The study of influence of structural inhomogenities upon optical parameters of zinc sulphide optical ceramic

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The aim of present paper was to find out the influence of structural inhomogenities upon the main parameter of optical ceramic obtained from zinc sulphide by hot pressing, IR transmission. It is directly influenced of microstructure characteristics of ceramic material. Microstructure of studied optical ceramic from zinc sulphide is influenced by starting powder parameters (purity, particle size distribution, stoechiometry) and processing conditions. Taking into account the experimental results we tried to relate transmission and microstructure, the last one being function of pressure, temperature, time, particle size distribution and purity.

1. Introduction

The optical ceramic obtained by hot-pressing is now used for optical instruments and IR radiation technique, because of its interesting properties, as: chemical inertia; low refraction; good mechanical processing.

The thermal and mechanical properties of the window material must be near optimum if the windows are to survive environmental conditions. IR windows should therefore meet the following requirements for optimum thermal, mechanical and optical properties, namely, high melting point, low coefficient of thermal expansion, large band gap, good transmission into the infrared, high hardness, and good strength.

In general, materials with strong chemical bonds exhibit good thermo-mechanical properties but poor infrared transmission, while materials that transmit very well possess weaker chemical bonds and poor thermal and mechanical properties.

The starting powders must have the following qualitative characteristics: high purity, submicronic particle size distribution (monodispersal powder); spherical shape of particles; weak tendency of agglomeration.

2. Experiments

An IR optic ceramic is a transparent aggregate of single crystal grains. The grain size can be varied over a wide range of values depending on chemical composition and method of fabrication. Although individual grains are anisotropic, the material is isotropic at a macroscopic scale, since crystallographic axes are oriented at random and anisotropy is averaged out. IR optic ceramics have a number of advantages over single crystals. These advantages are:
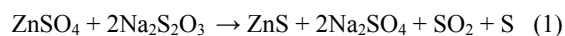
1. less expensive fabrication procedures;
2. possibility of preparing a wide range of sizes and shapes;
3. controlled orientation of optic axis;
4. design of optical and electrooptical properties by properly adjusting composition and fabrication parameters.

Our target in the research work on this type of material was the high purity powders synthesis, hot-pressing technology and the study of the material and technological parameters influence on the optical and mechanical properties of the IR windows.

We have studied the forming process of the liquid phase and its influence during the hot-pressing process. We have studied the polycrystalline ZnS with transmission range 0.57–14.70μm.

We are used the following synthesis reactions of zinc sulphide polycrystalline powder:

$$ZnSO_4 + 2Na_2S_2O_3 \rightarrow ZnS + 2Na_2SO_4 + SO_2 + S \quad (1)$$

$$ZnSO_4 + 4Na_2S_2O_3 \rightarrow ZnS + 4Na_2SO_4 + 4S \quad (2)$$

$$ZnSO_4 + Na_2S \rightarrow ZnS + Na_2SO_4 \quad (3)$$

The optical windows from polycrystalline zinc sulphide was obtained in the following conditions: high purity materials (5-6N); pressure (1-3t/cm^2); powder particle size distribution (5nm-1μm); heat treatment duration and heat treatment curve shape (between 15-60min); controlled work atmosphere.

Table 1. Purity characteristics of synthesised zinc sulphide.

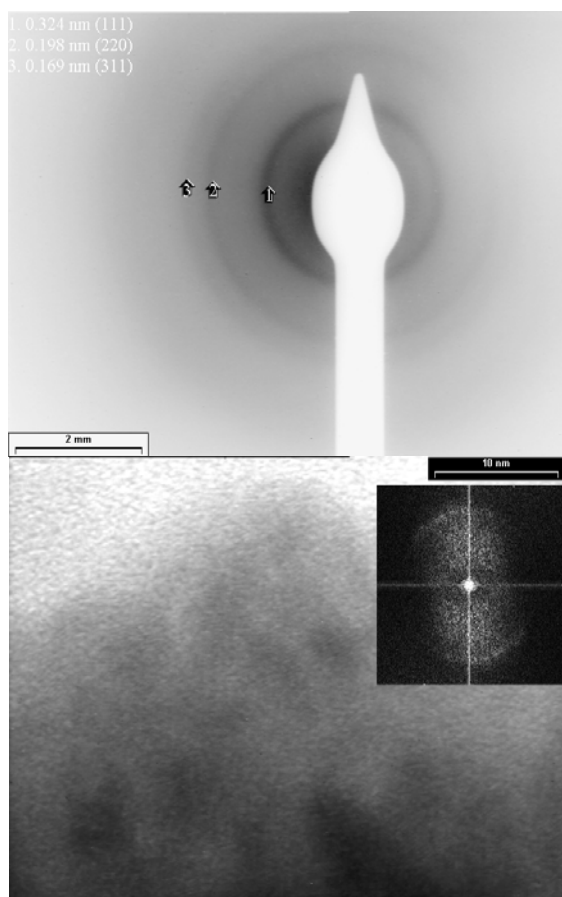| Batch	Fe(%)	Pb(%)	Mg(%)	Cd(%)	Cu(%)	Mn(%)	Ni(%)	Ca(%)	ZnS(%)
1	5.10^{-4}	2.10^{-3}	8.10^{-5}	4.10^{-3}	4.10^{-4}	6.10^{-4}	SLD	SLD	99.9924
2	SLD	1.10^{-3}	4.10^{-5}	1.10^{-3}	6.10^{-4}	4.10^{-3}	2.10^{-4}	5.10^{-4}	99.9927
3	6.10^{-4}	SLD	9.10^{-5}	2.10^{-3}	2.10^{-4}	SLD	3.10^{-4}	SLD	99.9978
4	9.10^{-4}	SLD	5.10^{-5}	5.10^{-4}	SLD	SLD	SLD	SLD	99.9985
5	7.10^{-4}	SLD	4.10^{-5}	2.10^{-4}	2.10^{-4}	8.10^{-4}	SLD	SLD	99.9981
6	8.10^{-4}	SLD	5.10^{-5}	2.10^{-3}	3.10^{-3}	SLD	3.10^{-4}	SLD	99.9938
7	1.10^{-3}	1.10^{-3}	1.10^{-4}	SLD	8.10^{-4}	1.10^{-4}	4.10^{-4}	SLD	99.9966
8	6.10^{-4}	2.10^{-3}	4.10^{-4}	4.10^{-3}	SLD	2.10^{-4}	3.10^{-4}	5.10^{-4}	99.9920
9	1.10^{-3}	1.10^{-3}	2.10^{-4}	9.10^{-4}	3.10^{-3}	SLD	5.10^{-4}	7.10^{-4}	99.9927
10	2.10^{-4}	SLD	3.10^{-5}	SLD	3.10^{-4}	SLD	SLD	3.10^{-4}	99.9992
11	1.10^{-3}	SLD	5.10^{-5}	SLD	4.10^{-3}	SLD	SLD	2.10^{-4}	99.9947
12	2.10^{-4}	7.10^{-4}	2.10^{-4}	4.10^{-4}	SLD	5.10^{-4}	5.10^{-4}	7.10^{-4}	99.9968
13	5.10^{-4}	7.10^{-4}	1.10^{-4}	2.10^{-4}	2.10^{-4}	SLD	3.10^{-4}	3.10^{-4}	99.9977
14	2.10^{-4}	3.10^{-4}	6.10^{-5}	SLD	3.10^{-4}	SLD	SLD	3.10^{-4}	99.9988
15	3.10^{-4}	SLD	SLD	6.10^{-4}	SLD	SLD	SLD	SLD	99.9990

Fig. 1. SAED and HRTEM image and Fourier transform of 5nm precipitated ZnS.

We have established optimal conditions for all the samples, in order to obtain increased optical transmissions and mechanical resistance.

The purity analysis was made with an Induced Coupled Plasma Spectrophotometer. The optical ceramic material was characterised by VIS and IR transmission. The particle size distribution was measured on a Laser Granulometric Analyse, Optical Microscopy, Transmission Electron Microscopy and Scanning Electron Microscopy.

3. Results

We have studied the influences of the working conditions on the parameters of the optical ceramic materials. As seen in the following table, the time and the pressure have a drastic influence on the IR transmission parameter.

Table 2. Influence of the time and pressure on IR transmission level.

Sample	Diameter (mm)	Force (kgf)	Temperature (°C)	Time (min)	Transmission (%)
1	20	5500	1000	15	29
2	20	5500	1000	30	26
3	20	5500	1000	45	33
4	20	5500	1000	60	29
5	20	5500	1000	25	37
6	20	6000	1000	45	40
7	20	2100	1500	50	19
8	20	2200	1500	50	43
9	20	2200	1500	30	20
10	45	8000	1500	50	17

We observed an increase of the particle size during the heat treatment. This has an important influence on the IR transmission parameters.

The thermal treatment at low temperature is needed because particle size increases by heating. We can calculate heating time, based on previously obtained graph (fig. 2), to get the desired crystallization structure with small grain size.
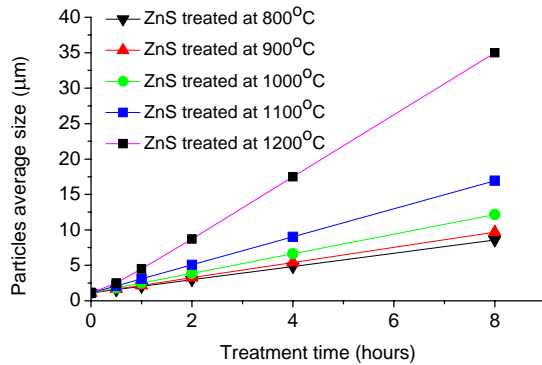
We have also studied the purity influence on the transmission parameters.

We noticed that any kind of impurity promoted the crystal growth by increasing of liquid phase, guiding the process of recrystallization.
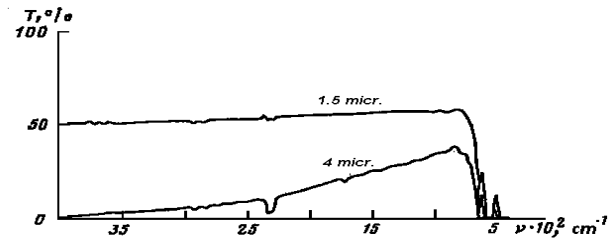

Fig. 2. The increase of ZnS particle size distribution, function of thermal treatment at different temperatures

Fig. 3. The dependence of the IR optical transmission function of the ceramic particle size distribution for windows made from ZnS powder free of SO_4^{2-} and ZnO [6].
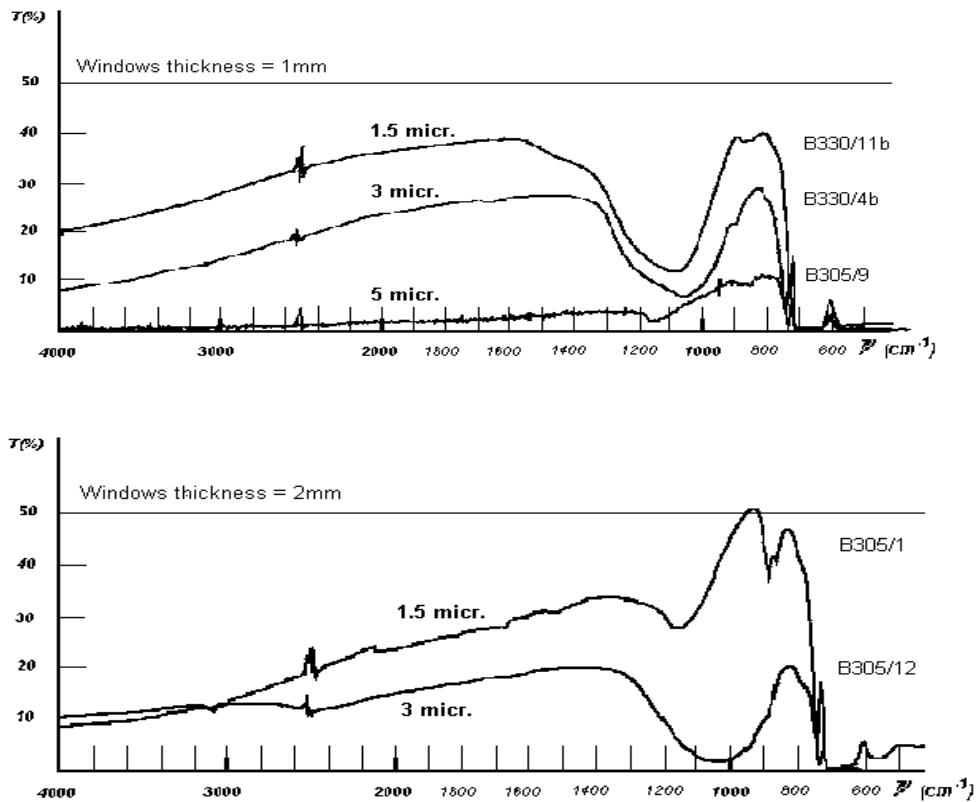

Fig. 4. The dependence of the optical transmission function of the ceramic particle size distribution and the windows thickness.
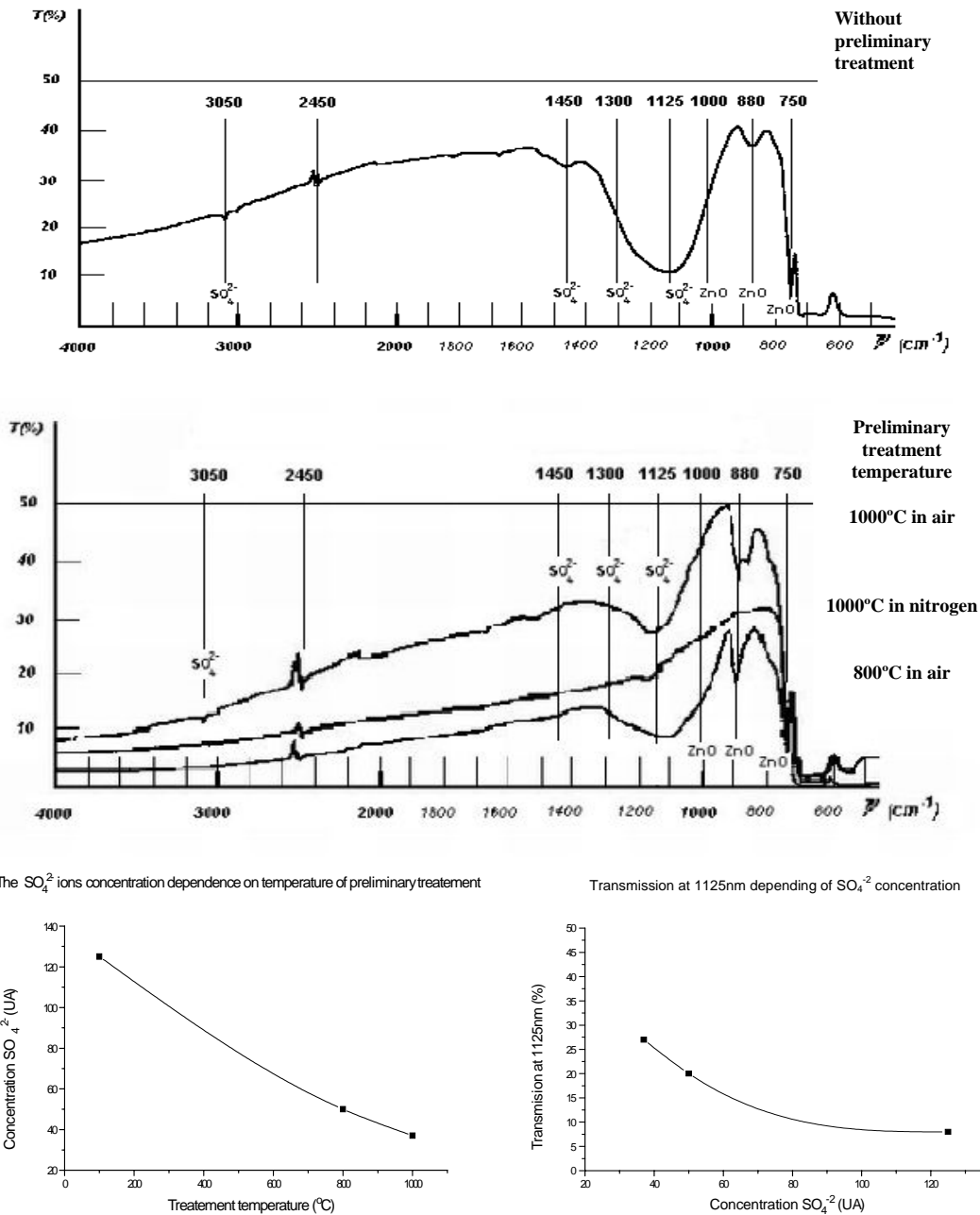
Fig. 5. The dependence of the optical transmission function of the impurity contents (HO^-, H_2O, SO_4^{2-}).

4. Conclusions

There was established a method that allows the synthesis of high purity zinc sulphide (99.9-99.999 %), with a controlled granulation fit for application connected to IR optics (5nm – 2μm).

It was carried out a study regarding the evolution of zinc sulphide granulation from submicronic dimensions (obtained by wet synthesis) up to 50-100 μm (as a result of the thermal treatments)

The starting powders must have the following qualitative characteristics: fine granulometric distribution (mono-dispersal powder); medium submicron diameter; spherical shape grains; minimum tendency of agglomeration.

The optical windows' manufacture was possible in the following conditions: high purity materials (99.999-99.9999%); pressure (1-3t/cm^2); particle size distribution (0.01-1μm); heat treatment duration and heat treatment curve shape (between 15-60 min); controlled working

atmosphere. We have established the optimal conditions for all the samples, in order to obtain increased optical transmittance and mechanical resistance.

We have studied the influences of the working conditions on the parameters of the optical ceramic materials. We observed an increase of the particle size during the heat treatment. This has a drastic influence on the IR transmittance parameter.

The influence of the purity on the transmittance parameter is very important. We noticed that any kind of impurity promoted the crystal growth by increasing of liquid phase fraction, guiding the process of recrystallization. This has, also, a drastic influence on the IR transmittance parameter.

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