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Structural Properties of Screen Printed Thick Films of $Zn_xCd_{1-x}S$ Prepared by Flux Technique

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Abstract: All possible compositions of $Zn_xCd_{1-x}S$ [$0.1 \leq x \leq 0.9$] were prepared by flux technique using Na_2S-S flux for first time. Thick films of each composition are prepared by screen printing technique. Interplaner spacings, lattice parameters, unit cell volume of these compositions were determined using XRD patterns. X-ray studies show that Wurtzite structure is the only stable phase throughout the composition. The latice parameters vary with composition in accordance with vegard's law.

Key words: $Zn_xCd_{1-x}S$, flux method, solid solutions, thick films, screen printing, lattice constants

Introduction

Cadmium sulphide, zinc sulphide, zinc-cadmium sulphide have widespread applications in the field of electronics ranging from phosphors to photovoltaic cells. $Zn_xCd_{1-x}S$ have in recent years aroused keen interest since their structural, optical and electronic properties can be suitably tailored for optimum device performance by choosing the desired composition. $Zn_xCd_{1-x}S$ films are of considerable interest in heterojunction solar cells and photovoltaic application (Romeo *et al*., 1978; Burton *et al*., 1979).

Many workers have studied this material in thin film form. There are no reports on properties of $Zn_xCd_{1-x}S$ in thick film form. Thick film forms of $Zn_xCd_{1-x}S$ have become the subject of renewed research interest due to the potential of their use in solar cells.

Flux method is simple technique to synthesize high quality homogeneous solid solutions with potentials of up-scaling. Flux technique permits the synthesis of solid solutions well below the melting point of the material (Bidnaya *et al*., 1962; Scheel, 1974; Patil *et al*., 1998; Patil and Wani, 2001; Garner *et al*., 1970). Na_2S_x solvents are reported as suitable fluxes to synthesize metallic sulphides. The advantages of Na_2S_x solvents are the presence of common anion and insignificant incorporation of sodium into the material to be synthesized. The liquidus temperature of Na_2S (978°C) decreases to the eutectic with Na_2S_4 at 65 wt. % S and 230°C. Melting points and eutectics of Na_2S_4, Na_2S_5 and Na_2S_6 lie between 230 and 300°C. Sodium polysulphides are soluble in cold water and can be easily separated from the final product. Doping of suitable elements can be easily achieved by flux method and non-stoichiometric forms of solid solutions are obtainable. Equipments required are simple and within the financial scope of the most laboratories. There are no reports on synthesis of $Zn_xCd_{1-x}S$ solid solutions by flux method.

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Efforts have therefore been made to synthesize $Zn_xCd_{1-x}S$ ($0.1 \leq x \leq 0.9$) solid solutions and to study the properties of thick films useful for functional applications. Following properties are studied as a function of composition: (a) phase transformation, (b) lattice parameters.

Materials and Methods

Preparation of $Zn_xCd_{1-x}S$ Solid Solutions by Flux Method

The hydrated sodium sulphide ($Na_2S.9H_2O$), high purity sulphur and an appropriate wt. % of coarse zinc and cadmium powders were used as starting materials. Preparation procedure of one of the compositions (x = 0.1) is explained as follows.

Preparation of $Zn_{0.1}Cd_{0.9}S$

The 0.1 weight % of Zn, 0.9 weight % of Cd were mixed throughly into an appropriate amount of sulphur and $Na_2S.9H_2O$. The mixture was transferred into platinum crucible. The crucible was placed in kanthol wound muffle furnace. The space around and above the crucible was filled with coarse corrundum powder. The furnace temperature was increased to 600°C. This temperature was then maintained for an hour. The furnace was then cooled to room temperature. Excess sulphur evaporated and removed the residual oxygen and water as SO_2 and H_2S, respectively. The product in the crucible was washed with double distilled water. Sodium polysulphides got dissolved in water and separated out easily. The final product was dried. Same procedure was adopted to synthesize the other compositions (x = 0.2 to 0.9). CDs and ZnS powders were also prepared using same procedure.

Preparation of $Zn_xCd_{1-x}S$ Thick Films

Thick films of each composition were prepared by screen printing technique. The powder of a particular composition prepared using the method as mentioned above was ballmilled in ethanol for 24 h to ensure sufficiently fine particle size. The thixotropic paste was formulated by mixing fine solid solution powder with solution of ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butyl cellulose, butyl carbitol acetate and terpineol (Amalnerkar *et al*., 1980; Yang and Im, 1986; Patil *et al*., 1998; Fu *et al*., 1985a,b). The ratio of inorganic part to organic part was kept as 75:25 in formulating the paste. The paste was screen printed on glass and alumina substrate in the pattern suitable for measurements. The films were fired at 550°C in air for 10 min.

Structural Analysis of the Films

X-ray diffraction patterns of the films corresponding to each composition were recorded with Phillips X-ray diffractometer Model PW-1730 using CuK_α radiations with Ni filter (λ = 1.5418 Å). X-ray patterns of all compositions were arranged in a single figure for comparison. The lattice constants of each composition were determined and represented graphically.

Results and Discussion

X-ray Diffraction Patterns of $Zn_xCd_{1-x}S$

Figure 1 represents XRD patterns of CDs, $Zn_xCd_{1-x}S$ (x ranging from 0.1 to 0.9) and ZnS. CDs generally shows dimorphism of: (I) zinc blend type (cubic form) and wurtzite (hexagonal) type at relatively low temperature and (ii) only wurtzite type at relatively high temperature. Cubic phase is

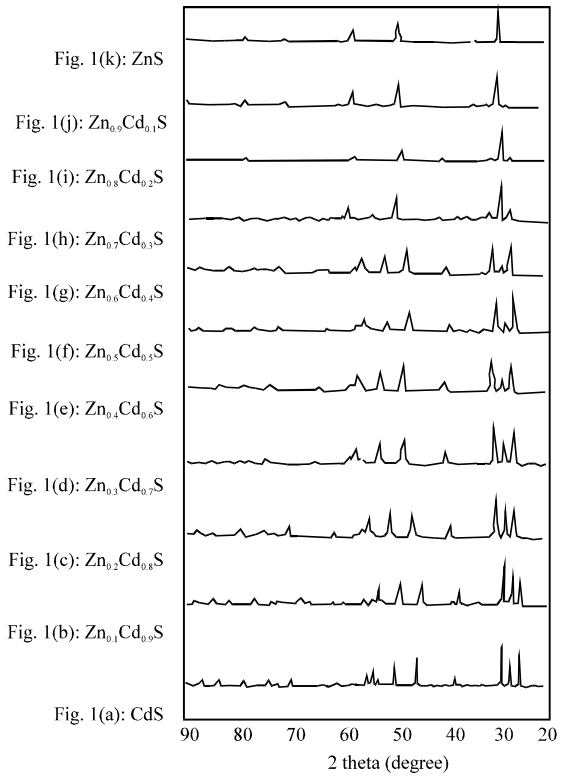

Fig. 1 : XRDs of $Zn_xCd_{1-x}S(0 \leq x \leq 1)$ thick films

unstable at temperature sufficiently high (Amalnerkar *et al*., 1985; Jakimavicious *et al*., 1972; Patil *et al*., 1998, 1999). ZnS can crystallize either in cubic (sphalerite) structure or as a hexagonal (wurtzite) structure. Wurtzite is a high temperature phase of ZnS.

XRD patterns show the wurtzite structure as the stable phase throughout the composition range of $Zn_xCd_{1-x}S$. This could be attributed to the high temperature flux method adopted for the synthesis of the compounds XRD patterns showed no cubic phase. The presence of single phase (wurtzite) showed that the homogeneous phase of $Zn_xCd_{1-x}S$ was formed and CDs and ZnS were completely miscible in each other. This observation is in conformity with the results of other workers (Burton *et al*., 1976; Vankar *et al*., 1978; Kane *et al*., 1966).

Figure 1a-g indicate the presence of CDs wurtzite phase (≤60 wt.% Zn) with XRD patterns observed to be similar to that of CDS and films of higher Zn concentrations(above 70 wt.% Zn), Figs. 1h-k, also exhibited the ZnS wurtzite phase with XRD patterns similar to that of ZnS. There is no evidence of the phase transformation similar to that reported by Banerjee *et al*. (1978).

It is reported (Cherin *et al*., 1970) that sphalerite (cubic) form predominates only when the concentration of zinc sulphide nears 100%. We were unable to observe such transformation throughout the range of Zn concentrations. It may be because of high temperature flux method of synthesis of $Zn_xCd_{1-x}S$.

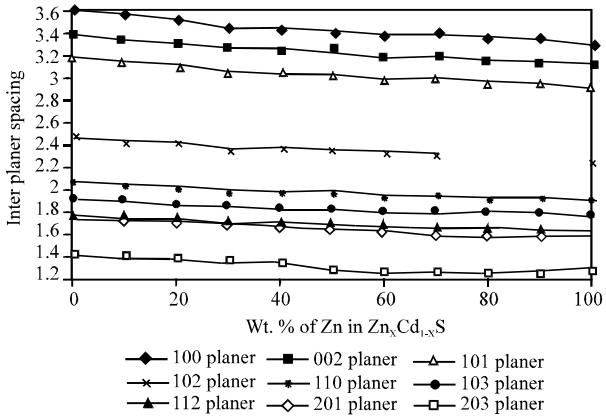

Fig. 2: Variation of interplaner spacing with wt.% of Zn in $Zn_XCd_{1-X}S$

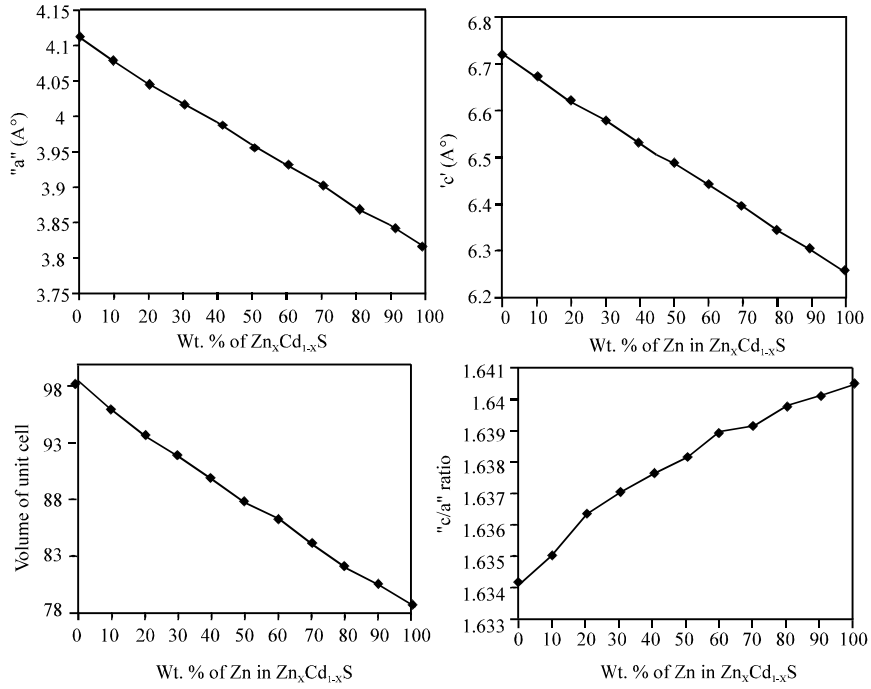

Fig. 3a: Variation of Lattice costant "a" with Zn content. (b) Variation of Lattice Constant "c" with Zn content. © Variation of unit cell volume with Zn content. (d) Variation of axial ratio "c/a" with Zn content

Variation of Interplaner Spacing 'D' with the Variation of Wt. % of Zn and Cd Concentrations in $Zn_xCd_{1-x}S$

The values of interplanner spacing of some planes recorded from XRD patterns of thick films of CDs, $Zn_xCd_{1-x}S$ and ZnS. It is clear from Fig. 2 that there was a gradual change in the interplanner spacing and no discontinuity in the variation (except some values) of any particular plane with the addition of Zn (or Cd) into $Zn_xCd_{1-x}S$.

Figure 2 represents the variation of interplanner spacing of some planes with the change in Zn concentration in the $Zn_xCd_{1-x}S$.

Dependence of Lattice Parameters on Zn or Cd Concentration in $Zn_xCd_{1-x}S$

The lattice parameters a, c and unit cell volume of hexagonal structure were computed using the XRD data by method of successive refinement and plotted as a function of composition. The values of a, c and unit cell volume were decreasing with the increase of Zn content in $Zn_xCd_{1-x}S$ as depicted in Fig. 3a-c, respectively. The variations were obeying Vegard's law.

The c/a ratios were calculated for each composition. The variation of c/a was nearly linear and was increasing with Zn concentration in the compositions as represented in Fig. 3d. The values of c/a ratios were nearly equal to or larger than the theoretically expected value of 1.633(critical value for close hexagonal packing of hard spheres). The linear (nearly) variation of c/a may be due to : (I) the absence of an unknown phase in the films, (ii) formation of no new compound, (iii) no excess of Zn or Cd ions and no sulphur vacancies. It may also be attributed to perfect stoichiometric compositions possible by flux technique. Hume-Rothery's rules were observed to be almost satisfied between hexagonal forms of ZnS and CDs as complete range of solid solutions were formed.

Conclusions

- Flux method was advantageous for the synthesis of high quality ternary compounds of sulphides using Na_2S_x as fluxing agent.
- Thick films could be prepared at room temperature without affecting the materials properties.
- Properties of bulk materials were obtainable through the thick films.
- $Zn_xCd_{1-x}S$, ZnS and CDs, synthesized at high temperature exhibited only hexagonal wurtzite structure.
- Throughout the composition range of $Zn_xCd_{1-x}S$, the wurtzite structure was the only stable phase.
- Lattice parameters obeyed Vegard's law.
- Hume Rothery's rules were almost satisfied between hexagonal forms of ZnS and CDs, as complete range of solid solutions can be formed between two sulphides.

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