

Preparation & Characterisation of IR Window Grade Zinc Sulphide Powder

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ABSTRACT

Zinc sulphide (ZnS) is an important II-VI compound well-known for the electrooptic applications. It is also one of the most suitable materials for the fabrication of IR transmitting domes and windows because of its transmission in the IR region ($2-12 \mu$) of the spectrum as well as its excellent thermo-mechanical properties. The ZnS domes and windows are prepared by hot pressing or hot isostatic pressing (HIP) of optical quality grade ZnS powder. This paper describes the preparation of optical quality grade ZnS powder using a modified acid process maintaining a constant pH. The resulting ZnS powder is subjected to thermal treatment in different atmospheres and at different temperatures. The ZnS powder thus obtained has been characterised by chemical analysis, particle size measurement, IR spectrophotometry, XR-D and XR-F analysis. The role of various experimental parameters involved, e.g., concentration of $ZnSO_4$ solution, firing temperature and firing atmospheres is investigated. A transmission of 69 per cent was achieved after HIP of the ZnS powder prepared by this method.

1. INTRODUCTION

Zinc sulphide (ZnS) is one of the most suitable materials for the fabrication of IR transmitting windows and domes¹. This is so because of its excellent thermo-mechanical properties along with very good transmission in the $2-12 \mu m$ IR region. However, very little information is available in the literature on the preparation of optical quality ZnS material (Showing IR transmission in window form touching theoretical limit ~70 per cent in the $8-12 \mu m$ range of IR, for ZnS) and the fabrication of IR transmitting domes/windows from the material.

Pure ZnS can be prepared by bubbling H_2S gas in a $ZnSO_4$ solution at a pH 3.0. This when fired in nitrogen N_2 at $650^\circ C$ and $1150^\circ C$ yield β - ZnS (cubic sphalerite phase) and α - ZnS (hexagonal-wurtzite phase) respectively². Luminescent grade ZnS has been prepared using acid process and alkali process³. However, no pH control has been exercised in these two processes; Eastman Kodak has produced IR transmitting windows from acid process-made ZnS powder and marketed them as IRTRAN-2 windows⁴. The effect of

pH, concentration of Zn^{++} ions, H_2S flow rate and temperature on the particle size and morphology of ZnS precipitate has been studied by Brown⁵. Again, pH has not been kept constant during the reaction in these studies. Recently, ZnS powder has also been prepared using thioacetamide as the precipitant⁶. However, in all these investigations, the resulting ZnS powders are poorly characterised and no attempt has been made to study the effect of firing temperatures and atmospheres on the IR characteristics and other properties of the ZnS powder.

As indicated in Ref. 2 above, ZnS precipitation from an aqueous $ZnSO_4$ solution through the use of H_2S gas as per the reaction



becomes reversible after a certain stage. To overcome this difficulty, it has been suggested to use a very dilute $ZnSO_4$ solution. Using very dilute $ZnSO_4$ solution results in poor quantities of ZnS . It is known⁷ that ZnS does not dissolve above pH 2.4. It is obvious that precipitation at a higher pH may incorporate some

undesired hydroxides of zinc. The use of buffers containing Na^+ ions will result in the contamination of ZnS powder with Na^+ ions.

It was thus thought worthwhile to precipitate ZnS using the acid process with the modification that ammonia was added dropwise during the precipitation to keep the pH constant at 2.4 ± 0.1 .

The resulting ZnS powder was then fired in pure dry nitrogen gas or argon at different temperatures and the resulting ZnS powders were characterised by chemical analysis, particle size measurement, IR spectrophotometry, XR-D and XR-F techniques.

EXPERIMENTAL DETAILS

2.1 Materials

(a) $ZnSO_4$ solution - ZnO (E Merck, CP grade 99 per cent pure, (India) was dissolved in 2M H_2SO_4 (AR Grade E. Merck, India) till saturation. The filtered solution was left in contact with AR grade (Glaxo) Zn granules for a week to remove the less electropositive metallic impurities. The resulting 2M $ZnSO_4$ solution was used as stock solution.

(b) H_2S gas : H_2S gas was prepared using usual Kipps apparatus. The FeS sticks (E. Merck, India) and H_2SO_4 (AR Grade E. Merck, India) were used for the preparation of the gas. The gas was bubbled through scrubbers of 50 per cent HCl , $Ba(OH)_2$ solution and finally through double distilled water before reaching the precipitation vessel.

(c) All other chemicals used were of AR grade.

2.1.2 Process

A 3l $ZnSO_4$ solution of known concentration (0.25M, 0.5M or 0.8M) was prepared by dilution of the stock solution (a) above. A few drops of 6 per cent H_2O_2 solution were added and dilute NH_3 solution was added to it till a faint precipitate is formed. The precipitate is filtered off and the filtrate is taken into a precipitation vessel shown in the Fig. 1.

The precipitation vessel is fitted with three joints (a) one for dropping dilute NH_3 , (b) the central one being the inlet for H_2S gas and (c) the third one for inserting the pH electrode.

The H_2S gas was bubbled into the filtrate in the vessel. As soon as the gas started flowing through the

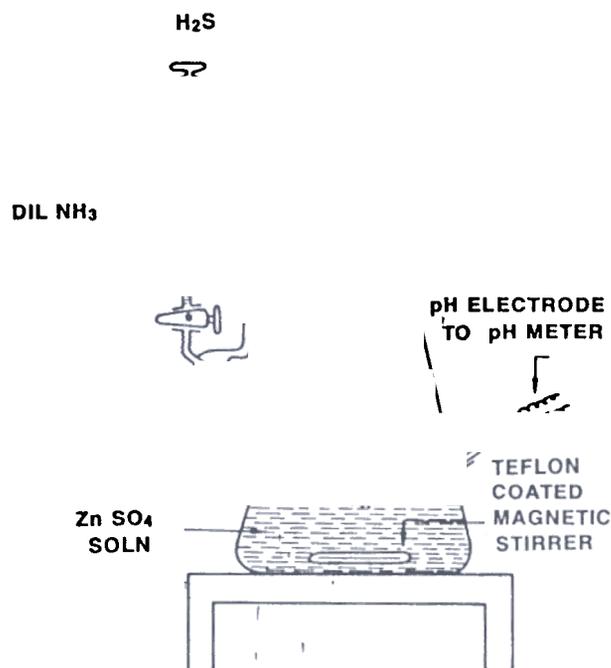


Figure 1. Precipitation vessel.

$ZnSO_4$ solution, the pH started receding from the original value of about 5.7 - 5.8. As the pH reached 3.0, the H_2S supply was cut off and the precipitate obtained (first precipitate) was filtered off. In the filtrate, H_2S gas was again bubbled. As the pH started falling below 2.4, a dilute NH_3 solution (25 per cent NH_3 solution : $H_2O = 1:2$) was added dropwise from the side funnel at such a rate that pH remains steady at the value 2.4 ± 0.1 . The precipitation was continued for about 30 min. The H_2S supply was stopped, the precipitate removed and washed free of SO_4^{--} ions and then dried at $120^\circ C$.

2.2 Firing of ZnS Powder

The ZnS powder obtained as above was taken in a quartz tube and heated in an electrical furnace at a predetermined temperature while an inert gas nitrogen or argon (IOLAR-I grade) (purified further by passing through KOH -pyrogallol solution followed by silica gel and molecular sieves) was flowing over it.

2.3 Characterisation

2.3.1 Chemical Analysis

A weighed quantity of ZnS was dissolved in 4N H_2SO_4 . The solution was made up to 250 ml with double distilled water. The percentage of zinc in the ZnS sample was then determined titrimetrically against $K_4Fe(CN)_6/K_3Fe(CN)_6$ solution using diphenyl benzidine as indicator⁸. From this, the percentage of ZnS in the sample was calculated.

2.3.2 Particle Size Measurement

The particle size measurement of the powder was carried out with a Seishin Particle Size Analyser (Model 2000) using sedimentation technique.

2.3.3 Trace Analysis

Trace analysis for various metallic impurities in the ZnS sample was carried out using X-ray fluorescence analysis. A Philips X-ray fluorescence spectrometer (Model PW 1400) was used for this purpose.

2.3.4 IR Spectrophotometry

The IR spectra (4000 cm^{-1} to 800 cm^{-1}) of various ZnS samples were recorded in the pure state by pressing the powder in the form of a pellet using Perkin Elmer spectrometer (Model 599B).

2.3.5 X-ray Diffraction Studies

X-ray diffractograms for various ZnS samples were recorded using Philips X-ray diffractometer (Model PW 1550).

3. RESULTS & DISCUSSION

3.1 Chemical & Trace Analysis

The ZnS powder obtained after drying the precipitate at 120°C on chemical analysis revealed the presence of about 90 per cent ZnS and the rest consisted of impurities, such as free S, sulphate, etc. The ZnS sample after firing in nitrogen or argon gas at 700°C or 900°C revealed the percentage of ZnS in the sample to be 99.9 per cent. The XR-fluorescence analysis indicated the following trace impurity content $CO < 20$ ppm $Cr < 30$ ppm $Cu < 25$ ppm $Mn < 3$ ppm $Ni < 10$ ppm $Pb < 10$ ppm and $Ti < 30$ ppm.

3.2 Particle Size Measurement

The weight 50 per cent average of the powder (fired at 700°C) particle size has been found to be 1.71 microns.

3.3 IR Spectrophotometric Studies

The ZnS powder obtained after drying the precipitate at 120°C produced the IR spectrum shown in Fig. 2. The spectrum reveals (i) a sharp absorption peak at 1600 cm^{-1} (6μ), (ii) a broad absorption band at $3000\text{--}3600\text{ cm}^{-1}$ ($3.3\text{--}2.8\mu$), and (iii) reduced transmission in $1200\text{--}700\text{ cm}^{-1}$ ($8\text{--}14\mu$) range. Whereas the former two are due to the presence of water molecules and various hydroxide species, the loss of transmission in $8\text{--}14\mu$ region is probably due to SO_4^{2-} ions (9μ)⁹ and free sulphur etc.

3.4 Concentration Effect

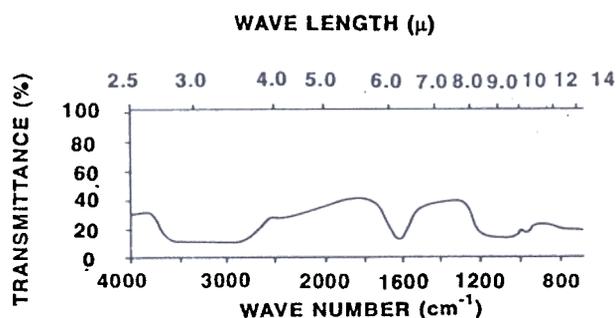


Figure 2. IR spectrum of raw zinc sulphid.

Using three different concentrations of $ZnSO_4$ solution, viz., 0.25M, 0.5M and 0.8M produced little change in the spectral characteristics of the resulting ZnS powder. Hence, for a better control of pH, 0.25M $ZnSO_4$ solution was taken for further investigations.

3.5 Firing Conditions

The 120°C dried ZnS powder (Raw ZnS powder) was purified by heating the powder in pure nitrogen at three temperatures, viz., 500°C , 700°C and 900°C . The IR spectra of the resulting powder are shown in Fig. 3.

It is clear from Fig. 3 that optimum temperature for firing the ZnS powder is 700°C . The powder fired at 500°C shows incomplete removal of water and other impurities. At 700°C the water content is very much reduced. The powder fired at 900°C shows

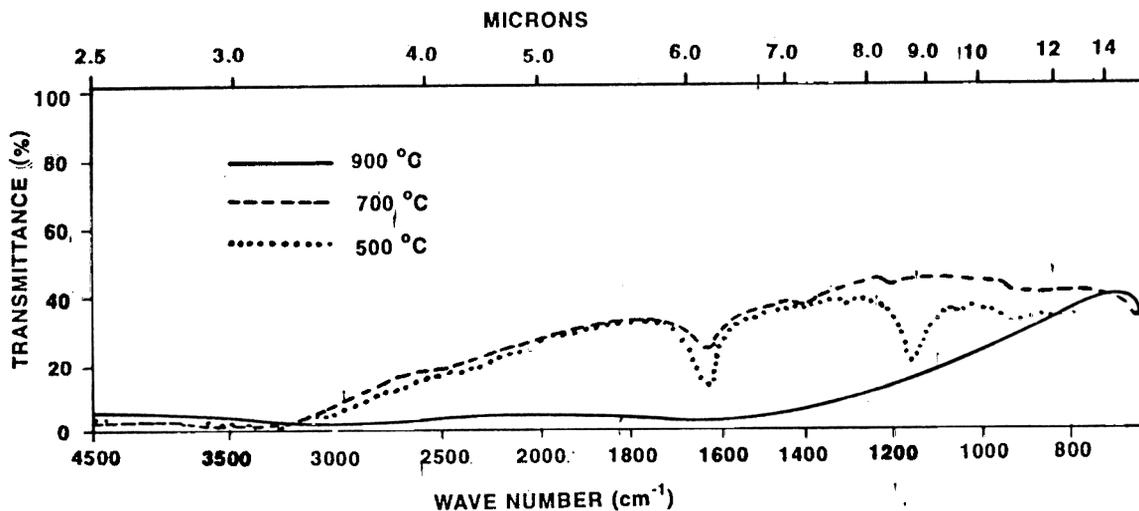


Figure 3. IR spectra of zinc sulphide fired in nitrogen

deterioration of transmission, probably due to scattering losses caused by an increase in grain size and increased α -content as shown by X-ray diffraction studies discussed later.

3.6 X-ray Diffraction Studies

The X-ray diffractograms for raw ZnS powder as well as the ZnS powder fired in nitrogen at 500 °C, 700 °C and 900 °C are shown in Figs 4 and 5. The unfired ZnS powder obtained is predominantly β -phase (Sphalerite). However, in the fired ZnS samples, α -phase (Wurtzite) is also present, and it goes on increasing with the firing temperature. The volume percentage of α -phase in the ZnS samples has been calculated by the method used by Xue and Raj¹¹. The content of α -phase in the unfired ZnS and the ZnS

powders fired at 500 °C, 700 °C, and 900 °C have been estimated to be 6 per cent, 7 per cent, 9 per cent and 16 per cent, respectively. Thus, as the powder fired at 700 °C shows about 9 per cent presence of α -phase as well as best transmission, it can be inferred that up to about 10 per cent, α -phase is not detrimental to the transmission behaviour. Higher percentage of α -phase causes scattering losses due to mismatch of refractive indices of the two phases. The ZnS samples fired in argon at 700 °C exhibit similar XR-D pattern as the one fired in nitrogen at 700 °C.

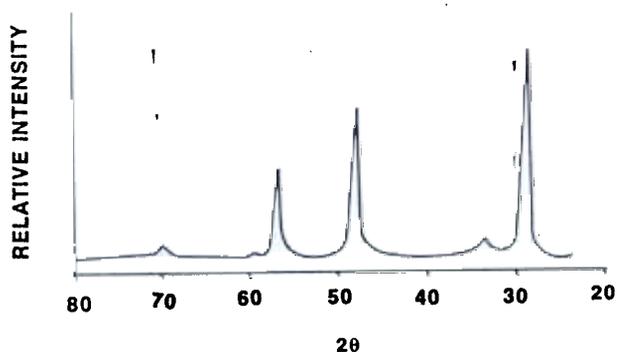


Figure 4. X-ray diffractogram of raw zinc sulphide.

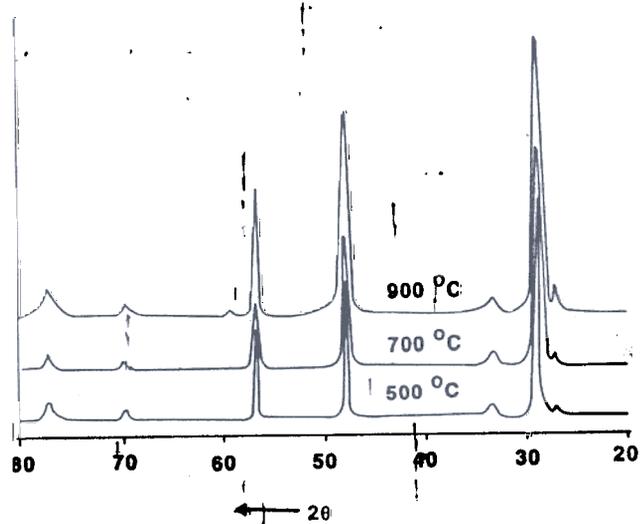


Figure 5. X-ray diffractogram for zinc sulphide fired in nitrogen at different temperatures.

It has been found that ZnS powder prepared by the authors after HIP gives a window having density 4.05 g cm^{-3} (> 99 per cent of the theoretical density of ZnS) showing up to 69 per cent transmission in the IR region (HIP of ZnS powder was carried out at the Defence Metallurgical Research Laboratory (DMRL), Hyderabad. The results of HIP studies on this ZnS powder will be presented in a separate paper).

4. CONCLUSIONS

A modified acid process has been developed for preparing IR window grade ZnS powder. The ZnS has been precipitated using ZnSO_4 (aqueous) - H_2S (gas) reaction at a constant pH maintained by controlled addition of dilute ammonia solution during the course of precipitation. The ZnS powder thus obtained has been purified by heating it in an inert atmosphere (nitrogen or argon). Optimum conditions are (i) 0.25 M concentration of ZnSO_4 solution, (ii) 2.4 pH, and (iii) firing in nitrogen at 700°C . The process leads to a 99.9 per cent pure, predominantly β -phase (Sphalerite) ZnS suitable for use in the fabrication of an IR-window.

The X-ray diffraction studies reveal that the presence of up to 10 per cent α -phase (Wurtzite) ZnS is tolerable for its application as an IR window material.

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