Preparation and hot pressing of ZnS nano powders for producing transparent ceramics

ZHU SHIZEN[a,b], M. A. HONGLI[b], R. JEAN[b], M.-C. ODILE[b], A. JEAN-LUC[b], L. JACQUES[b], Z. XIANGHUA [b*]
[a]*School of Material Science and Technology, Beijing Institute of Technology, Beijing, China,100083*
[b]*Laboratoire de Verres et Céramiques, UMR CNRS 6226 « Sciences Chimiques de Rennes», Université de Rennes I, Campus de Beaulieu, 35042 Rennes cedex, France*

Mono dispersed cubic nano ZnS powders have been successfully prepared by using thioacetamide (CH_3CSNH_2) as source of S^{2-}. The use of Na_2S as sintering agent allows to lower the sintering temperature and to keep the cubic structure, leading to hot pressing sintered ZnS ceramics with approximately the theoretical density. The morphology and optical properties of the sintered ceramics have been studied.

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1. Introduction

ZnS is a widely studied material having numerous interesting applications such as phosphorescence, photoelectric device, infrared window [1-6]. The commonly used method for preparing bulk product is Chemical Vapour Deposition (CVD) which allows obtaining highly transparent materials. However, this technique is complex, time consuming, leading to expensive products. Many works have been done in order to prepare transparent ZnS directly from powders by hot pressing [7-11] with more or less success. The difficulty to obtain highly densified ZnS is associated with the fact that this compound tends to sublimate when the temperature is higher than 1200 °C.

The quality of starting powders is critical to the quality of sintered samples. Polycrystalline YAG ($Y_3Al_5O_{12}$) ceramics, as transparent as single crystals have been successfully prepared by sintering high quality nano powders without pressure [12-15]. The sintered samples have even better mechanical properties compared to those of the single crystals.

In this paper, we report the preparation and sintering of nano ZnS powders which should allow to lower the sintering temperature.

2. Experimental

Zinc sulphide nano powders are generally prepared with the following three techniques: solid phase, liquid phase and vapour techniques. The solid phase technique consists of mixing and grinding together the raw materials which react to give nano particles. The advantages of this technique are mainly simplicity, high productivity and high reproducibility of particle size [16-17].

Liquid phase technique includes sol-gel method, chemical precipitation, and dissolution of organo–metallic complexes. It is generally easy to control the size and the composition of the produced nano particles [18-19].

Chemical or physical vapour deposition, sputtering and thermal vapour decomposition are the commonly used vapour phase techniques for producing nano powders. The produced nano particles are generally spherical with narrow size distribution[20-21].

We have decided to use the liquid phase technique for producing ZnS nano powders, mainly because of its simplicity with high yield.

2.1 Preparation of ZnS nano powders

The raw materials for this preparation are thioacetamide CH_3CSNH_2 (TAA) (99%), $ZnCl_2$ (99.9%), hydrochloric acid (HCl), aqueous ammonia ($NH_3.H_2O$), surfactant (polyoxethylene isooctylphenyl ether, OP-10), from Aldrich.

In order to study the influence of preparation technique on the overall quality of ZnS nano particles, we have used three different methods of synthesis.

2.1.1 Fast Homogenous Precipitation (FHP)

This preparation technique is typically the following: 90 ml of 0.5 mol/l of ZnCl2 solution is firstly prepared and the PH is adjusted to 0-2 with addition of hydrochloric acid. This solution is then mixed with filtrated 90 ml of 1.0 mol/l TTA solution (because of the relatively low solubility of TAA). This mixture is kept at room temperature for 2 hours for nucleation. 120 ml of ammonia solution with different concentrations is mixed up thoroughly with 0.5 vol% of OP and cooled to a temperature between 0-2 °C.

The ammonia solution is poured rapidly into the $ZnCl_2$ solution with strong stirring during 10 minutes. The precipitate is then separated from the solution by centrifugation, washed with deionised water and ethanol, dried under vacuum at 600 °C for 2 hours. Nano powder of ZnS is obtained.

2.1.2 Slow homogenous precipitation (SHP)

90 ml of 0.5 mol/l $ZnCl_2$ solution is mixed up with 90 ml of 1.0 mol/l TAA and the PH is adjusted to around 1.5. The mixture is heated to 75°C for 8 hours. The precipitate is separated, washed and dried as described above.

2.1.3 Classical precipitation (CP)

At room temperature, the pH of $ZnCl_2$ solution of 0.5 mol/l is adjusted to 1-2 with addition of HCl acid. The same volume of Na_2S solution of 0.5mol/l is then slowly mixed up with the $ZnCl_2$ solution with continuous stirring. The precipitate is always separated, washed and dried as previously described.

2.2 Characterisation

The crystal structure of the obtained nano powders is examined by X-ray diffraction (Philips PW3020). Their thermal stability is studied by a combined thermo-gravimeter (TG)/differential thermal analyser (DTA) (SDT2960 from TA instrument) with a heating rate of 10°C/minute and Al_2O_3 powder as reference. The microstructure is observed by using a scanning electron microscope (JSM-6301 from JEOL)

2.3 Sintering of ZnS nano powders

A typical quantity of 5 g of ZnS powder is introduced in a graphite die (20 mm in diameter). The sintering is performed in vacuum of about 10^{-2} mbar. The sintering process is the following: the furnace is continuously pumped under vacuum and the heating rate is 20°C/minute. The applied pressure is 25 MPa during the heating and it is increased to 50 MPa when the sintering temperature is reached. Different sintering temperatures between 950°C and 1200°C and different dwell times (between 1 and 4 hours) have been used to study their influence on the sintering quality. Sintering agent, Na_2S has also been used for some tests. In these cases, Na_2S is firstly dissolved in water and mixed with ZnS powder. The mixture is then dried in vacuum at 500°C for 2 hours before hot pressing.

The density of sintered samples is measured by using the Archimedes principle. The crystalline phases are determined by X-ray diffraction. The infrared transmission is measured with FTIR spectrometer (Bruker Vector 22)

3. Results

3.1 The influence of preparation technique on the microstructure

The X-ray diffraction patterns indicate that the obtained powder is the low temperature β-phase ZnS (sphalerite), having the cubic structure (Fig. 1). However, if the drying temperature is 600°C, then a small quantity of hexagonal wurtzite will be produced with the apparition of a small diffraction peak at 27° (2θ). This phenomenon is observed with the three methods of synthesis. The cubic structure is preferable for obtaining transparent ceramics, because high symmetry is favourable for homogeneous grain growth.

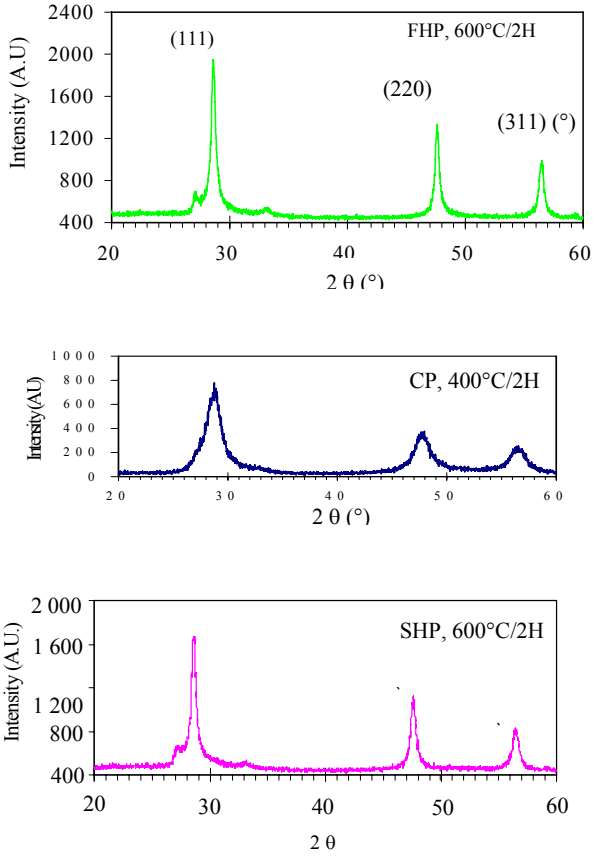


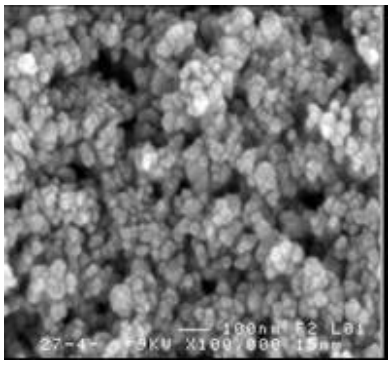
Fig. 1. X-ray diffraction of ZnS nano powders obtained by using different preparation techniques with drying temperature and time.

The preparation technique has a strong influence on the grain size of ZnS powder, as shown in Fig. 2. Different observations and sintering tests lead to the following comments:

- The ZnS powders obtained with the FHP and CP are relatively fine, with an average grain size of approximately 30 nm. The grain size is much bigger (several microns) when the SHP technique is used (Fig. 2b).
- After being dried, the powders obtained with CP are closely stuck together and it is difficult to get fine powder later by milling.
- With the SHP, TAA is used as the source of S^{2-}, by slow dissolution in water. The nucleation rate is controlled by the slow dissolution rate, leading to very few nuclei and relatively big grain size. This type of powder is also not favourable for sintering because large grain is synonym of small surface free energy. In addition this

technique requires long time and consequently is not efficient due to the very low dissolution rate of TAA in acid environment.

- With the FHP, the ammonia solution neutralise the H^+ generated by the dissolution of TAA which is greatly speeded up, leading to much higher productivity. The introduction of the surfactant creates a protective thin film on the ZnS grain, lowering down its growth rate. In addition, the whole reaction takes place at relatively low temperature (typically 0-2°C) leading to low thermal agitation energy and solubility product. With this technique, we have obtained homogeneous and fine ZnS powder. This preparation technique has been studied in detail.



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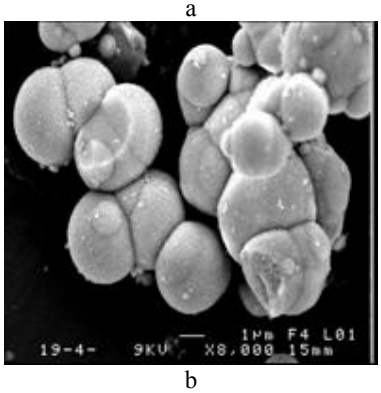

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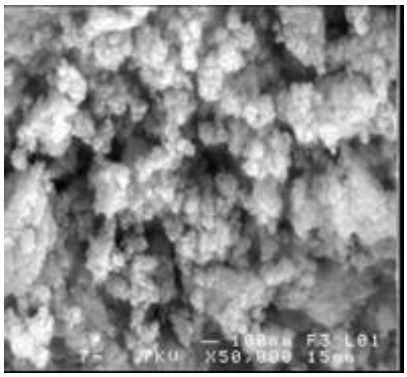


c

Fig. 2. Observation of different ZnS powders under scanning electronic microscope a)Fast homogenous precipitation, b) Slow homogenous precipitation, c) Classical precipitation.

3.2 Influence of the preparation parameters on the quality of the ZnS powder

For sintering transparent ZnS ceramics, it is important to have cubic and well crystallised ZnS powder with as low as possible ZnO content.

The FHP technique for preparing ZnS nano powders is based on the control of dissolution rate of TAA by controlling the acidity of the solution. TAA is firstly thoroughly mixed with $ZnCl_2$ solution with a pH value between 0-2. In this acid solution, the decomposition of TAA is negligible (reaction (1)). By introducing ammonia into the solution, a high number of S^{2-} is produced (reaction (2) and (3)) and in contact with a high number of Zn^{2+}, leading to fine precipitation of ZnS. Different ammonia concentrations have been used and their influence on the quality of the obtained powder is summarized in Table 1. The powders have been washed and dried at 600°C for 2 hours. The pH value is the value of the final solution after reaction. The ZnO and hexagonal ZnS contents are determined qualitatively by X-ray diffraction.

$$CH_3C(S)NH_2 \xrightarrow{H_3O^+} CH_3C(O)NH_2+H_2S \quad (1)$$

$$H_2S+H_2O \rightleftharpoons HS^-+H_3O^+ \quad (2)$$

$$HS^-+H_2O \rightleftharpoons S^{2-}+H_3O^+ \quad (3)$$

From Table 1, it can be seen that the pH value of the solution has a strong influence on the overall quality of the ZnS powders. For obtaining pure cubic ZnS without hexagonal wurtzite and ZnO, the pH should be higher than 10. In a general way, a higher pH value leads also to better crystallized powder with narrower and more intense x-rays diffraction peaks.

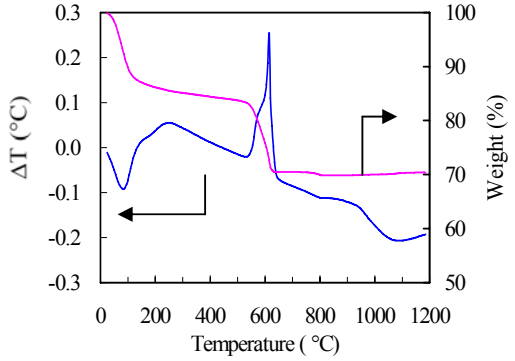
Table 1. Influence of the PH value on the quality of the ZnS nano powder.

PH value	ZnO content	Hexagonal ZnS	Intensity of X ray diffraction (29°)	Full Width at half maximum (°)
7.7	Observable	Present	350	0.90
8.8	Observable	Present	350	0.92
9.6	Non	Very few	600	0.70
10.5	Non	Non	500	0.70
10.5	Non	Non	500	0.64
10.8	Non	Non	500	0.62
11.1	Non	Non	1000	0.36
11.4	Non	Non	1000	0.36

3.3 Thermal analysis of ZnS nano powders

Differential thermal analysis and thermo-gravimetry analysis of the ZnS powders have been performed under normal air condition (Fig. 3a) or under protective nitrogen atmosphere (Fig. 3b). In both cases, the weight decreases quickly at the beginning because of the loss of water. In

normal air condition, zinc sulphide is oxidized at 615°C and this reaction is accompanied by a strong exothermic peak and a weight loss of about 16% corresponding to the complete transformation of ZnS to ZnO. Under nitrogen atmosphere, the cubic ZnS is rather stable until 1010°C at which the cubic phase is transformed to the undesired hexagonal phase. At temperatures higher than 1100 °C, ZnS begins to sublimate.



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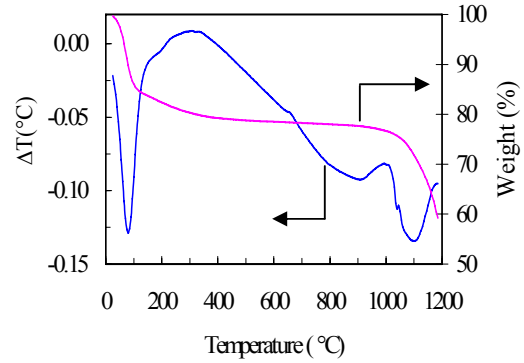

b

Fig. 3. Different thermal analysis and thermo gravity analysis of ZnS nano powder under normal air condition (a) and under nitrogen atmosphere (b).

In summary, ZnS precipitate can be dried in air at temperature lower than 500 °C to avoid risk of oxidation. Sintering of ZnS should be done preferably under 1000 °C to minimize the cubic to hexagonal structure transformation.

3.4 Sintering of ZnS powders

The influence of the sintering agent Na_2S on the quality of the obtained ceramic is shown in Fig. 4. It is clear that the porosity, observed on the polished surfaces is significantly higher for the sample without sintering agent (Figs. 4a and 4b), even with higher sintering temperature (1200 °C). The density is about the same for both samples: 4.09±0.07 g/cm^3 for the sample without sintering agent and 4.04±0.04 g/cm^3 with Na_2S. Observations on the fracture surfaces (Fig. 4b and 4d) indicate that the crystal grains are much bigger when sintering agent is used.

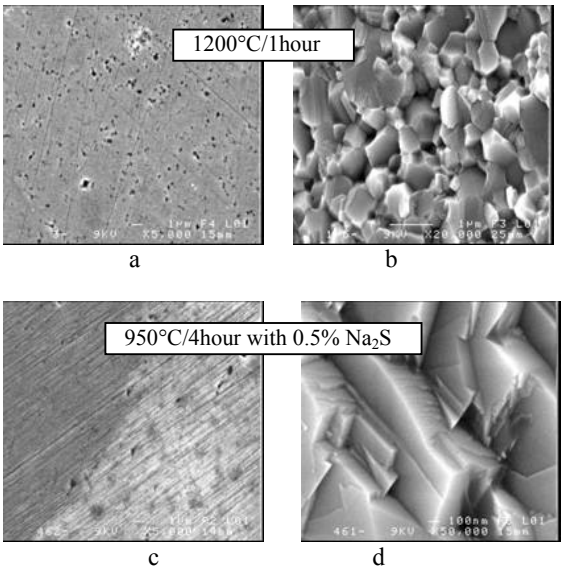

Fig. 4. Observation under scanning electronic microscope of hot pressed ZnS on polished surface (a and c) and on fracture surface (b and d)

The X ray diffraction patterns (Fig. 5) show that when the sintering temperature is higher than 1100°C, the obtained phase is a mixture of sphalerite and wurtzite, as sphalerite to wurtzite transformation temperature is known to be 1023°C. When the sintering temperature is low, 950°C for example, the cubic phase can be maintained. In this case, sintering agent is indispensable to get high densification.

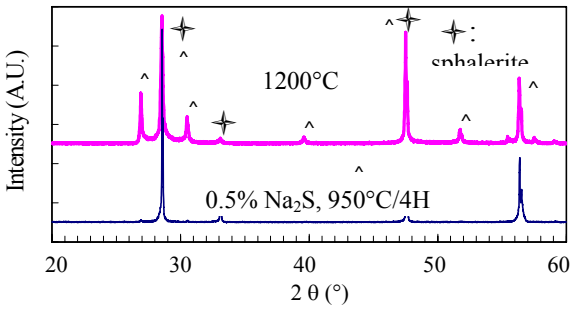

Fig. 5. X-ray diffraction of hot pressed ZnS with different conditions.

The density of sphalerite and wurtzite is respectively 4.04 g/cm^3 and 4.09 g/cm^3, which corresponds exactly to the density of low and high temperature sintering samples. Considering the precision of the measurement, the sintered samples are close to the theoretical densification.

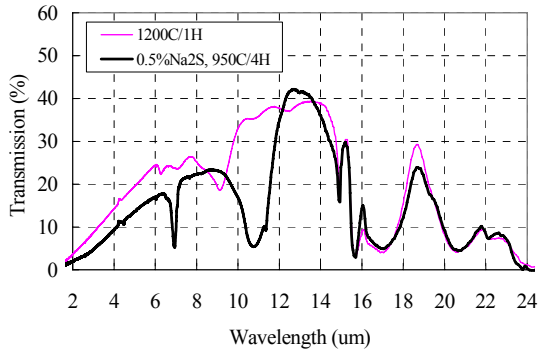

Fig. 6. Infrared transmission of hot pressed ZnS (thickness 0.4 mm).

The objective of this study is to obtain transparent ZnS ceramics. The transmission spectra are shown in Fig. 6 with a thickness of about 0.3 mm and lead to the following comments:

- The two samples show similar low transmittance and this is particularly true in the short wavelength region due to optical losses by scattering which is caused by the presence of porosity and grain boundary. This is not in contradiction with the density measurement, as very low porosity is enough to make the ceramic completely opaque.
- The sintering agent, Na_2S, brings addition absorptions located at 7 and 11 µm and removes the absorption at 9 µm. These absorptions are all linked to chemical bond S-O in different structure configurations [22]. The chemical purity of the obtained ZnS powder and of Na_2S must be increased to remove these absorptions.

4. Conclusion

Mono dispersed nano ZnS powders have been successfully prepared with the so-called fast homogenous precipitation technique by using TAA (CH_3CSNH_2) as source of S^{2-}. The grain size is typically around 50 nm with cubic structure which is preferable for sintering high transparent ceramics. The sintering of ZnS is difficult because of two reasons: firstly, ZnS tends to sublimate above 1200°C and secondly the low temperature cubic structure is transformed into hexagonal structure above 1023°C. The use of 0.5% of Na_2S as sintering agent allows to lower the sintering temperature and to keep the cubic structure. Highly densified ZnS ceramics have been obtained with approximately the theoretical density.

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*Corresponding author: xzhang@univ-rennes1.fr