contrôler le processus de cristallisation au cours du frittage. La technique SPS permettant de réduire les temps de frittage a donc été envisagé afin de contrôler efficacement le processus de cristallisation.

| Nom   | composition  | Méthode        | т<br>(°С) | Pression<br>(Mpa) | Durée<br>(min) | Liner  | Epaisseur<br>(mm) | Densité<br>(g/cm³) |
|-------|--------------|----------------|-----------|-------------------|----------------|--------|-------------------|--------------------|
| CC369 | G20+10%CdS-1 | SPS            | 330       | 50                | 10             | Та     | 0,81              | 3,23±0,012         |
| CC370 | G20+10%CdS-1 | SPS            | 320       | 50                | 5              | Papyex | 1,16              | 3,19±0,023         |
| CC371 | G20+10%CdS-1 | SPS            | 320       | 50                | 5              | Та     | 1,06              | 3,21±0,022         |
| CB115 | G20          | HP             | 370       | 31                | 240            | BN     | 0,72              | 3,13±0,021         |
| CD213 | G20+10%CdS-2 | HP             | 385       | 31                | 240            | BN     | 0,67              | 3,23±0,004         |
| CD214 | G20+10%CdS-2 | HP             | 380       | 31                | 420            | BN     | 0,56              | 3,24±0,004         |
| CD001 | G20+10%CdS-2 | Melt-quenching | 750       |                   | 300            |        | 0,74              | 3,26±0,008         |

Tableau 2 Paramètres des échantillons synthétisés par SPS et HP



Figure 5. Courbes de transmission des échantillons frittés par SPS (a) et Hot Pressing (b)

Enfin, le dernier moyen étudié pour former une vitrocéramique transparente est de faire fondre le verre de base et les cristaux de CdS à une température relativement basse (750°C) dans un tube de silice scellée sous vide. La transmission de l'échantillon CD001 obtenu en utilisant ce processus atteint 70% (voir la Figure 5 (b)). Cependant, il se forme de manière assez hétérogène des cristaux de Cd<sub>4</sub>GeS<sub>6</sub>, cristaux à propriétés non linéaires moins élevées que celles du CdS.



Figure 6. Franges de Maker obtenues dans les vitrocéramiques (a), Franges de Maker obtenues dans le quartz comparé avec l'échantillon CD001(b)

Une forte absorption à 0,9 µm est observée dans les échantillons CD213, CD214 et CD001 ce qui affecte la détection de génération de signal de seconde harmonique (SH). Sur la Figure 6 (a), le profil des Franges de Maker semble typique de celui d'une génération aléatoire de seconde harmonique (poudres) avec un plateau au centre et une décroissance du

signal aux grands angles qui résulte des coefficients de Fresnel. Malheureusement, l'intensité obtenue est trop faible, ne permettant pas de calculer la susceptibilité. Il sera donc impératif d'améliorer la transmission des échantillons aux basses longueurs d'ondes pour pouvoir optimiser les mesures de non linéarité.

#### 3. Synthèse de verre GeS<sub>2</sub> et vitrocéramique Ge<sub>15</sub>Ga<sub>20</sub>S<sub>65</sub> par mécano-synthèse

La technique combinant la mécano-synthèse au frittage par Spark Plasma Sintering a préalablement démontré la possibilité de synthétiser des verres et vitrocéramiques de chalcogénure. Dans cette partie, un nouveau verre se situant en dehors du domaine vitreux classique a été synthétisé. Les matières premières Ge, Ga, S de rapport stoechiométrique 15:20:65 ont été broyés pendant 80 et 120 heures. Avec l'augmentation de la durée de broyage, une réaction a progressivement eu lieu entre les éléments. Les DRX des phases Ge et S disparaissent progressivement (voir la Figure 7) et on observe une température de transition vitreuse qui augmente par analyse thermique (voir la Figure 8). Cependant, une poudre parfaitement amorphe n'a pas été atteinte en utilisant cette méthode puisque des pics de Ga<sub>2</sub>S<sub>3</sub> cristallins ont été détectés après 120 heures de broyage. Néanmoins, la majorité de la poudre synthétisée présente un caractère amorphe.



Figure 7. Diagramme de RX des poudres broyées selon différentes durées. Ainsi que les fiches PDF card no. 72-2402 S; PDF card no. 65-333 Ge; PDF card no. 84-1441 Ga<sub>2</sub>S<sub>3</sub>



Figure 8. Evolution de la température de transition vitreuse des poudres broyées selon une durée croissante

Certaines de ces poudres ont ensuite été frittés par SPS afin d'obtenir un matériau massif. Connaissant le fait qu'une poudre contenant une partie résiduelle de cristaux avait été obtenue, l'intérêt était ici de synthétiser une nouvelle vitrocéramique. Les paramètres de frittage sont listés dans le Tableau 3.

|      | Tableau 3 Param    | etres de mittage | e des poud | es broye | es pendant | 80 n et 120 | ) n                  |
|------|--------------------|------------------|------------|----------|------------|-------------|----------------------|
| Nom  | Composition        | Température      | Pression   | Durée    | Linor      | Epaisseur   | Densité              |
| NOTT | Composition        | (°C)             | (MPa)      | (min)    | Liner      | (mm)        | (g/cm <sup>3</sup> ) |
| GGS1 | 65S-15Ge-20Ga 80h  | 430              | 50         | no       | papyeux    | 0,68        | 3,164±0,007          |
| GGS2 | 65S-15Ge-20Ga 80h  | 420              | 50         | 5        | Та         | 0,87        | 3,153±0,010          |
| GGS3 | 65S-15Ge-20Ga 80h  | 400              | 50         | 5        | Та         | 0,87        | 3,132±0,014          |
| GGS4 | 65S-15Ge-20Ga 120h | 420              | 50         | 5        | Та         | 1,32        | 3,169±0,014          |
| GGS5 | 65S-15Ge-20Ga 120h | 400              | 50         | 5        | Та         | 1,17        | 3,165±0,016          |
| GGS6 | 65S-15Ge-20Ga 120h | 380              | 50         | 5        | Та         | 1,4         | 3,172±0,007          |
| GGS7 | 65S-15Ge-20Ga 120h | 360              | 50         | 5        | Та         | 1,35        | 3,135±0,007          |

1001

Les échantillons frittés à partir des poudres broyées pendant 80 h présentent des transmissions plus élevées que les poudres broyées pendant 120 h (voir la Figure 9). La faible transmission est liée à la forte densité de cristaux présent dans le matériaux. De nombreuses bandes d'absorption liées aux impuretés de type O-H, H<sub>2</sub>O sont observées. Bien que le résultat puisse être optimisé, ce résultat laisse entrevoir la possibilité de synthétiser de nouvelles vitrocéramiques transparentes impossible à obtenir jusqu'à présent.



Figure 9. Courbes de transmission des échantillons frittés par SPS



Figure 10. Photos MET de l'échantillon GS3

La phase et la taille des cristaux dans l'échantillon GGS3 sont déterminées par microscopie électronique en transmission (voir la Figure 10). L'indexation des cristaux est

affiché sur la Figure 10 (a), elle correspond parfaitement à la phase  $Ga_2S_3$  de la fiche No. 84-1441. La taille des cristaux est proche de 50 nm (voir la Figure 10 (b)).

Pour une telle composition, qui ne peut être synthétisée par la méthode traditionnelle, nous avons démontré la possibilité de synthétiser une poudre majoritairement amorphe après broyage ainsi qu'une vitrocéramique massive contenant une très forte densité de cristaux et maintenant une transparence dans l'infrarouge après frittage de cette poudre.

En utilisant le même moyen, le verre  $GeS_2$  a été fritté à partir des poudres de verre obtenue par mécanosynthèse dans un moule en graphite par SPS. Les poudres présentent la phase amorphe après avoir été broyées pendant 120 heures (voir la Figure 11).



Figure 11. Diffractogramme de RX des poudres GeS2 broyés pendant différentes durées

L'échantillon le plus transparent, GS1, a été fritté à 520°C sous une pression de 50 MPa pendant 30 minutes en utilisant des couches protectrices de Ta des deux côtés pour éviter la pollution du moule graphite. Les paramètres de frittage sont listés dans le Table 4.

|                          | Table               | eau 4 Paramètre   | s de frittage d | es poudres | GeS <sub>2</sub>  |                                 |
|--------------------------|---------------------|-------------------|-----------------|------------|-------------------|---------------------------------|
| Échantillon              | Température<br>(°C) | Pression<br>(MPa) | Durée<br>(min)  | Liner      | Épaisseur<br>(mm) | Densité<br>(g/cm <sup>3</sup> ) |
| GS1                      | 520                 | 50                | 30              | Та         | 1,00              | 2,777±0,008                     |
| GS2                      | 540                 | 50                | 30              | Та         | 1,22              | 2,943±0,006                     |
| GS3                      | 530                 | 50                | 5               | Та         | 1,23              | 2,771±0,012                     |
| Verre GeS <sub>2</sub>   | -                   | -                 | -               | -          | -                 | 2,750±0,006                     |
| Poudre                   | -                   | -                 | -               | -          | -                 | 2,619                           |
| Cristal GeS <sub>2</sub> | -                   | -                 | -               | -          | -                 | 2,94                            |

Même si la transmission est faible aux courtes longueurs d'onde, la transmission maximale atteint jusqu'à 14% à 10  $\mu$ m (voir la Figure 12 (a)). Cette transmission est très faible comparée aux 78% de transmission atteint par la méthode de traditionnelle. Les images MEB (voir la Figure 12 (b)) ont montré que quelques nano-cristaux sont présents dans la matrice vitreuse, même si aucun pic n'est observé sur le diffractogramme de RX (voir la Figure 13).



Figure 12. Courbes de transmission des échantillons GS1-3 (a) et leurs structures observées par microscopie électronique à balayage (b)



Figure 13. Diffractogramme de RX des échantillons GS1, GS2, GS3 en compaison avec le cristal GeS<sub>2</sub> PDF card No. 26-693

Jusqu'à présent, des verres ou des vitrocéramiques de chalcogénure parfaitement transparents n'ont pas été réalisées par la technique combinant la mécanosynthèse avec le frittage SPS. Plusieurs raisons peuvent expliquer les fortes diffusions qui provoquent la perte de transmission: la présence de cristaux, une hypothèse qui devra être étudiée plus profondément est la présence de joints de grains ayant une forte différente d'indice de réfraction avec les grains vitreux ou cristallins. On devine que la contamination de l'air est l'une des raisons principales qui affecte la transmission. Pour de futures expériences, le processus de broyage mécanique devra être réalisé dans une boîte à gants dénuée d'eau et d'air.

# Partie II Matériaux luminescents avec des bandes d'absorptions et d'émissions larges et ajustables

#### 4. Verres et céramiques

L'objectif de ce travail est de développer des matériaux luminescents avec des bandes d'absorptions et d'émissions larges et ajustables. Deux types d'ions actifs ont été considérés: les ions de métaux de transition et les ions de terres rares bivalents en raison des transitions électroniques impliquant des électrons de la couche *d*. Deux types de matériaux hôtes, des verres et des céramiques ont également été testés.

Les ions de métaux de transition possèdent généralement des bandes d'absorption larges et intenses. Il n'est cependant pas toujours facile de contrôler leur valence qui détermine leur propriété de luminescence. Le Fer, le manganèse et le nickel ont été sélectionnés pour cette étude et le verre de base est un verre d'alumino-phosphates bien connu au laboratoire. Les courbes d'absorption de ce verre dopé par les différents ions sont montrées sur la Figure 14. Les bandes d'absorption ont été identifiées et plusieurs valences peuvent être constatées. Aucune luminescence n'a pu être détectée avec ces échantillons.

Avec ces ions de métaux de transition, nous avons conclu qu'il est plus difficile de contrôler la valence de ces ions dans le verre en raison de l'existence d'environnements mixtes. Le verre semble être une matrice peu efficace pour la luminescence des ions de métaux de transition.

En se basant ces constations, l'étude s'est ensuite orientée vers les ions divalents de terres rares, en occurrence les ions Eu<sup>2+</sup> avec cette fois-ci des matrices en céramiques à base de sulfure ou/et de séléniure qui possèdent une faible énergie de phonon. De plus, des travaux antérieurs ont démontré que l'absorption des ions de terres rares est beaucoup plus efficace dans un environnement de sulfure ou de séléniure que dans un environnement de fluorure. Enfin, les ions de terres rares dans un environnement cristallisé montrent une luminescence beaucoup plus efficace que dans une matrice vitreuse. Des céramiques à base d'oxydes et de fluorures ont également été testées pour comparaison. Les principales compositions étudiées sont rassemblées dans le Tableau 5.



Figure 14. Courbes d'absorption du verre 10Ca<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>-10Al<sub>2</sub>O<sub>3</sub>-80NaPO<sub>3</sub> dopé par différents ions des métaux de transition Fe (a), Mn (b) et Ni (c)

| Tableau 5 I | Les céramiques dopées par des ions Eu <sup>2</sup> |
|-------------|--|
| Échantillon | Composition  |
| EZBS1       | 0,667BaS-0,33ZnS-0,003EuCl <sub>3</sub>            |
| EZCS1       | 0,667CaS-0,33ZnS-0,003EuCl <sub>3</sub>            |
| EZCSe2      | 0,9CaS-0,1ZnSe-0,003EuCl <sub>3</sub>              |
| EZSrS1      | 0,667SrS-0,33ZnS-0,003EuCl <sub>3</sub>            |
| EZCO1       | 0,497CaO-0,5ZnO-0,003Eu                            |
| EZCF        | 0,89CaF2-0,1ZnF2-0,01Eu                            |

Des émissions larges et parfois intenses ont été obtenues avec les céramiques étudiées. La largeur à mi-hauteur peut même dépasser 100 nm. Il a également été démontré que la position d'émission des ions Eu<sup>2+</sup> dépend fortement de son environnement chimique, comme le montre la Figure 15.



Figure 15. Émissions des céramiques dopées aux Eu<sup>2+</sup>, mesurées dans les mêmes conditions sauf pour EZCF et EZCO qui émettent faiblement.

Avec les ions Eu<sup>2+</sup> dans différentes matrices à base de sulfure en changeant uniquement le cation, la longueur d'onde du pic d'émission peut déjà être ajustée dans un grand domaine de longueur d'onde de 610 nm à 730 nm, comme le montre la Figure 16. Si on change complètement de matrice, en passant par exemple des oxydes aux sulfures, le pic d'émission peut être déplacé de plus de 300 nm.



Figure 16. Bandes d'émission normalisées des échantillons à base de sulfure (de Ca, Sr ou Ba) dopé aux Eu<sup>2+</sup> (a) et des céramiques d'oxyde, de sulfure et de fluorure de calcium (b).

Il est cependant à souligner que l'intensité d'émissions de différentes céramiques est très différente. Pour le dépôt de couches minces, les deux céramiques, EZSrS (SrS/ZnS :Eu<sup>2+</sup>) et EZCS (CaS/ZnS :Eu<sup>2+</sup>) qui ont une intensité d'émission comparable ont été sélectionnées comme cibles.

# 5. Couches minces à basse énergie de phonon avec des bandes d'émission ultra larges et ajustables

Les deux céramiques, EZSrS (SrS/ZnS :Eu<sup>2+</sup>) et EZCS (CaS/ZnS :Eu<sup>2+</sup>), sélectionnées comme cibles sont montrées sur la Figure 15. Différentes couches minces contenant des ions Eu<sup>2+</sup> ont été déposées avec une ou deux cibles en utilisant la technique de pulvérisation cathodique assistée par magnétron. Avec les paramètres de dépôt utilisées (pression Ar de 0,033 mbar, puissance de 60 W), le vitesse de dépôt avec une est d'environ 2 nm/min, ce qui est assez faible. Toutes les couches minces obtenues sont amorphes comme le montre les diffractions aux rayons X (Figure 17). Un traitement thermique est nécessaire pour cristalliser les couches. Pour la couche SrS15 (SrS/ZnS:Eu<sup>2+</sup>), la cristallisation commence à 300°C et la phase cristallisée est principalement du SrS. Quand la température de recuit augmente, du ZnS peut aussi apparaitre. Le meilleur résultat a été obtenu avec une température de recuit de 500°C. Cette température correspond à la température maximale possible, imposée par l'utilisation des substrats en BK7. Les couches recuites présentent une luminescence intense et large centrée autour de 615 nm avec une FWHM d'environ 80 nm sous excitation à 467 nm. Cette émission est attribuée à la transition des Eu<sup>2+</sup>  $4f^{6}5d^{1} \rightarrow 4f^{7}$  (voir la Figure 18). Le pic d'émission des couches minces est proche de celui de la cible SrS/ZnS:Eu<sup>2+</sup> indiquant un bon transfert de composition de la cible vers le substrat.

On peut noter aussi que les couches minces peuvent également émettre de la lumière sous l'excitation à 430 nm avec des émissions larges entre 400-500 ou 500-700 nm. Elles sont attribuées au ZnS ou plus précisément aux défauts dans le ZnS (voir la Figure 18 (c)). Les émissions fines à 500 nm proviennent vraisemblablement d'un artefact de l'appareil. La couleur des couches minces sous excitation à 430 nm ou à 467 nm est présentée à la Figure 19.

En ce qui concerne la couche mince obtenue avec la cible  $CaS/ZnS:Eu^{2+}$ , une température de recuit à 500°C ne provoque pas une cristallisation visible aux diffractions de rayons X (voir la Figure 17 (b)) et n'améliore pas non plus la luminescence (voir la Figure 20).



Un substrat avec une meilleure résistance thermique doit être utilisé dans le futur pour pouvoir recuire les couches à des températures plus élevées.

Figure 17. Diffractions aux rayons X des couches minces SrS15 et CaS1 avant et après le recuit à différentes températures.



Figure 18. Spectres d'émission des couches SrS15 recuit à 400°C sous excitation à 467 nm (a); et des couches SrS15 recuit à différentes températures sous excitation à 467 nm (b) et à 430 nm (c)



#### Excited at 340 nm

Figure 19. Photos des couches SrS15-(1-5) excités @ 340 nm (a) et excités @ 467 nm (b). La lumière d'excitation est filtrée



Figure 20. Spectres d'émission des couches CaS1 recuit à 500°C sous excitation à 467 nm (a); et à 430 nm (b)

Les couches minces co-déposées avec différents ratios de Sr/Ca, ont été préparées en appliquant de différentes puissances sur chaque cible. Les couches minces obtenues présentent une excellente uniformité. Avec la couche mince CSSr2 ayant un rapport Sr/Ca élevé (estimé à 85%), une phase cristalline SrS est observée après un recuit à 500°C (Figure 21). Pour l'autre couche CSSr5 avec un rapport Sr/Ca plus faible (estimée à 79%), même si le recuit ne change pas significativement la diffraction aux rayons X de la couche (Figure 21), sa luminescence est cependant très nettement améliorée, comme le montre la Figure 22.

Toutes les couches recuites montrent une émission relativement intense et large avec une FWHM typique de 80 nm. La longueur d'onde d'émission maximale des couches minces dépend directement du rapport Sr/Ca. Les deux couches minces co-déposées ont un pic d'émission relativement proche de celui de la cible contenant du SrS, et par conséquent relativement éloigné de celui de la cible contenant du CaS. Deux raisons pourraient probablement expliquer cette observation: la première est que, dans les deux couches, les atomes de Sr sont toujours nettement majoritaires par rapport aux Ca et la deuxième raison est que la phase cristallisée est celle du SrS.



Figure 21. Diffraction aux rayons X des couches CSSr2 et CSSr5 avant et après le recuit



Figure 22. Spectres d'émission des couches CSSr2, CSSr5 avec ou sans recuit à 500°C sous excitation à 467 nm.

En conclusion, il est possible d'ajuster la longueur d'onde du pic d'émission en modifiant le rapport Sr/Ca dans les couches minces. Il semble que la luminescence des couches codéposées provient essentiellement des ions Eu<sup>2+</sup> dans l'environnement de SrS, plus au moins influencé par les ions calcium. Le FWHM de la bande d'émission ne change pas significativement. Pour les travaux futurs, il sera important de préparer des couches minces ayant des cristaux de SrS et de CaS si un élargissement de la bande d'émission est souhaité.

CONTENTS

| General Introduction | 1   | 1 - |
|----------------------|-----|-----|
|                      | , . |     |

### Chapter I: Non linear glass-ceramics based on GeS<sub>2</sub>

| 1. Introduction  | 5 -  |
|--|------|
| 2. Glass-ceramic   | 6 -  |
| 2.1 Manufacturing of glass-ceramics                                      | 6 -  |
| 2.2 Transparent glass-ceramics   | 9 -  |
| 3. Non-linear optics and second harmonic generation                      | 10 - |
| 3.1 Introduction of non-linear optics                                    | 10 - |
| 3.2 The second harmonic generation                                       | 11 - |
| 3.3 Second order non-linear chalcogenide glass-ceramics                  | 12 - |
| 3.4 The measurement of second order non-linear                           | 12 - |
| 4. Introduction on sintering   | 13 - |
| 4.1 Sintering mechanism  | 13 - |
| 4.2 Sintering factors  | 14 - |
| 4.3 Sintering methodSpark Plasma Sintering                               | 15 - |
| 5. Synthesis of the GeS <sub>2</sub> glass-ceramic                       | 16 - |
| 5.1 Synthesis by thermal treatment method                                | 16 - |
| 5.2 Synthesis of glasses or glass-ceramics by powder sintering method    | 19 - |
| 5.2.1 Synthesis of $\beta$ -GeS <sub>2</sub> crystals                    | 21 - |
| 5.2.2 Mixing of glass powder with $\beta$ -GeS <sub>2</sub> crystals     | 23 - |
| 5.2.3 SPS process  | 24 - |
| 6. Properties studied on the pastilles made by melt-quenching and by SPS | 25 - |
| 6.1 Optical transmission   | 25 - |
| 6.2 Morphology   | 27 - |

| 6.3 Second order nonlinearity | 29 -   |
|-------------------------------|--------|
| 6.4 Photo-induced phenomenon  | - 30 - |
| 7. Conclusion                 | - 35 - |
| 8. References                 | 37 -   |

## <u>Chapter II: Glass-ceramics Ge-Sb-S+CdS preparation and non linear</u> properties

| 1. Introduction   | 41 - |
|---|------|
| 2. The choice of the base glass   | 42 - |
| 3. Synthesis of the powders for sintering   | 46 - |
| 3.1 Static way to prepare CdS-glass mixture   | 47 - |
| 3.2 Stirring way to prepare CdS-glass mixture   | 51 - |
| 4. Sintering of Ge <sub>20</sub> Sb <sub>12</sub> S <sub>68</sub> -CdS glass-ceramics by SPS and HP | 54 - |
| 4.1Properties of the samples sintered by SPS  | 54 - |
| 4.1.1 Optical transmission  | 54 - |
| 4.1.2 X-ray diffraction   | 55 - |
| 4.1.3 Scanning Electron Microscope  | 56 - |
| 4.2 Properties of the samples sintered by Hot Pressing  | 58 - |
| 4.2.1 Introduction of Hot Pressing (HP)   | 58 - |
| 4.2.2 Optimal HP temperature  | 59 - |
| 4.2.3 Optical transmission  | 62 - |
| 4.2.4 X-ray diffraction   | 63 - |
| 4.2.5 Scanning Electron Microscope  | 64 - |
| 4.2.6 Non-linear analysis   | 67 - |
| 5. Conclusion   | 69 - |

| 6. Reference 71 | l |  | - |  |
|-----------------|---|--|---|--|
|-----------------|---|--|---|--|

## <u>Chapter III: Mechanical milling for synthesizing chalcogenide glass</u> <u>GeS<sub>2</sub> and glass-ceramic Ge<sub>15</sub>-Ga<sub>20</sub>-S<sub>65</sub></u>

| 1. Introduction   | 74 - |
|---|------|
| 2. Mechanical synthesis   | 75 - |
| 2.1 Background  | 75 - |
| 2.2 Technical considerations  | 76 - |
| 3. Synthesis of the glass-ceramic Ge <sub>15</sub> -Ga <sub>20</sub> -S <sub>65</sub> | 79 - |
| 3.1 Synthesis by conventional melt-quenching technique                                | 81 - |
| 3.2 Synthesis by mechanical method  | 83 - |
| 3.2.1 Experimental preparation  | 83 - |
| 3.2.2 Color variation of the powders  | 83 - |
| 3.2.3 X-ray diffraction of the powders  | 84 - |
| 3.2.4 Thermal analysis of the powders   | 85 - |
| 3.3 Ge <sub>15</sub> Ga <sub>20</sub> S <sub>65</sub> glass-ceramics made by SPS      | 87 - |
| 3.3.1 X-ray diffraction   | 87 - |
| 3.3.2 Optical properties  | 89 - |
| 3.3.3 Scanning Electronic Microscope  | 91 - |
| 3.3.4 Transmission Electron Microscope  | 93 - |
| 4. Synthesis of the GeS <sub>2</sub> glass  | 95 - |
| 4.1 Experimental preparation  | 95 - |
| 4.2 The color variation of the powders  | 95 - |
| 4.3 X-ray diffraction of the powders  | 96 - |
| 4.4 Thermal analysis of the powders   | 97 - |

| 4.5 Granulometry analysis of the powders              | 99 -  |
|---|-------|
| 4.6 Synthesis of bulk GeS <sub>2</sub> glasses by SPS | 101 - |
| 4.6.1 X-ray diffraction                               | 101 - |
| 4.6.2 Optical properties                              | 102 - |
| 4.6.3 Scanning Electronic Microscopy analysis         | 103 - |
| 5. Conclusion   | 105 - |
| 6. Reference  | 107 - |

## <u>Chapter IV: Glasses and ceramics with ultra-broad absorption and</u> <u>emission bands for efficient frequency conversion</u>

| 1. Introduction  | 110 -          |
|--|----------------|
| 2. The state-of-the-art of luminescent materials with broadband absorption and   | emission-111 - |
| 2.1 Generation of white light for lighting   | 111 -          |
| 2.2 Improvement of photovoltaic solar cell's efficiency  | 113 -          |
| 2.3 Bandwidth increase for telecommunication   | 116 -          |
| 3. Theory of luminescence  | 117 -          |
| 3.1 Basic consideration  | 117 -          |
| 3.2 Cases of broad emission  | 118 -          |
| 3.2.1 $d \rightarrow d$ emission   | 118 -          |
| 3.2.2 $d \rightarrow f$ emission   | 119 -          |
| $3.2.3 \ s \rightarrow p \text{ emission}$   | 119 -          |
| 4. Transition metal ions-doped phosphate glasses   | 120 -          |
| 4.1 Fe ions doped 10Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> -10Al <sub>2</sub> O <sub>3</sub> -80NaPO <sub>3</sub> glass           | 121 -          |
| 4.2 Mn ions doped phosphate glass 10Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> -10Al <sub>2</sub> O <sub>3</sub> -80NaPO <sub>3</sub> | - 123 -        |
| 4.3 Ni ions doped phosphate glass 10Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> -10Al <sub>2</sub> O <sub>3</sub> -80NaPO <sub>3</sub> | 124 -          |

| 5. $Eu^{2+}$ doped ceramics based on MX (M = Ba, Sr, Ca; X = S, Se, F, O)             | 126 - |
|---|-------|
| 5.1 BaS/ZnS: Eu <sup>2+</sup>   | 126 - |
| 5.2 CaS/ZnS(Se):Eu <sup>2+</sup>  | 129 - |
| 5.2.1 CaS/ZnS: Eu <sup>2+</sup>   | 129 - |
| 5.2.2 CaS/ZnS(Se): $Eu^{2+}$  | 131 - |
| 5.3 SrS/ZnS(Se):Eu <sup>2+</sup>  | 137 - |
| 5.4 CaO/ZnO:Eu <sup>2+</sup> and CaF <sub>2</sub> /ZnF <sub>2</sub> :Eu <sup>2+</sup> | 139 - |
| 5.5 Comparison of the emission band of $Eu^{2+}$ in different chemical environments   | 141 - |
| 6. Conclusion   | 144 - |
| 7. Reference  | 145 - |

## <u>Chapter V Low phonon-energy thin films with tunable and ultra wide</u> <u>emission bands</u>

| 1. Introduction  | - 152 - |
|--|---------|
| 2. The thin film deposition                                    | - 153 - |
| 2.1 Basic description of magnetron sputtering                  | - 153 - |
| 2.2 Preparation of the targets                                 | - 154 - |
| 2.3 Preparation of the substrates                              | 155 -   |
| 2.4 Thin film deposition                                       | 155 -   |
| 2.4.1 Description of the equipment                             | 155 -   |
| 2.4.2 Determination of deposition parameters                   | 157 -   |
| 2.4.3 Thin film deposition process                             | 157 -   |
| 2.5 Determination of the film's thickness and refractive index | 159 -   |
| 3. Characterization of the thin films                          | 162 -   |
| 3.1 Presentation of the films                                  | 162 -   |

| 3.2 X-ray diffraction of the thin films               | 162 - |
|---|-------|
| 3.3 Optical properties of the thin films              | 163 - |
| 4. Thermal treatment of the thin films                | 165 - |
| 4.1 Single target-deposited thin films                | 165 - |
| 4.1.1 Description of the set-up for thermal treatment | 166 - |
| 4.1.2 X-ray diffraction                               | 167 - |
| 4.1.3 Luminescence measurement of the thin films      | 168 - |
| 4.2 Co-sputtered thin films                           | 172 - |
| 4.2.1 Transmission measurement                        | 172 - |
| 4.2.2 X-ray diffraction analysis                      | 174 - |
| 4.2.3 Luminescence measurement                        | 176 - |
| 5. Conclusion   | 181 - |
| 6. Reference  | 183 - |
| General Conclusion                                    | 185 - |

**General Introduction**
Light source has always been an important issue for humanity. In modern society, frequency conversion is a frequently used technology for generating new light sources. This conversion can be realized through frequency doubling by using materials with high optical non-linearity or by means of photoluminescence.

Second-harmonic generation (SHG) is a nonlinear optical process. When a light source with a frequency  $\omega$  is injected into a nonlinear material, a light with frequency  $2\omega$  can be obtained after the interaction between the photons and the nonlinear material. In this process, a light with higher energy is obtained. SHG was firstly discovered in quartz sample by Peter Franken et al at the University of Michigan, in 1961. This process is reserved to materials with non centro-symmetric structure. Glasses however are macroscopically isotropic and consequently non second-order nonlinear susceptibility  $\chi^{(2)}$  can be expected. In 1986, Österberg and Margulis have detected the frequency doubling in Ge and P doped optical fiber.

Because of the inherent advantage associated with glasses (easy fabrication and shaping), SHG has also been widely studied in glasses even if this family of materials does not show any intrinsic 2<sup>nd</sup> order non linearity. Chalcogenide glasses having high linear and non linear refractive index are particularly interesting for this application. To destroy the intrinsic isotropy associated with glass, external excitations such as thermal/electrical poling, optical poling and electron beam irradiation are needed. In many cases, the induced  $\chi^{(2)}$  in glass is not stable and decreases with time. One way to create durable 2<sup>nd</sup> order non linearity in glass is to generate non centro-symmetric crystals inside the glasses, leading to a composite material, the glass ceramic. Since a decade, many works have been published on chalcogenide glass-ceramics. All these glass-ceramics are made by thermal treatment of glass samples at a temperature above glass transition temperature ( $T_g$ ) during a certain time to induce nucleation and crystal growth.

By definition, therefore, glass-ceramics are composite materials produced through controlled crystallization of the base glass. Glass-ceramics have an amorphous phase with one or more crystalline phases. In most cases, glass-ceramics contain 30% to 90% of crystalline phases homogeneously dispersed in the amorphous phase. However, for some thermally very "stable" or very unstable glasses, it is difficult to obtain such glass-ceramics. The crystallization process can hardly be controlled. Crystals might be formed only on the surface or close to the defects where less energy is needed for the crystallization. The traditional

thermal annealing technique is not efficient for obtaining this kind of glass-ceramics. New technique is necessary in this case.

Because of the high vapor pressure and the risk of reaction with oxygen during the melting process, chalcogenide glasses are generally synthesized in a vacuum-pumped silica tube and heated at a high temperature for several hours to allow all the raw materials to react. The silica tube which is not reusable is one of the important parts in the production cost of chalcogenide glasses. In case of thermally unstable glasses, only small samples can be produced because of the low quenching rate crossing the silica tube. This melt-quenching method can strongly affect the chalcogenide glasses' size and the glass forming region. So, there is a strong motivation to develop new fabrication technique for chalcogenide glasses.

Photoluminescence is a process that a matter absorbs excitation energy (photon) and then emits a radiation. Luminescent material has been developed mostly for display and lighting.

General lighting based on LEDs is a hot research topic during the last decade. For this application, the emission of white color is required. The invention of blue emitting LED received a huge success. White light was obtained with the combination of GaN-based LED, peaking at about 465 nm, and the  $Y_3Al_5O_{12}$ : Ce<sup>3+</sup> phosphor, emitting widely between 500-700 nm. Even it showed high efficiency and good light-distribution character, the "white" light was bluish as lacking of red color. For being comparable with day light, a material with a broad and intense luminescence covering the whole visible wavelength range is desirable.

Energy crisis is one of the biggest issues for humanity. Efficient use of solar energy can completely meet the human needs. The most matured and the most efficient technology today is the photovoltaic (PV) solar cells with high growth over a decade, even taking the recent slowdown into account. The solar cell efficiency is limited to 30% because of the mismatch between the solar spectrum and the response of the solar cells. Many solutions are proposed to correct this mismatch. The most efficient one is the use of multi-junction cells. Generally, it contains 2-5 junctions. But this technique is very complicated and expensive. Meanwhile, other approach has been proposed, for example by modifying the solar spectrum. Rare earth ions-doped luminescent materials using  $Pr^{3+}-Yb^{3+}$ ,  $Er^{3+}-Yb^{3+}$ ,  $Ho^{3+}-Yb^{3+}$ ,  $Tm^{3+}-Yb^{3+}$  and  $Nd^{3+}-Yb^{3+}$  ions have been studied for converting the solar light as much as possible to the light around 1 µm where the silicon based solar cell is highly efficient. However, the

absorption and emission of rare earth ions are generally narrow and weak due to the f-f transitions and energy transfer efficiency between the  $RE^{3+}-Yb^{3+}$  is usually low. Materials with wide and strong absorption as well as intense luminescence are the key for this application.

Wavelength division multiplexing (WDM) is an efficient and widely used technology to increase the data transmission capacity of optical fiber network. Wideband optical amplifier is a key component in this technology. In nowadays' telecommunication industry, the most successful and widely used amplifier is the erbium doped fiber amplifiers (EDFAs) operating around 1550 nm. Due to the 4f-4f transition of  $\text{Er}^{3+}$ , the working bandwidth is narrow. Optical amplifier with larger bandwidth will be indispensable to meet the increasing demand of data transmission.

All the applications mentioned above require materials with broad and efficient emission bands. Generally, transition metal ions and divalent rare earth ions present large and strong absorption bands. A well-know example is the  $Eu^{2+}$  with large and adjustable absorption and emission bands, depending on its chemical environment. This divalent rare earth ion will be particularly studied in this work.

The selection of the host is also very important for efficient emission. Glasses have the advantages of easy fabrication, large size as well as easy shaping. Phosphate glasses doped with luminescent ions have been studied since a long time as they have many interesting properties: low chromatic dispersion, high transparency for ultraviolet light, high rare earth ions and transition metal ions doping concentration as well as large emission and absorption cross section. Crystals are generally a more efficient host for active ions and they are mainly used in form of single crystals. Sulfide can be a good host mainly for two reasons in addition to its low phonon energy. Firstly, previous studies have demonstrated that the absorption of rare earth ions is much more efficient in sulfide environment than in fluoride environment for example. Secondly, the feasibility of sulfide based transparent glass-ceramics has been recently demonstrated with efficient luminescence when doped with rare earth ions.

The first objective of this work is to develop a new technique to synthesis chalcogenide glasses and glass-ceramics with high non linearity, which cannot be synthesized by using classic melt-quenching technique.

The first chapter is devoted to the synthesis of  $GeS_2$  glasses and glass-ceramics by using the technique associating mechanical milling and spark plasma sintering. The densification of mechanically grinded powders and the controlled crystallization will be particularly studied with regards to the non linear properties.

The second chapter deals with the preparation of chalcogenide glasses containing a well-known and highly non linear compound which is CdS.

The third chapter will report on the preparation of a glass with strong tendency to crystallization by using the mechanical milling technique.

The second objective of this work is to develop materials with broad and tunable absorption and emission bands.

In chapter four, photo-luminescence studies will be carried out on transition metals ions such as Mn, Fe and Ni in phosphate glasses, and divalent rare earth ion  $Eu^{2+}$  in sulfide ceramics.

The objective of the final chapter is to create a material with diffident chemical environment for  $Eu^{2+}$  ions in order to obtain ultra wide and tunable absorption and emission bands. Magnetron assisted co-sputtering technique will be used for obtaining thin films with modifiable composition profile.

Chapter I: Non linear glass-ceramics based on GeS<sub>2</sub>

| 1. Introduction   | 5 -  |
|---|------|
| 2. Glass-ceramic  | 6 -  |
| 2.1 How to make glass-ceramics  | 6 -  |
| 2.2 Transparent glass-ceramics  | 9 -  |
| 3. Non-linear optics and second harmonic generation                   | 10 - |
| 3.1 Introduction of non-linear optics                                 | 10 - |
| 3.2 The second harmonic generation                                    | 11 - |
| 3.3 Second order non-linear chalcogenide glass-ceramics               | 12 - |
| 3.4 The measurement of second order non-linear                        | 12 - |
| 4. Sintering  | 13 - |
| 4.1 Sintering mechanism   | 13 - |
| 4.2 Sintering factor  | 14 - |
| 4.3 Sintering methodSpark Plasma Sintering                            | 15 - |
| 5. Synthesis of the GeS <sub>2</sub> glass-ceramic                    | 16 - |
| 5.1 Synthesis by thermal treatment method                             | 16 - |
| 5.2 Synthesis of glasses or glass-ceramics by powder sintering method | 19 - |
| 5.2.1 Synthesis of $\beta$ -GeS <sub>2</sub> crystals                 | 21 - |
| 5.2.2 Mixing of glass powder with $\beta$ -GeS <sub>2</sub> crystals  | 23 - |
| 5.2.3 SPS process   | 24 - |
| 6. Properties studied on the pastilles made by SPS                    | 25 - |
| 6.1 Optical transmission  | 25 - |
| 6.2 Morphology  | 27 - |
| 6.3 Second order nonlinearity   | 29 - |
| 6.4 Photo-induced phenomenon  | 30 - |
| 7. Conclusion   | 35 - |
| 8. Reference  | 37 - |

# **1. Introduction**

Last decades, a strong interest has been dedicated in the development of chalcogenide glasses because of their wide transparency in the infrared (IR) range covering the 3-5  $\mu$ m and 8-12  $\mu$ m atmospheric windows. They can both be used for passive (IR lenses) and for active (non-linear phenomenon, luminescence...) optical applications [1, 2]. These materials are widely used as potential candidates for infrared optics, photonic devices, all-optical switching, etc... [2-5].

Second-harmonic generation (SHG) can be easily produced in chalcogenide glasses as their macroscopic inversion symmetry can be easily destroyed by external excitation. This external excitation can be produced by thermal/electrical poling, optical poling [6] and electron beam irradiation. However, the induced  $\chi^{(2)}$  is not stable and decreases with time. Another way which consists in the introduction of non centro-symetric crystals presenting non-linear phenomenon was found [1, 7]. This kind of glass-ceramic shows a permanent SHG, becoming an attractive route to make chalcogenide glass-ceramics for optical converter applications in the mid-IR region. Since a decade, many works have been published on chalcogenide glass-ceramics [8, 9]. These glass-ceramics are all made by heat treatment of glass samples at a temperature above glass transition temperature ( $T_g$ ) during a certain time to induce nucleation and growth of crystals [1, 9-11].

In this chapter, GeS<sub>2</sub> has been chosen as the base glass for studying non linear properties because of its large transparency window, from 0.45  $\mu$ m to 11  $\mu$ m. Moreover, it is known that  $\beta$ -GeS<sub>2</sub> crystals which presents evident second order non-linear phenomenon can be generated in a chalcogenide glassy matrix [1, 12]. Because of the close composition between glass and crystals, the difference of refractive index is small, that should strongly reduce the scatterings induced by the crystalline phase [13]. In this work, glass-ceramics were firstly synthesized by annealing glassy matrix in a furnace just above  $T_g$ , leading to heterogeneous crystallization. Considering the results of preliminary experiments, we modified the innovative way of synthesis combing mechanical milling and Spark Plasma Sintering (SPS) technique recently elaborated in our lab [14].

Consequently, in order to synthesize  $GeS_2$  glass-ceramics by mechanical milling and SPS,  $GeS_2$  glass and  $\beta$ -GeS<sub>2</sub> crystals were separately fabricated.  $\beta$ -GeS<sub>2</sub> crystals were homemade by heat treatment and then mechanical milling was used to reach  $\beta$ -GeS<sub>2</sub> crystals with size of hundreds of nanometer. Crystalline powder and glass were thoroughly mixed in a planetary grinder in order to obtain a homogenous powder before being densified into glassceramic by spark plasma sintering for a few minutes. In fact, SPS has already demonstrated its ability to form bulk chalcogenide glasses from powders [14-16].

Besides, this chapter also presents the photoinduced phenomenon on  $\text{GeS}_2$  glass-ceramic. It evaluates the magnitude of the photoinduced absorbance and refractive index variations induced by two different wavelengths at 532 nm and 10.6  $\mu$ m. This study should give additional information about the mechanisms responsible for the observed phenomenon as well as concerning the possible applications of these photo-induced effects in optically operated delay lines, triggers, sensors etc.

### 2. Glass-ceramic

Glass-ceramics are composite materials composed of glass and crystals. The percentage of crystals within the glassy matrix can range from several % to more than 90% depending on the targeted applications. Their size can vary from tens of nanometer to several micrometers. Glass-ceramics are made of an amorphous phase and one or more crystalline phases and are produced by controlled crystallization process during annealing treatment. They present the main interest to combine simultaneously the properties of crystals and glasses. In fact, glass-ceramics can present good mechanical properties (high strength, toughness), high temperature stability, high chemical durability, low thermal expansion, and can be easily shaped.

### 2.1 Manufacturing of glass-ceramics

Usually, the preparation of glass-ceramics includes two steps: the formation of nuclei in the glassy matrix, and the growth of crystals. For successfully preparing glass-ceramic, it is important to ensure the formation of a large number of nuclei homogeneously dispersed throughout the bulk glass and their growth at a second step.

Three types of nucleation may occur in bulk glasses: homogeneous nucleation, heterogeneous nucleation, and photo-nucleation [17]. Homogeneous nucleation defined as the nucleation occurs throughout the matrix without any preferential sites for nucleus formation. It requires that the matrix phase is very homogeneous, without any defects, neither on chemically nor on structurally. But in reality, there is barely such perfect phase. The nucleus

of a new phase formed on the surface of an already existing phase boundary is termed heterogeneous nucleation. In bulk crystallization of glass-ceramic materials, it demands that the nucleation sites be homogeneously distributed throughout the whole matrix. By photo-nucleation, nuclei are formed by radiation. The glasses with the ions Au, Ag or Cu together with sensitizers Ce<sup>3+</sup>, Sn<sup>4+</sup> dispersed uniformly may be irradiated at a certain wavelength with subsequent thermal treatment, leading to separation of metal particles distributed throughout the glassy matrix, which can be utilized in the heterogeneous nucleation of a further principal crystalline phase with conversion of the glass into a glass ceramic material.

After the formation of nuclei in the glassy matrix, crystallization proceeds by growth of the new phase. Usually the growth process proceeds at a higher temperature, but with some glass composition, the temperature to form nuclei and to grow the crystal can be approximately the same. It depends strongly on the temperature dependence curve of nucleation rate and that of crystal growth rate. Fig.1.1 presents the relation between nucleation rate, crystal growth rate, crystal number per volume, particles radius against the change of temperature [18]. At lower temperature,  $T_N$ , the nuclei formed in large quantities. The crystal number per volume increases rapidly at this temperature. For those glasses that are very stable, no intersection between the crystal growth rate curve and the nucleation rate curve, their crystals growth needs much more energy, at much higher temperature,  $T_G$ . Two step thermal treatment is suitable for these stable glasses.



Fig.1.1 Temperature dependence curves of nucleation rate (n(T)), crystal growth rate (g(T)), crystal number per volume (N), particles radius (R), transition temperature  $(T_g)$ , melting temperature  $(T_m)$ ; two step thermal treatment [18]



Fig.1.2 One step heat treatment of nucleation and crystal growth [18]

Fig.1.2 presents the one step heat treatment for a system showing an overlap of nucleation rate and crystal growth rate curves [18]. For those glassy systems that are very sensitive to the temperature and composition, the crystallization and crystal growth can be realized at one temperature,  $T_{NG}$ . To obtain the nucleation rate and crystal growth curves is important to control the process of crystallization of glasses. Glasses will be treated at a suitable temperature which depends on the curve to obtain an expected glass-ceramic.

The introductions of nucleus by thermal treatment, as described above, are suitable for glasses which have somehow tendency to be crystallized. The tendency of crystallization depends on the composition of the glass. For some compositions, the rate of homogeneous nucleation is low or zero at any temperature. The glass system would be too stable to be crystallized. Even heated above the glass transition temperature, crystallization process can only be initiated on the surface of the sample through heterogeneous nucleation. The growth of the surface crystals into the bulk leads to coarse grains which deteriorate the properties of the glass ceramics. On the opposite extreme, for some compositions the overlap of nucleation and crystallization curves is so large that the nucleation process cannot be deliberately controlled, that means nucleation and crystal growth occur simultaneously during the quenching of the melt. This kind of glasses is not available to be formed or should be formed with a higher cooling rate of the melt, such as cooled in ice-water or nitrogen. Conclusively, the feasibility of thermal treatment for glass ceramics is quite limited by the composition of the glass system.

Besides the heat treatment, the nuclei can also be introduced within the glassy matrix by focusing a laser beam inside the glassy matrix without inducing any cracks. With a following heat treatment, transparent glass ceramics can be obtained. Controlled patterns like dots and lines can be made, which can be used as laser waveguides, grating or wavelength conversion devices. For example, crystals  $Ba_2TiSi_2O_8$  were obtained within the system  $BaO-TiO_2-SiO_2$ , doped by  $Dy_2O_3$  [19-21].

### 2.2 Transparent glass-ceramics

Transparent glass-ceramic is a material containing homogeneously dispersed nanoparticles. Currently, the commercial transparent glass-ceramic has excellent thermal properties, especially low coefficient of expansion, high thermal stability, and high thermal shock ability. It is used in the cooking plate, kitchenware, glass chimneys, oven, and fire doors... [22].

The transparency of glass-ceramics is significantly associated with the scattering processes. To describe the scattering processes, the glass-ceramics are divided into two groups [13, 23, 24]. In the first group, the crystals are independent and well separated. The scattering obeys the Rayleigh–Gans model. The coefficient of light extinction can be described as follow

$$\alpha \approx \frac{2}{3} NV \kappa^4 R^3 (n\Delta n)^2 \tag{2-1}$$

where N is the quantity of the crystals, V is the volume of the crystals, R is the radius of the crystals,  $\kappa = 2\pi/\lambda$  ( $\lambda$  is wavelength), n is the refractive index of the glassy phase,  $\Delta n$  is the refractive index difference between the crystals and glass.

In the second group, the distance between the crystals *L* is comparable with the crystal sized *R*, where  $R < L \le 6R$ . Another scattering model was proposed by Hopper:

$$\alpha \approx \frac{2}{3} \times 10^{-3} \kappa^4 L^3 (n\Delta n)^2 \tag{2-2}$$

Besides, Hendy [13] published recently another formula:

$$\alpha \approx \frac{14}{15\pi} \varphi(1-\varphi) \left(\frac{\Delta n}{n}\right)^2 \kappa^8 R^7 \tag{2-3}$$

where  $\varphi$  is the volume fraction of the crystals.

According to these equations, the extinction coefficient strongly depends on the crystals' radius. The size of the crystals must be controlled, normally less than 15-30 nm. Besides, transparent glass-ceramic can also be obtained as long as the refractive index difference is small enough (less than 0.1). For example, a glass-ceramic SiO<sub>2</sub>-CaO-Na<sub>2</sub>O with 97% volume fraction of the crystal and grain size as large as 5-7  $\mu$ m, can keep transparent due to the small refractive index difference between the crystals and glass [25].

# 3. Non-linear optics and second harmonic generation

### 3.1 Introduction of non-linear optics

Non-linear optics is the study of phenomena that occur as a consequence of the modification of the optical properties of a material by the presence of light [26]. When an electric field is applied to a dielectric medium, if the intensity is very weak, the dipole will just oscillate around its equilibrium position with the same frequency as the electric field. When the electric field reaches a value near that of the coulomb attraction between the nucleus and the electrons, a separation of bound charges is induced as presented in Fig.1.3 [26]. The dipole will oscillate in an anharmonic way.



Fig.1.3 Schematic of the electronic polarization of an atom relative to the nucleus under the influence of an external field E [26], x: the shift of the electron

In the non-linear optical effect, the emitted light intensity is proportional to incident light intensity, such as square or cubic relationship. There is an interaction between the lights with different frequency, including the exchange of energy. Many interesting phenomena can be found in the field of non-linear optics. Second harmonic generation is one of the second non-linear optical properties. It exists in the materials which possess non centro-symetric crystals.

### 3.2 The second harmonic generation

The second harmonic generation can be generally described as the production of a pulse wave of  $2\omega$  from the incident pulse wave of  $\omega$  as shown in Fig.1.4. We assume that the medium is lossless both at the incident frequency  $\omega_1$  and at the double frequency  $\omega_2$ .



Fig.1.4 Schematic illustration of second harmonic generation, Z: direction; d: non-linear coefficient; L: length of material.

Second harmonic generation was firstly discovered in quartz sample by Peter Franken et al at the University of Michigan, in 1961 [27]. It has been widely used in diagnostic of the surface properties of optical materials [28]; in nonlinear optical microscopy [26]; in frequency converters, etc. Glasses however are macroscopically isotropic and consequently non secondorder nonlinear susceptibility  $\chi^{(2)}$  can be expected. In 1986, Österberg and Margulis have detected the frequency doubling in Ge and P doped optical fiber [29]. Because of the inherent advantage associated with glasses (easy fabrication and shaping), external induced SHG has also been widely studied in glasses even if this family of materials does not show any intrinsic  $2^{nd}$  order non linearity. Chalcogenide glasses having high linear and non linear refractive index are particularly interesting for this application.

# 3.3 Second order non-linear chalcogenide glass-ceramics

Chalcogenide glasses have more defects and local deformations and can be poled more easily by using various methods. They can be normally polarized by thermal/electrical poling, optical poling [6], electron beam irradiation [30] and thermal treatment. In which, by the means of thermal treatment [1, 11], the permanent second order nonlinear can be obtained. In 2007, M. Guignard [1] has detected second order nonlinear effects in a Ge-Sb-S glass-ceramic containing a few  $\beta$ -GeS<sub>2</sub> crystals. The nonlinear susceptibility observed was about 0.01 of that of  $\alpha$ -quartz. The size of the crystals ranges from 1 to 6  $\mu$ m, which is not large enough to reveal the phase-matchable or the non-phase-matchable character of GeS<sub>2</sub>. In 2009, C. Lin prepared crystals  $\beta$ -GeS<sub>2</sub> in GeS<sub>2</sub> using the thermal treatment, the second order nonlinear susceptibility  $\chi^{(2)}$  was estimated to be ~7.3 pm/V [11]. However, the presented glass-ceramics were thoroughly inhomogeneous as the crystallization only took place on the glass surface inducing a strong and fast deterioration of the transparency. Moreover, it is well known that heterogeneous crystallization taking place onto the surface is an uncontrollable and not reproducible process. In 2008, also transparent surface-crystallized glasses containing CdGa<sub>2</sub>S<sub>4</sub> nonlinear optical crystal were prepared by the GeS<sub>2</sub>-Ga<sub>2</sub>S<sub>3</sub>-CdS chalcogenide glass [31]. By using the Maker fringe measurement, prominent second-harmonic generation was observed from these crystallized glasses. The  $\chi^{(2)}$  was calculated to be 38.85 pm/V. Permanent second order optical nonlinearity up to 5.79 pm/V was found in the IR transparent bulkcrystallized AgGaGeS<sub>4</sub> chalcogenide glass [32].

### 3.4 The measurement of second order non-linear

Maker has found that the second harmonic signals presented by a rotating sample will present curves showing different shapes with the changes of the incidence angle. It can be used for measuring the second harmonic coefficient for the glasses that cannot realize phase matching. This measurement method is called Maker fringe method [33]. Fig.1.5 shows the principle of montage. The output of the wavelength of the fundamental frequency is pumped by Nd:YAG pulsed laser operating at 1064 nm with a 10 Hz repetition rate. An optical parametric oscillator (OPO) outputs a signal and idler (pump) which has the wavelength set at 1800 nm. The samples are fixed on a rotating table whose vertical rotation axis crossed the pump. After filtering through different filters rejecting the signals at 900 nm (frequency

doubled) that are generated through the OPO, the different optical pump is focused on the samples. The double-frequency signal generated is then detected by a photomultiplier (PM). Different filters before the PM are used to filter signal from the pump. The Maker fringes setup is configured and calibrated using an  $\alpha$ -quartz crystal [14].



Fig.1.5 Diagram of the experimental setup [14]

# 4. Introduction on sintering

For some "stable" glasses, it is difficult to achieve homogeneous crystallization in the bulk sample. Instead surface crystallization may occur [11]. Sintering the glassy powders with crystals already doped can be a solution to solve this problem.

Sintering is a technique used to synthesize bulk samples from powders. This process is based on atomic diffusion by heating the powders below the melting point. The atoms in the powders diffuse across the boundaries of the particles, bonding the particles together, creating one solid piece. Because of the synthesizing temperature is much lower than the melting point, sintering is often used as the shaping process for materials with extremely high melting point.

# 4.1 Sintering mechanism

Sintering is the control of both densification and grain growth. The whole process can mainly be divided into three periods (Fig.1.6):

1) Initial stage of sintering: This is generally a surface diffusion process. The atoms are just re-ranged. No obvious change happened on the shape of the particles and the gap between the particles.

2) Formation of necks: In this stage, the "neck" begins to grow, the particles deform. The gap begins to form an open pore surrounded by particles.

3) Evolution of necks and grain boundaries: The grain boundaries form, the particles grow up. The pores eliminate and form a network of open pores.

4) Isolation of pores: This is the final stage of sintering. The pores are isolated. The ideal situation is that the pore is surrounded by four particles, in a spherical shape. The particles have grown up. Through sintering, the porosity is effectively reduced and the density could be achieved to more than 99%.



Fig.1.6 Grain growth during the sintering process

# 4.2 Sintering factors

Quite a lot of facts can affect sintering.

1) Powder's granularity. Normally smaller the particles, shorter the diffusion distance of the atoms and higher solubility of the particles in the liquid phase, then speed-up the sintering process.

2) Sintering temperature. In the crystal, when the lattice energy is greater, the ions bonding will be stronger. Then the ions are more difficult to diffuse. The sintering temperature required is much higher.

3) Dwell temperature. At higher temperature, sintering is dominated by volume diffusion. But at lower temperature, surface diffusion takes the dominate position. Longer duration at lower temperature cannot densify but cause the surface diffusion and destroy the pores' shape. So it is possible to rise to high temperature quickly to cause volume diffusion.

4) Atmosphere. Usually the sintering should be carried out under vacuum or inert gas atmosphere to protect the powders.

5) Pressure. Generally speaking, greater is the pressure, the contact between the particles will be bigger, and then the sintering process will be enhanced.

# 4.3 Sintering method---Spark Plasma Sintering

Different routes of sintering process can be carried out. In this work, we mainly focus on a new sintering technique which is the Spark Plasma Sintering (SPS). The scheme of the process of SPS is presented in the Fig.1.7.



Fig.1.7 The scheme of the SPS[14]

Spark Plasma Sintering is a form of sintering where both external pressure and an electric field are applied simultaneously to enhance the densification of the metallic/ceramic powder compacts. With this method, it could rise to a certain temperature rapidly at a rate of 100°C/min, the densification uses lower temperature and hence the sintering process is very fast, usually several minutes. This speed of the process can ensure that it has the potential of

densifying powders with nanosize without enlarging their size or inducing undesirable crystalline phase.

#### 5. Synthesis of the GeS<sub>2</sub> glass-ceramic

GeS<sub>2</sub> has a large transparency window from 0.45  $\mu$ m to 11  $\mu$ m.  $\beta$ -GeS<sub>2</sub> crystal, which has the same composition with the GeS<sub>2</sub> glass, can present evident second order non-linear phenomenon. Close refractive index between them can lead their combination being a new chalcogenide glass-ceramic that can be used in second harmonic generation.

Two synthesis methods have been investigated to prepare  $GeS_2$  glass-ceramics. The first one is the conventional thermal treatment method in ventilated furnace and the second one is based on the powder sintering method.

### 5.1 Synthesis by thermal treatment method

To prepare the glass-ceramic by thermal treatment method, the base glass was firstly synthesized by the conventional melt-quenching method. High purity raw elements Ge and S were used. Their purity and their origin are listed in the Table1.1. Sulfur was additionally purified in the laboratory by distillation at 180°C first to remove the impurities such as O-H, S-H. Then evaporate the sulfur at 220°C to leave the other impurities which have higher melt-point, like CS<sub>2</sub>[34]. The concentration of group X-H, [X-H]<sub>ppm</sub> can be calculated by the function

$$\alpha_{cm^{-1}}(\lambda) = \frac{1}{x} ln \frac{l_0}{l}$$
$$[X - H]_{ppm} = \frac{\alpha_{cm^{-1}}}{\varepsilon_{cm^{-1}/ppm}}$$
(2-1)

- *x*: the thickness of the sample;
- *I*<sub>0</sub>: intensity incident;
- *I*: the maximum transmission;
- $\alpha$ : the absorption coefficient;

ε: the extinction coefficient at the impurity's wavelength.

The extinction coefficients of the group [S-H] and [O-H] are already known before [35]. So, in this GeS<sub>2</sub> glass,  $\varepsilon_{S-H}$ =0.025 ppm at 4.01 µm, and  $\varepsilon_{O-H}$ =0.025 ppm at 2.92 µm.

| Product   | Supplier | Purity |
|-----------|----------|--------|
| Sulfur    | Strem    | 5N     |
| Germanium | Umicore  | 5N     |

In order to avoid the loss of sulfur due to evaporation and the pollution of oxygen and water in the air, the glass was synthesized in silica tubes under vacuum. The set-up is presented in the Fig.1.8.



Fig.1.8 Schematic graph of vacuum pumping process and rotating furnace for preparation of chalcogenide glasses

About 10 g of raw materials were transferred into the silica tube of 10 mm diameter which was sealed under a vacuum of  $10^{-3}$  Pa. Then, the sealed tube was put into a rocking furnace following a heating process as show in Fig.1.9. Firstly the tube was heated up to 500°C at a rate of 1°C/min and kept at this temperature for 2 hours. This process is necessary because the boiling temperature of sulfur is about 444°C. The high vapor-pressure in the silica tube creates a risk of explosion. Maintaining the mixture for two hours at this temperature can let the sulfur reacts preliminarily with germanium to reduce the vapor-pressure. Then the tube was heated up to 930°C and kept at this temperature for about two days in order to complete the reaction and to homogenize the melt. At the end, the tube was quenched in water and annealed at  $T_g$ -30°C (450°C) before being slowly cooled down to room temperature (RT). In order to facilitate analysis, the glass rod was cut into pieces of about 2 mm thick using a diamond wire saw and the slices were carefully polished with the carpet of silicon carbide. The chalcogenide glass slices are presented on Fig.1.10.



Fig.1.9 Typical heating curve for the fabrication of chalcogenide glasses



Fig.1.10 GeS $_2$  base glass prepared by melt-quenching method

Thermal analysis was performed using a differential scanning calorimeter (DSC TA Q20) with samples of 10 mg and a heating rate of 10°C/min. Characteristic temperatures, the glass transition temperature,  $T_g$ , can be determined from the curves in Fig.1.11.



Fig.1.11 DSC curve of glass GeS<sub>2</sub>, temperature transition  $(T_g)$  is pointed out

Glass-ceramic of GeS<sub>2</sub>-βGeS<sub>2</sub> was fabricated by heat-treatment in ventilated furnace which presents an accuracy of  $\pm 2^{\circ}$ C. Depending on the  $T_g$ , the as-prepared glass was kept at 490°C for 96 hours. Table1.2 lists the parameters of the glass and glass-ceramic by thermal treatment.

Name Annealing  $T(^{\circ}C)$ Annealing time (h) Thickness (mm) GS No No 2.22 GS1 96 490 2.34

Table1.2 Parameters of glass-ceramic made by thermal treatment method

### 5.2 Synthesis of glasses or glass-ceramics by powder sintering method

Powder sintering provides a new method to synthesize the chalcogenide glasses and glass ceramics. This method is generally composed of two steps, the mechanical milling to obtain a mixture of amorphous powder and the following sintering process to compact it. The main aim is to induce a slight heterogeneous crystallization process on glass surface during the sintering process, so that a homogeneous bulk material should be obtained with inner crystallization. In our experiment, the glass rod was grinded into powders and well-mixed with the crystal powders by a planetary grinder (Retsch PM100). The grinding jar and grinding balls are made of tungsten carbide. Depending on the volume of the grinding jar, 125 ml, the fillings should be consisted of 1/3 sample, 20 g sample, and 1/3 grinding balls charge,

6 grinding balls on diameter 20 mm. The remaining 1/3 is left for the free movement of the grinding balls. These data were supplied by the provider. For not destroy the crystal structure, the rotation speed was set as 300 rpm. It worked every 3 minutes with a 3-minute interval to avoid the over-heat. The machine was kept in the glove box to protect powders from the pollution of oxygen and water. Then the powders were sintered under secondary vacuum by using Spark Plasma Sintering (SPS) equipment (Dr. Sinter 505 Syntex). The melt-quenching technique is limited by the diameter of the silica tube and the quenching speed. For some unstable glasses,  $T_x$ - $T_g$ <100°C [36], because of the low thermal conductivity of silica, heterogeneous crystallization occur and hence reduce the glassy domain. Using SPS, the size of the sample is only limited by the diameter of the mold. Fast heating rate can prevent the glass from undesirable crystallization. Besides, the sintering temperature used to be below  $T_g$  as the application of a uniaxial compaction pressure could lead to a decrease in the  $T_g$  value [37]. Lower synthesis temperature causes cost savings. It is also possible to synthesize glasses or glass-ceramics by controlling the sintering time [38, 39].

So, SPS technique is supposed to be efficient to make IR glasses and glass ceramics from amorphous powders.

The Planetary Ball Mill is presented in Fig.1.12. The machine posted in the Fig.1.12 is the planetary grinder, PM100. The tungsten carbide grinding jar (photo bottom right) which loaded with raw materials and grinding balls is fixed at the center by a quick-action clamping device.



Fig.1.12 The Planetary Ball Mill

The grinding jars are arranged eccentrically on the sun wheel of the Planetary Ball Mill. The direction of movement of the sun wheel is opposite to that of the grinding jars. The difference in speeds between the grinding balls and grinding jars produces an interaction between frictional and impact forces, which releases high dynamic energies. The interplay between these forces produces the high and very effective degree of size reduction of the planetary ball mill.

### 5.2.1 Synthesis of $\beta$ -GeS<sub>2</sub> crystals

To prepare the glass ceramics of  $GeS_2/\beta$ -GeS<sub>2</sub>, the corresponding glass and crystals powders were prepared. For the first experiment, GeS<sub>2</sub> glass grains were prepared by milling the glassy rod made by melt-quenching method.  $\beta$ -GeS<sub>2</sub> crystals were synthesized by controlled crystallization of GeS<sub>2</sub> glassy powders in a vacuumed tube using a thermal treatment at 493°C for 250 h. The vacuumed tube was used here to protect the powders from the pollution of oxygen and water in air which significantly deteriorates the glass-ceramics transparency in the infrared range. To achieve a thorough transition from glass to  $\beta$ -GeS<sub>2</sub> crystals, two points have to be considered. Firstly, the glass powders should be well grinded to increase the specific surface area to fasten the crystallization process. This is due to the fact that  $\beta$ -GeS<sub>2</sub> tends to be formed on the surface of the GeS<sub>2</sub> glass by hetero-nucleation. Secondly, the temperature of the heat treatment should be well chosen.



Fig.1.13 Phase-transformation diagram of GeS<sub>x</sub> glasses, (x=1~2.1) [40]

It is well known that GeS<sub>2</sub> crystals can present two different phases. According to the phase-transition diagram of GeS<sub>x</sub> (Fig.1.13) [11, 40], below 497°C, the stable structure is  $\beta$ -GeS<sub>2</sub> phase which has a non-centro-symmetric structure, and can present second order non-linear effects. The heat treatment operated at higher than 497°C will generate the phase  $\alpha$ -GeS<sub>2</sub>.

The powders obtained after heat treatment shows yellow color as presented in Fig.1.14. To identify the phase, the powders were analyzed by X-ray diffraction using a Phillips PW3020 diffractometer operating with Cu K $\alpha$ , voltage 40 kV, current 30 mA, with a step width of 0.02°. Both polished disk and grinded powders were used for XRD measurements. Fig.1.15 presents the powders' diffraction patterns. On comparing with the PDF card, the yellow powders perfectly match with the  $\beta$ -GeS<sub>2</sub> phase.



Fig.1.14 Photo of  $\beta$ -GeS<sub>2</sub> crystals powder



Fig.1.15 XRD patterns of  $\beta$ -GeS<sub>2</sub> crystals and JCPDF card No. 26-693 ( $\beta$ -GeS<sub>2</sub>, orthorhombic system)

# 5.2.2 Mixing of glass powder with $\beta$ -GeS<sub>2</sub> crystals

Then, 15 mol% of  $\beta$ -GeS<sub>2</sub> crystals were mixed thoroughly in a planetary grinder with 85 mol% of GeS<sub>2</sub> glass grains for about 3 hours to obtain an homogeneous matrix. Grinding mechanically can mix the powders more homogenously, but there is still a risk of milling the crystals into amorphous phase [41]. In order to check the evolution of crystallization, a small quantity of mixture was taken out every one hour and was analyzed by XRD to observe the possible amorphization or phase changes (Fig.1.16). On comparing the XRD patterns, the peaks intensity slightly decrease with increasing milling time. To prevent from turning into amorphous phase, 3 hours of milling was sufficient.



Fig.1.16 XRD patterns of mixed GeS<sub>2</sub>/β-GeS<sub>2</sub> powders grinded for different durations

Fig.1.17 presents the distribution of particles size measured in Limoges. The size of the particles, especially the size of crystals, affects mostly the transparence of the glass-ceramic. From the Fig.1.17, the mixtures size was at the order of micrometer. Along with the grinding duration, particles size is decreased from about 100  $\mu$ m at the beginning, to 10  $\mu$ m after 3 hours of grinding. In fact a compromise has to be found between the decrease of particle size and the possibility to amorphization. Considering these two parameters, an optimal time of 3 hours of grinding has been chosen.



Fig.1.17 Size of mixtures  $GeS_2/\beta$ -GeS<sub>2</sub> grinded with different durations

# 5.2.3 SPS process

The powder was sintered under primary vacuum using SPS equipment (Dr. Sinter 505 Syntex). Mixture of powders was introduced in an 8 mm diameter graphite die. Ta layer was used to cover the mold in graphite to protect the samples from the pollution of carbon. Sintering parameters were slightly modified to produce two different glass-ceramics: GC1 and GC2. The SPS parameters were as follows: temperature at 450°C (heating rate of 100°C/min up to 400°C and then 50°C/min until 450°C), dwell time of 10 minutes (GC1) and 15minutes (GC2), pressure at 50 MPa. The temperature of sintering was determined to be the  $T_g$  of the glass. Table1.3 lists all the parameters of the disks made by SPS.

| sample | T /°C | Pressure<br>/MPa | Duration<br>/min | φ/mm | $\rho/g \cdot cm^{-3}$ | Liner | Grinding<br>atmosphere | Thickness (mm) |
|--------|-------|------------------|------------------|------|------------------------|-------|------------------------|----------------|
| GC1    | 450   | 50               | 10               | 8    | 2.80                   | Та    | Glove box              | 0.57           |
| GC2    | 450   | 50               | 15               | 8    | 2.75                   | Та    | Air                    | 0.57           |

Table1.3 Parameters of the SPS experiments and characteristics of the glass-ceramic

# 6. Properties studied on the pastilles made by melt-quenching and by SPS

### 6.1 Optical transmission

For optical characterization, transmission spectra were recorded using a Perkin Elmer Lambda spectrophotometer in the UV/Visible/NIR region and using a Bruker Vector 22 Spectrophotomer in the infrared region. Measurements were performed with well polished samples of 2.2 mm thick.



Fig.1.18 Transmission curves of the as-prepared and heat-treated samples in the Visible and near IR region; the inset is the photo of these two samples

Optical transmission spectra in the visible and near infrared region of glasses made by conventional melt-quench method and heat-treated are presented in Fig.1.18. After crystallization at 490°C for 96 hours, a decrease of transmission is observed in the visible range due to scatterings of crystals having a size close to the micrometer (inset photo in the Fig.1.18). Crystals are mostly generated on the surface of the bulk glass. It is noteworthy that the maximum of transmission beyond 2.5  $\mu$ m remains almost unchanged in comparison with the base glass. Moreover, the transmission cut-off remains unchanged after crystallization treatment; glass-ceramics keeping a high transparency up to 11.5  $\mu$ m. Also, the absorptions due to vibration modes of O-H bonds at 2.8  $\mu$ m and 4  $\mu$ m of the glass-ceramic were stronger than those of the parent glass. This can be explained by the fact that the crystallization step was conducted in air atmosphere during the annealing process.

Optical transmission of the GC1 (10 min, 450°C, 50 MPa) and GC2 (15 min, 450°C, 50 MPa) samples made by SPS was presented in Fig.1.19. On comparing these two samples, one can observe that the transmission of GC1 glass-ceramic is higher than that of GC2, especially in the shorter wavelength. There are barely any signals before 3  $\mu$ m on the GC2. Before 7  $\mu$ m, the transmission of GC1 is much higher than GC2 while the maximum of transmission is the same at 10.5  $\mu$ m reaching 30%. At this stage, several hypotheses can be proposed: scatterings due to pores at the boundary glass/crystal, to aggregates of crystals, diffusion of C graphite within the glassy matrix, uncompleted sintering, etc. These scatterings still affect the lower wavelength but are minimized in the GC1 sample as crystals are homogenously dispersed within the glassy matrix and present a smaller size (about 500 nm).



Fig.1.19 IR transmission spectrum of the glass-ceramics prepared by SPS and then polished on both faces (the inset are the photos of the samples)

Moreover the carbon that diffused from the die during the SPS process can explain the scatterings in the GC1 glass-ceramic. As observable in the inset of the Fig.1.19, the obtained glass-ceramics are black instead of yellowish. Moreover, some absorption bands are observable in the transmission curves. The large specific area of powders induces a fast and strong reaction with the atmosphere inducing absorption due to water and oxygen. Even by grinding the mixture in the glove box free of water but not free of oxygen (which in our case only decreases the water content not the oxygen as no oxygen getter is installed), absorption bands are still remaining. The very low transmission in the visible and infrared range does not

allow making measurement of second order non-linear phenomenon in the glass-ceramics. One can guess that the oxidation of powder induces a difference of refractive between the grain boundaries because of the difference of oxygen content with the inner part of the grain. As mentioned earlier in Hendy's equation, this difference of refractive index will cause strong scatterings. Moreover the carbon that diffuses within the glassy matrix is detrimental for optical applications.

# 6.2 Morphology

The crystals size and distribution as well as pores existing in the samples made by sintering process were observed by Scanning Electronic Microscope (SEM). Freshly broken sections were made and coated by a gold layer to enhance the contrast.



Fig.1.20 Photos of GS1 sample prepared by annealing the as-prepared glass at 490°C during 96 h (magnification of x350, x1000, x5000 and x10000).

The Fig.1.20 presents the SEM images of sample GS1 which were prepared by annealing the as-prepared glass at 490°C during 96 h observed by SEM. As shown, a thin crystallized layer, not perfectly homogeneous in thickness, was generated at the glass surface in the thickness range of 3-10  $\mu$ m, with individual crystals having a size lower than 1 $\mu$ m. The volumic ceramisation of GeS<sub>2</sub> base glass to generate  $\beta$ -GeS<sub>2</sub> crystals is an uncontrollable process. From the curve of DSC, on Fig.1.11, the  $T_c$  (crystallization temperature) of GeS<sub>2</sub> glass is about 659°C,  $T_g$  of glass is about 481°C. The  $\Delta T$  ( $T_c$ - $T_g$ ) is larger than 170°C, this kind of glass could be identified as thermal stability ( $\Delta T$ >100°C) and consequently are not suitable for controlled crystallization treatment [42]. Crystallization can only be initiated on the surface through heterogeneous nucleation.

SEM pictures of GC1 and GC2 glass-ceramics obtained by sintering of powder are presented in Fig.1.21. In the GC2 sample, there are remaining pores at the boundary between glass and crystals leading to lower density (Table1.3). Both GC1 and GC2 bulk presents crystals which are slightly smaller in the GC1 sample (about 500 nm). However, a high amount of closed pores of hundreds of nanometers are clearly present in the GC2 glass-ceramic (Fig.1.21). This residual porosity can be linked to the presence of oxide on the powder surface as mechanical milling was performed under air in contrary to the GC1 sample.



Fig.1.21 Photos of the GC1 (a) and GC2 (b) slices prepared by SPS observed by SEM,)

Both polished disk and grinded powders were used for XRD analysis. As shown in Fig.1.22, X-Ray Diffraction patterns of the glass-ceramics slices obtained after SPS treatment indicate that the bulk is still mainly amorphous. The initial amount of  $\beta$ -GeS<sub>2</sub> crystal was 15 mol%, showing that the sintering process by SPS can be controlled to make glasses or glass-ceramics without uncontrolled crystallization. In fact, as shown in Fig.1.22, with longer SPS



treatment time, a growth of crystals is induced as bigger peaks of diffraction characterizing  $\beta$ -GeS<sub>2</sub> phase start to appear.

Fig.1.22 X-ray diffraction patterns of the glass-ceramic slices prepared by SPS

### 6.3 Second order nonlinearity

Non-linear measurement was carried out by Maker fringe method [33] at  $\lambda$ =1.8 µm, signals were recorded at 0.9 µm. The Maker fringes setup was configured and calibrated using an  $\alpha$ -quartz crystal. This measurement was carried out in the University of Lille by Professor Y. Quiquempois (Laboratoire de Physique des Lasers, Atomes et Molécules).

Fig.1.23 presents the Maker fringes pattern of sample GS1, the sample annealed at 490°C for 96 hours. The signal was directly compared with the signal obtained from the quartz which is used as a reference. Non-linear signals only exist in the glass-ceramic GS1, nothing was observed in the base glass sample GS. The SH intensity slightly increases until the incidence angle reaches roughly  $35^\circ$ , and then decreases. This decrease can be attributed to Fresnel losses that occur at high angles [1]. The Second Harmonic intensity is approximately 6 times lower than the one recorded in 1 mm-thick quartz sample, but is generated in a very thin layer (<10 µm), leading to higher values for the non-linear coefficient than that of quartz. Further investigations are needed to better understand the Maker fringe



pattern and extract the nonlinear coefficient since the contribution of the nonlinear layers to the SH signal can results from partial orientation of the crystals [43, 44].

Fig.1.23 Maker fringe patterns of the glass-ceramic GS1 heated at 490°C during 96 h. The signal was compared with that of quartz reference.

Besides, the ceramisation of base glass GS to generate  $\beta$ -GeS<sub>2</sub> crystals is an uncontrolable process. According to the function of turbidity mentioned earlier, large size of particles may cause the glass opacity rapidly [13] and inhibit all the non-linear signal.

Unfortunately, the transmissions of GC1 or GC2 samples obtained by sintering were too low in the visible and infrared region, there are barely any second order non-linear signals that can be detected.

### 6.4 Photo-induced phenomenon

Chalcogenide glass is an interesting photo-induced material. Such material with or without crystals in the glassy matrix presents different responses under the irradiation of laser. The photo-induced absorption was measured by a set-up using an optical fibre spectrophotometer (Ocean Optics) with spectral resolution of about 0.2 nm within the 400 nm–1000 nm spectral range. While the transmission measurement was going on, the samples were irradiated by a laser beam with an incident angle of about 12-15°. A doubled frequency CW Nd:YAG laser with power density equal to about 42 W/cm<sup>2</sup> and a pulsed 2  $\mu$ s CO<sub>2</sub> laser emitting at 10.6  $\mu$ m with power density about 0.3 MW/cm<sup>2</sup> were used. The optical density difference  $\Delta D$  before and after the illumination was used to characterize the photoinduced absorption. The changes of refractive indices were carried out using a double-modulated polarimetry set-up which allows registering the phase shift delay, corresponding to the refractive indices variation up to 10<sup>-8</sup>, during the illumination as well as after its interruption. Simultaneously, the temperature at the surface of the samples was controlled by laser pyrometer with accuracy up to 0.2 K. The variation of the Gaussian-like laser beam profile does not change the observed photo-induced modifications not more than 0.8%.

The Fig.1.24 depicted that the photo-induced changes of absorption corresponding to the difference between the absorption of "fresh" and irradiated samples for two irradiation duration (30 s and 15 min) with the CW 532 nm laser. After 30 s of irradiation, drastic changes of the optical density can be observed which are accentuated with time increase. By integrating the area of the modifications, the changes are substantially more important for glass-ceramic GS1sample comparing to the glass GS sample. The first one presents several spectral resonances (462, 575 and 702 nm) whereas the latter has only one main peak centered at 455 nm which can be caused by a transient photo-darkening effect. The principal spectral differences of absorbance behavior between glass and glass-ceramic are observed at higher wavelengths than the lonely peak observed in glass. It should be a consequence of the occurrence of crystallized/amorphous interfaces between the crystallites and the glass matrix which are source of new deeper levels located within the forbidden energy band-gap, similarly to molecular crystals [45]. Particular attention should be paid to the spectral band at 530-560 nm range which is obviously much weaker than that of the glass-ceramic sample. The additional absorption for glass-ceramic is likely caused by the occurrence of crystalline long-range ordered sub-bands which maybe main source of additional absorption from the valence band to these sub-bands. More quantitative analysis will require the use of chemical quantum calculation of the electronic states density taking into account the formation of crystallites inside the GeS<sub>2</sub> glass matrix.



Fig.1.24 Irradiation by CW 532 nm green laser of GS (black) and GS1 (grey) for two durations (30 s and 15 min); in inset: absorption coefficient of GS and GS1 recorded from 300 nm to 800 nm.

During illumination by impulse of 2  $\mu$ s from the IR laser which is absorbed in the spectral domain of multi-phonon absorption, the feature of spectral changes are comparable for the glass and glass-ceramic samples presenting mainly a central peak. It is worthy to note that in this case, the magnitude of  $\Delta D$  changes is more crucial in the case of glass compared to glass–ceramics. Successive enhancement of the illumination time leads to a substantial increase of the photo-induced optical density changes, as it was already observed in the case of CW 532 nm laser. The phonon subsystem should play here a crucial role, as it is shown from the inserted FTIR spectra, with the observed multi-phonon absorption at 10.6  $\mu$ m. A different behavior of absorption changes caused by IR irradiation occurs for the glass and glass-ceramic in comparison with 532 nm laser excitation. It is obviously observed in the case of glass sample for the longest irradiation time on Fig.1.25 There is a sign inversion of spectral changes at higher wavelength; the deeper trapping levels seems to be depleted, during the vibration excitation caused by CO<sub>2</sub> laser, likely in favor to trapping levels of energy closer to the band-gap energy.


Fig.1.25 Changes of absorption in GS and GS1 by infrared 10.6  $\mu$ m laser irradiation; in inset: absorption coefficient of GS and GS1 recorded within 2.5  $\mu$ m to 12  $\mu$ m wavelengths.



Fig.1.26 Relaxation of absorption photoinduced changes ( $\Delta D$ ) in GS irradiated by infrared 10.6  $\mu m$  laser (1 min, 5 min and 10 min).

Finally considering the experimental irradiation conditions used for these samples, there is no irreversible absorption observed as a relaxation of photoinduced changes which is systematically detected for the glasses and glass–ceramics using the two green or IR laser (Fig.1.26). This one excludes classical quasi-permanent photo-darkening/bleaching mechanisms or at least, the phenomenon reaches only a metastable state of polarization with

own specific lifetime. It is necessary to mention that the relaxation processes seems to be similar for the two laser excitation which may be explained by the same mechanisms for the two types of the excitations caused by the electron–phonon interactions.

The relaxation times of the photo-induced changes are longer for the glass-ceramics than for the glasses; the main differences between the glass and glass-ceramics concern the excitation or relaxation of deeper levels depending on used laser. The changes of the metastable photo-induced time decays are certainly related to the presence of deep trapping levels created at the surface of the crystallites which will affect the state density of defects. It seems that for the both kind of illuminations the electron-phonon relaxations are dominant. However this hypothesis requires additional studies to be confirmed which will be a subject of a separate work in a future. The absence of irreversible part in the refractive index variation just after the switch-off of the laser irradiation (see Fig.1.27) may indicate that we are in presence of transient effects observed during the photo induced refraction changes which not involve additional permanent mechanisms as photoinduced plasticity or crystallization.



Fig.1.27 Refractive index change induced by CW 532 nm green laser irradiation of GS and GS1 (490°C-96h).

### 7. Conclusion

In this chapter, GeS<sub>2</sub> glasses and glass-ceramics were synthesized using two different processes: the traditional melt quenching method and mechanical milling combined with Spark Plasma Sintering. Optical transmission, second order nonlinear, photo-induced properties and morphology properties were studied to observe the influence of crystals growth within the glassy matrix.

The usual crystallization process by annealing the base glass led to the inhomogeneous crystallization of micrometric crystals on the glass surface (glass-ceramic GS1). Scatterings are observed in the short wavelength while transparency in the infrared range remains almost unchanged. The thickness layer of crystals is about 3 to 10  $\mu$ m. Due to the high transmission at 0.9  $\mu$ m and 1.8  $\mu$ m, and the presence of non-centro-symetric crystals  $\beta$ -GeS<sub>2</sub>, the second order nonlinear signal can be detected on sample GS1.As expected due to the isotropy of the glass, no non-linear signal was observed with the base glass.

Moreover, photo-induced phenomenon was observed with the samples GS and GS1 on charge of microsecond pulsed  $CO_2$  and CW green laser. The changes of absorption are very sensitive to the presence of crystallization in the GeS<sub>2</sub> glass matrix. During the irradiation by green laser, the principal phenomenon at the origin of the photoinduced effects is certainly related to a pure electronic transition involving the trapping levels intra the energy band-gap while for the IR laser, these levels are excited via the interaction with the phonons of the network. The similarity of the relaxation processes caused by the green or IR lasers may be a consequence of the principal role played by electron–phonon mechanisms inducing the vanishing of photoinduced phenomena. Relaxation studies of photo-induced refractive index and absorption changes show the absence of irreversible modifications which allow to use these materials for application as optically operated materials for visible and IR lasers.

On the other hand, the GC1 and GC2 glass-ceramics synthesized by mechanical milling and sintering permit to choose the crystalline phase wanted to be incorporated within the glassy matrix. On comparing these two samples, glass-ceramic prepared from powder made in air present high porosity after sintering, glass-ceramics obtained from powders milled in the glove box present a densification rate higher than 99%. On contrary to the GC2 glass-ceramic, the GC1 present a relatively good transparency in the infrared range. Residual scatterings are mainly due the presence of crystals of about 500 nm size but also might be due to the change of refractive index at the grains boundaries after sintering where oxygen can be accumulated. Moreover, the diffusion of carbon within the glass-ceramic is an important fact to consider as it is probably the main reason of such strong scatterings. Nevertheless, grinding in the glove box is an efficient way to decrease the pollution by water. Consequently, the feasibility to make transparent chalcogenide glass-ceramics using mechanical milling combined with Spark Plasma Sintering has been demonstrated. But according to the transmission curve and SEM picture of GC1, there is still a long way to achieve to make perfect infrared transparent samples by combining ball milling and Spark Plasma Sintering.

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Chapter II: Glass-ceramics Ge-Sb-S+CdS preparation and non linear properties

| 1. Introduction  | 41 -   |  |  |  |  |  |
|--|--------|--|--|--|--|--|
| 2. The choice of the base glass  | 42 -   |  |  |  |  |  |
| 3. Synthesis of the powders for sintering  | 46 -   |  |  |  |  |  |
| 3.1 Static way to prepare CdS-glass mixture  | 47 -   |  |  |  |  |  |
| 3.2 Stirring way to prepare CdS-glass mixture  | 51 -   |  |  |  |  |  |
| 4. Sintering of Ge <sub>20</sub> Sb <sub>12</sub> S <sub>68</sub> -CdS glass-ceramic by SPS and HP |        |  |  |  |  |  |
| 4.1Properties studied of the samples sintered by SPS   | 54 -   |  |  |  |  |  |
| 4.1.1 Optical transmission   | 54 -   |  |  |  |  |  |
| 4.1.2 X-ray diffraction  | 55 -   |  |  |  |  |  |
| 4.1.3 Scanning Electron Microscope   | 56 -   |  |  |  |  |  |
| 4.2 Properties studied of the samples sintered by HP   | 58 -   |  |  |  |  |  |
| 4.2.1 Introduction of HP   | 58 -   |  |  |  |  |  |
| 4.2.2 Determine the temperature of HP  | 59 -   |  |  |  |  |  |
| 4.2.3 Optical transmission   | 62 -   |  |  |  |  |  |
| 4.2.4 X-ray diffraction  | - 63 - |  |  |  |  |  |
| 4.2.5 Scanning Electron Microscope   | 64 -   |  |  |  |  |  |
| 4.2.6 Non-linear analysis  | 67 -   |  |  |  |  |  |
| 5. Conclusion  | 69 -   |  |  |  |  |  |
| 6. Reference   | 71 -   |  |  |  |  |  |

## 1. Introduction

The results presented in the last chapter show that the GeS<sub>2</sub>- $\beta$ GeS<sub>2</sub> glass-ceramic is able to deliver second order non-linear signals due to their non centro-symetric crystals of  $\beta$ GeS<sub>2</sub>. However, comparing a glass-ceramic sample of 1 mm thick to a reference  $\alpha$ -quartz crystal, the non-linear effect is much lower in GeS<sub>2</sub> glass-ceramic. Thus, materials with large second order non-linear optical coefficient should be found. Bibliographic research presents that CdS crystal is a very important optical and electronic semiconducting material [1, 2] and it also owns a large second order optical nonlinear coefficient. At the wavelength of 1.064  $\mu$ m, its nonlinear susceptibility is about +44±12.6 pm/V [3], while that of  $\beta$ GeS<sub>2</sub> is about 7.3 pm/V [4].

Several studies aiming to induce second order non-linearity in glasses by introducing CdS crystals were performed. For example, second harmonic generation (SHG) activity was detected in borosilicate glasses containing Cd and S after being thermally poled [5]. This thermal poling method was also used to induce second order nonlinear susceptibility  $\chi^{(2)}$  in GeS<sub>2</sub>-Sb<sub>2</sub>S<sub>3</sub>-CdS chalcogenide glasses [6]. This second order non-linearity observed in these glasses is attributed to the reorientation of certain bonds during thermal poling, such as Ge-S, Sb-S, Cd-S dipoles in GeS<sub>2</sub>-Sb<sub>2</sub>S<sub>3</sub>-CdS glasses. However, the second order non-linearity usually decays over time [7]. Recently, GeS<sub>2</sub>-Ga<sub>2</sub>S<sub>3</sub>-CdS chalcogenide glass-ceramics containing CdGa<sub>2</sub>S<sub>4</sub> nonlinear optical crystals heat treated for 48h at 405°C, permitted to generate second-harmonic signals, with a  $\chi^{(2)}$  reaching 38.85 pm/V [8]. However, the inhomogeneous crystals form on the surface with 15-µm depth conduct to a strong decrease of the optical transmittance. SHG was also observed within glasses belonging to the GeS<sub>2</sub>-In<sub>2</sub>S<sub>3</sub>-CdS system using electron-beam irradiation. The SHG increased with the increase of the irradiating current and time [9]. Until now, no papers have reported the formation of glass-ceramic which should induce permanent SHG only caused by CdS crystals.

In the chapter I, the mechanical milling process followed by sintering has been demonstrated to be efficient for the preparation of glass-ceramics with homogenously distributed crystals. Thus in this chapter this technique will be chosen to homogeneously introduce CdS crystals within a chalcogenide glassy matrix. In order to perform analysis of second order nonlinearity, the glass-ceramic must be transparent in the visible and near infrared ranges, at least at the detection wavelength of 0.9  $\mu$ m [10, 11]. So, the difference of refractive index between the base glass and CdS crystals should be lowered as the extinction

coefficient is proportional to the square of the refractive index difference [12]. The refractive index of CdS at 0.9  $\mu$ m is 2.359. Thus the choice of a base glass who owns a refractive index near 2.359 is firstly discussed in this chapter. Then the details of the preparation of fine and uniform CdS crystals, the way to mix it within the base glass, the techniques and parameters of sintering will be reported. Series of optical analysis, morphology analysis and nonlinearity analysis are carried out on these glass-ceramic samples.

#### 2. The choice of the base glass

As already mentioned, in order to choose base glasses suitable for making transparent glass-ceramics with CdS particles, close refractive index is the most important factor to be considered. Table2.1 lists several refractive indexes of glasses close to that of CdS.

| Composition   | n (at 1.064 µm)           |  |  |  |
|---|---------------------------|--|--|--|
| GeS <sub>2</sub>  | 2.059 (at 1.3 µm)         |  |  |  |
| $35La_2S_3-65Ga_2S_3$   | 2.5 [13]                  |  |  |  |
| 87.3GeS <sub>2</sub> -12.7Ga <sub>2</sub> S <sub>3</sub>  | 2.19 [13]                 |  |  |  |
| 7.5BaS-17.5Ga <sub>2</sub> S <sub>3</sub> -70GeS <sub>2</sub>   | 2.22 [14]                 |  |  |  |
| $Ge_{31}Sb_9S_{60}$   | 2.32 [15]                 |  |  |  |
| $Ge_{31}Sb_9S_{50}Se_{10}$  | 2.4 [15]                  |  |  |  |
| $Se_{93}Te_5Zn_2$   | 3.1 [16]                  |  |  |  |
| 50(0.75GeS <sub>2</sub> -0.25In <sub>2</sub> S <sub>3</sub> )-50(In <sub>2</sub> S <sub>3</sub> -AgI) | 2.386 (at 0.6328 µm) [17] |  |  |  |

On considering the difficulty and security of synthesizing the base glasses, system Ge-Sb-S comes into our attention [18]. Ge-Sb-S glasses are generally transparent in a wide range, from 0.5  $\mu$ m to 11  $\mu$ m, having a high glass transition temperature from 250°C to 360°C [19], low phonon energy, high solubility of rare-earth elements [20], and high non-linear optical characteristics [6]. Other advantages of these materials are that they are much more resistant to decomposition by reaction with air humidity than glasses of Ge-S system, more safety to synthesize than La<sub>2</sub>S<sub>3</sub>-Ga<sub>2</sub>S<sub>3</sub> or glasses contain In<sub>2</sub>S<sub>3</sub>, BaS, which can cause explosion when heating up to a very high temperature in silica tube [13, 14, 17].

In the Ge-Sb-S system only one glass forming region appears [21], shown in Fig.2.1, located in the neighborhood of the Ge-S side and sulfur rich part of the Ge-Sb-S triangle, extending to composition with about 40% Sb. The glass  $Ge_{31}Sb_9S_{60}$  whose refractive index is 2.32 [15] as reported, is close to that of CdS. So investigations were made on three compositions around the reported composition  $Ge_{31}Sb_9S_{60}$  [15] in the glass forming region. The following glass compositions:  $Ge_{31}Sb_9S_{60}$ ,  $Ge_{20}Sb_{12}S_{68}$ , denoted as G31, G28 and G20 respectively are marked in Fig.2.1. Their transmission in the visible region, glass transition temperature, and refractive index were studied. Refractive index was measured by total reflection with a Metricon model 2010/M prism coupler, the error was 0.0001.



Fig.2.1 Glass forming region Ge-Sb-S system, (-) glass forming region for rapidly cooled samples, (---) glass forming region for slowly cooled samples [21]

By changing the composition, obvious variation of the glass transition temperature and the glass absorption can be observed from Fig.2.2. Along with the increase of Ge content, the  $T_g$  increases. In Ge-Sb-S glasses, structure of Ge-S is GeS<sub>4</sub> tetrahedron [22] while that of Sb-S is trigonal SbS<sub>3</sub> pyramid in the case of Sb<sub>2</sub>S<sub>3</sub> glass [23]. The addition of Ge increases the amount of Ge-S, so that increases the network connectivity thus increases the  $T_g$ . The cut-off edge of G20 is the lowest, at 550 nm, while that of G28 and G31 located at 700 nm and 712 nm. As observable in the inset of Fig.2.2, the variation of the cut-off edge leads to the fact that



glass G20 is partially transparent in the visible range while G28 and G31 appear black color to naked eye.

Fig.2.2 DSC curves and absorption curves of glasses G28, G31, G20; the photo inset is the photos of these three samples

The variations of band-gap and  $T_g$  of these glasses are plotted in Fig.2.3 for clear and easier comparison. Along with the addition of germanium, the glass has trend to be opaque in the visible region. Moreover, considering the addition of nanoparticles of CdS crystals in a glassy matrix to obtain glass-ceramic can induce scatterings, a special attention has to be paid to choose the base glass in order to keep a high transparency for SHG measurements. In fact, scatterings will occur by adding crystalline particles inducing optical losses in the short wavelength, which can be prohibitive for SHG measurements [24]. As already shown in the first chapter, in order to measure the second order non-linear signals, the glass-ceramics have to be transparent at 0.9  $\mu$ m [11]. As a consequence, the most transparent sample in the visible region has been chosen to perform experiments, meaning the G20 base glass.



Fig.2.3 Band-gap of the glasses (left side) and glass transition temperature  $(T_g)$  (right side) according to the glass composition

Moreover, the glass transition temperature of G20, 270°C, is the lowest among the three samples, facilitating its shaping at lower temperature. Thus, glass-ceramic pellets were synthesized by mixing mechanically the glass powders with CdS crystals and pressing them by hot pressing in a stainless mold. The temperature to shape the pellets was usually set as  $T_g$ +100°C as it permits to reach a viscosity low enough (10<sup>7</sup> Pa•S) to allow the shaping process.

The refractive indexes of the three glasses at different wavelength are shown in Fig.2.4. These points are fitted by the Cauchy dispersion equation

$$n(\lambda) = A + B \times \lambda^{-2} + C \times \lambda^{-4}$$
(3-1)

*n* is the refractive index,  $\lambda$  is the wavelength, *A*, *B*, *C* are coefficients that can be determined for a material by fitting the equation to measured refractive indices at known wavelengths. The refractive index of CdS at 0.9 µm is known to be 2.359. The refractive index at 0.9 µm of the glasses can be determined from the fitting curves in Fig.2.4. At this typical wavelength, the refractive index of G31, G28 and G20 samples are 2.343, 2.373 and 2.273 respectively.



Fig.2.4 Refractive index of G20, G28 and G31samples; and the curves fitted by the Cauchy dispersion equation

Even if the difference of the refractive index between CdS and the host glassy matrix is of 0.086, on considering the transmission, temperature of glass transition and refractive index, the  $Ge_{20}Sb_{12}S_{68}$  glass composition appears to be the best candidate for further experiments.

#### 3. Synthesis of the powders for sintering

The cadmium sulfide nano-particles were synthesized from basic cadmium solution strongly complexed by amine. Thioacetamide (CH<sub>3</sub>CSNH<sub>2</sub>) decomposes homogeneously in basic solution to form  $S^{2-}$  which, in presence of complexed metals such as amine complexed cadmium, induces the precipitation of the metal sulfide [1, 2, 25-27]. The formula of the reaction is as follow:

$$Cd^{2+} + CH_3CSNH_2 + H_2O \rightarrow CdS \downarrow + CH_3C(O)NH_2 + 2H^+$$
(3-2)

Two routes have been followed to prepare the CdS powders and to mix it with the base glass powders. The details of the synthesis are presented in the following.

# 3.1 Static way to prepare CdS-glass mixture

For the first try, CdS was synthesized in a 500-ml beaker containing 0.5 mol/L in  $CH_3CSNH_2$ , 1 mol/L in  $NH_4Cl$ , and 0.1 mol/L in  $CdCl_2$ . The droplets of concentrated ammonia were slowly added into the solution at room temperature without stirring. The solution is then left to stand to complete the precipitation of CdS about 1 g.

Fig.2.5 presents the reaction process. The color of the solution turned from colorless to yellow in 2 minutes. Then, the solution became turbid with prolonged reaction time. Hours later, the CdS began to precipitate. The solution was completely precipitated after 40 hours, as presented in the photo. The obtained particles were washed by de-ionized water three times to completely wash off the reaction solution and then by ethanol three times to wash off the H<sup>+</sup> ions. The preliminary powders were dried in an oven at 150°C for about 12 hours, leading to yellow powders. The powders obtained are denoted as CdS-1 in the following text.



Fig.2.5 Synthesis of the CdS-1 powder according to the time of reaction

Thermal treatment under H<sub>2</sub>S flow was then conducted for CdS-1 to improve its crystallinity. Powders were placed in a silica tube, which can be heated by a furnace up to 600°C, similar work has been done by Chlique [28]. The melting point of the CdS crystal is 1750°C. The temperature chosen to perform the recrystallization should be around 0.35% of the melting point. It should also consider the pyrolysis temperature of H<sub>2</sub>S, which is around 600°C [29]. The running gas, nitrogen and following a gas mixture (90% nitrogen and 10% H<sub>2</sub>S) was introduced into the tube from one end [28], and guided out to the other end into a KOH solution which was used to absorb the residual H<sub>2</sub>S gas. The progress of the sulfidation

is schematized in Fig.2.6. During the first 15 minutes, a nitrogen flow passed through the tube to get rid of the air. During the following 15 minutes the gas mixture of  $N_2/H_2S$  was introduced to fill the silica. Then the tube was heated up to 600°C within one hour. The reaction between powders with  $H_2S$  lasted for two hours, and was then cooled down to room temperature.



Fig.2.7 XRD patterns of the CdS-1 before and after the sulfidation; PDF card 41-1049 CdS (hexagonal); PDF card 75-1546 CdS (cubic).

XRD analysis was performed to identify the phase present in the synthesized powders. As shown in Fig.2.7, the pattern of the powder before sulfidation consists of two kinds of diffraction peaks. The broad peaks at 26.5°, 44.0° and 51.9° are in good accordance with the three strongest peaks of cubic CdS (PDF card 75-1546). The broadening of the peak implies the small crystal size or poor crystallinity of the cubic CdS in CdS-1. Additionally, the sharp peaks at 38.2°, 44.4° and 64.8° correspond neither to the two possible phases of CdS (cubic and hexagonal). It is hard to exactly identify the structure of the generated phase. Significant changes from the XRD pattern can be observed after sulfidation in Fig.2.7. The pattern after sulfidation corresponds well to that of hexagonal CdS (PDF card 41-1049). Therefore, a phase transition from cubic to hexagonal occurs during the 600°C thermal treatment. Moreover, all the peaks are sharp and intense, indicating a growth of crystals and the improvement of the powder crystallinity during the sulfidation process.



Fig.2.8 SEM photos of the powders CdS-1 before (a,b) and after (c) the sulfidation on the scale of 1 µm, and the mixture 90 mass% G20+ 10 mass% CdS-1 (d,e)

Fig.2.8 shows the SEM photos of the powders before (a, b) and after the sulfidation (c). The size of the primary particles of the sample before sulfidation is tens of nanometers. This is in agreement with the broad diffraction peaks in XRD patterns which could be previously observed. In the magnified picture (b) it can be seen that the primary particles are of spherical shape. However, these particles are heavily aggregate up to several micrometers. The aggregation might occur during the precipitation due to the high specific surface of the particles and the long time aging. After sulfuration, the size of the particles increases to hundreds of nanometers as shown in Fig.2.8 (c). Meanwhile the form of the particles turns to more complete crystal structure.

Then, the glassy powders which were made by melt-quenching technique and grinded into powders by mechanical milling were thoroughly mixed with the sulfured CdS-1 powders using a planetary grinder. The ratio between the glassy powder and CdS powder is 9:1 (in mass). The mixture was grinded for about one hour at a low rotation speed (200 rpm) to avoid breaking the CdS crystals into amorphous phase [30]. The mixture's XRD pattern is shown in Fig.2.9. The broad peaks correspond to the pattern of the G20 glassy phase, while the sharp peaks belong to hexagonal CdS crystals. The SEM photos of the mixtures are shown in the above Fig.2.8 (d), (e). As observable in Fig.2.8 (d), the big grains (tens of micrometers) are glassy powders. These big size grains like in Fig.2.8 (e) are still presented at the last step of the process demonstrating that aggregates have not been grinded into smaller size during the mechanical milling.



Fig.2.9 XRD patterns of the  $Ge_{20}Sb_{12}S_{68}$  base glass and of the powder (90 mass% G20 + 10 mass% CdS-1) after mixing by planetary grinder.

3.2 Stirring way to prepare CdS-glass mixture

In the second process, CdS was synthesized in a 500-ml beaker and be stirred at room temperature. The starting solution contained 0.5 mol/L CH<sub>3</sub>CSNH<sub>2</sub>, 1 mol/L NH<sub>4</sub>Cl, and 0.1 mol/L CdCl<sub>2</sub>. The pH was adjusted around 9.5 by buffer solution formed by 1 mol/L NH<sub>4</sub>Cl and concentrated ammonia [26]. The reaction was lasted for 40 hours. This sample was called CdS-2.

Fig.2.10 shows instruments used for synthesis of CdS-2 powder. Magnetic stirring was used to obtain crystals with homogenous size. The centrifuge can help the turbid liquid to precipitate rapidly, that prevents the aggregation during long time aging which happened in the static way. The precipitates were washed three times with deionization water and three times with ethanol.



Fig.2.10 Instruments used for the synthesis of CdS-2 crystals, magnetic stirring (left); centrifuge (right)

In Fig.2.11, the XRD pattern shows that CdS-2 powder is mainly constituted of pure hexagonal CdS phase. Additionally, an evident broadening of the diffraction peaks is observed. It implies a small primary particles size of powder. On calculating by the XRD analyze software Jade, according to (1 0 1) peak, the size of the CdS crystal is around 12 nm.



Fig.2.11 XRD pattern of the CdS-2 powder, compared with the PDF card 41-1049 CdS (hexagonal)

The particles' morphology is revealed in the SEM photos (Fig.2.12 (a), (b)). The size of the aggregate particles is homogeneously distributed of about 100 nanometers. Comparing with Fig.2.8 (a), it can be seen that the aggregation of CdS particles is much lighter using the stirring way of investigation. The addition of buffer solution together with stirring can prevent a high local pH value due to the inhomogeneous addition of the base. The sudden addition of the base without stirring can create a large number of nuclei locally. This results in so small particles that they are more likely to aggregate.

Before being dried in an oven, the CdS powder was mixed with the glassy powder (90 mass% G20) in ethanol and stirred to well homogenize the mixture. Using this way, the CdS crystals will be separated by the glassy powders. The mixture is stirred until the ethanol is fully evaporated and they were dried in an oven at 70°C for 12 hours to volatilize the residual ethanol adsorbed on the powder surface.

Fig.2.12 (c) and (d) show the SEM photos of the mixture. The big size particles are the glassy powders while the smallest ones, about dozens of nanometers to one hundred nanometers, are the CdS crystals. The key point is that not much aggregate are observed in Fig.2.12 (c) which should guarantee to reduce the scattering.



Fig.2.12 SEM photos of the CdS-2 powder (a), (b); and the mixture of powder of 90 mass% G20 + 10 mass% CdS-2, (c), (d)



Fig.2.13 XRD patterns of mixture powders (90 mass% G20 + 10 mass% CdS-2) compared with the G20 glass, and PDF card 41-1049 of CdS.

XRD diffractogram of the mixture powder is compared with the G20 glass in Fig.2.13. As observable, the form of the X-ray pattern shows that the major part of the mixture powder is amorphous. This corresponds well with the photo presented in Fig.2.12 (c). The small quantity and size (shown in Fig.2.12 (c) and (d)) of CdS particles do not permit to observe clear diffraction peaks at 25°, 26° and 28°, but only a broad peak located between 25° and 30°.

#### 4. Sintering of Ge<sub>20</sub>Sb<sub>12</sub>S<sub>68</sub>-CdS glass-ceramics by SPS and HP

Spark plasma sintering (SPS) and hot pressing (HP) techniques were used to compact the samples. The different parameters of sintering are listed in the Table2.2. Samples CC369 to CC371 were sintered close to  $T_g$  by SPS. Sample CB115 was made in order to know the best conditions to synthesize CD213 and CD214 by HP. Sample CD213 and CD214 were sintered at different temperatures for different durations to get the densest sample. Meanwhile, sample CD001 was made by re-melting the mixed powders in a sealed silica tube under vacuum at 750°C for about 5 hours.

| Name  | composition   | Method         | т (°С) | Press<br>(Mpa) | Time<br>(min) | Liner  | Thickness<br>(mm) | Density<br>(g/cm <sup>3</sup> ) |
|-------|---|----------------|--------|----------------|---------------|--------|-------------------|---------------------------------|
| CC369 | G20+10%CdS-1  | SPS            | 330    | 50             | 10            | Та     | 0.81              | 3.23±0.012                      |
| CC370 | G20+10%CdS-1  | SPS            | 320    | 50             | 5             | Papyex | 1.16              | 3.19±0.023                      |
| CC371 | G20+10%CdS-1  | SPS            | 320    | 50             | 5             | Та     | 1.06              | 3.21±0.022                      |
| CB115 | G20(Ge <sub>20</sub> Sb <sub>12</sub> S <sub>68</sub> ) | HP             | 370    | 31             | 240           | BN     | 0.72              | 3.13±0.021                      |
| CD213 | G20+10%CdS-2  | HP             | 385    | 31             | 240           | BN     | 0.67              | 3.23±0.004                      |
| CD214 | G20+10%CdS-2  | HP             | 380    | 31             | 420           | BN     | 0.56              | 3.24±0.004                      |
| CD001 | G20+10%CdS-2  | Melt-quenching | 750    |                | 300           |        | 0.74              | 3.26±0.008                      |

Table 2.2 Parameters of the samples made by HP and SPS

### 4.1Properties of the samples sintered by SPS

### 4.1.1 Optical transmission

The transmission curves of the samples sintered by SPS are presented in Fig.2.14. Those samples of about 1 mm thickness were sintered at different temperature with a different duration and then polished on both surfaces. A typical photo of the samples is shown in the inset of Fig.2.14 while the base glass without CdS is red colored and has a maximum transmittance of 75% after sintering. All the sintered samples are black and present a low

transmittance (30% around 10  $\mu$ m). Unfortunately these glass-ceramics are too opaque in the near infrared region to perform the second order non-linearity measurement.

The absorption peaks at 4  $\mu$ m, 4.26  $\mu$ m and 6.63  $\mu$ m are caused by O-H, CO<sub>2</sub>, and H<sub>2</sub>O respectively. Strong scatterings which increased with shortening of wavelength cause the low transmission of as-made glass-ceramics. These scatterings can be ascribed to several parameters: presence of crystals or impurities, of bubbles or a difference of refractive index between the glassy grains and the grain boundaries.



Fig.2.14 Transmission curves of the CC369, CC370, CC371 samples compared with the base glass from 0.5  $\mu$ m to 12  $\mu$ m; photo of the sample sintered by SPS (inset photo)

# 4.1.2 X-ray diffraction

It is known that by varying the sintering process, phase changes can occur. Thus, in order to see if other crystals are formed, the samples were observed by X-ray diffraction. Fig.2.15 presents their XRD patterns. The hexagonal CdS phase can be observed after sintering and no other crystals are detected. The relative intensity between the diffraction peaks changes, indicating a partial orientation of the CdS crystals which might be attributed to the uniaxial pressure applied during the sintering, especially in the sample CC370, the most intense peak is 002-oriented according to the phase CdS (PDF card 41-1049). Compared with the diffraction pattern of the base glass, the XRD patterns of the sintered samples show the

same shape, except for the peaks belonging to CdS. It means that after sintering, the samples is still composed of amorphous major phase with hexagonal CdS particles dispersed inside.



Fig.2.15 XRD patterns of the CC369, CC370, CC371 samples compared with the initial powders (G20+10 mass% CdS-1) and base glass; PDF card 41-1049 CdS (hexagonal)

## 4.1.3 Scanning Electron Microscope

The microstructure of the three samples was observed by SEM. For sample CC369, crystals of tens of microns can be seen from the photo of the Fig.2.16 (a). Moreover, while the glass seems to be perfectly compact (smooth surface) without defects, the inner part of grains present residual porosity, meaning that the glass viscosity reached during the sintering process is not sufficient to fill in all the voids. The CdS aggregate can also be found in photo (b). The size of aggregate (40  $\mu$ m) is larger than that of initial powder (10  $\mu$ m) showing a second step of crystals aggregation during the sintering process.



Fig.2.16 SEM photos of the CC369, CC370 and CC371 samples after sintering

Sample CC370 presents smooth interface between the glass and crystal in the photo (a). Besides that, CdS aggregates can also be found in CC370 (b). These CdS crystals are still of small size, about 550 nm, but the aggregates are of about 10 micrometers. These aggregates are also observed in the sample CC371 as shown in the SEM image.

According to the revealed microstructure, it is reasonable to attribute the low transmission to the strong scatterings of the defects in the samples. These defects include the

fissures between the uncompleted sintered glassy powders, the micrometric CdS crystals, and especially the holes in the CdS aggregates.

This low transmission might also be attributed to the pollution by carbon. The powders were sintered in a graphite mold and coated by tantalum layer or papyex on both sides to prevent the diffusion of carbon from the mold. With the increasing temperature during the sintering, the carbon could diffuse into the samples. However it is difficult to detect the diffusion of carbon since the element C was too light to measure. Not much difference exists among these three samples. They all present smooth surface but include fissures and big grains. So, sintered at 320°C during 5 minutes seems to be enough. But the CdS particles need to be less in size, less aggregate and dispersed more homogeneously.

In conclusion, the key point to increase the transmission of the glass-ceramic is to reduce the scattering. This can be achieved by reducing the aggregation of CdS crystals and by avoiding the diffusion of carbon within the glassy matrix. WC mold is therefore expected to be used in future experiments.

# 4.2 Properties of the samples sintered by Hot Pressing

# 4.2.1 Introduction of Hot Pressing (HP)

Hot pressing is a high-pressure, low-strain-rate powder metallurgy process for forming of powder at a temperature high enough to induce sintering and creep processes. This is achieved by the simultaneous applications of heat and pressure. Photo of the homemade HP equipment and the stainless steel mold are presented in Fig.2.17. The homemade HP machine includes the heating controller, the pump, the vacuum chamber, the pressurized system, cooling water and protective gas which was not used in this chapter.

The powder was put in a stainless steel mold with an inner diameter of 20 mm. It was placed between two removable pistons. The protective plates and/or powders BN were used to avoid the diffusion pollution from the piston to the powders. The mold was pumped in the vacuum chamber using a load of 1 MPa for about half an hour and then was heated to a certain temperature with the heating rate of 10°C/min. Then, one launches the pressurized system, and a pressure of 31 MPa was applied. After a few hours, the pressure is unloaded

and the heating system is stopped in order to let the mold slowly cool down to room temperature.



Fig.2.17 The scheme of Hot Pressing set-up

## 4.2.2 Optimal HP temperature

The temperature of pressing was determined by performing experiments on the glassy powders first. Thus, the G20 glass (Ge<sub>20</sub>Sb<sub>12</sub>S<sub>68</sub>) was synthesized first by the conventional melt-quenching method, and then milled by mechanical milling machine into powder. The glassy powder, about 2 g, was put in a stainless mold with a diameter of 20 mm. At the two ends, BN powders were applied to prevent the pollution from the mold and to prevent the sample sticking with the mold. As already seen in Fig.2.2, the  $T_g$  of the base glass G20 is of about 270°C. The temperature of HP was set at  $T_g$ + 100°C. i.e. 370°C. The applied pressure is of 31 MPa. After 4 hours of HP, the sample CB115 was obtained. The temperature chosen is a compromise because higher temperature presents the risk of crystallization during the sintering, while a lower temperature cannot be sufficient to reach a viscosity low enough to shape the sample.

A picture of the CB115 sample before polishing is presented in Fig.2.18. The color of the two sides of the sample is different. On one side, it presents brown color and is glass-like while the other side presents yellow color and is ceramic-like. This difference might be caused by inhomogeneous temperature field in the furnace under vacuum. It is found that the ceramic-like surface can be removed easily by polishing.



Fig.2.18 Optical transmission curve of the sample CB115 after polishing of the ceramized surface compared with the glass G20

The transmission curve of CB115 sample after polishing compared with the transmission of glass made by melt-quenching in Fig.2.18 shows that scatterings occur both in the short and long wavelength ends. Different causes of scatterings can be mentioned in a first step: generation of crystals and/or holes of inhomogeneous size, grain boundaries present different refractive index than the glassy grains. Moreover, the smaller thickness (0.72 mm) of CB115 causes its cut-off edge at longer wavelength than the base glass (1.3 mm), but does not affect the optical band-gap.

To further identify the morphology of the CB115 glass sample, SEM images of sample obtained without polishing are presented in Fig.2.19. The different morphologies previously described can be clearly observed on SEM images. On the glass-like side, a low densification of the material has occurred as a large amount of holes are detected (Fig.2.19 (b)). According to the fact that the sintering process has not been completely established, one can guess that the sintering temperature reached on this side is not high enough to reach a enough low viscous flow ( $10^7 \text{ Pa} \cdot \text{S}$ ) to reduce surface energy of a porous compact [31].

On the ceramic-like side, crystals can be observed within a thin layer on the surface (Fig.2.19 (d)). Beneath this layer, a dense glass phase is identified (Fig.2.19 (c)). The

temperature reached on this side is close to that of the crystallization temperature of the base glass ( $T_x$ =380°C) and consequently uncontrollable crystals are formed. Fortunately, only a thin lay of crystals is generated. So, temperatures a little higher than 370°C were tried to sinter the samples containing CdS crystals reaching a low enough viscous flow to fully sinter the glass.



Fig.2.19 SEM photos of the two sides of sample CB115, photos (a) and (b) are the glassy side; photos (c) and (d) are the yellow side, photo (d) is an enlarged view of the crystal region of the photo (c)

Thus, the base glass and CdS powders, mixed in ethanol and dried in an oven at 70°C, were sintered at two different temperatures, 380°C and 385°C. The pressure is maintained at 31 MPa. The HP lasted for 7 hours and 4 hours respectively. The obtained glass-ceramic samples are denoted as CD213 (385°C, 31MPa, 4h) and CD214 (380°C, 31MPa, 7h).

In parallel to this way of synthesis, the mixed powders (base glass and CdS crystals) were re-melted in a silica tube using the melt-quenching process on heating up to 750°C for 5 hours. The obtained glass-ceramic is denoted as CD001. In fact, this temperature of synthesis has been chosen as it is assumed that CdS particles would not be melt at 750°C because its

melting point is 1750°C. However, the main risk of this type of synthesis is the agglomerate of CdS particles at high temperature in the melt bath or even a relatively bad homogeneity of the glass-ceramic because of the difference of density between the crystals ( $\rho$ =4.82 g/cm<sup>3</sup>) and the glass ( $\rho$ =3.14 g/cm<sup>3</sup>) which may lead to a sedimentation of the crystals.

### 4.2.3 Optical transmission

To well detect the optical signals, glass-ceramic samples were thinly polished to 0.5 - 0.7 mm thick. The photos of the samples and their transmission curves are presented in Fig.2.20. Samples CD213 and CD214 are black, even if the sample CD001 is red colored it is not transparent for the naked eyes showing some strong light scatterings.

It can be seen from the transmission curves that, before 1  $\mu$ m, optical signals through CD213 and CD214 can be partially detected. We proposed that these scatterings could be attributed to the defects (e.g. the pores) and CdS particles in the samples which will be shown later in the SEM images. Absorption peak situated at 3.2  $\mu$ m is the absorption of -OH; at 4  $\mu$ m is the absorption of S-H; 4.3  $\mu$ m corresponds to the absorption of CO<sub>2</sub>; 6  $\mu$ m, 7.2  $\mu$ m and 7.5  $\mu$ m are the absorption of H<sub>2</sub>O. Broad band of absorption located from 8  $\mu$ m to 10  $\mu$ m might be a combination effects from H<sub>2</sub>O, carbon, etc. One can notice that these impurities directly come from the introduction of CdS within the base glass, as this one presented almost a perfect transmission curve after sintering. These impurities are caused by the residual ethanol which helped to well mix the CdS crystals with the base glass powders.

On comparing the curves of CD213 and CD214, the maximum transmission of CD214 achieves 60% at 10.5  $\mu$ m, a little higher than that of CD213. The longer time used for the CD214 sample can be high enough to improve the densification of the material, reducing the scatterings due to the presence of holes at the interface between the glassy matrix and crystals. The transmission curves of both CD213 and CD214 are very characteristic of usual chalcogenide glass-ceramics [32] containing submicron crystals as a slight increase of the transmittance is observed with increasing wavelengths. However, the non linear shape can be affected by the strong absorption bands due to impurities of water and oxygen.



Fig.2.20 Transmission curves of the samples CD213 and CD214 sintered at 385°C and 380°C compared to the base glass and the CD001sample

CD001 sample was made to observe what the transmission should be if no pores present in the sample using the conventional technique of synthesis. Sample CD001 is much more transparent than the other two samples made by hot pressing, having a maximum of transparency almost identical to the base glass. The loss of transmittance in the visible and near infrared region can be attributed to the scattering of CdS crystals. However, the strong absorptions at 2.8  $\mu$ m, 4  $\mu$ m, 6.3  $\mu$ m and 7.6  $\mu$ m respectively are attributed to O-H, S-H, H<sub>2</sub>O coming from CdS crystals. Further experiments by perfectly drying the CdS crystals from residual water have to be performed at higher temperature than 70°C for the whole day in order to fully evaporate the ethanol.

### 4.2.4 X-ray diffraction

XRD experiments were performed on CD213, CD214 and CD001 samples and their patterns are presented in Fig.2.21. For the sample CD214, the small peaks at 26.52° and 28.26° belong to CdS while they are well observable, but cannot be identified clearly in the initial powders. It means that CdS crystals grew larger and its structure performs better after

sintering. But for samples CD213 and CD001, their patterns are slightly changed compared to the CD214 glass-ceramic. Besides the peaks belonging to CdS at 26.52° and 28.26°, peaks belonging to Cd<sub>4</sub>GeS<sub>6</sub> crystals at 25.2°, 26°, 29.11° and 30.56° are observed in CD213. Thus, a temperature of 385°C used for sintering is the highest temperature to retain the CdS phase. At this temperature, the base glass reacts with the CdS crystals leading to the Cd<sub>4</sub>GeS<sub>6</sub> phase which presents a monoclinic structure, Cc space group [10]. The emergence of this new phase is not prohibitive in concern of making non linear glass-ceramics as M. Guignard et al have already demonstrated the existence of non linear signals with such a crystalline phase [10]. Thus, concerning the CD001 sample, even re-melting under the melting point of CdS, the reaction between base glass and CdS has occurred. The Cd<sub>4</sub>GeS<sub>6</sub> crystals are mainly presented in the final glass-ceramic.



Fig.2.21 XRD patterns of CD213, CD214 and CD001 samples compared to the Ge-Sb-S base glass and the initial mixture powder synthesized by the second route

#### 4.2.5 Scanning Electron Microscope

SEM images of sample CD214 (380°C, 31MPa, 7h) are presented in Fig.2.22. An overall looking on Fig.2.22 (a) taken with a magnification of 300 shows the presence of big crystals and of grain boundaries in light color. The EDS measurements have demonstrated these big crystals are SiO<sub>2</sub> coming from dust of the silica tube when opened (the white point shown in Fig.2.23 (a)).
The grain boundaries can be further seen from Fig.2.22 (b) with a magnification of 20000. As observable in this picture, CdS crystals are mainly concentrated between the glassy grains as in the initial powder mixtures, CdS crystals were mainly adsorbed on the surface of the glassy grains. Details among the glass powders and crystals are clearly observed from Fig.2.22 (c) and (d). The Fig.2.22 (c) presents a region not perfectly sintered containing glass and crystal grains. A magnification of 10000 (Fig.2.22 (d)), permits to know that the glass does not fill in perfectly the crystals aggregate. In fact, among the crystals, holes can be seen, demonstrating that a temperature of 380°C was not high enough to making the glass viscous flow through the crystals. It seems that the glass powders start to go through the crystals, but the energy was not high enough.



Fig.2.22 SEM photo of sample CD214 on the scale of 100  $\mu m$  and 1  $\mu m$ 

More interesting are the pictures observed during EDS measurements (Fig.2.23). The composition of the white point in Fig.2.23 (b) is 12%Ge-18%Sb-70%S while the grain boundaries, see the white point of Fig.2.23 (c), are composed both of crystals and glasses. Its composition is 13%Ge-10%Sb-67%S-10%Cd.



Fig.2.23 EDS images of the CD214 sample measured at different places (the white points)

The low homogeneity of the microstructure at a micro scale causes scattering and consequently affects a lot the transmittance.

The morphology of sample CD213 (385°C, 31MPa, 4h) is presented in Fig.2.24. Boundaries formed by glass grains and CdS crystals are clearly observed. The Fig.2.24 (b) also shows that the interspaces between glass and crystals are almost completely vanished.

As observable in Fig.2.21, sintering the mixed powders at  $385^{\circ}$ C makes the sample denser and with less defects, but it leads to the formation of heterogeneous crystals in the matrix as a mixture of CdS and Cd<sub>4</sub>GeS<sub>6</sub>. The duration of HP (4 hours) might be too long. Thus, another sintering way using SPS can reduce the sintering time to several minutes, which should permit to control the crystallization process efficiently.



Fig.2.24 SEM photos of sample CD213 sintered by HP sintering on the scale of 10  $\mu$ m and 1  $\mu$ m

#### 4.2.6 Non-linear analysis

Second order non-linear measurements were carried out on sample CD213, CD214 and CD001 by Y. Quiquempois and G. Martinelli in the IRCICA Research Institute. The measurement instrument is already introduced in the last chapter.

As demonstrated in Fig.2.20, these three samples have a very low transmittance at 0.9  $\mu$ m and the extinction of the glass-ceramic is very important when measuring the second harmonic signals at 0.9  $\mu$ m. So, it can be foreseeable that the signals should be very weak. The practical Maker Frange shown in Fig.2.25 indicates that the signals detected from these samples were indeed very weak as the signals detected at 0.9  $\mu$ m are strongly extinct which makes the estimation of the susceptibility very difficult. The shape of the curves is typically the random generation of second harmonic pattern with a typical center plate and a signal decrease at large angles that Fresnel coefficients resulting.

For comparing, Maker frange patterns of the quartz and CD001 samples are presented in Fig.2.26. The black curve represents the Maker frange patterns obtained from standard sample, the quartz. And the red one is the Maker frange patterns obtained from sample CD001. It is important to note that their intensities are not in the same order of magnitude.

For the moment, the transmittance at 0.9  $\mu$ m is so low that it is difficult to estimate the real susceptibility through the weak SHG signals. Improvement of the transmission at short wavelength is necessary for further researches. Otherwise, they can also be useful in the infrared region while using the CO<sub>2</sub> laser with the principal wavelength bands centering around 10.6  $\mu$ m.



Fig.2.25 Maker frange patterns of the sample CD001, CD213 and CD214



Fig.2.26 Maker frange patterns of the sample CD001 compared with the reference one quartz

## 5. Conclusion

In this chapter, CdS was found to be an ideal material to generate second order nonlinearity phenomenon. Because of its non centro-symetric structure it can present large second order optical nonlinear coefficient.  $Ge_{20}Sb_{12}S_{68}$  glass was chosen as an optimal base glass to be doped by CdS crystals.

CdS crystals were fabricated using two synthesis ways, one with static reaction and precipitation (CdS-1 crystals), the other one reaction occurred in a pH=9.55 solution with stirring and particles are precipitated with centrifugation to avoid further growing (CdS-2 crystals). According to the SEM photos, the size of the CdS-1 crystals was not homogeneous ranging from tens of nanometer to micrometers. Different structures are also presented and they formed big size aggregates during the reaction process. CdS made by the second route is less aggregate, and its morphology is more uniform, about hundred nanometers and its hexagonal structure is well defined. The CdS-1 crystals, sulfurized at 600°C in the flow of H<sub>2</sub>S, were mixed with Ge<sub>20</sub>Sb<sub>12</sub>S<sub>68</sub> glass powder by mechanical grinding for one hour at a low rotation speed. However, even using this technique, the CdS aggregates cannot be grinded into smaller size. The CdS-2 crystals (before drying) were mixed with glassy powders with the help of analysis ethanol by stirring. Crystals were adsorbed on the glass powders decentralized.

Mixed powders were sintered by Spark Plasma Sintering and Hot Pressing separately at different temperature during different durations. Samples CC369, CC370 and CC371 made by SPS had low transmittance. The aggregates and the possible presence of carbon within the glass-ceramics caused strong scatterings. Unfortunately, these three samples were too opaque in the visible and near IR range to measure second order non-linear signal.

The maximum transmittance of sample CD213 and CD214, sintered by HP, achieves 60% at around 10.5  $\mu$ m. But at shorter wavelength, their transmittance is relatively low, close to 30%. Before 1  $\mu$ m, there barely any signals. Strong scatterings are caused mostly by the holes formed among the glassy grains and CdS crystals. Besides, the inevitable contaminations from residual ethanol and air strongly affect the transmission. CO<sub>2</sub>, O-H, and H<sub>2</sub>O cause big optical absorption. While a temperature of sintering of 380°C does not seem to be sufficient to fill in perfectly the CdS aggregates, the sintering performed at 385°C can make sample denser but the matrix is unstable that forms Cd<sub>4</sub>GeS<sub>6</sub> crystals. It is difficult to control the

crystallization process during the sintering process. Thus, SPS technique using other molds such as WC should be experimented to enhance the transmission.

Finally, the last way investigated to form glass-ceramics was to melt the base glass and CdS crystals at a barely low temperature (750°C) in a sealed silica tube maintained under vacuum. The transmission of CD001 sample obtained using this process reaches 70%. It forms heterogeneous  $Cd_4GeS_6$  crystals, which was undesirable to enhance the non-linear phenomenon even it showed non-linear signals.

Strong absorption at 0.9  $\mu$ m in sample CD213, CD214 and CD001 affects the second harmonic generation signals detection. Their Maker frange patterns represent well with the random generation of second harmonic, but their intensity is too weak to estimate the real susceptibility. Their transmittances should be improved in the further research.

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Chapter III: Mechanical milling for synthesizing chalcogenide glass GeS<sub>2</sub> and glass-ceramic Ge<sub>15</sub>-Ga<sub>20</sub>-S<sub>65</sub>

| 1 Introduction  | - 74 - |
|---|--------|
|   | /4 -   |
| 2. Mechanical synthesis   | 75 -   |
| 2.1 Background  | 75 -   |
| 2.2 Technical considerations  | 76 -   |
| 3. Synthesis of the glass-ceramic Ge <sub>15</sub> -Ga <sub>20</sub> -S <sub>65</sub> | 79 -   |
| 3.1 Synthesis by conventional melt-quenching technique                                | 81 -   |
| 3.2 Synthesis by mechanical method  | 83 -   |
| 3.2.1 Experimental preparation  | - 83 - |
| 3.2.2 The color variation of the powders  | - 83 - |
| 3.2.3 X-ray diffraction of the powders  | 84 -   |
| 3.2.4 Thermal analysis of the powders   | 85 -   |
| 3.3 Ge <sub>15</sub> Ga <sub>20</sub> S <sub>65</sub> glass-ceramics made by SPS      | 87 -   |
| 3.3.1 X-ray diffraction   | 87 -   |
| 3.3.2 Optical property  | 89 -   |
| 3.3.3 Scanning Electronic Microscope  | 91 -   |
| 3.3.4 Transmission Electron Microscope  | - 93 - |
| 4. Synthesis of the GeS <sub>2</sub> glass  | 95 -   |
| 4.1 Experimental preparation  | 95 -   |
| 4.2 The color variation of the powders  | 95 -   |
| 4.3 X-ray diffraction of the powders  | 96 -   |
| 4.4 Thermal analysis of the powders   | 97 -   |
| 4.5 Granulometry analysis of the powders  | 99 -   |
| 4.6 Synthesis of bulk GeS <sub>2</sub> glasses by SPS                                 | 101 -  |
| 4.6.1 X-ray diffraction   | 101 -  |
| 4.6.2 Optical properties  | 102 -  |
| 4.6.3 Scanning Electronic Microscopy analysis   | 103 -  |
| 5. Conclusion   | 105 -  |

| 6. Reference 1 | 0 | 7 | - |
|----------------|---|---|---|
|----------------|---|---|---|

### 1. Introduction

In the last two chapters, base glasses were made by traditional melt-quenching technique. The traditional synthesis of chalcogenide glasses is performed under a high vacuum silica tube. Such kind of silica tube which is not reusable costs approximately 30% of the final glass [1]. In addition, the raw materials need to be melted at a temperature above their melting-point and hold for hours to ensure that all the raw materials have reacted homogeneously. For some special glasses, the synthesis needs to be performed at a very high temperature. For example, synthesis of sulfide based glasses containing germanium has to be performed upper than 900°C, which is highly energy consuming. Moreover, chalcogenide glasses can be produced with a limited diameter because of the low quenching rate reached during quenching. Additionally, glasses synthesized by melt-quenching are limited by the diameter of silica tube and their thermal stability. So, it is necessary to develop an entirely new way to synthesize chalcogenide glasses in order to reduce the cost of chalcogenide glasses, save energy and enlarge the glass forming region.

Mechanical synthesis combined with Spark Plasma Sintering (SPS) technique was used to prepare glass-ceramics in the last two chapters. In this chapter, raw materials weighted in stoichiometric ratio are mechanical milled directly for certain duration to achieve a homogeneous amorphous phase. Following with sintering by SPS, a chalcogenide glass or glass-ceramic can be obtained in a few minutes. Mechanical milling permits to obtain the amorphous chalcogenide powders at room temperature due to the high mechanical energy of this process. Meanwhile, fast heating rate reached by SPS prevents the glass from undesirable crystallization. Moreover the glass powders are shaped in a graphite mold that can fit the desired size of samples [2]. Glass compositions out of the conventional glass forming region and big dimension samples could be synthesized using this technique, as the mechanical energy given to the system appears higher than the classical quenching technique.

Thus, in this chapter, the study on the preparation of  $Ge_{15}Ga_{20}S_{65}$  glass-ceramics and  $GeS_2$  glasses using the mechanical synthesis technique will be presented. The Ge based glasses usually show good thermal stability and good mechanical properties, but also need a relatively high synthesis temperature with conventional method [3]. The incorporation of Ga in the Ge–S system improves the solubility of rare-earth ions, which makes this glass a good matrix for luminescence applications [1, 4-6]. However, the content of Ga is limited by the glass forming ability [7]. These problems are expected to be solved by using mechanical

synthesis to prepare these glasses. For each glass, the condition of mechanical milling is firstly studied to obtain the desired amorphous particles with a certain size distribution. Then the parameters of SPS sintering are controlled to optimize the optical property of the products.

### 2. Mechanical synthesis

### 2.1 Background

Mechanical synthesis is a powder processing technique that permits the production of a homogeneous material from the blended elemental powder mixtures. It is also known as highenergy ball mills in literatures. Different devices can be used to conduct the mechanical mills, such as shaker mills, planetary ball mills, attritor mills, cannon-ball type mills, etc. Despite of different configuration, capacity and milling efficiency, all these devices have a common feature: using the mechanical motion of milling balls to transfer the mechanical energy to the milled materials [8].

Mechanical synthesis was firstly developed by Benjamin and his colleagues in order to synthesize the oxide dispersion strengthened nickel-based superalloys for gas turbine application around 1966 [9]. Three steps are involved in their technique. Firstly, the raw materials are combined in a ball mill and ground to a fine metallic powder containing homogeneously dispersed oxide particles. A hot pressing process is then applied to simultaneously compress and sinter the powder. A final heat treatment helps removing the residual stress. The application of the mechanical synthesis was later extended to even wide fields in the role of a non-equilibrium processing technique. This technique has been developed to synthesize a variety of metastable phases including supersaturated solid solutions, crystalline and quasicrystalline intermediate phases and amorphous alloys [8]. Thanks to the high mechanical energy induced during the processing, the mechanical synthesis has also been used to activate the solid state reaction at lower temperature compared with classic synthesis methods [10-12]. Another important application of mechanical synthesis is for synthesizing certain components of lithium-ion battery, including the nanocrystalline cathode materials such as LiMnPO<sub>4</sub>, xLi<sub>2</sub>M'O<sub>3</sub>.(1-x)LiMO<sub>2</sub> (M'=Mn, Ti; M=Mn, Ni. Co) [2, 13], the well crystallized ultra-fine carbonaceous anode material [14], and the novel amorphous solid electrolytes with extended composition range which was achieved by mechanical synthesis [15].

- 75 -

In general, there are two different processing of powder particles in high-energy ball mills: mechanical milling and mechanical alloying. For mechanical milling, the frontal impact and tangential shock of the milling ball induce hydrostatic and shear stress in the milled material. This leads to work hardening and fracture of the milled material which decreases the particles size. On the other hand, the new surface increases the surfaces energy of the system, leading to the aggregation of the created particles, which is also known as cold welding for metallic milled material. As a result of the balance between the two opposite processes, a limited particles size is reached after a certain time of milling. At this stage, the larger particles reduce the size while the smaller particles increase the size, which narrows the size distribution. An addition effect of mechanical milling is the mechanical disordering. Large amounts of plastic deformation results in the generation of a variety of defects structures and these destabilize the ordered nature of the lattice leading to the formation of a disordered nano-crystalline phase or amorphous phase.

Different from mechanical milling, when mechanical alloying occurs, material transfer happens during the mixing of powders, and a homogeneous phase will be finally obtained. With mechanical alloying, alloys or compounds can be synthesized from elemental starting materials at room temperature or at much lower temperature compared with other synthesis methods. Generally, two aspects result in this enhanced reactivity. Firstly, a refined microstructure, which could be down to nanometer dimension, can be obtained by the repeat deformation of the raw materials during mechanical alloying. This decreases the diffusion distances. Secondly, the formation of a variety of crystal defects such as dislocations, vacancies, stacking faults and increased number of grain boundaries enhances the diffusivity of the elements.

## 2.2 Technical considerations

The technique of mechanical synthesis used in this chapter is the planetary ball mill. For the process of mechanical synthesis, the elements in stoichiometric amounts are first put into a bowl with several grinding balls for helping fracturing the elements. The bowls then rotate at a rotation speed  $\omega$  on a tray moving in the opposite way at a speed  $\Omega$  (Fig.3.1 (a)). During the high speed rotation, two types of shocks occurs (Fig.3.1 (b)). The tangential shocks involve important friction phenomena, whereas frontal shocks induce compression. These shocks decrease the particle size of the milled materials down to a limited value, as a balance between the fracture and the aggregation is established. After, the milled powders are consolidated into a bulk shape by Spark Sinter Plasma or Hot Pressing along with heat treatment to obtain a desired property.

The properties of the powders obtained by planetary ball mills are intimately associated with several milling parameters, including the materials and size of the grinding medium, the speed and duration of the milling, the charge ratio and the filling rate of the milling bowl, and the milling atmosphere.

Grinding bowls and balls are made of different materials, like steel, alumina, oxide zirconium, agate or tungsten carbide, etc. Here tungsten carbide bowl and balls are used to match the hardness of germanium. The hardness of germanium is 6 Mohs, and that of tungsten carbide is 9 Mohs. But the hardness of other materials for grinding bowl and balls is lower or not higher enough than germanium. Even these elements will be milled to small particles at the order of micrometer in a few minutes with a high speed of rotation, the size of the elements should not be beyond that of the balls, especially for those high hardness elements.



Fig.3.1 (a) Scheme of planetary ball mills and (b) Two types of shocks occurring during the milling process.[8]

The speed and duration of the milling process should be considered. The faster the mill rotates, the higher the energy is transferred to the powders. But while increasing the rotation speed, the speed of the balls inside the mill will increase also. When a critical speed is

achieved, the balls will stick to the inner walls of the bowl and not fall down to collide with the powders [8]. Therefore, the maximum speed should be controlled so that the balls can fall down to collide with the powders efficiently and provide the maximum collision energy. More detailed considerations of the rotation speed involve the ratio between  $\omega$  and  $\Omega$  (the rotation speed of the bowl and the tray, respectively). A according to a modeling study [16], this ratio determines the predominant type of shock during the milling process. If this ratio is small, the type is qualified as chaotic: as soon as the ball strikes the wall, it is immediately pushed back. Inversely, when the ratio is high, the ball remains on the wall and the type is a friction mode.

The duration of the milling process is less important because the particles size of the raw materials decreases exponentially with time and generally reaches a small value of a few microns after a few minutes of milling. The criteria is that the duration should be as short as possible, since a long time milling increases the risk of contamination and the consumption of the energy.

The charge ratio specifies the ratio between balls and powders weights (or volume). A high charge ratio increases the frequency of the shocks between balls and powders, which favors the fracture of the powders and consequently reduces the duration of milling. Additionally, a too high charge ratio leads to a too large intensity of the milling, and an amorphization of the materials may occur. The filling rate is the ratio between the balls and powder volumes and the total volume of the bowl. If the filling rate is small, the production rate is small. On the other hand, if the filling rate is large, then there is not enough space for the balls to move around and so the energy of the impact is less. In our experiments, the volumetric charge ratio is 19:1 and the filling rate is 1:3.

To avoid the contamination from air, a controlled atmosphere can be used during the milling. It is better to mill in the protection of argon or helium but not nitrogen, which can react with powders to form nitrides. The glove box is usually repeatedly evacuated and refilled with argon gas, so it is an ideal place for carrying out the mechanical alloying. Milling with a liquid medium can usually obtain fine particles. New surfaces created during the milling process increase the surface energy that leads to aggregation of the particles. With the solvent molecules, which absorbed on the newly formed surface of the particles, the surface energy can be lowered and the possibility of aggregation becomes less. However the liquid

medium can introduce additional contamination. So, most of the mechanical alloying is carried out without the adding of liquid medium.

#### 3. Synthesis of the glass-ceramic Ge<sub>15</sub>-Ga<sub>20</sub>-S<sub>65</sub>

The systems studied in last two chapters, led to Ge-S and Ge-Sb-S-CdS glass-ceramics presenting second order non-linear properties, which can be applied for second harmonic generation, fiber-optic amplifiers, infrared lasers, etc... The essence of all these applications is to change the wavelength of the incident light and generate a new source of light [17, 18]. Glasses or glass-ceramics doped with rare-earth ions can also successfully achieve this aim through photo-luminescence. For example, the glasses belonging to the Ge-Ga-S system doped with Tm<sup>3+</sup>/Ho<sup>3+</sup> [13] emits at 2.02 µm due to the fluorescence from Ho<sup>3+</sup>:  ${}^{5}I_{7} \rightarrow {}^{5}I_{8}$  transition; moreover, Ge-Ga-S glasses doped with Dy<sup>3+</sup> or Pr<sup>3+</sup> could be used as materials for fiber-optic amplifiers at 1.3 µm [19, 20].

The glass-forming domain of  $GeS_2-La_2S_3$  for example extends to 60-100 mol% of  $GeS_2$  [21, 22]. With increasing  $GeS_2$  concentration in the glass, there is an evidence of phase-separation. Low solubility of rare-earth can result in clustering and crystallization which strongly limits their optical properties [23]. For the system Ge-As-S, the maximum solubility was approximately of 0.5 wt% of Ho<sub>2</sub>S<sub>3</sub> [24]. Compared with the system of other chalcogenide glasses based on germanium with the addition of As or Sb, Ge-Ga-S glasses have the largest rare-earth solubility [13, 19, 20], up to 1 wt% of  $Dy^{3+}$  or  $Pr^{3+}$  can be incorporated in Ge-Ga-S glasses [24].

Adding  $Ga_2S_3$  within a  $GeS_2$  glass network could help forming a more stable glassy structure [23, 25]. Because the bond strength [26] and the electronegativity difference [27] between Ge-S are lower than those of Ga-S, the dissociation of the Ge-S bonds is easier than the Ga counterpart. One sulfur originally connecting two  $GeS_4$  tetrahedral is transferred to Ga side to provide extra sulfur for forming  $GaS_4$  tetrahedral and forming Ge-Ge bonds. Meanwhile, the GaS<sub>4</sub> tetrahedral has one negative charge [25].

With an addition of rare-earth sulfide into the Ge-Ga-S system, it firstly dissociates the metal-metal bonds, and provides sulfur which acts as non-bridging sulfur to convert the energetically unstable  $S_3Ge(Ga)$ -(Ga)GeS<sub>3</sub> type connection to a more stable  $Ge(Ga)S_4$  tetrahedra. Then charge compensation by rare-earth ions becomes necessary due to the

presence of the  $GaS_4^{-1}$  tetrahedral. The rare-earth sulfide acts as a modifier and charge compensation. As a consequence, the  $Ga_2S_3$  provides a special structure unit for increasing the solubility of rare-earths [7, 23].

Fig.3.2 shows the glass-forming region in the Ge-Ga-S system [28]. Easy glass-forming by cooling in air is limited while up to 15% of Ga can be introduced in the glassy network using a violent quenching in ice water. A high content of Ga (larger than 20 at %) leads to the devitrification of the system and consequently to opaque ceramics. Thus, considering the fact that addition of Ga<sub>2</sub>S<sub>3</sub> can improve the rare-earth solubility of this system, it is interesting to study Ge-Ga-S glass with high Ga content. Although this kind of glass is very difficult to synthesize by traditional technique because of the high risk of crystallization when cooled down, it is expected that the mechanical synthesis is a possible way to achieve this goal. A composition Ge<sub>15</sub>Ga<sub>20</sub>S<sub>65</sub> out of the normal glass-forming domain when made by quenching in water, marked as a red point in Fig.3.2, was synthesized both by conventional melt-quenching technique and mechanical synthesis technique associated with SPS to check our hypothesis.



Fig.3.2 Glass-forming domain of the Ge-Ga-S system [28], (•) vitrified by cooling in air, (Δ) vitrified by quenching in ice water, and (•) crystallized.

# 3.1 Synthesis by conventional melt-quenching technique

The composition  $Ge_{15}Ga_{20}S_{65}$  was firstly synthesized by conventional method. Starting materials were commercial high purity Ga (5N), Ge (5N), and S (5N). The sulfur was purified to remove the impurities such as O-H. 10 g of raw materials were weighed in the glove box and transferred into a well dried silica tube with 9-mm internal diameter. Then the tube was sealed under a vacuum of  $10^{-3}$  Pa. The sealed tube was heated in a rocking furnace at 800°C and 900°C for 10 hours respectively. Then, the tube was quenched in water without a step of annealing process. The final products are shown in Fig.3.3.



Fig.3.3 Photos of the Ge<sub>15</sub>Ga<sub>20</sub>S<sub>65</sub> materials synthesized by conventional melt-quenching technique at 800°C (a) and at 900°C (b) for 10 hours.

As observable in the Fig.3.3 (a), the final material is constituted of two parts, the yellow part seems to be a part of mixture of glass and crystal while the black one shows a metallic luster, putting forward the evidence that there are still un-reacted starting materials. The Fig.3.3 (b) shows that the compound is completely crystallized after quenching. The phase diagram of the GeS<sub>2</sub>-Ga<sub>2</sub>S<sub>3</sub> binary system [27] is presented in Fig.3.4.



Fig.3.4 Phase diagram of the GeS<sub>2</sub>-Ga<sub>2</sub>S<sub>3</sub> binary system. The glass transition temperature  $T_g$  and the crystallization temperature  $T_x$  are also presented [27]. x=0.25 gives the critical concentration where intensive cristallisation occurs

According to the phase diagram in Fig.3.4 we can assume that the properties of the studied  $Ge_{15}Ga_{20}S_{65}$  glass are similar to  $0.43(GeS_2)-0.57(GaS_{3/2})$ , its liquidus temperature is about 890°C. This high liquidus temperature requires a much higher temperature of synthesize to make the reactants melt so that the reaction can be favored. But even reaching a temperature of synthesis of 900°C for 10 hours under vacuum is not sufficient to make a transparent glass, as demonstrated in Fig.3.3 (b), the presented ceramic is fully opaque in the visible as well as in the infrared region. Additionally, Fig.3.4 shows that the glass transition temperature and the crystallization temperature of  $0.43(GeS_2)-0.57(GaS_{3/2})$  is quite close, so the glass phase is thermally unstable. These two facts result in an inhomogeneous and crystallized product by melt-quenching method in our experiment. Conclusively, the selected composition out of the glass forming domain cannot be synthesized by the conventional method.

## 3.2 Synthesis by mechanical method

## 3.2.1 Experimental preparation

20 g of raw elements of high purity, Ge (5N), Ga (5N), and re-purified S (5N) were weighed according to the ratio of the designed composition and transferred into tungsten carbide grinding bowl. Then six tungsten carbide grinding balls were added into the bowl. The total mass in the bowl was 375 g that gave the ratio of powder: grinding balls as 1: 17. As mentioned in a previous part, the volume of the powders should not exceed 1/3 of the total volume; the volume of the balls should be also controlled at 1/3. The vacancy space should be reserved for the movement of the balls for efficiently milling. The planetary ball mill was conducted in the air at this stage.

The program set for the milling process was a repetition of 3 min at 400 rpm, then stopped for 3 minutes, and followed with 3 min at 400 rpm in the opposite direction. This setting was suggested by the manufacturer Retsch, so that overheat in the center of the grinding balls can be avoided. Because most of the energy is lost in form of heat, only a small amount is used in the deformation of the powders. A small amount of powders (approximately 200 mg) were taken out at 3 h, 5 h, 15 h, 40 h, 60 h and 80 h respectively to verify their morphology by XRD and their characteristically temperatures ( $T_g$ ,  $T_x$ ,  $T_m$ ) by thermal analysis.

# 3.2.2 Color variation of the powders

Powders taken out during the milling are shown in Fig.3.5. A variation of the color is observed from black, mostly due to the presence of metallic germanium and gallium, to light gray with prolonged milling time up to 40 h. Finally after 60 h of grinding, the powders look like yellow, typical color of grinded sulfide based glasses. Even if the change of color can be due to the decrease in size of the powders, we can assume that a reaction between Ge, Ga and S occurred progressively.



Fig.3.5 Color variation of the powders milled for different duration

3.2.3 X-ray diffraction of the powders

X-Ray diffraction pattern obtained from the different powders are presented in the Fig.3.6.



Fig.3.6 XRD patterns variation of the powders milled for different time; PDF card no. 72-2402 S; PDF card no. 65-333 Ge; PDF card no. 84-1441 Ga<sub>2</sub>S<sub>3</sub>

After 5-hour of milling, the peaks intensity belonging to  $Ga_2S_3$  phase starts to decrease, so does the phase S and Ge. It is a sign that the reaction of Ge with Ga and S starts. 10 hours later, the peaks belonging to S can barely be found. Additionally, the decrease in intensity of the Ge and  $Ga_2S_3$  peaks is accompanied with a broadening of the peaks. It indicates that these crystalline phases were deformed along with the time. Big changes occurred after 40 h of milling, as the S and Ge peaks totally disappear meaning that Ge has totally reacted with sulfur and gallium. Only the Ga<sub>2</sub>S<sub>3</sub> phase remains at that time. With prolonged time, the peak at  $31.7^{\circ}$  decreases and disappears after 80 h. The peak at  $29.6^{\circ}$  is barely seen at 120 h. But the peaks at  $28^{\circ}$ ,  $49.5^{\circ}$  and  $54^{\circ}$  are always present. The background signals of the powders milled for 80 h and 120 h mainly looks like an amorphous diffractogram. Until 120 h, the composition was not yet been completely grinded into amorphous, always mixed with crystals Ga<sub>2</sub>S<sub>3</sub>. However the small intensity and the broad shape of peaks indicate that the residual crystalline phase is strongly minority and is constituted of submicron particles. On calculating by Jade software, the size of the Ga<sub>2</sub>S<sub>3</sub> crystals in [1 0 0] orientation in the powders grinded for 80 h is around 19.5 nm while that in the powders grinded for 120 h is around 18.5 nm.

### 3.2.4 Thermal analysis of the powders

The DSC curves of the powders milled at different times are shown in Fig.3.7. Powders of about 10 mg were heated at a rate of 10°C/min. Through the curves in Fig.3.7 (a), when milled for 5 hours and 15 hours, there are two transition temperatures. The first one is at about 110°C, the second one is at about 130°C. The transition at 110°C might be the phase transition of sulfur. After 40 hours, no more peaks at 110°C appear, but only a large glass transition around 140°C. To observe the glass transition clearly, the powders milled for 40 h, 60 h and 80 h were re-heated up to 400°C after cooling down to the room temperature from the first heating process at a rate of 10°C/ min. There is no longer peak around 150°C (Fig.3.7 (b)), but a subtle change around 350°C, which should be the glass transition temperature of Ge-Ga-S.

To verify the transition observed at 110°C, pure sulfur was measured by DSC. About 10 mg sample was encapsulated in an aluminum crucible, heated up to 140°C first, then cooled down to room temperature and again heated to 140°C. Fig.3.8 presents the curves. The black one presents the heat flow of the first heating process. The red one presents the heat flow of the second heating process.

Two transition temperatures are observed in Fig.3.8. One is at 102°C, another one is at 118°C. After re-heating to 140°C, only one transition around 102°C appears during the second heating process. So, the  $T_g$  at 110°C in Fig.3.7 (a) belong to sulfur, but that at 140°C is not. This second phenomenon might be attributed to the evaporation of water which can be adsorbed on the particles surface during the ball milling process.



Fig.3.7 (a) DSC of the powders milled for different duration showing the variation of the glass transition temperature; (b) DSC curves obtained with the process of re-heating after cooling down to room temperature.



Fig.3.8 DSC curves of sulfur heated directly to 140°C (black one); re-heated to 140°C after cooling down to room temperature (red one).

# $3.3 \ Ge_{15}Ga_{20}S_{65}$ glass-ceramics made by SPS

In order to be molded into bulk samples by SPS, two powders were prepared by mechanical milling with different duration. One is 80 hours of grinding and the other is 120 hours. It is important to notice that all the milling process was carried out in the air.

These two powders were sintered by SPS under different conditions. The powders milled for 80 hours were mainly sintered under secondary vacuum and heated at 400°C, 420°C and 430°C at a rate of about 100°C/min then held for 5 minutes. They were denoted as GGS1, GGS2 and GGS3 respectively. Ta layer was used to cover the mold in graphite but the sample GGS1 was covered by papyex (flexible graphite sheet [29]) and without dwell. A pressure of 50 MPa was applied during each process. The powders milled for 120 hours were sintered using the similar process at 420°C, 400°C, 380°C and 360°C for comparison. All these sintering conditions are listed in the Table 3.1. In order to facilitate the various characterizations, the samples of 1mm thick were then polished on both faces.

| Name | Composition        | Temperature<br>(°C) | Press<br>(MPa) | Duration<br>(min) | Liner   | Thickness<br>(mm) | Density<br>(g/cm³)  |
|------|--------------------|---------------------|----------------|-------------------|---------|-------------------|---------------------|
| GGS1 | 65S-15Ge-20Ga 80h  | 430                 | 50             | no                | papyeux | 0.68              | 3.164±0.007         |
| GGS2 | 65S-15Ge-20Ga 80h  | 420                 | 50             | 5                 | Та      | 0.87              | $3.153 {\pm} 0.010$ |
| GGS3 | 65S-15Ge-20Ga 80h  | 400                 | 50             | 5                 | Та      | 0.87              | $3.132{\pm}0.014$   |
| GGS4 | 65S-15Ge-20Ga 120h | 420                 | 50             | 5                 | Та      | 1.32              | $3.169 {\pm} 0.014$ |
| GGS5 | 65S-15Ge-20Ga 120h | 400                 | 50             | 5                 | Та      | 1.17              | $3.165 {\pm} 0.016$ |
| GGS6 | 65S-15Ge-20Ga 120h | 380                 | 50             | 5                 | Та      | 1.4               | $3.172 {\pm} 0.007$ |
| GGS7 | 65S-15Ge-20Ga 120h | 360                 | 50             | 5                 | Та      | 1.35              | $3.135 {\pm} 0.007$ |

Table 3.1 Parameters of the samples made by SPS

## 3.3.1 X-ray diffraction

The XRD patterns of samples GGS1-GGS3 are presented in Fig.3.9. For an overall looking, except for the crystals  $Ga_2S_3$  which were already existed in the powders, there is no other extra crystalline phase.

When sintered at 400°C, the shape of the curve is almost unchanged comparing to the initial powder. That is to say, during the sintering, the crystals  $Ga_2S_3$  did not grow larger in sample GGS3. However, the peaks at 28° and 49.5° are much sharper and with higher intensities if we consider the GGS1 and GGS2 samples. Furthermore, the peaks at 29.7°, 31.7°

and 41.2° begin to grow while they almost disappear in the initial powder. These two samples were sintered at a higher temperature than GGS3. Thus, Ga<sub>2</sub>S<sub>3</sub> crystals might grow up during the sintering process leading to a partial modification of their structure.



Fig.3.9 X-ray diffraction patterns of the GGS1-GGS2-GGS3 samples compared with the initial powders which were mechanically milled for 80 hours; PDF card 84-1441 Ga<sub>2</sub>S<sub>3</sub>



Fig.3.10 X-ray diffraction patterns of the samples GGS4 to GGS7 compared with the initial powders which were mechanically milled for 120 hours; PDF card 84-1441 Ga<sub>2</sub>S<sub>3</sub>

The XRD patterns of the samples made from the powders milled for 120 hours are shown in Fig.3.10. It is important to mention that the three peaks shown in sample GGS6 at 38.4°, 44.6° and 65.1° belong to the sample holder made by aluminum. Through these curves, one can determine that no new crystals phases are formed during the sintering. The peak intensity is similar to the sintered samples, which may be due to the lower temperature used than the GGS1-GGS3 samples. However the peaks are sharper than the initial powder, indicating an annealing effect during the sintering process.

### 3.3.2 Optical properties

The samples GGS1, GGS2 and GGS3 were polished to 0.67 mm, 0.87 mm and 0.87 mm respectively. Optical transmission was measured from 250 nm to 12  $\mu$ m and is presented in Fig.3.11. As observable, the samples are totally opaque before 1  $\mu$ m. Then, the transmission increases up to 20% around 8 to 9  $\mu$ m. Strong scatterings occur at short wavelength, probably caused by the crystals and the holes formed during the sintering, which affects the transmission especially in the visible region. Comparing the transmission spectra of these three samples it can be seen that higher transmittance can be achieved in the samples sintered at higher temperature. Even if the crystals should be of bigger size, the lower viscosity reached at a higher temperature should permit to reduce the residual porosity and consequently enhanced the compactness. This point will be further detailed by the morphology study thereafter.

Besides, there are many absorption peaks which could be attributed to the impurities which were adsorbed on the surface of the initial powders during the milling process. Around 3  $\mu$ m, 3.9  $\mu$ m, 6.3  $\mu$ m and 7.5  $\mu$ m, the absorption peaks are caused by OH which is introduced by the H<sub>2</sub>O from air. A narrow peak at 4.26  $\mu$ m is an extrinsic signal which is caused by CO<sub>2</sub> in the air when doing the measurement. The intense absorption between 9  $\mu$ m to 10  $\mu$ m is caused by many reasons. They might be due to the presence of oxygen, water or carbon which might diffuse into the samples from the graphite mold. However, since the carbon is not crystallized in our samples, it cannot be detected by XRD. Moreover, scatterings can also occur between the interface of two grains as the difference refractive index between the glassy grain and the crystal boundary. It can be strongly affected if the presence of impurities such as oxygen is mainly concentrated in the boundaries.



Fig.3.11 Optical transmission of the samples sintered from powders milled for 80 h under different conditions



Fig.3.12 Optical transmission of the samples sintered from powders milled for 120 h at different temperatures for 5 minutes under 50MPa

The optical transmission curves of the samples GGS4 to GGS7 are recorded in Fig.3.12. Compared with Fig.3.11, the transmission signals of these samples can barely be detected even in the infrared range. With materials milled for much longer time, the slices sintered even at the same conditions have a lower transparency. With much longer milling time, the opportunity to be polluted by the oxygen and water in the air is strongly increased. That results in the sintered materials being mostly opaque.

## 3.3.3 Scanning Electronic Microscope

Fig.3.13 and Fig.3.14 present the SEM images of the samples sintered by SPS. The first three images in Fig.3.13 are in 20,000 times magnification; the fourth is 50,000 times magnification. The fracture surface of the three samples is rough, indicating the existence of crystalline phases or of unreacted glassy grains. It can be seen from the two previous figures (Fig.3.13 GGS1 and GGS2) that there exists a smooth area characteristic of dense vitreous phase. On comparing with these two previous photos, there are less smooth areas in the photo of GGS3, which indicates the presence of higher amount of particles. It is difficult to figure out the size of the crystals from these images. Thus, Transmission Electron Microscope pictures will have to be performed to have a better understanding of the material structure. These crystals might cause the big scatterings in the visible region, which is in accordance with the results obtained from the transmission curves.

In Fig.3.14, images are all taken with a magnification of 20,000. Sintering process at 360°C does not permit to reach a viscosity low enough to reduce the surface energy of the porous pellets as a large amount of holes can be observed in the sample GGS7 [30]. Moreover, whatever the sintering process used, few large area of glasses perfectly sintered are observed (smooth surfaces). In fact, in comparison with powders milled for 80h and then sintered in the same conditions, a higher amount of holes is observed here which can explain the low transmission.



Fig.3.13 SEM images of the samples GGS1, GGS2 and GGS3



Fig.3.14 SEM images of the samples GGS4, GGS5, GGS6, GGS7

For example, on comparing Fig.3.13 with Fig.3.14, GGS2 is more compact than GGS4, even sintered at the same conditions (same conclusion if we compared GGS3 with GGS5).

One possible explanation is that the contaminations adsorbed on the surface of the 120-hour milled powders can reduce the surface energy which reduces consequently the driving force of diffusion during the sintering. Furthermore, atmosphere pollution can be trapped during sintering in closed holes. Conclusively, the slices sintered from the powders milled for 80 hours were much denser than that sintered from the powders milled for 120 hours. Future experiments of mechanical milling have to be performed in controlled atmosphere or under vacuum to avoid such a contamination.

## 3.3.4 Transmission Electron Microscope

Fig.3.15 shows the selected area electron diffraction (SAED) pattern (a) and bright field image (b) of sample GGS3 (5 min, 400°C, and 80-hour milling). This analysis was carried out by M. Allix in Orléans (CEMHTI-CNRS3079). The bright spots observed in the diffraction pattern are characterics of the presence of crystals. Besides these spots, halos representative of amorphous phase can also be found, confirming that sample GGS3 is a glass-ceramic. Analysis of these bright spots and comparison with PDF cards, show that they only fit with the Ga<sub>2</sub>S<sub>3</sub> crystal phase 84-1441, which confirms the results of x-ray diffraction previously described. The crystals can be seen clearly in the TEM picture (Fig.3.15-b). The bright points represent the crystals while the other area represents glassy phase. Crystal size of Ga<sub>2</sub>S<sub>3</sub> is approximately of 50 nm.

Considering this impressive amount of crystals within the glassy matrix, the transmission reached considering the milling conditions (ambient atmosphere) is of great interest. This exploratory study demonstrates the possibility to make infrared transparent glass-ceramics from new compositions out of the usual glassy domains. It also offers the possibility to mainly control the generated crystalline phase considering the base glass composition.



Fig.3.15 Selected area electron diffraction pattern (a) and bright field image (b) of sample GGS3

## 4. Synthesis of the GeS<sub>2</sub> glass

In the first chapter,  $GeS_2$  glasses were synthesized by melt-quenching technique. The raw materials needed to be melted at 900°C for over 48 hours under vacuum. This process is energy consuming. Moreover, with such unstable composition, the possibility to make homogeneous glass without uncontrolled crystallization is very low. Another important parameter to be considered is that usually, the dimension of the glass strongly depends on the silica tube size, because of its low thermal conductivity. Thus, mechanical synthesis is conceived to be an interesting alternative way to solve these problems.

GeS<sub>2</sub> has been chosen for studying because of its large transparency window, from 0.45  $\mu$ m to 11  $\mu$ m. Moreover,  $\beta$ -GeS<sub>2</sub> crystals which presents evident second order non-linear phenomenon can be generated in a chalcogenide glassy matrix [31, 32]. Because of the close composition between glass and crystals, the difference of refractive index is small, that strongly reduces the scatterings induced by the crystalline phase [33].

## 4.1 Experimental preparation

20 g of raw materials with high purity Ge (5N) and pre-purified S (5N) weighed on stoichiometric (GeS<sub>2</sub>) ratio were put into a tungsten carbide grinding jar with 6 tungsten carbide grinding balls. The grinding jar was installed in the planetary milling machine. Similar conditions of grinding previously described in the section 3.2.1 were used. Raw materials were milled up to 120 hours. Powders sample (200 mg) were taken out every 24 hours for the thermal and morphology analysis.

## 4.2 The color variation of the powders

The photos of the powders are shown in Fig.3.16. As expected, the powders changed from black to yellow with increasing milling time duration, indicating the reaction is carried out progressively.


Fig.3.16 Color variation of the powders milled every 24 hours

After several hours of milling, colors changed from dark gray to dark yellow, suggesting that the quantity of the crystalline germanium decreases. After milling for 120 hours, the elements were reacted thoroughly and no change of color is observed for further milling duration. The final powder presents the color of glassy powder of  $GeS_2$ . The variation of the phase will be determined from the XRD curves as presented below.

# 4.3 X-ray diffraction of the powders

Fig.3.17 shows the variation of the X-ray diffraction patterns of the powders milled for different durations. On comparing with the PDF card, one can find out that within 24 hours after starting, the powder was still a mixture of crystalline sulfur and germanium. When milled for 48 hours, the peak intensity of sulfur is much weaker than before, indicating the progressive amorphization of sulfur. However, the intensity of the peaks belonging to germanium is still very intense. Diffractogram of powder milled for 72 hours shows a weakening in the intensity of crystalline germanium peaks. Meanwhile, peaks belonging to GeS phase begin to appear. These two features are the signals of the reaction between Ge and S. After 96 hours, peaks belong to GeS increases rapidly. When milled until 120 hours, surprisingly no diffraction peaks are observed, presenting anamorphous state where all the raw materials have been completely reacted. However, further experiments have to be performed to confirm that the amorphous powder obtained after 120h of milling is a GeS<sub>2</sub> glassy phase.



Fig.3.17 Evolution of the X-ray diffraction patterns as a function of milling duration, the powders taken out every 24 hours were compared with PDF card 72-2402 S, PDF card 65-333 Ge and PDF card 24-460 GeS

# 4.4 Thermal analysis of the powders

The DSC curves obtained by heating ~10 mg powder at a rate of 10°C/min are shown in Fig.3.18. It reveals the evolution of  $T_g$  according to the milling time up to 48 hours, peaks around 100°C typically belong to sulfur. This result is in a good agreement with the XRD curves previously showed in Fig.3.17. After 72 hours, peaks due to sulfur chains are vanished. In order to better identify the thermal characteristics such as  $T_g$ , the Fig.3.19 presents their variation as a function of milling durations. With increasing milling time, the  $T_g$  shifts towards higher temperature, increasing from 153°C to 337°C which confirms the progressive reticulation of the glass network.



Fig.3.18 DSC curves of the powders milled for different duration; and their  $T_g$  variation



Fig.3.19 Variation of the characteristic temperature  $T_g$  of the powders milled for different durations

The progressive polymerization of the network is due to the progressive incorporation of fourth-fold coordinated germanium within the amorphous sulfur. This progressive increase of  $T_g$  has already been observed in recent works made in the lab and very recently published [34].

## 4.5 Granulometry analysis of the powders

The size of powders milled for different duration was measured in Limoges by G. Delaizir using laser diffusion technique (Mastersizer 2000; Malvern Instruments, Orsayn France). Fig.3.20 presents the particles size distribution and Fig.3.21 shows the variation of the average particles size. In the first hours of milling process, the particles size was broad from tens of microns to hundreds of microns. But with increased milling duration, the average particles size reduces rapidly in the first step and then slowly decreases to reach a constant average size of 10  $\mu$ m. Additionally, the particles size distribution became narrower up to 96h. This is the result of the equilibrium between the fracture and the aggregation of the powders. It is important to put forward the fact that after 120-hour milling, the particles size distribution became a little wider although the average size does not change. These changes can be associated with the change of the nature of the powder from crystalline GeS to completely amorphous. The amorphous phase facilitates the aggregation instead of the fracture resulting in big aggregate of several hundreds of microns.



Chapter III Mechanical milling for synthesizing chalcogenide glass GeS<sub>2</sub> and glass-ceramic Ge<sub>15</sub>-Ga<sub>20</sub>-S<sub>65</sub>

Fig.3.20 Particles size distribution according to increasing milling time



Fig.3.21 Evaluation of the average size of the particles milled for different duration

# 4.6 Synthesis of bulk GeS2 glasses by SPS

Amorphous powders milled for 120 hours were sintered by SPS. The process is almost the same as the previous one used to synthesize  $Ge_{15}Ga_{20}S_{65}$  glass-ceramics. Table3.2 lists the various sintering conditions used and the name of the respective bulk materials. Samples were sintered at different temperatures while the pressure and the duration remain the same. All samples were protected with a sheet of Tantalum on both sides to prevent from the pollution by the graphite mold. Compact samples of about 1mm thick were then polished.

| Table 3.2 Sintering conditions of the different samples |             |          |          |       |           |             |
|---|-------------|----------|----------|-------|-----------|-------------|
| Sample  | Temperature | Pressure | Duration | Liner | Thickness | Density     |
|   | (°C)        | (MPa)    | (min)    |       | (mm)      | $(g/cm^3)$  |
| GS1   | 520         | 50       | 30       | Та    | 1.00      | 2.777±0.008 |
| GS2   | 540         | 50       | 30       | Та    | 1.22      | 2.943±0.006 |
| GS3   | 530         | 50       | 5        | Та    | 1.23      | 2.771±0.012 |
| GeS <sub>2</sub> glass                                  | -           | -        | -        | -     | -         | 2.750±0.006 |
| Powder  | -           | -        | -        | -     | -         | 2.619       |
| GeS <sub>2</sub> crystal                                | -           | -        | -        | -     | -         | 2.94        |

Table 3.2 Sintering conditions of the different samples

The error of density is calculated by the following formulate:

$$\sqrt{\frac{(\rho_1-\overline{\rho})^2+(\rho_2-\overline{\rho})^2+\cdots(\rho_{10}-\overline{\rho})^2}{9}}$$

# 4.6.1 X-ray diffraction

The x-ray diffraction patterns are showed in Fig.3.22. Sample GS1 does not present peaks of diffraction meaning that an amorphous state is maintained even during the sintering process. For the other two samples obtained from a sintering at higher temperatures, crystalline phases were detected. It is important to note that the peak observed at 28.9° in sample GS3 might belong to carbon (PDF card 72-2091 C<sub>8</sub>). A fast increase of the crystallization process occurs only 20°C higher than 520°C. Several diffraction peaks are observed in the sample GS2, corresponding to the formation of  $\beta$ -GeS<sub>2</sub> crystals. The generation of crystalline particles induce a strong increase of the sample density as the sample GS2 is the densest of the series, 2.94 g/cm<sup>3</sup> while GS1 and GS3 has a density of about 2.77

g/cm<sup>3</sup>. Thus, a shorter duration of sintering at a slightly higher temperature than the one used for the GS1 sample permits to reach the same density.



Fig.3.22 X-ray diffraction patterns of the GS1, GS2 and GS3 samples sintered by SPS

## 4.6.2 Optical properties

Fig.3.23 shows the transmission curves of the samples sintered at different temperatures. As expected, the numerous crystals present in the GS2 glass-ceramics induce stronger scatterings, so that its transmission is the lowest. That of GS3 is better, but still lower than that GS1. The maximum transmission obtained with the GS1sample is of about 24% at 10  $\mu$ m. Through the figures, contamination from the oxygen and water is important since they cause strong absorption at 2.8  $\mu$ m, 4  $\mu$ m, 7.5  $\mu$ m and around 9  $\mu$ m. Absorption peak at about 4.26  $\mu$ m is caused by CO<sub>2</sub>. So, even if the transmission is relatively low compared to what we should expect for a GeS<sub>2</sub> glass (around 78% of transparency) according to its refractive index, the feasibility to make IR transparent GeS<sub>2</sub> glasses is demonstrated. To remind, this glass composition is very difficult to make with classical technique.



Fig.3.23 Transmission curves of the samples GS1, GS2 and GS3

### 4.6.3 Scanning Electronic Microscopy analysis

These three samples were observed by SEM. Images taken with a magnification of 20 000 and 50 000 are shown in Fig.3.24. As observable the GS2 sample seems completely crystallized, which is surprising as it is till transparent in the infrared range. Crystal size is about hundred nanometers. Consequently, it is understandable that its density is very close to the density of the crystal GeS<sub>2</sub> which is of 2.94 g/cm<sup>3</sup>.

It can also be seen from the images of GS1 and GS3 that their surfaces are smooth after making a crack. It comes out that the majority part is glassy. But in the GS1 sample, several defects such as small crystals of about tens of nanometers and few places not well sintered are found. In the images of GS3, several small crystals of tens of nanometers are also observed. These results match well with that of X-ray diffraction patterns and optical transmission. However the presence of such small crystals is not sufficient to explain the strong scatterings which affect a lot the transmission, especially at short wavelength. We can assume that a small amount of carbon and the presence of oxygen are the primarily responsible of scatterings.



Fig.3.24 SEM images of the GS1, GS2 and GS3 samples

## **5.** Conclusion

In this chapter, a new technique combining mechanical milling and Spark Plasma Sintering was introduced to synthesize chalcogenide glass and glass-ceramics usually not possible to obtain with classical techniques. Raw materials Ge, Ga, S, on stoichiometric ratio 15:20:65 were milled for 80 and 120 hours. With increasing milling duration, a progressive reaction between elements occured which is put forward by various analyses: XRD patterns of crystalline Ge and S progressively disappear and an increasing glass transition temperature is observed. However, a perfectly amorphous powder was not reached using this method as diffraction peaks belonging to Ga<sub>2</sub>S<sub>3</sub> phase are still detected even after 120 hours of milling. For such composition, which cannot be synthesized by traditional method, we have demonstrated the possibility to synthesize in large amount of amorphous phase using a glass composition which it is identified out of the glass forming domain with traditional techniques. Moreover, this amorphous powder can be sintered by SPS into translucent pellets of glassceramics in the mid-infrared range.

Using the same process, GeS<sub>2</sub> glasses were sintered from the glassy powders in a graphite mold by SPS. The synthesized powders present amorphous XRD pattern after being milled for 120 hours. The most transparent pellet, GS1, was sintered at 520°C under the pressure of 50 MPa during 30 minutes using shield of Ta layers on both sides to prevent the pollution from the graphite mold. Even if the transmission is very low at short wavelength, the maximum transmission reached up to 14% at 10 µm. Such transmission is very low compared with that of the glass made by tradition method which can reach 78% and which is fully transparent to the naked eyes when made in small diameter. The SEM images revealed that nano-crystals are present in the glassy matrix even if no peaks can be detected in the XRD diffractogram. Until now, very transparent chalcogenide has not been made glass by combining mechanical milling and SPS. Several parameters can be advanced to explain the strong scatterings causing the loss of transmission: the presence of crystals, a rate of densification slightly inferior to a full compactness and finally an assumption which will have to be investigated is the presence of carbon and of grain boundaries having a strong difference of refractive index from the glassy grains. Some very recent results have demonstrated in another system the presence of grain boundaries having a chemical composition different from the glassy phase. We can guess that the contamination from air is one of the main parameter which affects the transmission. For further experiments, the mechanical milling

process should be carried out in the glove box to avoid being polluted from air and the sintering conditions should be further optimized using tungsten carbide molds for example.

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Chapter IV: Glasses and ceramics with ultra-broad absorption and emission bands for efficient frequency conversion

| 1. Introduction  | - 110 - |
|--|---------|
| 2. The state-of-the-art of luminescent materials with broadband absorption and emissio   | n-111 - |
| 2.1 Generation of white light for lighting   | 111 -   |
| 2.2 Improvement of photovoltaic solar cell's efficiency  | - 113 - |
| 2.3 Increase of bandwidth of telecommunication   | - 116 - |
| 3. Theory of luminescence  | - 117 - |
| 3.1 Basic consideration  | - 117 - |
| 3.2 Cases of broad emission  | - 118 - |
| 3.2.1 $d \rightarrow d$ emission   | 118 -   |
| $3.2.2 d \rightarrow f \text{ emission}$   | - 119 - |
| $3.2.3 \ s \rightarrow p \text{ emission}$   | 119 -   |
| 4. Transition metal ions doped phosphate glasses   | - 120 - |
| 4.1 Fe ions doped 10Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> -10Al <sub>2</sub> O <sub>3</sub> -80NaPO <sub>3</sub> glass           | - 121 - |
| 4.2 Mn ions doped phosphate glass 10Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> -10Al <sub>2</sub> O <sub>3</sub> -80NaPO <sub>3</sub> | - 123 - |
| 4.3 Ni ions doped phosphate glass 10Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> -10Al <sub>2</sub> O <sub>3</sub> -80NaPO <sub>3</sub> | - 124 - |
| 5. $Eu^{2+}$ doped chalcogenide ceramics based on MX (M = Ba, Sr, Ca; X = S, Se, F, O)   | - 126 - |
| 5.1 BaS/ZnS: $Eu^{2+}$   | - 126 - |
| $5.2 \text{ CaS/ZnS(Se):Eu}^{2+}$  | - 129 - |
| 5.2.1 CaS/ZnS: Eu <sup>2+</sup>  | - 129 - |
| $5.2.2 \text{ CaS/ZnS(Se):Eu}^{2+}$  | - 131 - |
| 5.3 $SrS/ZnS(Se)$ : $Eu^{2+}$  | - 137 - |
| 5.4 CaO/ZnO: $Eu^{2+}$ and CaF <sub>2</sub> /ZnF <sub>2</sub> : $Eu^{2+}$  | - 139 - |
| 5.5 Comparison of the emission band of $Eu^{2+}$ in different chemical environments  | - 141 - |
| 6. Conclusion  | - 144 - |
| 7. Reference   | 145 -   |

#### **1. Introduction**

Materials for frequency conversion have been studied for decades for different applications such as laser generation, fiber optic communication systems [1, 2], display, fluorescent lamps and more recently for lighting and for increasing efficiency of photovoltaic solar cell.

Such materials are synthesized by doping transition metal ions or rare-earth ions in crystalline or glassy matrix. Crystals are generally a more efficient host for active ions and they are mainly used in form of single crystals which are relatively difficult to synthesize. Recently developed transparent YAG ceramics [3, 4] have demonstrated many advantages over single crystals: easier fabrication, larger size, higher rare earth ion content and better mechanical properties with the same transparency. The transparent ceramics are for the moment limited to very few compositions with cubic structure. The main advantages of glasses are associated with the possibility of easy fabrication and shaping of very large size samples. Glass-ceramic is a relatively new luminescent material group that has been developed in recent years. It can combine the advantages of the glasses and crystals. Its conversion efficiency and emission intensity increase greatly when the rare-earth ions are embedded into the crystalline phase [5-11].

For increasing the photovoltaic solar cell's efficiency, one of the most interesting ways is to have a frequency converter which absorbs, as wide as possible, inefficient or useless frequencies of the solar spectrum [12, 13] and converts them to efficient frequency. LEDs for lighting are generally based on UV [14] or more frequently on Blue LEDs fabricated with GaN [15]. The biggest challenge is to efficiently obtain white light with acceptable or better tunable color rendering index (CRI). Phosphors with high conversion efficiency and tunable emission are the subjects of many studies. Broadband optical amplifier is the key component to increase the data transmission capability of optical fiber network by increasing the number of channels of wavelength division multiplexing (WDM) [1]. These amplifiers will necessitate luminescent materials with wide emission in the telecommunication bands.

Rare earth ions are considered as effective luminescent centers. However, the generally narrow absorption and emission bands are attributed to the 4f-4f electronic transitions which prevent the trivalent rare earth ions from applications where broad emission is necessary [16]. Divalent rare earth ions have usually large absorption and emission bands thanks to the

 $5d\rightarrow 4f$  transition and the well-known example is the Eu<sup>2+</sup>. Depending on the chemical environment, it can emit in a very large spectral band from near ultraviolet to yellow. Transition metal ions can have the same absorption and emission features. For example, the emission of Mn<sup>2+</sup> can vary from green to deep red due to the  ${}^{4}T_{1}\rightarrow {}^{6}A_{1}$  transition [17]. In addition, the emission position strongly depends on the host lattice [16]. These properties make possible absorption and emission tuning by changing the crystal field surrounding the active ions. The strength of the crystal field increases with the charge of the ligands and decreases with the size of the ligands, the size of the substituted cation, the coordination number of the site and the degree of covalency [16].

In this chapter, our objective is to demonstrate the feasibility of materials with wide and tunable absorption and emission bands by creating different environments around the active ions. Phosphate glasses, sulfide materials are considered as the base matrix. Transition metal ions namely Fe, Mn, Ni, and divalent Eu ions are used as the doping ions.

# 2. The state-of-the-art of luminescent materials with broadband absorption and emission

These materials have been studied mainly for the following applications.

#### 2.1 Generation of white light for lighting

Luminescent material started to attract attention probably since the discovery, around 1600, of the natural barite mineral which emits yellow to orange light with long duration when subjected to sunlight [18]. However, before the  $19^{th}$  century, the luminescent materials were only used for decoration. After then, the luminescent devices were first realized through gas discharge, electron beam in evacuated glass tube by Geissler and Braun, as well as the x-rays by Röntgen [19, 20]. Among the most-known luminescent devices are cathode-ray tube, stimulated during the world war for radar screen, fluorescent lamp for illumination and x-ray intensifying screen for medical imaging [18]. The early luminescent materials contained only a single phosphorescent material which generally does not emit white light. One example is CaWO<sub>4</sub> [16, 21] with blue light emission. In 1925, black-and-white television was fabricated by subjecting ZnS: Ag<sup>+</sup>; (Zn, Cd)S: Ag<sup>+</sup> to the cathode ray [18], while the color television was produced in 1960 with the use of the luminescent material (Zn, Cd)S: Cu<sup>+</sup>, Al<sup>3+</sup> [18].

The emission of white light is required for general lighting. The first fluorescent lamp was invented in 1926 with a single-phosphor which can emit more or less continuously over the whole visible spectral range. It contained halo-phosphates such as  $Ca_5(PO_4)_3(Cl, F)$ :  $Sb^{3+}/Mn^{2+}$  which are still in use today [22]. Although its efficiency is high, the lumen equivalency of their emission, taking the sensitivity of the human eyes into account, is low compared to daylight [16, 18, 23].

White light can be generated by mixing different color light. The most common method is to use the three fundamental colors: red, green and blue or two complementary colors (blue and orange for example). The di-phosphor lamp has the highest efficiency (120 lm/W), but the lowest color rending capacity. The tetra-phosphor device is the opposite. It has the best color rending, but poor overall efficiency. The tri-phosphor lamp can be considered as a compromised solution. The phosphor contains generally  $BaMgAl_{10}O_{17}$ : $Eu^{2+}$  emitting blue light [24],  $LaPO_4$ :  $Ce^{3+}$ ,  $Tb^{3+}$  emitting green light [25] and  $Y_2O_3$ :  $Eu^{3+}$  emitting red light [26]. These rare earth doped luminescent materials were used until 1971 by Koedam and Opstelten [27]. Because of the "line-type" f-f transitions, the emission bands are narrow. They have high efficiency and high lumen equivalency with however low color rendering index. The stability at relatively high temperature is also a big issue for long term application.

Color rendering is a way to describe the color quality of an object appears under a given light source. The measure is called the "color rendering index (CRI)", which is a quantitative measure of the ability of a light source to produce the colors of various objects in comparison with an ideal or natural light source. A low CRI indicates that the objects may appear unnatural under the source, while the light with a high CRI rating will allow an object to present colors to appear more natural. Obviously, the narrow emission bands of florescent lamps don't give a high CRI. The materials with broad emission bands are particularly interesting for lighting.

The first high-brightness blue-emitting LED based on InGaN [28] was invented in 1994 by Nakamura. White light can be obtained by combining the GaN-based LED, peaking at about 465 nm, and the  $Y_3Al_5O_{12}$ : Ce<sup>3+</sup> phosphor, emitting widely between 500-700 nm. With the same brightness, the consumed energy is only 1/8 of that of incandescent lamps or 1/2 of that of fluorescent tubes with life time of respectively 20-30 times or 10 times longer. It shows a higher efficiency and much better light-distribution character compared with the

RGB LEDs. This is the currently most used technique for generating white light form LEDs with however long term stability issue and unsatisfying color rendering. Materials that can emit efficiently over a large spectrum and with tunable emission wavelength are still necessary in order to improve the CRI and to adapt the CRI to different application requirements.

#### 2.2 Improvement of photovoltaic solar cell's efficiency

Clean and renewable energy as well as energy saving are clearly among the biggest social challenges for humanity. Solar energy is today the object of worldwide active research and development effort for the reason that the solar energy reaching the Earth every year corresponds to 10 000 years of fossil fuel use at current rate [29]. The most matured and the most efficient technology is the photovoltaic solar cells. However, the efficiency of the solar cell is still low with relatively high production cost. For example, the cost of solar energy in USA is about 0.2 \$/kWh while the nuclear electrical energy is produced at the cost of about 0.04 \$/kWh [30].

The photovoltaic effect is the creation of voltage or electrical current in a material upon exposure to light. The electrons in the valence band are excited by the sunlight or any other light which illuminates the surface of a material, jump to the conduction band and then become mobile. A solar cell is an electrical device that forces, by means of a p-n junction, the electrons and the holes, created in the valence band, to move toward two opposite faces of a device instead of simply recombining. The solar cell efficiency limit is currently estimated to be 34%, known as the Shockley-Queisser limit. Such low efficiency of the solar cell is mainly due to the mismatch between the solar spectrum and the response of the solar cells. Taking the silicon solar cell for an example, two intrinsic spectral limitations exist. The first limitation is energy loss by thermalization. The band-gap of silicon is 1.12 eV,  $\lambda$ =1100 nm. When a photon with energy higher than 1.12 eV is absorbed by silicon, one electron-hole pair will be created and the excess energy will be lost when the electron is relaxed to the lower level of the conduction band. These energies turn into heat in the cell. Secondly, photons with energy lower than 1.12 eV will not be absorbed by the silicon cell and all these photons will be transmitted through the cells without creating any electron-hole pair. These two losses, due to the spectrum mismatch, in a single junction silicon solar cell can be as large as 50% [31]. Another reason is the poor UV response of silicon based photovoltaic devices. The external quantum efficiency, EQE describes the  $\lambda$ -dependent response of a PV device defined as the ration of the number of electron-hole pairs generated to the number of photons incident on the front surface of the cell [31]. Fig.4.1 shows representative EQEs of various PV technologies. At short wavelengths,  $\lambda$ <500 nm, the EQE is very low, especially for thin film device.



Fig.4.1 (A) EQEs of wafer-based device C-Si, single junction GaAs and Mc-Si. (B) EQEs of thin film devices DSSC, copper indium gallium diselenide (CIGS), cadmium telluride (CdTe), triple junction a-Si, single junction a-Si and organic poly (3-hexylthiophene) phenyl-C<sub>61</sub>-butyric acid methyl ester (P3HT: PCBM) [31]

Different approaches have been tested for increasing the conversion efficiency of the photovoltaic solar cells. The most efficient, also the most expensive way is to use multi-junction cells. The best example of multi-junction cells has demonstrated performance over 35.8% at 1 sun [32]. It contains several p-n junctions. Each junction is tuned to absorb light in a specific spectral region, reducing therefore the mismatch between the solar spectrum and the cell's response. However, this technology is highly complicated. Its high price and low performance/price ratio limits its large commercial use. Another more simple and convenient approach is to modify the solar spectrum in order to reduce the above-mentioned mismatch.

Fig.4.2 presents the mismatch between the solar spectrum and the energy absorbed by silicon-based solar cells. It is clear that only energy in the 1  $\mu$ m region can be efficiently used.



Fig.4.2 The mismatch between the solar spectrum (the blue region) and the light which can be efficiently absorbed by solar cell (the green region) [33]

Consequently, the idea to improve the efficiency of PV solar cells is to convert the solar spectrum, as much as possible, to light around 1  $\mu$ m. The solar spectrum can be modified through the following luminescent process: down-conversion (DC), in which one high energy photon ( $\lambda$ <500 nm) is cut into two lower energy photons; up-conversion (UC), in which two or more low energy photons ( $\lambda$ >1100nm) combine to create one higher energy photon; downshifting (DS), in which photons in the region of 300-500 nm are absorbed and re-emit at a longer wavelength.

Rare earth ions are widely studied to achieve DC. They can have many energy levels, which may facilitate the energy division of the incident light.  $Tb^{3+}$ ,  $Yb^{3+}$  co-doped YPO<sub>4</sub> is firstly used to demonstrate the DC by Vergeer et al [34]. Zhang et al have found another couple, the  $Pr^{3+}-Yb^{3+}$  couple which has also achieved DC [35]. The couples  $Er^{3+}-Yb^{3+}$  [36],  $Ho^{3+}-Yb^{3+}$  [37, 38],  $Tm^{3+}-Yb^{3+}$  [39, 40] and  $Nd^{3+}-Yb^{3+}$  [41] have also been studied for DC. However, these ion couples cannot be used for improving the efficiency of the solar cells, because the absorption of these rare earths is narrow and weak due to the f-f transitions and the energy transfer efficiency between the  $RE^{3+}-Yb^{3+}$  is generally low [16]. Large and intense absorption is desirable.  $Ce^{3+}$  ion seems to be an ideal candidate because of its 4f-5d transition [42].

In 1979, Hovel et al [43] have proposed another way to increase the solar cell's efficiency, by shifting the light to the region where the EQE of the solar cells is much higher.

Numbers of luminescent materials have been investigated for DS, they can mainly be divided into three categories: quantum dots [44], organic dyes and rare-earth ions/complexes [45]. Quantum dots are nano-size semiconducting crystals. They have tunable absorption and emission with the change of the crystal size. They also exhibit broad absorption band, high emission intensity and good stability. The widely used materials are CdSe quantum dots in a polymeric matrix [46], Si-doped InAs quantum dots [46]; non-stoichiometric silica (SiO<sub>x</sub>) [48, 49] and silicon nitride (SiN<sub>x</sub>) [49, 50] layers containing silicon nano-structures.

## 2.3 Bandwidth increase for telecommunication

Wavelength division multiplexing (WDM) is a technology which multiplexes a number of optical carrier signals into a single optical fiber by using different wavelengths of laser light. The most successful and widely used amplifier is the erbium doped fiber amplifiers (EDFA). The first erbium-doped fiber laser has been realized in 1986 at Southampton University by Mears et al. [51]. They showed a 3-meter fiber delivering a peak gain of 28 dB at 1536 nm. The installation of EDFAs in WDM networks has led to tremendous increase of data communication speed from 100 Mb/s to more than 5 Tb/s over the last 25 years. However, the bandwidth is limited by the optical amplifier because the 4f-4f transition of  $\text{Er}^{3+}$ ions is narrow with a gain bandwidth of less than 100 nm [52-54]. Optical amplifiers with large bandwidth are one of the key devices for increasing the data transmission capacity of the optical fiber network.

Numerous researches have been carried out for achieving broadband amplification. Rare-earth and transition metal-doped amplifiers have been considered. Some interesting results have been obtained. For example,  $Bi_2O_3$  doped  $65SiO_2-20Al_2O_3-15La_2O_3$  glass presents emission band centered at 1160 nm with a FWHM of 300 nm [55];  $Er^{3+}$ -Tm<sup>3+</sup> co-doped  $Bi_2O_3$ -GeO<sub>2</sub>-Na<sub>2</sub>O glasses demonstrated a broad emission from 1.3 µm to 1.65 µm with a FWHM of 160 nm [2], etc.

#### 3. Theory of luminescence

#### 3.1 Basic consideration

Photoluminescence is a process that a matter absorbs excitation energy (photon) and then emits a radiation. Upon the excitation of light, the electrons located on the fundamental energy level will absorb the energy and be excited to a higher energy level (excited level). This process is called "absorption". The "emission" process is the reverse process. The excited photons fall down to a lower energy level and the excess energy is transformed into light. The shape of an optical absorption band can be described by the configuration coordinate diagram. Such a diagram shows the energy of luminescent center in the crystal lattice as a function of the configuration coordinate. Fig.4.3 shows a schematic configuration coordinate diagram where E is plotted versus the metal-ligand distance R.



Fig.4.3 Configurational coordinate diagram. The ground state (g) has the equilibrium distance  $R_0$  with the vibrational states v=0, 1, 2. The excitation state (e) has the equilibrium distance  $R_0^{'}$  with the vibrational states v'=0, 1, 2.  $\Delta R = R_0^{'} - R_0$ . [16]

The absorption process is indicated as  $g \rightarrow e$ . After absorption of light, the system reaches a high vibrational level of the excited state. Then, it relaxes to the lowest vibrational level v'=0 and is then de-excited from  $e \rightarrow g$  by emitting light.

This parabolic shape corresponds to the fact that the vibrational motion is assumed to be harmonic.  $E = \frac{1}{2}k(R - R_0)^2$ . The minimum  $R_0$  of the parabola corresponds to the equilibrium distance in the ground state. For the excited states, their shape is also parabolic, with however different values of the equilibrium distance  $(R'_0)$ . In this model, the transitions between the two parabolas are electronic transitions. In Fig.4.3, after having absorbed light, electrons in the ground state (g) are excited and enter into an excited state (e). These excited electrons tend to be quickly relaxed to the minimum energy of the excited state. There is usually a shift between the minimum energy point of the excited state and that of the ground state. This difference is induced by the fact that the chemical bond in the excited state is different from that in the ground state, leading to a relative displacement over a value  $\Delta R$ , as shown in Fig.4.3. Thus, the absorbed photon energy is usually higher than the emitted photon energy. The energy difference is called Stock shift ( $E_s$ ). When  $\Delta R=0$ , the vibrational overlap will be the maximal for the level v=0 and v'=0. The absorption spectrum will be a fine line, corresponding to the transition from v=0 to v'=0. However, when  $\Delta R \neq 0$ , the v=0 level will have the maximal vibration overlap with several level's v'>0, and a broad absorption band will be observed. The broader the absorption band, the larger the value of  $\Delta R$  and the larger the Stokes shift. The value of  $\Delta R$  measures the strength of the interaction between the electrons and its environment.  $\Delta R=0$  corresponds to a weak-coupling scheme,  $\Delta R>0$  the intermediate-coupling scheme and  $\Delta R \gg 0$  a strong-coupling scheme.

#### 3.2 Cases of broad emission

#### 3.2.1 $d \rightarrow d$ emission

Transition metal ions have an incompletely filled *d* shell. The transition between levels of the *d* shell can be forbidden or allowed. One of the best examples is the first red ruby laser with  $Cr^{3+}$  in Al<sub>2</sub>O<sub>3</sub> host under excitation in visible. The Mn<sup>2+</sup> doped Ba<sub>2</sub>ZnS<sub>3</sub> [56] is a red emitting phosphor widely studied for white LED and display applications. Its emission spectrum shows a broad band with emission maximum at 625 nm under excitation of 358 nm.

As the outside electron shell is d shell, its energy level is strongly affected by its chemical environment. The position of the absorption and emission bands depends largely on the crystal field and the coordination number.

The luminescence of  $Cr^{3+}$  in Al<sub>2</sub>O<sub>3</sub> is a line and red emission due to the transition  ${}^{2}E \rightarrow {}^{4}A_{2}$ . The red color of ruby for high crystal field strength is due to the two broad and strong absorption peaks respectively centered at 400 nm and 550 nm. But when the  $Cr^{3+}$  ions are added into Mg<sub>4</sub>Nb<sub>2</sub>O<sub>9</sub>, the emission becomes broad, attributed to the transition  ${}^{4}T_{2} \rightarrow {}^{4}A_{2}$ . The color is green for low crystal field strength. The  ${}^{2}E$  is not always the lowest excited state. For relatively low crystal fields, the  ${}^{4}T_{2}$  level is lower. Tetrahedrally coordinated  $Mn^{2+}$  (weak crystal-field) gives a green emission, while the octahedrally coordinated  $Mn^{2+}$  (strong crystal-field) shows an orange to red emission.

#### 3.2.2 $d \rightarrow f$ emission

Several rare earth ions show broad band emission because of its transition from 5*d* orbital to 4*f* orbital [16]. The outside electron shell is 5*d* which is sensitive to its local environment. Since the  $5d \rightarrow 4f$  transition is parity allowed, the emission transition is a fully allowed one. Its emission should be intense. Some trivalent rare earth ions such as Ce<sup>3+</sup>, Pr<sup>3+</sup>, Nd<sup>3+</sup> and divalent rare earth ions such as Eu<sup>2+</sup>, Sm<sup>2+</sup>, Yb<sup>2+</sup> are in this case [16].

The most famous example is  $Ce^{3+}$  ion  $(4f^4)$  with wide application for general lighting based on blue LEDs in the form of  $Ce^{3+}$ : YAG. Its excited configuration is  $5d^1$ , the crystal field has split it into five crystal-field components; the  $4f^4$  ground state configuration yields two levels. Usually the  $Ce^{3+}$  emission is located in the ultraviolet or blue region, but in  $Ce^{3+}$ : YAG, it shows broad emission peaks in the range of 480-640 nm with maximum intensity at 524 nm because of the crystal-field effect; while in CaS, the  $Ce^{3+}$  emit red color because of the covalence effect.

The emission of  $\text{Eu}^{2+}(4f^7)$  ions varies from blue to red, depending on its chemical environment. It is due to the transitions between the  ${}^8S_{7/2}(4f^7)$  ground state and the crystal field components of the  $4f^65d$  excited state. In BaAl<sub>2</sub>O<sub>4</sub>, Eu<sup>2+</sup> ions show emission centered at 510 nm; while in SrAl<sub>2</sub>O<sub>4</sub>, it emits at 520 nm [57]. In CaAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, a blue emission at 440 nm is observed [58].

## 3.2.3 $s \rightarrow p$ emission

Ions with outer  $s^2$  configuration like Ti<sup>+</sup>, Pb<sup>2+</sup>, Bi<sup>3+</sup> (all  $6s^2$ ) and Sn<sup>2+</sup>, Sb<sup>3+</sup> (both  $5s^2$ ) are strongly affected by the host lattice. Mainly two different types of interaction act on the <sup>3</sup>P state which is yielded from the excited *sp* configuration, namely spin-orbit (SO) interaction

and Jahn-Teller (JT) (electron-lattice) interaction [59]. The SO interaction split the <sup>3</sup>P state into the <sup>3</sup>P<sub>0</sub>, <sup>3</sup>P<sub>1</sub>, <sup>3</sup>P<sub>2</sub> levels. The strength of this interaction increases with nuclear charge. The JT effect causes also a splitting of the <sup>3</sup>P state due to coupling of this state with vibrational modes. If the SO coupling is strong, the influence of the JT effect is weaker.

The emission of  $Cs_2NaYCl_6:Bi^{3+}$  [16] consists of a narrow band with considerable vibrational structure and a small Stokes shift of 800 cm<sup>-1</sup>. Small Stokes shift happens with octahedral coordination. The Bi<sup>3+</sup> ions are too big to relax to a different equilibrium distance [16]. But the emission of LaPO<sub>4</sub>:Bi<sup>3+</sup> consists of a broad band without any vibrational structure and with a large Stokes shift of 19 200 cm<sup>-1</sup>. Such large Stokes shift happens in large site. The Bi<sup>3+</sup> ions can obtain its preferred asymmetrical coordination when there is enough space and can relax to the center of the coordination polyhedron.

#### 4. Transition metal ions-doped phosphate glasses

In this work, we have firstly selected the phosphate glasses as host for transition metal ion doping in order to get broad and tunable absorption and emission. These glasses doped with luminescent ions have been studied since a long time as they have many interesting properties: low chromatic dispersion, high transparency for ultraviolet light, high rare earth ions and transition metal ions doped concentration as well as large emission and absorption cross section [47, 60, 61].

We have selected Fe<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub> and NiO which have been introduced into a previously studied phosphate glass with the composition  $10Ca_2(PO_4)_2$ - $10Al_2O_3$ - $80NaPO_3$  to verify the valence state, the absorption position and the emission of these transition metal ions. Table4.1 lists different doped glass samples. The selected glass matrix presents an interesting compromise between  $T_f$  (melting temperature) and low  $T_g$  (glass transition temperature) and good chemical durability. Furthermore, it has high transmittance facilitating optical measurements. These glasses were made by melt-quenching method. The raw materials were weighted in the stoichiometric ratio and mixed thoroughly and then were put in an alumina crucible which is placed then in a furnace at  $1000^{\circ}C$  in air for 30 minutes. The melt was then quenched in air by pouring it onto a polished and preheated brass plate and pressed with

another brass plate before annealing at 475°C. The obtained glasses are transparent with different colors as function of doping ions.

Transmission spectra were recorded by using a Perkin Elmer Lambda spectrophotometer in the UV/Visible/NIR region and by using a Bruker Vector 22 spectrophotometer in the infrared region.

| Sample                   | Composition  |  |  |  |  |
|--------------------------|--|--|--|--|--|
| ТСР                      | 10Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> -10Al <sub>2</sub> O <sub>3</sub> -80NaPO <sub>3</sub>   |  |  |  |  |
| FeTCP1                   | TCP+0.1 wt% Fe <sub>2</sub> O <sub>3</sub>   |  |  |  |  |
| FeTCP2                   | TCP+0.5 wt% Fe <sub>2</sub> O <sub>3</sub>   |  |  |  |  |
| MnTCP                    | TCP+0.1 wt% MnO <sub>2</sub>   |  |  |  |  |
| NiTCP                    | TCP+0.1 wt% NiO <sub>2</sub>   |  |  |  |  |
| FeTCP2<br>MnTCP<br>NiTCP | TCP+0.5 wt% Fe <sub>2</sub> O <sub>3</sub><br>TCP+0.1 wt% MnO <sub>2</sub><br>TCP+0.1 wt% NiO <sub>2</sub> |  |  |  |  |

Table4.1 List of different transition metal ions-doped phosphate glasses

4.1 Fe ions doped 10Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>-10Al<sub>2</sub>O<sub>3</sub>-80NaPO<sub>3</sub> glass

Previous studies have shown that iron ions in this type of glass act as both vitreous network modifier and former. The addition of iron ions can influence the glass's optical and structural properties [62]. It is well known that Fe ions exist in different valence states with different local symmetries in different glass networks. For example, Fe<sup>3+</sup> ions exist in octahedral symmetry and tetrahedral symmetry and play an intermediate role; Fe<sup>2+</sup> exists in octahedral symmetry form [FeO<sub>6</sub>] and acts as a glass modifier [62-64]. The iron ions' valence and local coordination depend on the nature and concentration of the iron ions added in the glass network [65] and on the nature of the glass network as well as on the strength of the crystal field. In the glass Li<sub>2</sub>O-MgO (CaO)-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>, a strong absorption band of Fe<sup>3+</sup> is observed at 457 nm due to the transition  ${}^{5}T_{2g} \rightarrow {}^{5}E_{g}$  and at 2250 nm due to the transition  ${}^{5}T_{2g} \rightarrow {}^{5}E_{g}$  and at 2250 nm due to the transition  ${}^{5}A_{1}(e^{2}t_{2}^{3}) \rightarrow a^{4}T_{1}(e^{3}t_{2}^{2})$ , and the absorptions are generally attributed to the transitions of Fe<sup>3+</sup> ions  ${}^{6}A_{1}(t_{2g}^{3}e_{g}^{2}) \rightarrow a^{4}T_{1}(t_{2g}^{4}e_{g})$ ,  ${}^{6}A_{1}(t_{2g}^{3}e_{g}^{2}) \rightarrow a^{4}T_{2}(t_{2g}^{4}e_{g})$  and  ${}^{6}A_{1}(t_{2g}^{2}e_{g}^{3})$  respectively [68].

In this study,  $Fe_2O_3$  was added into the phosphate glass with two different concentrations, 0.1 wt% and 0.5 wt%. They are respectively denoted as FeTCP1 and FeTCP2 (Fig.4.4).



Fig.4.4 Photos of samples FeTCP1 and FeTCP2 respectively doped with 0.1 wt% and 0.5 wt% of Fe $^{3+}$ 

The sample FeTCP2 is pale-yellow color and FeTCP1 is almost colorless. These samples were polished to a thickness around 1.5 mm for optical measurement.

Fig.4.5 shows the absorption spectra of the samples FeTCP1 and FeTCP2 compared with the glass matrix TCP without any doping. The base glass TCP shows important optical losses at short wavelengths due to the presence of small bubbles in the glass. The absorption due to iron ions is weak in the sample FeTCP1. A large but weak absorption peak is observed between 700 nm to 1200 nm. The absorption peaks of sample FeTCP2 are significantly stronger. There are peaks at 522 nm, 1020 nm and peaks between 2000 nm to 2400 nm. According to the works of M. Elisa et al [62], W. E. Jackson et al [66], Z. V. Gareyeva et al [67] and T. G. V. M. Rao et al [68], the weak absorption peak at 522 nm might belong to Fe<sup>3+</sup>, attributed to the transition  ${}^{6}A_{1} \rightarrow {}^{4}T_{1}$ . The strong absorption peak at 1.02 µm might belong to Fe<sup>2+</sup>, due to the transition  ${}^{5}T_{2g} \rightarrow {}^{5}E_{g}$ . The peak around 2 µm seems like a combination of two peaks. It might correspond to the transition  $E \rightarrow T_{2}$  of Fe<sup>2+</sup>.



Fig.4.5 Optical loss spectra of the phosphate glasses without doping and with 0.1 or 0.5 wt% Fe ions

4.2 Mn ions doped phosphate glass 10Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>-10Al<sub>2</sub>O<sub>3</sub>-80NaPO<sub>3</sub>

0.1 wt%  $MnO_2$  is added into the phosphate glass TCP and the sample is denoted as MnTCP1 (Fig.4.6). The color of the sample is purple.  $Mn^{2+}$  ions have an extinction coefficient 100 times lower than that of  $Mn^{3+}$ . The color of the glass largely depends on the color of  $Mn^{3+}$ . The color of the doped glass indicates clearly the presence of  $Mn^{3+}$  ions in the glass [69].

Fig.4.6 presents the absorption spectra of the sample MnTCP1, doped by 0.1 wt%  $MnO_2$  compared with the base glass without doping. The small absorption peak located at 490 nm is attributed to the d-d electronic transition of  $Mn^{3+}$  (d<sup>4</sup>) ions, the spin allowed  ${}^{5}E_{g} - {}^{5}T_{2g}$ . Normally, the transition of  $Mn^{2+}$  (d<sup>5</sup>) ions is around 410 nm in this type of glasses [69]. It depends of course on its environment. It can be seen in Fig.4.6 that the cut-off edge of the base glass is around 350 nm. No absorption peak of  $Mn^{2+}$  ions around 410 nm can be observed. The high optical losses of the base glass are again due to the presence of small bubbles.



Fig.4.6 Optical loss spectra of 10Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>-10Al<sub>2</sub>O<sub>3</sub>-80NaPO<sub>3</sub> doped with0.1 wt% MnO<sub>2</sub> (photo in the insert) compared with the base glass

4.3 Ni ions doped phosphate glass 10Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>-10Al<sub>2</sub>O<sub>3</sub>-80NaPO<sub>3</sub>

 $Ni^{2+}$  is a very important activator since it has a broadband luminescence in the near infrared region. Unlike the other transition metals, Ni presents in divalent state in almost all hosts. 0.1 wt% NiO<sub>2</sub> is added into the phosphate glass TCP (denoted as NiTCP1). Its photo is presented in Fig.4.7 with an orange color due to the strong absorption of nickel ions.

In Fig.4.7, different absorption peaks with different intensities can be clearly seen. The broad absorption bands centered at 434 nm, 816 nm and 1380 nm are respectively due to transitions of  ${}^{3}E'(F) \rightarrow {}^{3}E''(F)$ ,  ${}^{3}E'(F) \rightarrow {}^{3}A'_{2}(F)$  and  ${}^{3}E'(F) \rightarrow {}^{3}A'_{1}(P)$  of the trigonal bipyramid five-fold Ni<sup>2+</sup> [70, 71]. The small absorption band at around 712 nm could be attributed to the tetrahedral fourfold Ni<sup>2+</sup>.



Fig.4.7 Absorption spectra of the sample NiTCP doped by 0.1 wt% NiO<sub>2</sub> (photo), compared with the base glass TCP without doping

The luminescence of these phosphate glasses doped by Fe, Mn and Ni ions has been studied without any measurable signal. Obviously, the excited electrons were nonradiatively relaxed.

The selection of host for transition metal ion doping is complex process. At least two important considerations should be taken into account: the first one is to select appropriate coordination environment. For example, the best environment is tetrahedral for  $Cr^{4+}$  [72]; for Ni<sup>2+</sup>, the best environment is octahedral [73]. The second consideration is to minimize the non-radiative decay process, which of course limits the quantum efficiency of transition metal ions. Glasses seem not to be the best host materials for the transition metal ions with obviously high probability of non-radiative relaxation [74].

# 5. Eu<sup>2+</sup> doped ceramics based on MX (M = Ba, Sr, Ca; X = S, Se, F, O)

With the general finding that it is more difficult to control the valence of transition metal ions or rare earth ions in glass due to the existence of mixed environments, we have reoriented our study to crystallized materials. In addition, glass seems less efficient as luminescent host.

Europium ions have two kinds of valence,  $Eu^{3+}$  and  $Eu^{2+}$ . The emission of  $Eu^{3+}$  ions is typically line emission due to transitions within the  $4f^6$  configuration. In contrast, the emission of ions  $Eu^{2+}$  is associated with an allowed f-d transition  $4f^65d^1 \rightarrow 4f^7$  and the emission peak is usually large and depends on the host. In this study,  $Eu^{2+}$  ions have been introduced into different matrix BaS, CaS (Se), SrS (Se), CaO (F, Se) based on different studies [75-78] in order to tune the absorption and emission of  $Eu^{2+}$  ions by modifying the environment. The sulfide based ceramics are chosen mainly for three reasons. Firstly, it has low phonon energy and secondly, the absorption of rare earth ions is much more efficient in sulfide environment than in fluoride environment as demonstrated in the previous works [79]. Finally, the rare earth ions in crystallized environment show much stronger luminescence than in glasses [80].

The ceramic materials have been prepared as follows: Raw materials were thoroughly grinded and mixed in a glove box to avoid moisture. ZnS or ZnSe was used as a sintering agent to lower the sintering temperature because the melting point of CaS or SrS is too high. The studied compositions are listed below. Eu<sup>2+</sup> ions were added in the form of EuCl<sub>3</sub>. All of the samples are sintered at 950°C under a pressure of 50 MPa for 2 hours in vacuum in a graphite mold with the protection of BN to facilitate the release of the sintered samples. The sintered ceramic discs were polished to eliminate the BN on the surface. The crystalline phases of all samples have been studied by X-ray diffraction and the fluorescence of these samples has been measured.

# 5.1 BaS/ZnS: Eu<sup>2+</sup>

The composition of the two samples, one doped with europium ions and the other without any doping, is collected in Table4.2.



Table4.2 The composition of two samples with and without europium ions

Composition (mol%)

0.667BaS-0.33ZnS-0.003EuCl<sub>3</sub>

Sample

EZBS1

Fig.4.8 X-ray diffraction patterns of ZBS and EZBS1 compared with the PDF card 65-309 ZnS and PDF card 74-132  $Ba_2ZnS_3$ .

Fig.4.8 presents the X-ray diffraction patterns of the sample EZBS1 with europium ions  $Eu^{2+}$  and the ZBS without doping as a reference. The photos of these two samples show clearly two different colors. The sample doped by  $Eu^{2+}$  ions (this will be confirmed by luminescence measurement) shows bright yellow, while the sample without doping is grey. The sample EZBS1 is synthesized from the powder mixture BaS/ZnS=2 doped by 0.3 mol% EuCl<sub>3</sub>. By Comparison with the PDF card, it is found out that the diffraction pattern corresponds well to the phase Ba<sub>2</sub>ZnS<sub>3</sub> which is the major phase in the ceramic. However, there exists some diffraction peaks located at 28.45°, 47.43° and 56.19° corresponding to cubic ZnS and the peaks at 24° and 29° fit well with PDF card 75-896 BaS. With these sintering conditions, the majority of BaS and ZnS has reacted together with however some residual starting compounds.
Fig.4.9 represents the excitation and emission spectra of the samples with (b) and without (a) doping ions. A fast examination indicates that the emission around 420 nm can be attributed to the host materials BaS/ZnS. In fact, ZnS based materials have been studied as luminescent materials [81, 82]

The doped and undoped ceramics show significantly different second emission peak. For the undoped ceramic, the 2<sup>nd</sup> emission peak is centered around 630 nm with a Full Width at Half Maximum (FWHM) of about 50 nm. For the europium doped BaS/ZnS, this peak is much larger and centered around 670 nm. In order to elucidate the origin of this emission, an excitation spectrum, monitored at 670 nm has been realized, leading to a large excitation peak around 436 nm. If the europium doped ceramic is excited at this wavelength (436 nm), a broad emission band, centered at around 700 nm is observed. No emission can be observed if the ceramic without europium doping is excited at the same wavelength (Fig.4.9 a). Consequently, this emission can be attributed to the presence of Eu<sup>2+</sup> ions due to the allowed transition  $4f^65d^1 \rightarrow 4f^7$ .



Fig.4.9 The excitation and emission spectra of samples ZBS (a) and EZBS1 (b) collected at room temperature.

The ionic radius of  $Eu^{2+}$  and that of  $Ba^{2+}$  are very close, respectively 0.130 nm and 0.135 nm. Even the europium ions are introduced as  $EuCl_3$ , Ba offers the environment of valence two in the matrix, and  $Eu^{3+}$  will be reduced according to the following mechanism already proposed elsewhere [83]:

$$\blacksquare 3Ba^{2+}+2Eu^{3+}=V^{2-}_{Ba}+2Eu_{Ba}^{+}+3Ba^{2+}$$

$$\blacksquare V^2_{Ba} = V + 2e^{-1}$$

 $\blacksquare 2Eu_{Ba}^{+} + 2e^{-} = 2 Eu^{2+}$ 

It is interesting to note the presence of some fine peaks on the excitation spectrum of europium doped ceramic, monitored at 670 nm. These peaks are caused by the Xe lamp.

# 5.2 CaS/ZnS(Se):Eu<sup>2+</sup>

5.2.1 CaS/ZnS: Eu<sup>2+</sup>

The element calcium is located in the same group IIA as barium. The radius of ions  $Ba^{2+}$  is 0.135 nm, while that of  $Ca^{2+}$  is 0.1 nm. The electronegativity of Ca is higher than that of Ba. The substitution of Ba by Ca will change the environment of doping ions  $Eu^{2+}$ . The crystal field will also be changed. The emission of  $Eu^{2+}$  is expected to change. Table4.3 lists the compositions of different samples which have been studied.

Table4.3 Different compositions doped with Eu ions

| Sample | Composition (mol%)                           |
|--------|--|
| EZCS1  | $0.667CaS$ - $0.33ZnS$ - $0.003EuCl_{3}$     |
| EZCS2  | $0.89 CaS\text{-}0.1 ZnS\text{-}0.01 EuCl_3$ |
| EZCS3  | $0.85 CaS\hbox{-}0.1 ZnS\hbox{-}0.05 EuCl_3$ |

Sample EZCS1 keeps the same ratio as sample EZBS1 with the only change of the cation (from  $Ba^{2+}$  to  $Ca^{2+}$ ). Sample EZCS2 and EZCS3 are designed for studying the luminescent properties as the function of the doping concentration of  $Eu^{2+}$ . The X-ray diffraction pattern of the sample EZCS1 in Fig.4.10 shows that the major phases are CaS and ZnS. No solid reaction happened between these two materials during the sintering. The photo of the sample EZCS1 in Fig.4.10 shows the red color of the sample. The color changes from bright yellow (see Fig.4.8) to red from  $Ba^{2+}$  to  $Ca^{2+}$ ,



Fig.4.10 X-ray diffraction pattern of the sample EZCS1 (photo) compared with the PDF card 65-894 for CaS and PDF card 65-1961 for ZnS.

The excitation and emission spectra of this series of samples are presented in Fig.4.11. Sample EZCS1 (0.667CaS-0.33ZnS-0.003EuCl<sub>3</sub>) can be excited at 378 nm and at 436 nm with the same emission peak centered at 661 nm. The emission band intensity, excited at 436 nm, is higher than that excited at 378 nm. The other samples, sample EZCS2 (0.89CaS-0.1ZnS-0.01EuCl<sub>3</sub>) and sample EZCS3 (0.85CaS-0.1ZnS-0.05EuCl<sub>3</sub>) have similar excitation and emission behavior: a very broad excitation band between 400- 600 nm with the same emission around 675 nm which is attributed to the transition  $4f^65d^1 \rightarrow 4f^7$  of Eu<sup>2+</sup>.

On the excitation spectrum, some fine absorption peaks can be observed in the region of 450 - 500 nm, which could indicate the presence of Eu<sup>3+</sup> ions (transition  ${}^{7}F_{0} \rightarrow {}^{5}D_{n}$ ). An emission spectrum is recorded with excitation at 467 µm (the most intense fine absorption peak) for two samples (Fig.4.11 b and c) and no fine emission peak of Eu<sup>3+</sup> can be observed. Consequently, these fine absorption peaks superimposed over the broad excitation band are likely due to the noise of the equipment.



Fig.4.11 The excitation and emission spectra of the sample EZCS1 (a), EZCS2 (b), EZCS3 (c) collected at room temperature and the emission intensity comparison of the samples(d)

In order to compare the emission intensity, the luminescence of the three samples was measured under the same experimental conditions, excited at 467 nm or 436 nm. The result is presented in Fig.4.11 (d). The emission intensity of sample EZCS1 is the strongest, even the excitation wavelength is slightly different. The excitation spectrum of the EZCS1 is quite flat in this wavelength region. The FWHM of the emission peak is about 62 nm. By comparing the emission curves of different samples, it can be seen that the emission intensity decreases significantly with increasing of  $Eu^{2+}$  concentration (from 0.3 mol% to 5 mol%) due to concentration quenching. A slight red shift is also observed for the emission peak due to structure modification induced by the insertion of europium ions.

# 5.2.2 CaS/ZnS(Se):Eu<sup>2+</sup>

In order to create more different environment for  $Eu^{2+}$  ions, Se is used to totally or partially substitute S. Selenium element is in the same group VIA as sulfur. Its radius is bigger than S with lower electronegativity. Since it is difficult to obtain CaSe, ZnSe was used to introduce Se. Four samples, along with the already discussed EZCS1 sample, have been synthesized with the compositions detailed in Table4.4. Sample EZCSe1 was designed with the same doping concentration of  $Eu^{2+}$  as sample EZCS1 but with ZnSe instead of ZnS. EZCSe2 was tried to study the influence of ZnSe by decreasing the ZnSe concentration from 33 mol% to 10 mol%. The EZCSe5 sample is for studying the influence of partial substitution of selenium by sulfur. The concentration of  $Eu^{2+}$  ions was increased up to 1% in sample EZCSe6 for comparison with sample EZCSe2.

| Sample | Composition (mol%)   |
|--------|--|
| EZCS1  | 0.667CaS-0.33ZnS-0.003EuCl <sub>3</sub>                        |
| EZCSe1 | $0.667 CaS - 0.33 ZnSe - 0.003 EuCl_3$                         |
| EZCSe2 | $0.9 CaS\text{-}0.1 ZnSe\text{-}0.003 EuCl_3$                  |
| EZCSe5 | $0.9 CaS\hbox{-}0.05 ZnSe\hbox{-}0.05 ZnS\hbox{-}0.003 EuCl_3$ |
| EZCSe6 | $0.89CaS$ - $0.1ZnSe$ - $0.01EuCl_3$                           |

Table4.4 compositions of europium doped samples in the CaS- ZnS(Se) system

Fig.4.12 shows the X-ray patterns of the series ZnSe/CaS:  $Eu^{2^+}$ . In sample EZCSe1, the peak at 27.68° fits well with ZnSe. But the peak at 30.95° is located between the phases CaS and CaSe. The peaks at 44.35° and 46.08° are also difficult to attribute. They cannot fit very well with ZnSe nor with CaS. The peak at 44.35° is between the phase CaS and CaSe, but closer to the CaS side. The peak at 46.08° is near the ZnSe side but is shifted slightly to larger diffraction angle. Obviously, these diffraction peaks do not correspond to known phases. These new crystalline phases are probably composed of a mixture of CaS and CaSe as well as ZnS and ZnSe. In sample EZCSe2, EZCSe5 and EZCSe6, the peaks at 31.46°, 45.09°, 55.63° fit very well with the phase CaS. But the peaks located at 28.26° and 47.04° have a shift to larger angles, between the peaks of ZnS and ZnSe. Consequently, europium ions can be in different environments. In case of Eu<sup>2+</sup> ion, it will probably substitute Ca<sup>2+</sup> with comparable ionic radius.



Fig.4.12 The X-ray diffraction patterns of the series ZnSe/CaS: Eu<sup>2+</sup>; PDF card 77-777 ZnSe, PDF card 65-292 CaS, PDF card 65-1691 ZnS and PDF card 77-2012 CaSe.

Fig.4.13 shows the excitation and emission spectra of the CaS/ZnSe:Eu<sup>2+</sup> series (a) and the comparison of theses emissions with that of EZCS1, containing ZnS (b). All the emissions are characterized by a broad emission band centered around 660 nm, attributed to the transition  $4f^65d^1 \rightarrow 4f^7$  of Eu<sup>2+</sup>. The emission intensity decreases and the maximum of emission moves from 662 nm to 651 nm when S is substituted by Se (by comparing the sample EZCS1 with EZCSe1). This shift is associated with the change of anion. Se offers a more covalent environment with a weaker crystal field, leading to blue shift of the emission.

The Se atom is bigger than S atom which is less polarisable. Upon excitation, the change of the d outer shell electronic cloud of Se is bigger than that of S. The Eu<sup>2+</sup> ions are more stable in the environment of S than in that of Se. The equilibrium distance of Eu-Se is longer than that of Eu-S. The  $\Delta R'$  is larger than  $\Delta R$  (see Fig.4.14). When the europium ions are excited, there are two processes of relaxation. The process ① is a radiative transition, followed by a non-radiative relaxation. The process ② is caused by thermal agitation. Electrons are firstly thermally excited by following the way ② and then the non-radiative

transition. It can been seen from Fig.4.14 that the energy necessary for  $Eu^{2+}$  ions to follow the way (2) is higher when the ions are in the S environment than in Se environment. It's consequently more difficult for  $Eu^{2+}$  ions to follow the way (2) in S environment. The probability of non-radiative relaxation is then higher for  $Eu^{2+}$  ions in Se. This can explain why the emission intensity of the  $Eu^{2+}$  ions is higher in CaS environment than in CaSe environment with the same composition.

With the same concentration of  $Eu^{2+}$  (0.3%), the emission intensity increases immediately when the ZnSe content is decreased from 33% (EZCSe1) to 10% (EZCSe2) as it can been seen in Fig.4.13 (b). At the same time, the emission maximum moves slightly from 651 nm to 656 nm. When the ZnSe concentration is further decreased to 5%, the emission intensity of sample EZCSe5 increases. The radius of Zn<sup>2+</sup> ion is 0.074 nm and that of Eu<sup>2+</sup>ion is 0.095 nm. It is difficult for Eu<sup>2+</sup> ions to enter into the lattice of ZnSe or ZnS. The radius of Eu<sup>2+</sup>ion is very close to that of Ca<sup>2+</sup> (0.099 nm). It is reasonable to assume that Eu<sup>2+</sup> ions occupy preferentially the site of Ca<sup>2+</sup>. Even the Eu<sup>2+</sup> concentration is the same in EZCSe2 and EZCSe1, the Eu<sup>2+</sup> ions are closer to each other in EZCSe1 than in EZCSe2 due the fact that Zn<sup>2+</sup> ions are smaller than Ca<sup>2+</sup>. The probability of concentration quenching of Eu<sup>2+</sup> is higher in EZCSe1.

With increasing concentration of Eu ions from 0.3% to 1%, the emission intensity decreases immediately (Fig.4.13 (b), comparison of EZCSe2 with EZCSe6). This confirms that the concentration quenching happens in this system even at relatively low concentration level. This phenomenon is probably linked to the fact that many quenching centers may exist in this kind of sintered ceramics with imperfections (porosity, grain boundaries...) and impurities.



Fig.4.13 Excitation and emission spectra of the CaS/ZnS(Se):Eu<sup>2+</sup> series (a) and emission intensity comparison (b). These samples were measured at the same time with the same experimental conditions.



Fig.4.14 Configuration coordination diagram of CaS:Eu<sup>2+</sup> and CaSe:Eu<sup>2+</sup>. The equilibrium distance R<sub>0</sub>, and the offset of the excited state equilibrium distance of CaS ( $\Delta$ R) and CaSe ( $\Delta$ R'). (1) is the radiative transition and non-radiative transition way; (2) is the thermal excitation and non-radiative transition way [16]

As mentioned in Fig.4.12, the doping ions  $Eu^{2+}$  can be located in a complex environment (typically sulfur or selenium environment). Consequently, the broad emission band can be deconvoluted into two parts fitted by the Gaussian function, as shown in Fig.4.15. One emission peak is centered at 680 nm and the other at 652 nm.



Fig.4.15 The EZCSe2 emission spectra decomposed into two curves using Gaussian function

# 5.3 SrS/ZnS(Se):Eu<sup>2+</sup>

Another element in the IIA group, the strontium, is also tested. Sample EZSrS1 is designed to keep the same ration as in sample EZCS1. EZSrSe1 is designed to study the influence of ZnS substitution by ZnSe. Table4.5 lists the studied compositions.

| <u>Fable4.5 Compositions of SrS/ZnS(Se) samples doped by 0.3% Eu</u> |   |  |
|--|---|--|
| Sample   | Composition                             |  |
| EZSrS1   | 0.667SrS-0.33ZnS-0.003EuCl <sub>3</sub> |  |
| EZSrSe1  | $0.667 SrS - 0.33 ZnSe - 0.003 EuCl_3$  |  |
| ZSrS   | 0.667SrS-0.333ZnS                       |  |

Fig.4.16 shows the X-ray diffraction patterns of EZSrS1, EZSrSe1 and ZSrS as well as the photos of the samples with and without doping ions. The sample without doping ions shows gray-white color while the sample doped by Eu<sup>2+</sup> shows light orange-pink color. In sample EZSrS1, the major phases are SrS and ZnS. There are still many small diffraction

peaks which do not correspond to any known phase. Some intermediate phases between SrS and ZnS are likely formed. In sample EZSrSe1, the major phases are between SrS and SrSe, ZnS and ZnSe.



Fig.4.16 X-ray diffraction patterns of samples EZSrS1, EZSrSe1 and ZSrS compared with PDF card 8-489 SrS, PDF card 89-2142 ZnS, PDF card 1-690 ZnSe and PDF card 10-182 SrSe. ZSrS is the matrix without doping ions, EZSrS1 is doped by 0.3 mol%Eu<sup>2+</sup>

Fig.4.17 shows the excitation and emission spectra of samples EZSrS1 and EZSrSe1. Sample EZSrS1 presents one broad emission peak centered at 618 nm with a FWHM of about 70 nm. The emission is attributed to the transition  $4f^65d^1 \rightarrow 4f^7$  of Eu<sup>2+</sup>. It presents also a broad excitation band attributed to 4f-5d transition of Eu<sup>2+</sup> ions. The maximum of excitation is located around 425 nm if the fine excitation peaks are not considered. Otherwise, the maximum is around 467 nm. These fine peaks have been discussed earlier. For the following experiments, we have selected 467 nm as excitation wavelength. Both wavelengths can be used without modifying significantly the emission spectra. Sample EZSrSe1 also shows a broad emission band centered at 598 nm. The emission measurement has been performed with the same experimental conditions for these two samples. It is clear that the emission of EZSrS1 is much stronger than that of sample EZSrSe1 with the same concentration of europium ions. As discussed earlier, sulfur environment is more favorable than Se environment in order to have strong emission of  $Eu^{2+}$  ions. The substitution of sulfur by selenium leads to blue shift of the emission of  $Eu^{2+}$ .



Fig.4.17 Excitation and emission spectra of the samples EZSrS1 and EZSrSe1

5.4 CaO/ZnO:Eu<sup>2+</sup> and CaF<sub>2</sub>/ZnF<sub>2</sub>:Eu<sup>2+</sup>

Always for modifying the environment for  $Eu^{2+}$  ions, oxide and fluoride have also been tested with the studied compositions listed in Table 4.6.

|        | Table 4.6 Oxide and fluoride for Eu <sup>2+</sup> doping |
|--------|--|
| Sample | composition  |
| EZCO1  | 0.497CaO-0.5ZnO-0.003Eu                                  |
| EZCF   | $0.89CaF_2$ - $0.1ZnF_2$ - $0.01Eu$                      |

Fig.4.18 presents the emission (a) and excitation (b) spectra of sample EZCF. It has three overlapped excitation bands centered at 337 nm, 353 nm and 367 nm attributed to the same f-d transition of the  $Eu^{2+}$  ion. The origin of these three excitation bands is not very clear. They may be caused by three different, but very similar sites for  $Eu^{2+}$ . The emission is however located at the same wavelength region with different intensity.



Fig.4.18 Emission (a) and excitation (b) spectra of Eu<sup>2+</sup>-doped fluoride sample EZCF

Fig.4.19 shows the emission and excitation spectra of the  $Eu^{2+}$ -doped oxide sample EZCO1. It has a broad excitation band centered at 502 nm with a broad emission centered at 733 nm. The FWHM for the emission is large, around 100 nm.



Fig.4.19 Emission and excitation spectra of sample EZCO1 excited @ 502 nm and monitored @ 738 nm

# 5.5 Comparison of the emission band of $Eu^{2+}$ in different chemical environments

Fig.4.20 (a) and (b) show the normalized emission spectra of the Eu<sup>2+</sup> doped samples with two groups of environments for facilitating the comparison. The first group, illustrated in Fig.4.20 (a), keeps the same anion S, but with changing cation from Ca to Sr and to Ba by keeping the same ration of Ba(Ca,Sr)/ZnS and the same doping concentration of Eu<sup>2+</sup>. The maximum emission wavelength is very significantly changed in the direction of SrS:Eu<sup>2+</sup> < CaS:Eu<sup>2+</sup> < BaS:Eu<sup>2+</sup>. The emission center of sample EZCS1 is located at a longer wavelength than that of sample EZSrS1. This can be attributed to the fact that the crystal field strength of SrS is weaker than that of CaS, leading to blue shift of the emission peak for SrS. However the emission center of sample EZCS1 (CaS) is located at shorter wavelength compared with the emission center of sample EZBS1. Normally, the crystal field strength of CaS is stronger than that of BaS and this should induce blue shift of the emission peak in BaS:Eu<sup>2+</sup>, which is not the case. The radius of Ba<sup>2+</sup> is 0.135 nm, which is larger than that of Ca<sup>2+</sup> (ionic radius of 0.099nm). The change of equilibrium distance in BaS will be longer than in CaS. In this case and as showed in Fig.4.21, the radiative

transition in BaS:Eu<sup>2+</sup> from the way (1) will emit light with longer wavelength than in CaS:Eu<sup>2+</sup>. CaS seems to be more appropriate than BaS for the emission of Eu<sup>2+</sup>. The Fig.4.21 can explain also why Eu<sup>2+</sup> emission is much weaker in BaS than in CaS.

If we keep the same cation and change the anion from F to S and to O (Fig.4.20 b), the maximum emission wavelength is considerably changed from 423 nm to 662 nm to 733 nm.

Fig.4.20 (c) shows the emission spectra of these samples measured at the same condition except for samples EZCO1 and EZBS1. The last two samples are measured with larger slit width as their emission is relatively weak. It can be seen that the intensity of the sample EZCF is the lowest. The emission intensity of samples EZCS1, EZCS2 and EZSrS1 are comparable with the order of EZCS2 > EZSrS1 > EZCS1.



Fig.4.20 Normalized emission spectra of Ba(Ca,Sr)-S:Eu<sup>2+</sup> (a), Ca-S(F,O):Eu<sup>2+</sup> (b) and emission spectra of Ba(Ca,Sr)-S(Se,F,O):Eu<sup>2+</sup> measured at the same conditions (c) except for the samples EZBS1 and EZCO1 with weak luminescence



Fig.4.21 Configuration coordination diagram of CaS:Eu<sup>2+</sup> and BaS:Eu<sup>2+</sup>. The equilibrium distance R<sub>0</sub>, and the offset of the excited state equilibrium distance of CaS ( $\Delta$ R) and BaS ( $\Delta$ R'). (1) is a radiative transition, followed by anon-radiative transition; (2) is the thermal excitation, followed by a non-radiative relaxation [16]

### 6. Conclusion

The objective of this work is to develop luminescent materials with broad and tunable absorptions and emissions bands. Two types of active ions have been considered: the transition metals ions and divalent rare earth ions because of their electronic transitions involving d-shell electrons. Two types of host materials, glasses and ceramics have also been tested.

Transition metal ions have the advantages of wide and strong absorption. It is however not always easy to control the valence. Iron, Manganese and Nickel have been selected for this study. The tested glass hosts are based on alumino-phosphates glasses. It turns out that these transition metal ions are not efficient for luminescence in the above-mentioned glass host.

 $Eu^{2+}$  ions have been studied mainly in different sulfide/selenide environments. Oxide and fluoride have also been tested. Broad and sometimes intense emissions have been obtained. The full width at half maximum can even exceed 100 nm. It has also been demonstrated that the position of the  $Eu^{2+}$  emission is strongly dependent of its chemical environment. The peak emission wavelength can be changed from 655 nm to 730 nm if the anionic environment is changed from sulfide to oxide. Two  $Eu^{2+}$  ions-doped hosts with strong and comparable emission intensity but different emission wavelength will be selected for further studies.

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Chapter V Low phonon-energy thin films with tunable and ultra wide emission bands

| 1. Introduction  | 152 - |
|--|-------|
| 2. The thin film deposition                                    | 153 - |
| 2.1 Introduction of magnetron sputtering                       | 153 - |
| 2.2 Preparation of the targets                                 | 154 - |
| 2.3 Preparation of the substrates                              | 155 - |
| 2.4 Thin film deposition                                       | 155 - |
| 2.4.1 Description of the equipment                             | 155 - |
| 2.4.2 Determination of deposition parameters                   | 157 - |
| 2.4.3 Thin film deposition process                             | 157 - |
| 2.5 Determination of the film's thickness and refractive index | 159 - |
| 3. Characterization of the thin films                          | 162 - |
| 3.1 Presentation of the films                                  | 162 - |
| 3.2 X-ray diffraction of the thin films                        | 162 - |
| 3.3 Optical properties of the thin films                       | 163 - |
| 4. Thermal treatment of the thin films                         | 165 - |
| 4.1 Single target-deposited thin films                         | 165 - |
| 4.1.1 Description of the set-up for thermal treatment          | 166 - |
| 4.1.2 X-ray diffraction  | 167 - |
| 4.1.3 Luminescence measurement of the thin films               | 168 - |
| 4.2 Co-sputtered thin films                                    | 172 - |
| 4.2.1 Transmission measurement                                 | 172 - |
| 4.2.2 X-ray diffraction analysis                               | 174 - |
| 4.2.3 Luminescence measurement                                 | 176 - |
| 5. Conclusion  |       |
| 6. Reference   | 183 - |

# 1. Introduction

Results in the last chapter show that the chalcogenide ceramics  $SrS/ZnS:Eu^{2+}$  and  $CaS/ZnS:Eu^{2+}$  exhibit broad and strong emission bands centered at 620 nm and 662 nm, both attributed to the  $4f^{6}5d^{1}\rightarrow 4f^{7}$  transition of  $Eu^{2+}$ . The FWHM of each emission band is about 60 nm. The emission band is not tunable and depends on the chemical environment of  $Eu^{2+}$  ions.

In this work, our objective is to obtain a wide emission band with still larger FWHM and tunable peak emission wavelength. To realize this objective, it is necessary to design a structure which can provide different environments for  $Eu^{2+}$ . It is relatively difficult to realize such structure in bulk material while thin film structure offers more flexibility as the composition of thin film can be continuously tuned during the deposition.

Radio frequency co-sputtering has been selected for thin film deposition. Two chalcogenide ceramics,  $SrS/ZnS:Eu^{2+}$  and  $CaS/ZnS:Eu^{2+}$  with comparable emission intensity but different emission wavelengths, have been selected as sputtering targets. This thin film fabrication technique allows controlling the thin film composition easily from the composition of one target progressively to that of the other target just by programming the power applied to each target. In this way, thin films with smooth composition gradient can be obtained, as shown in Fig.5.1. In this way, it should be possible to tune the peak emission wavelength of the thin film from that of  $SrS/ZnS:Eu^{2+}$  to that of  $CaS/ZnS:Eu^{2+}$  with still broader emission band.



Fig.5.1 schematic representation of thin film with composition gradient

# 2. The thin film deposition

# 2.1 Basic description of magnetron sputtering

Magnetron sputtering is an extremely flexible technique for thin film deposition that can be used to deposit almost any material [1]. Sputtering is based on removing atomized material from a solid by energetic bombardment of its surface layers by ions or neutral particles. The magnetic field is used to change the electron's moving direction and prolong the trajectory and this improves the working gas' ionization probability to enhance the sputtering efficiency. Magnetron sputtering can be divided into direct current (DC) sputtering and radio frequency (RF) sputtering. The DC sputtering is usually used for electrically conducting materials. The materials studied in this work are mainly insulators and consequently radio frequency magnetron sputtering is used [1-3]. RF discharge helps also to densify the sputtered films by bombing the films [4].

A magnetic field which is vertical to the electric field is loaded on the cathode. The electrons move in the direction vertical to both the electric field and magnetic field. The secondary electrons are under the constraint of the annular magnetic field at the target's surface. They move along the magnetic field line. Its cycloid line moving trajectory can increase the ionizing collision opportunity so that it can work under low sputtering pressure and voltage [1]. The sputtering process is usually carried out in low pressure of about 0.01 mbar or 0.1 mbar [5]. The working gas is an inert gas such as Ar. When a negative voltage is loaded on the target, plasma composed of electrons and ions ( $Ar^+$  for example) can be created. This negative voltage attracts positive ions to the target surface and the positive ions collide with atoms at the surface of a solid with energy transfer. When the transferred energy is greater than the binding energy, the atoms of the target will be ejected and deposited onto the substrate. During the transfer from the target to the substrate, these neutral atoms will collide with Ar and their energy will be reduced and their moving direction changed. The ejected atoms could arrive at the surface of the substrate in all direction by improving the uniformity of the thin films. Magnetron sputtering offers high deposition rate and allows low working pressure. Fig.5.2 is a schematic representation of a magnetron sputtering system [6].



Fig.5.2 Schematic representation of a magnetron sputtering system [6]

# 2.2 Preparation of the targets

The targets used in our systems are discs with diameter of 50 mm and thickness typically of 3-6 mm. Raw materials CaS or SrS: ZnS+EuCl<sub>3</sub> were weighed in a glove box. 30 g powders were thoroughly mixed by using the mechanical milling machine placed in a glove box in order to protect the powders from the pollution of moisture and oxygen. The mechanical milling machine is programmed at a speed of 200 rmp during 30 min. The target is sintered by hot-pressing in a carbon mold with an inner diameter of 50.5 mm at 1100°C with a pressure of 24 MPa for 4 hours under vacuum (about 2 Pa). The obtained targets are presented in Fig.5.3. The target EZSrS shows an orange color while the color of the target EZCS is red. They were smoothly polished to a thickness between 3-6 mm.



Fig.5.3 Photos of the targets EZSrS and EZCS

# 2.3 Preparation of the substrates

In this work, the thickness and refractive index of the film is determined from its transmission curve by measuring the interference minima and maxima. So it's important that the substrates present a good optical transmission over the wavelength region of interest, typically from 400 nm to 1700 nm. Two kinds of substrates are used: commercial glass microscope plates ( $20mm \times 18mm \times 1mm$ ) and BK7 glass ( $\varphi 25mm \times 2mm$ ). They have high transmission of about 92% with a short wavelength cut-off at about 320 nm. In order to improve the adherence of the thin films, the substrates are carefully cleaned as follows before use: Firstly, they were degreased in TFD4 solution under ultrasound agitation for 15 minutes. Then they were cleaned by acetone. Finally, they were rinsed by de-ionized water and dried by blow drier.

# 2.4 Thin film deposition

# 2.4.1 Description of the equipment

The magnetron sputtering used in this study is a Plassys MP600s with three cathodes. This system is composed of three major parts: the vacuum system, deposition system and PC controller. Fig.5.4 shows the deposition system of the magnetron sputtering. Three targets are placed in the vacuum chamber ( $\varphi$ 500 mm×445 mm) shown in Fig.5.4 (a). The chamber can be pumped down to a pressure close to 10<sup>-7</sup> mbar. The position of the targets is shown in Fig.5.4 (c). Fig.5.4 (b) shows the substrate holder. The positional relationship between the target and the substrate is shown in Fig.5.4 (d). The distance and the tilt between the substrate and the target can be adjusted through a mechanism depictured in Fig.5.4 (d).

The substrate can be heated in order to perform thermal annealing, if necessary, during the sputtering. The maximum annealing temperature is 800°C. There is a substrate transfer system, the square box on the right side of the Fig.5.4 (a), allowing changing the substrate without breaking the vacuum in the deposition chamber.



Fig.5.4 Magnetron sputtering equipment (a)(b)(c) and mechanism for adjusting the distance and the tilt between the target and the substrate (d)

#### 2.4.2 Determination of deposition parameters

The sputtering parameters can affect the deposition rate, the film's composition and the film's uniformity. The major parameters to be optimized are:

(1) The pressure of Ar. First, it should be high enough to guarantee the normal glow discharge. But if the Ar pressure is too high, there will be more opportunity for the particles to be scattered by the Ar atoms. That will reduce the energy of the atoms that arrive on the substrate. It will affect the film's density. If the Ar pressure is too low, there will be less opportunity for the secondary electrons to collide the Ar atoms. Usually, the working pressure of sputtering is around 0.01 mbar to 0.1 mbar. For magnetron sputtering, the working pressure can be lower to  $10^{-3}$  mbar. There is an optimized pressure for having the highest deposition rate.

(2) The power applied to the target. The deposition rate is proportional to the power applied to the target. But high stress could be induced by high sputtering power [7]. Considering that the targets used in this work are sintered ceramics and are relatively fragile with a high thermal expansion coefficient of about 13.8  $10^{-6}$  K<sup>-1</sup>, we have restricted the power to 100 W. Otherwise, the target can be broken because of the thermal shock as part of the power is wasted to generate heat during the deposition [8]. In fact, one side of the target is cooled by water and the other side is heated by argon ions.

(3) The distance between the target and the substrate. The deposition rate is inversely proportional to the distance between the target and the substrate when the other parameters are fixed. The film's uniformity depends also on the distance. Normally, longer the distance is, better the uniformity of the film will be.

(4) The temperature of the substrate [9]. The process of deposition is similar to the process of glass quenching. If the substrate is not heated, the temperature of the substrate is raised only by the sputtered particles. The temperature of the substrate is normally kept around 40°C during the deposition. The obtained thin films are usually amorphous. Annealing is necessary to allow the thin films to reorganize [7, 8, 10]. To a certain degree, higher the temperature of the substrate is, higher the film's density and compactness will be.

#### 2.4.3 Thin film deposition process

The thin film deposition process includes the following steps:

1) Cleaning the vacuum chamber including the shutters, covers, substrate holders, screws and so on in order to avoid cross contamination. This step is particularly important in case of target change. Those parts are cleaned by sandblasting which is a rapid and efficient way to remove the films on the contaminated parts. All the sand cleaned parts are again cleaned with detergent and acetone to eliminate all organic contaminants which are harmful to the adherence of the thin films.

2) Installing the targets. The diameter of the target should be adjusted to about 2 inches. The target is put on a copper holder, cooled by circulating water, and fixed by a ring. In order to well fix the target, its diameter should be larger than the inner diameter of the ring (Fig.5.5). It's important to fix well the target. Otherwise, the target will fall down. Then the barrel cover is installed. Attention should be paid to ensure a gap between the barrel cover and the ring. Their relative position is shown in Fig.5.5 (b). But the gap cannot be very big so as to avoid glow discharge.



Fig.5.5 Installation of the target on the target holder

3) Etching the substrate. It's a further process of cleaning. After having pumped the deposition chamber down to  $10^{-7}$  mbar, the well cleaned substrate can be introduced into the deposition chamber through the transfer chamber. The deposition process starts with the etching of the substrate by bombarding the substrate with  $Ar^+$  ions. The Ar gas flow was controlled at 30 Sccm. Plasma was usually initiated with a pressure of 0.1 mbar which is a typical pressure for magnetron sputtering [11]. The etching power was set to 100 W as the substrate is a borosilicate glass. If the substrate is changed to chalcogenide glass, the etching power cannot exceed 30 W. This etching duration is around 10 minutes.

4) Etching the target. Before depositing film, the target is etched in order to eliminate the surface contamination. The plasma initiation pressure was always 0.1 mbar which was then decreased to the working pressure of 0.033 mbar. In order to protect the target of the chalcogenide ceramics with relatively high thermal expansion coefficient of about 13.8  $10^{-6}/K$ , the deposition power is increased progressively to 60 W. This etching process, during which the target cover is closed, lasted for 10 minutes.

5) Depositing thin films. Two targets have been chosen for the deposition. The Ar flow rate was set to 30 Sccm. The working pressure was set to 0.033 mbar. The initial deposition power was set to 60 W. If the deposition power is higher than 100 W, there would be a high risk of breaking the target. The DC bias between the target and the substrate caused by the asymmetry between the electrodes was kept around 120 V. It is known that the bias has a certain influence on the compactness and uniformity of the films. An increase in bias voltage could enhance the adatom mobility on the surface via increasing the average energy of the free ions [8]. The temperature of the substrate during the deposition was between 40°C and 70°C due to the plasma and the ion/atom bombarding. At the end of the depositions, the power loaded on the target was decreased progressively to minimize the thermal shock of the targets.

#### 2.5 Determination of the film's thickness and refractive index

In this work, the thickness and the refractive index of the films are calculated based on the transmission curve [12]. The transmission spectra were recorded using a Perkin Elmer Lambda spectrophotometer in the UV/Visible/NIR region. A typical transmission spectrum is presented in Fig.5.6.

A thin film presents three different interfaces: air-film, film-substrate and substrate-air. These three mediums have different refractive index, leading to multiple reflections. The incident light arrives at a polished surface is either reflected or transmitted. For example, the specific case of a plane parallel to the substrate is considered and it is assumed that the illumination conditions of the surface can generate interference phenomena. This means that there will be multiple reflections at the various interfaces. With the example of Fig.5.7 below, there are two areas, one uncoated and the other coated.


Fig.5.6 Typical transmission curve of a thin film [13]

For each wavelength,  $R_s$  and  $T_s$  are respectively the reflectance and transmission of the substrate, with energy conservation ( $R_s+T_s=1$ ). The optical property of this single layer deposited on substrate is the factor of transmission T, reflection at the air side R and at the substrate side R'. With Spectrophotometry method, we have access only to flow quantities as shown in Fig.5.7, reflection and transmission flows. Flow expressions are given for uncoated and coated surfaces and depend on transmission T, reflections R and R',  $R_s$  and  $T_s$  of uncoated substrate.

In the case of single layer deposited on a substrate, if this thickness is comparable to the wavelength, interferences will appear. These interferences are characterized by a modulation of transmission as shown in Fig.5.6. Theory of optical coatings [14] demonstrates with a matrix approach that the optical admittance at each minimum of transmittance is equal to  $n^2/n_s$  where n and  $n_s$  are respectively the refractive index of the layer and that of the substrate. The maximum transmittance, when absorption is negligible, is equal to the transmittance of the uncoated substrate ( $T_{max}=T_s$ ). If we know the measured quantity of transmitted flow ( $\phi_{min}$ ) by

spectrophotometry, we can determinate, with these approximations, the refractive index for each minimum of transmission by using the expression (6-2). For more simplicity in the future, transmitted flow measured by spectrophotometer is called transmission.

$$n = \frac{\sqrt{-1 - n_s^2 + \frac{4n_s}{\phi_{min}} + \frac{\sqrt{-4n_s^2 \phi_{min}^2 + (-4n_s + \phi_{min} + n_s^2 \phi_{min})^2}}{phi}}}{\sqrt{2}}$$
(6-2)

The maximum transmission T=1-R<sub>s</sub>.



Fig.5.7 The schema of the incident light arriving at the coated and uncoated surface [15]

By supposing that we have no dispersion of refractive index and knowing the wavelength  $\lambda_1$  where the transmission is the minimum and  $\lambda_2$  corresponding to the adjacent maximum transmission, the thickness of the film *e* is:

$$e = \frac{\lambda_1 \lambda_2}{4(n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1)} \tag{6-3}$$

This method allows calculating the thickness and the refractive index of the films if the interference maxima and minima are measured. More precise measurement of the thickness and the refractive index of the film can be performed by M-lines or prism coupler method.

### 3. Characterization of the thin films

A series of films were deposited. Their transmission was measured with a UV/visible/NIR spectrometer to determine the films' thickness. X-ray diffraction was performed in order to determine if the film was amorphous or already crystallized. The luminescence of the films has also been measured. Table5.1 lists the deposition parameters of different films.

| Table5.1 Deposition parameters of different thin films |            |                 |                               |    |          |
|--|------------|-----------------|-------------------------------|----|----------|
| Film   | Target     | Pressure (mbar) | Power (W) Ar flow rate (Sccm) |    | Duration |
|  |            |                 |                               |    | (h)      |
| SrS21  | SrS/ZnS:Eu | 0.033           | 60                            | 30 | 3.3      |
| CaS1   | CaS/ZnS:Eu | 0.033           | 60                            | 30 | 2        |
| SrS15  | SrS/ZnS:Eu | 0.033           | 50                            | 20 | 19       |

### 3.1 Presentation of the films

The glass substrate was fixed on the substrate holder by screw. The BK7 glass substrate could be put in a specifically adapted substrate holder. The uniformity of the thin films depends on deposition parameters. With our experimental conditions, still to be optimized, a uniform area of about 25 mm in diameter can be obtained, as shown in Fig.5.8.



Fig.5.8 The substrate holder and the deposited films.

# 3.2 X-ray diffraction of the thin films

The XRD patterns of the films SrS21 and CaS1 are shown in Fig.5.9. They are obviously amorphous. During the sputtering process, the atoms were randomly ejected from the target onto the substrate. The substrate temperature was close to room temperature during

the sputtering process. These free atoms were suddenly fixed on the substrate and did not have enough energy to rearrange. Amorphous phase was formed.



Fig.5.9 X-ray diffraction patterns of the films SrS21 and CaS1

### 3.3 Optical properties of the thin films

For optical characterization, transmission spectra were recorded using a Perkin Elmer Lambda spectrophotometer in the UV/Visible/NIR region. The transmission curve of each substrate was recorded before the deposition.

The transmission curves of film SrS21 were recorded in Fig.5.10. Two areas were measured to check if the film was uniform. Film SrS21 appeared a little foggy after exposure in air during 20 minutes. This is probably because SrS is sensitive to moisture. The transmission curves present clearly scattering losses due to degradation of the film by moisture. Under the optical microscope, rough surface can be observed as shown in Fig.5.10. Through the transmission curve, the film's thickness can be calculated and the result is 217 nm. The refractive index of the substrate is 1.5 and that of the film is 2.23.

From figure 5.10, it can be seen that the transmission is different for the two measured areas. This is attributed to the sensitivity of the film to moisture which degrades randomly the quality of the film. This will be discussed later.



Fig.5.10 Transmission curves of the SrS/ZnS:Eu<sup>2+</sup> film and that of the substrate. The inset photo represents the film after 20 minute-exposure in air.

The transmission curves of CaS/ZnS: $Eu^{2+}$  film were recorded and shown in Fig.5.11. Again, two different areas were measured. This film looked much smoother than the SrS/ZnS: $Eu^{2+}$  film. The transmission curves of area a and area b coincide well with each other. It means that the film CaS1 is uniform and stable in air. The maximum transmission of the thin film is lower than the transmission of the substrate due to the scattering losses induced by the presence of small crystals inside the film. Through the transmission curves, the film's thickness is calculated as 189 nm. The refractive index of the film is 2.038.

With the following deposition condition: Ar pressure=0.033 mbar; Ar flow rate=30 Sccm; power loaded on the target=60 W, the deposition rate of the SrS/ZnS: $Eu^{2+}$  film is 1.11 nm/min and that of the CaS/ZnS: $Eu^{2+}$  film is 1.58 nm/min.



Fig.5.11 Transmission curves of the CaS/ZnS:Eu<sup>2+</sup> film and the substrate. The inset photo is the film observed under optical microscope

#### 4. Thermal treatment of the thin films

### 4.1 Single target-deposited thin films

It is widely known that crystalline environment is generally more favorable for having high intensity of luminescence. We have chosen to anneal the thin film after the deposition. Similar study has been already reported [16]. The film deposited with the target EZSrS (SrS/ZnS:Eu<sup>2+</sup>) during 19 hours (thickness of 2  $\mu$ m) is selected for this experiment. The same thin film was cut into four parts. One was kept as the reference. The other three parts were annealed in vacuum (10<sup>-3</sup> Pa), at different temperatures for 2 hours. The thermal treatment conditions are listed in Table5.2. Due to lack of thin film samples, SrS15-5 is the SrS15-2 sample annealed again at 500°C for 2 hours, as the sample SrS15-2 didn't have significant luminescence. Films deposited with the target EZCS (CaS/ZnS:Eu<sup>2+</sup>) was just annealed at 500°C for 2 hours thanks to the results obtained with the film SrS15. We could not use higher annealing temperature because of the use of glass substrate.

| Film                 | Annealing temperature | Duration (h) |
|----------------------|-----------------------|--------------|
|                      | (°C)                  |              |
| SrS15-1              | -                     | -            |
| SrS15-2              | 220                   | 2            |
| SrS15-3              | 300                   | 2            |
| SrS15-4              | 400                   | 2            |
| SrS15-5 <sup>*</sup> | 500                   | 2            |
| CaS1                 | -                     | -            |
| CaS1-2               | 500                   | 2            |

| Table5.2 The fil | m SrS15 anneal | led at different | temperature | for 2 | hours |
|------------------|----------------|------------------|-------------|-------|-------|
|                  |                |                  |             |       |       |

\*Sample SrS15-5 was the sample SrS15-2 annealed again

# 4.1.1 Description of the set-up for thermal treatment

Fig.5.12 shows the set-up used for annealing the films. The films were annealed in vacuum of about  $10^{-3}$  Pa to avoid contamination by air during the thermal treatment. The films were heated rapidly to the annealing temperature with the rate of  $10^{\circ}$ C/min and were kept at this temperature for 2 hours. The samples were then cooled down slowly, inside the furnace, to the room temperature.



Fig.5.12 The set-up used in the lab for annealing the films

#### 4.1.2 X-ray diffraction

The crystallized films were analyzed by X-ray diffraction and the results are shown in Fig.5.13. From the figures, we can see that there is no crystallization with the film annealed at 220°C. But significant diffraction peaks appear with the film annealed at 300°C. The diffraction peaks (2 $\theta$ ) at 25.7°, 29.7° and 42.5° can be attributed to the cubic SrS phase. There is not any diffraction peak which can be attributed to ZnS. When the annealing temperature is increased to 400°C, the peaks attributed to SrS didn't change significantly. Two new peaks appear at 28.6° and at 47.6°, corresponding to the cubic ZnS phase. With increasing annealing temperature, more ZnS is generated. ZnS phase can be clearly observed with the SrS/ZnS:Eu<sup>2+</sup> film annealed at 500°C. These experiments indicate that SrS tends to crystallize firstly and ZnS tends to remain amorphous.



Fig.5.13 (a) X-ray diffraction patterns of the SrS based films (SrS15) annealed at 220°C, 300°C, 400°C and 500°C respectively for 2 hours compared with the film without annealing, PDF card 8-489 SrS and PDF card 65-309 ZnS; (b) X-ray diffraction patterns of CaS based films without and with annealing at 500°C for 2 hours

With the CaS based thin film, the crystallization temperature is significantly higher, as the thin film stay amorphous even after an annealing at 500°C for 2 hours. The melting point of CaS is 2400°C while that of SrS is 2000°C. The radius of Ca is smaller than that of Sr. The bond energy of Ca-S is higher than that of Sr-S. This can explain why the CaS based film should be annealed at higher temperature than that of SrS based films.

#### 4.1.3 Luminescence measurement of the thin films

The luminescence of these thermally annealed films was measured by using the fluorimeter FLS920 with a Xe lamp as the light source. The width of the excitation slit and that of the emission slit are set as 3 and 3 respectively. The emission curves were recorded with a step of 1 nm and dwell of 0.3 s. A filter 495 nm was placed before the visible detector to filter the light before the wavelength of 495 nm which may arrive at the detector. The emission curves were corrected after the measurement with the correction files supplied with the equipment. The emission spectra of the films with and without annealing at 400°C are presented in Fig.5.14 (a), together with the emission spectra of the target as a reference. The same excitation wavelength as for the target (467 nm), determined previously, is used for the film before the thermal treatment, it didn't show any luminescence. After annealing at 400°C for 2 hours, the thin film shows a broad emission band centered around 615 nm, very similar to the emission band of the target.

The emission spectra of thin films annealed at different temperatures are presented in Fig.5.14 (b). The films without annealing or annealed at low temperature such as 220°C didn't exhibit emission signals. With increasing annealing temperature, the emission intensity increases. The emission intensity of the film annealed at 500°C is almost 3 times of the emission intensity of the film annealed at 300°C. All the emission spectra are centered around 610 nm with slightly different shape. As discussed for the target in Chapter 4, this emission is attributed to the  $4f^65d^1 \rightarrow 4f^7$  transition of Eu<sup>2+</sup>. Annealing at 500°C seems to be the most efficient temperature for the luminescence. Owing to the glass transition temperature of the substrate glass of about 550°C, the maximum annealing temperature cannot exceed significantly 500°C.

All these results lead to the following comments and discussions:

- It is essential to create a crystalline environment for the Eu<sup>2+</sup> ions to enhance their luminescence. It is well known that crystalline environment is more favorable to

have strong luminescence. Another parameter should also be taken into account. In fact, the as-deposited amorphous films generally contain defects (voids, composition deficiency, stress...). After thermal treatment, some of these defects will be removed. The  $Eu^{2+}$  ions will be incorporated in stoichiometric crystalline phase [7, 10]. All these parameters will help to enhance the luminescence of the  $Eu^{2+}$  ions.

- There is an excellent composition transfer from the target to the substrate during the sputtering process. The luminescence of the Eu<sup>2+</sup> ions, which is sensitive to the chemical environment, is similar to the target and to the thin films.
- The sensitivity of the Eu<sup>2+</sup> ions' luminescence to the chemical environment is also illustrated in Fig.5.14 (b). Slight difference can be observed on the emission spectra of the same thin film annealed at different temperatures.



Fig.5.14 Excitation and emission curves of the films SrS15 with and without annealing at 400°C and the emission band of the target (a), their intensity is not comparable as their slit width is not the same; emission curves of the films crystallized excited @ 467 nm (b) and @ 340 nm (c), measured at ambient temperature

The luminescence of all these films has also been studied with UV excitation at 340 nm. The emission spectra are shown in Fig.5.14 (c). The broad emission bands between 400-500 and between 500-700 nm are attributed to ZnS or more precisely to defects center of ZnS [17]. It was demonstrated that the thermal treatment will determine the emission wavelength. The origin of the band at 500 nm is not clear. It is present with all samples, including the one without annealing. It is probably due to an artifact of the equipment.

Fig.5.15 shows the luminescence taken by the camera (Canon 600 D) when the films were excited at 340 nm (a) and excited at 467 nm (b). In order to photograph the luminescence of the film, the excitation slit was opened to the maximum width. The film without annealing didn't present luminescence when excited at 340 nm. The color of the film annealed at 220°C was cold blue. When the annealing temperature is increased to 300°C and 400°C, the color change is small. The light emitted by the sample annealed at 400°C seemed to be warmer than that emitted by the sample annealed at 220°C. Big change happened with the sample annealed at 500°C. The color of the emission changed to green. These observations are in agreement with the Fig.5.14 (c). The sample SrS15-5 has a broad and relatively intense emission band centered at 500 nm. So, it presents a mix color of yellow and green. The sample SrS15-4 also has a broad emission band, but its intensity is much lower, leading to a bluish color with a little yellow component. The emission band of the samples SrS15-2, SrS15-3 is centered at 425 nm, leading consequently to blue color.



Fig.5.15 The color of the films SrS15-(1-5) excited @ 340 nm (a) and excited @ 467 nm (b). The excitation light is filtered.

When we took the photos of samples excited at 467 nm, a 495 nm filter was placed between the camera and the samples in order to eliminate the excitation light. Obvious

changes in color and brightness can be observed from Fig.5.15 (b). The film which is not annealed does not emit significantly. The film annealed at 220°C shows emission with very weak green color. When the annealing temperature is increased to 300°C, the color is changed to red-orange. The color of the film annealed at 400°C didn't change much compared with SrS15-3. The brightest one is the film annealed at 500°C and its color is turned to orange.



Fig.5.16 Emission bands of the films CaS/ZnS : Eu<sup>2+</sup> (CaS1) with and without annealing excited @ 467 nm (a) and excited @ 340 nm

The film deposited with another target, CaS/ZnS :Eu<sup>2+</sup> (EZCS) was annealed at 500°C for 2 hours. The emission spectra ( $\lambda_{ex}$ =340 nm and 467 nm) are shown in Fig.5.16. By comparison with the emission spectra of the substrate, it can be seen that the film without annealing didn't show any luminescence when excited at 467 nm. The annealed one exhibits a very weak emission band around 660 nm. When the films were excited at 340 nm, slight changes in emission can be observed. As discussed before, these emissions are attributed to ZnS.

Fig.5.13 (b) has indicated that 500°C is not high enough as annealing temperature to induce crystallization of the films based on CaS. This temperature was limited by the nature of the substrate. This annealing temperature starts to have an effect on ZnS which has lower temperature of crystallization. Higher annealing temperature should be tried later.

# 4.2 Co-sputtered thin films

The co-deposition is carried out to achieve the aim of tuning the emission band by adjusting the film's composition through changing the power loaded on the targets. The parameters of the co-deposited films on BK7 glass substrate are listed in Table5.3.

| Table5.3 The parameters of the film co-deposition |              |          |         |              |          |
|---|--------------|----------|---------|--------------|----------|
| Film  | Target       | Pressure | Power   | Ar flow rate | Duration |
|   |              | (mbar)   | (W)     | (Sccm)       | (h)      |
| CSSr2   | EZSrS - EZCS | 0.033    | 60 - 60 | 30           | 2        |
| CSSr5   | EZSrS - EZCS | 0.033    | 40 - 60 | 30           | 2        |

# 4.2.1 Transmission measurement

These co-deposited films were analyzed firstly by spectrophotometer. The transmission spectra are presented in Fig.5.17. Two zones of the same film were measured. By comparing the transmission spectra of these two zones, it can be found that these two spectra are perfectly identical, indicating that the films were very uniform. The Strong absorption in the wavelength region of 400-600 nm is due to the electronic transition of the thin films if we neglect the absorption due to Eu<sup>2+</sup> ions. Comparing the films CSSr2 with CSSr5, no obvious difference in band-gap can be observed. With CaS, ZnS and SrS as constituents, a band-gap of the targets can be estimated from the reflection spectra which can be seen in the Fig.5.18. The band-gap of target SrS/ZnS:Eu is expected to be 537 nm, that of target CaS/ZnS:Eu is 610 nm. The shift of the absorption edge of the deposited films, toward shorter wavelengths might attribute to the fact that the film is much thinner than the bulk target. Optical path length is shorter, and the optical loss is lower.



Fig.5.17 Transmission spectra of the co-deposited films (targets CaS/ZnS:Eu<sup>2+</sup> and SrS/ZnS:Eu<sup>2+</sup>)



Fig.5.18 Reflection spectra of the targets EZCS (CaS/ZnS:Eu<sup>2+</sup>) and EZSrS (Sr/ZnS:Eu<sup>2+</sup>)

From the knowledge of the maximum and minimum transmissions and the corresponding wavelengths, the thickness and the refractive index of the films can be calculated by using the equation 6-1, 6-2 and 6-3. The results are listed in Table5.4.

| Table5.4 The refractive index of the substrate and the films and the films' thickness are listed |                      |                           |                |  |
|--|----------------------|---------------------------|----------------|--|
| Film   | <i>n</i> of the film | <i>n</i> of the substrate | thickness (nm) |  |
| CSSr2  | 2.00                 | 1.51                      | 442            |  |
| CSSr5  | 2.07                 | 1.51                      | 313            |  |

4.2.2 X-ray diffraction analysis

Samples were cut into four parts and annealed in vacuum at 300°C, 400°C and 500°C for 2 hours. Their x-ray diffraction patterns are presented in Fig.5.19.



Fig.5.19 X-ray diffraction patterns of the films CSSr2 without annealing and annealed at 300°C, 400°C and 500°C for comparing with PDF card 2-659 SrS

The sample without annealing is amorphous. The diffraction peak around 43° grows up progressively with increasing annealing temperature. The same phenomenon is observed with the peak located at 25.8°. Another peak at 29.8° was hardly observable because of the noisy

base line. It has a tendency to appear when annealed at 300°C. This peak is more visible with the sample annealed at 500°C. These three peaks belong to the cubic SrS phase. No diffraction peak corresponding to CaS or ZnS can be found. It has been demonstrated earlier that ZnS tends to stay amorphous while CaS crystallize at higher annealing temperature. The other sample CSSr5 was annealed only at 500°C. Its x-ray diffraction pattern is presented in Fig.5.20.

Fig.5.20 shows that the diffraction patterns of the thin film does change significantly before and after annealing at 500°C. The peaks located at 26° and 43° belong to SrS already existed in the film without annealing. The annealing temperature of 500°C is not enough to promote further crystallization. In this film, power applied to the target EZCS (CaS/ ZnS:Eu<sup>2+</sup>) was higher than that loaded on the target EZSrS (SrS/ZnS:Eu<sup>2+</sup>). This film contains more CaS than the thin film just discussed before. It is consequently more difficult to crystallize.



Fig.5.20 X-ray diffractions of film CSSr5 with annealing at 500°C and without annealing, compared with PDF card 2-659 SrS

#### 4.2.3 Luminescence measurement

The emission spectra of the film CSSr2 annealed at 300°C, 400°C and 500°C are presented in Fig.5.21. They are excited at 467 nm. Obvious changes can be observed for the samples after a thermal treatment at 400°C or at 500°C. These annealed thin films show a broad emission band with a FWHM of 80 nm. The emission intensity increases with the increasing annealing temperature. The phenomenon is the same as for the bulk sample and the crystallization of SrS gives a more favorable environment for Eu<sup>2+</sup> ions. The emission band is centered at 623 nm. By comparison with the emission band of the thin film based on SrS/ZnS:Eu<sup>2+</sup>, shown in Fig.5.14, the peak emission wavelength is moved towards longer wavelength. As expected, this co-sputtered thin film, with the two targets SrS/ZnS:Eu<sup>2+</sup> and CaS/ZnS:Eu<sup>2+</sup>, has a peak emission wavelength (623 nm) between that of the two targets (610 nm and 662 nm). The co-sputtered thin film has a peak emission wavelength closer to that of the target based on SrS. One of the reasons is the main crystallized phase in the co-sputtered thin film is SrS.



Fig.5.21 Emission curves of the films CSSr2 annealed at 300°C, 400°C, and 500°C or without annealing.

Fig.5.22 shows the photography of different annealed films CSSr2 excited at 467 nm. The initial weak blue light which existed in all samples (see Fig.5.21) is probably due to the ZnS, as discussed previously. The sample annealed at 300°C presents a yellow-green color. And the color changes to red-orange when the sample is annealed at 400°C or 500°C. This observation is in fully agreement with the emission spectra and the observed color is the result of combination of two emissions, centered respectively at 623 nm and around 500 nm.



Fig.5.22 Photos of the films CSSr2 annealed at 300°C, 400°C and 500°C excited @ 467 nm

The emission bands of the as-prepared CSSr5 film and that of the same CSSr5 film annealed at 500°C are presented in Fig.5.23. The as-prepared film didn't show any significant emission while the film after the thermal treatment showed a strong emission band centered at 634 nm. The photos in Fig.5.24 show the color change of the films excited at 467 nm. The annealed film shows a red color.

Despite the fact that the annealing at 500°C does not induce significant change in the x-ray diffraction patterns (Fig.5.13), the annealing do have created more favorable local environment for  $Eu^{2+}$  ions probably with the generation of some nano-crystals containing these europium ions.



Fig.5.23 Emission spectra of the films CSSr5 with and without annealing excited @ 467 nm



Fig.5.24 Photos of the as-prepared and annealed CSSr5 films excited @ 467 nm

Fig.5.25 shows the normalized emission spectrum, with the same excitation at 467 nm, for four thin films:

- SrS15: thin film deposited with the target SrS/ZnS:Eu<sup>2+</sup>
- CaS1: thin film deposited with the target CaS/ZnS:Eu<sup>2+</sup>
- CSSr2: thin film co-deposited with the targets SrS/ZnS:Zu<sup>2+</sup> (60W) and CaS/ZnS:Eu<sup>2+</sup> (60W)

- CSSr5 : same as CSSr2 but with more CaS

All these films have been annealed at 500°C for 2 hours. It is clear that the peak emission wavelength depends directly on the ration of SrS/CaS. A higher content of CaS leads to a longer peak emission wavelength.

In order to estimate the different deposition rate of these two targets containing respectively SrS and CaS, and assuming that the deposition rate is lineally proportional to the applied power on the target, we can have the following equations by taking the data from Table5.4

 $60^*\alpha Ca + 60^*\alpha Sr = 442 \text{ nm}$ 

 $60*\alpha Ca + 40*\alpha Sr = 313 \text{ nm}$ 

 $\alpha$ Ca and  $\alpha$ Sr are respectively the deposition rate (nm/W for deposition duration of 2 hours) for the two targets containing CaS and SrS. By using the above equations, we can get the value of  $\alpha$ Ca and  $\alpha$ Sr which is respectively 0.91 nm/W and 6.45 nm/W for two hours. These deposition rates cannot be compared with the rate of single-target deposition, because the condition is totally different.

By using these deposition rates, we can estimate the ratio of Sr/Ca in the two cosputtered films as indicated in the Table5.5.

| Tubles is composition estimation of co-spatieled time in |              |           |       |  |  |
|--|--------------|-----------|-------|--|--|
| Film   | Target       | Power (W) | Sr/Ca |  |  |
| CSSr2  | EZSrS - EZCS | 60 - 60   | 87%   |  |  |
| CSSr5  | EZSrS - EZCS | 40 - 60   | 82%   |  |  |

Table5.5 Composition estimation of co-sputtered thin films

Consequently, it seems that the Sr atoms are always by far the majority, compared to Ca atoms, in both films. This is probably the main reason why the peak emission wavelength of the co-sputtered films is quite close to that of the target containing SrS. In addition, SrS tends to crystallize the first.



Fig.5.25 Normalized emission band of the single-target deposited and double-target deposited thin films, excited at 467 nm

# 5. Conclusion

Different thin films containing  $Eu^{2+}$  ions have been deposited with one or two targets by using magnetron sputtering technique. With the used deposition parameters (Ar pressure of 0.033 mbar, power of 60 W), the single-target deposition rate is typically about 2 nm/min which is quite low and this is mainly due to the 3-target configuration of the sputtering system. The as-prepared thin films are amorphous. Thermal treatment was necessary to crystallize the films. For the SrS/ZnS:Eu<sup>2+</sup> films, it starts to crystallize when annealed at 300°C and the best results have been obtained with the annealing temperature of 500°C. The cubic SrS phase was the major crystallized phase. The annealed films present an intense and broad luminescence centered at around 615 nm with a FWHM of about 80 nm.

Concerning the film obtained with the target CaS/ZnS:Eu<sup>2+</sup>, a annealing temperature of 500°C do not induce any crystallization and the enhancement of luminescence, due to the annealing is small. The used substrate was BK7 with a glass transition temperature of 550°C, preventing the use of significantly higher annealing temperature. A substrate with higher  $T_g$  should be used in the future.

The co-deposited films with different ratios of Sr/Ca, realized by applying different power on each target, have been prepared with excellent uniformity. With the film having a high Sr/Ca ratio (estimated as 87%), the crystalline SrS phase is observable upon annealing at 500°C. For the other film with lower Sr/Ca (estimated as 82%), even the annealing does not lead to observable crystallized phase, the luminescence is greatly enhanced. All the annealed films show relatively intense and broad emission with a typical FWHM of 80 nm. The peak emission wavelength of the thin films depends directly on the Sr/Ca ratio. The two co-sputtered thin films have the peak emission wavelength relatively closer to that of the target containing SrS than that of the target containing CaS probably for two reasons: the 1<sup>st</sup> one is that in both films, Sr atoms are always by far in majority and the 2<sup>nd</sup> reason is that the first crystallized phase is SrS.

In conclusion, it is possible to adjust the peak emission wavelength by modifying the ratio of Sr/Ca of the thin films. It seems that the luminescence of the co-sputtered films comes essentially from  $Eu^{2+}$  ions in SrS environment, more or less influenced by Ca ions. The FWHM of the emission band does not change significantly. In the future, it will be important to prepare thin films with crystallized CaS if the peak emission wavelength should been tuned

in a large domain. If a very broad emission band is necessary, then a mixed and crystallized SrS and CaS environment would be a good solution.

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**General Conclusion** 

The objective of this work is to develop materials for efficient frequency conversion. Two types of materials for two modes of frequency conversion have been studied.

The first conversion mode is frequency doubling by using second harmonic generation, necessitating materials with high 2<sup>nd</sup> order non linearity. We have selected chalcogenide glass-ceramics for this study by using a new fabrication technique associating mechanical milling with Spark Plasma Sintering. This technique allows the fabrication of chalcogenide glasses even with strong tendency to crystallize, which is often necessary for obtaining glass-ceramics. In addition, this technique can also considerably lower the production cost of these glasses and glass-ceramics.

A new glass  $Ge_{15}Ga_{20}S_{65}$ , located outside the glass forming region delimited with the classic melt-quenching method using sealed silica tube, is selected for demonstrating the feasibility of this new fabrication technique. Raw materials Ge, Ga and S were mechanically milled for 120 hours. During the milling process, there is a progressive reaction between the starting elements. The phase  $Ga_2S_3$  can still be found in the final powder. This powder has been sintered and pressed with SPS and the obtained sample was not transparent in the visible. The maximum transmission in the infrared region was also low due to the presence of scattering centers such as crystals, non-reacted grains and porosity. In addition, impurities such as oxygen and water have also been introduced into the glass ceramic during the mechanical milling process in air. This process should be carried out in glove box under inert atmosphere.

Another glass-ceramic GeS<sub>2</sub>+ $\beta$ GeS<sub>2</sub> was also synthesized by this technique. The GeS<sub>2</sub> glass can be synthesized with traditional melt-quenching technique. However, it was impossible to homogeneously generate crystals inside the glass. The crystallization is mostly superficial with a thickness of about 10 µm, leading to weak second harmonic generation. With this new technique, glass-ceramics containing homogenously dispersed  $\beta$ GeS<sub>2</sub> were obtained. Samples obtained with mechanical milling in air and in controlled atmosphere have been compared. The later shows a higher densification rate (> 99%). The optical transmission of such samples is still low due to the scattering losses induced by imperfections such as porosity, graphite (mould) contamination. Its transmission at the wavelength of 0.9 µm was too low to carry out any experiment of second harmonic generation.

In order to increase the transmission of the samples, especially at 0.9  $\mu$ m, it is essential to decrease the scattering losses. For achieving this objective and in addition to the reduction

of defects induced by the sintering process, it is also important to minimize the refractive index difference between the glassy matrix and the doping crystals as well as to control the size of the crystals.  $Ge_{20}$ -Sb<sub>12</sub>-S<sub>68</sub>+CdS system has been selected with closely matching refractive index between the glass and CdS.

The cadmium sulfide nano-particles were synthesized from basic cadmium solution strongly complexed by amine. During the synthesis process, they were continuously stirred and precipitated with centrifugation to avoid further growing. Finally, fine and pure CdS crystal powders were obtained. These crystals were thoroughly mixed with the glassy powders and sintered into a disc which presented relatively high transmission of 60% at 10.6  $\mu$ m. At shorter wavelengths, its transmission was much lower, indicating the presence of small scattering centers. Second harmonic generation has been confirmed in this sample, with however very weak signal. At the signal detection wavelength of 0.9  $\mu$ m, the transmittance was very low. Future works will include two research directions. The first one is to improve the transmission at 0.9  $\mu$ m and the second direction is to perform the SHG measurement at 10.6  $\mu$ m by using CO<sub>2</sub> laser as pumping source.

The second part of this work is focused on the development of materials with ultrabroad and tunable absorption and emission for efficient frequency conversion through photoluminescence.

Two types of active ions have been considered: the transition metal ions and divalent rare earth ions because of their electronic transitions involving d-shell electrons. Transition metal ions have the advantages of wide and strong absorption. But it is always difficult to control their valence. Transition metals Fe, Ni and Mn have been tested in aluminophosphates glass and no luminescence has been detected.

Divalent europium ions in different sulfide/selenide ceramics have been studied. Oxide and fluoride environment have also been tested for comparison. Broad and intense emission bands have been obtained with  $Eu^{2+}$  ion in sulfide and selenide ceramics. The full width at the half maximum (FWHM) can exceed 100 nm. It is also demonstrated that the peak emission wavelength of  $Eu^{2+}$  strongly depends on its chemical environment. In sulfide environment, this wavelength can be tuned from 620 nm to 733 nm if the cation is changed from Sr to Ba. The peak emission wavelength can change from 425 nm to 733 nm if the anion is changed from fluoride to oxide. In order to benefit from the fact that the emission of Eu<sup>2+</sup> ions is different in various environment, thin film structures with tunable composition have been designed. The ultimate objective is to achieve ultra wide and tunable emission. Two chalcogenide ceramics, SrS/ZnS:Eu<sup>2+</sup> and CaS/ZnS:Eu<sup>2+</sup> with comparable emission intensity, but different emission wavelength have been selected as sputtering targets. Different thin films have been obtained by single or co-deposition. It has been found that all as-prepared amorphous thin films do not show any noticeable luminescence. An increasing annealing temperature leads to increasing luminescence intensity. The annealing temperature was limited, by the use of BK7 glass substrate, to 500°C. Intense and broad luminescence bands, centered around 615 nm with a FWHM of about 80 nm, have been measured.

For the co-deposited films, the peak emission wavelength depends directly on the Sr/Ca ratio. The co-deposited film with high ratio of Sr/Ca showed the emission center located at 622 nm while the low ratio of Sr/Ca showed the emission center located at 634 nm. It has been demonstrated that the deposition rate of SrS/ZnS:Eu<sup>2+</sup> is much higher than that of CaS/ZnS:Eu<sup>2+</sup>. The difference of Sr/Ca ratio between the two above-mentioned thin films is quite small. The crystallized phase is always SrS in our annealing conditions, limited by the use of BK7 glass substrates. In the future, it is important to generate, at the same time, CaS crystals in order to still enlarge the emission band.

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# RÉSUMÉ

L'objectif de ce travail est de développer des matériaux pour une conversion efficace de fréquences. Deux types de matériaux ont été étudiés.

Le premier type concerne des matériaux pour le doublage de fréquence par la génération de second harmonique. Nous avons sélectionné des vitrocéramiques de chalcogénures  $GeS_2+\beta GeS_2$  et  $Ge_{20}Sb_{12}S_{68}+Cds$  pour cette étude avec une différence d'indice faible entre la phase vitreuse et les cristaux. Ces vitrocéramiques ont été élaborées avec une technique originale en associant la mécano-synthèse et le pressage flash (Spark Plasma Sintering). Elles présentent une grande compacité supérieure à 99,9%. Les pertes optiques par diffusion, en particulier dans les courtes longueurs d'onde, doivent encore être améliorées pour rendre possible les mesures de génération de second harmonique.

Cette nouvelle technique de synthèse a également permis la fabrication des verres de chalcogénures qui ont une forte tendance à cristalliser. L'exemple a été donné par la synthèse du verre  $Ge_{15}Ga_{20}S_{65}$ , situé en dehors du domaine vitreux déterminé par la méthode de synthèse classique (fusion-trempe).

Le deuxième type de matériaux étudiés concerne des matériaux luminescents à large bande d'absorption et d'émission. Les ions de métaux de transition Fe, Ni et Mn et l'ion de terre rare bivalent Eu ont été sélectionnés en raison des transitions électroniques impliquant des électrons de la couche d.

Des émissions larges et parfois intenses ont été obtenues avec des ions  $Eu^{2+}$  dans les céramiques SrS/ZnS et CaS/ZnS. La largeur à mi-hauteur peut même dépasser 100 nm. Il a été démontré que la position de l'émission dépend fortement de l'environnement chimique des ions  $Eu^{2+}$ . Afin d'ajuster continuellement la position de cette émission, des couches minces contenant différents rapports Sr/Ca ont été déposées par co-pulvérisation cathodique assistée par un magnétron. Des émissions larges et ajustables ont été obtenues.

#### ABSTRACT

The objective of this work is to develop materials for efficient frequency conversion. Two types of materials were studied.

The first type relates to materials for frequency doubling by using second harmonic generation. We selected chalcogenide glass ceramics  $GeS_2+\beta GeS_2$  and  $Ge_{20}Sb_{12}S_{68}+CdS$  for this study with a low difference of refractive index between the glass phase and the crystals. These ceramics were synthesized by melt-quenching technique and by combination of mechanical milling and Spark Plasma Sintering. The obtained glass ceramics have a high compactness greater than 99.9%. The optical losses due to scattering, particularly at shorter wavelengths, must be further improved before measurement of second harmonic generation.

This new synthesis technique also allowed the manufacture of chalcogenide glasses which have a strong tendency to crystallize. The example was given by the synthesis of the glass  $Ge_{15}Ga_{20}S_{65}$ , located outside of the glass forming region determined by using the conventional melt-quenching method.

The second type of the studied materials was related to luminescent materials with broadband absorption and emission. Transition metal ions, Fe, Ni and Mn, and divalent rare earth ion Eu were selected for its electronic transitions involving d-shell electrons.

Wide and intense emissions were obtained with  $Eu^{2+}$  ions in CaS/ZnS and SrS/ZnS ceramics. The FWHM may exceed 100 nm. It has been demonstrated that the position of the emission strongly depends on the chemical environment of  $Eu^{2+}$  ions. In order to continuously adjust the position of the emission, thin films containing different Sr/Ca ratios were deposited by magnetron sputtering. Wide and adjustable emissions were obtained.