INFLUENCE OF LEAD ON STRUCTURE AND MORPHOLOGY OF $Zn_{1-x}Pb_xS$ SEMICONDUCTOR COMPOUND PREPARED BY CO-PRECIPITATION TECHNIQUE

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Abstract: $Zn_{1-x}Pb_xS$ (x=0 to 0.4 in steps of 0.1) ternary semiconductor compounds were synthesized by co-precipitation technique. XRD studies revealed that all the compounds have polycrystalline nature and possess Hexagonal crystalline structure. The variation in lattice parameter(s) with Pb concentration was found to obey Vegard's law. Bulk density, dislocation density, lattice strain and average grain size of all samples were calculated with the change in Lead concentration. Surface morphology and chemical homogeneity studies were also carried out by using SEM and EDAX.

Keywords: **$Zn_{1-x}Pb_xS$ semiconductor; co-precipitation technique; XRD; SEM; EDAX; Bulk density and Grain size.**

I. INTRODUCTION

The application of a semiconductor in the area of device fabrication is primarily based on the energy gap of the semiconductor. In this context, ZnS is an important II-VI semiconductor with a large energy gap 3.66eV at room temperature [1] and possess potential applications in UV light emitting diodes [2-4], thin film electro luminescence [5-7], anti-reflecting coatings [8] etc. Doping / replacing one of the elements in such compounds with a suitable element, in a limited quantity, improves their electrical properties. Replacing few Zn metal ions with Pb ions in ZnS crystalline material results in to $Zn_{1-x}Pb_xS$ semiconductor compound. This can also be achieved by mixing ZnS and PbS binary compounds, in limited quantities. The mixed compound may consist an intermediate energy gap between 0.4 eV of PbS [9] and 3.66 eV of ZnS [1] and modified lattice parameters compared to PbS ($5.936A^0$) and ZnS ($a=3.82A^0$, $c=6.26A^0$) with a specific crystalline structure. Many researchers reported properties of doped ZnS with Mn [10], with Cu [11], with Co [12, 13], with Cr [14] etc. Literature review reveals that there are only few reports on Pb doped ZnS that too on thin films [15-20]. So the authors have taken up synthesis of $Zn_{1-x}Pb_xS$ bulk compounds by simple and low cost co-precipitation method with x=0, 0.1, 0.2, 0.3 and 0.4. This paper reports the synthesis and structural characterization studies of ternary $Zn_{1-x}Pb_xS$ semiconductor compounds.

II. EXPERIMENTAL

$Zn_{1-x}Pb_xS$ bulk compounds with x=0 to 0.4 in steps of 0.1 were prepared by controlled co-precipitation method. The detailed experimental procedure to grow similar ternary compounds like $Cd_xZn_{1-x}S$ was described in our earlier articles [21-24].

Analytical reagent grade (SD fine) chemicals Zinc acetate, Lead acetate and Thiourea were used in the synthesis process as source materials for Zn, Pb and S ions respectively. The source materials were weighed according to the stoichiometry as per the target compositions (x = 0, 0.1, 0.2, 0.3, 0.4) and were dissolved in doubled distilled water to make 1 M solutions. The solutions were mixed in the stoichiometric proportion under continuous stirring process. 1 M solution of Triethanylamine (TEA), a complexing agent was added to the solution mixture. The solution mixture was made alkaline by adding 25% of Ammonium hydroxide under constant stirring process to maintain pH of the solution about 10. The solution mixture was heated at 80^0C with a constant stirring process for one hour till the colour of the solution changed from pale yellow to grey, indicating the formation of precipitation. The bath was further heated for 3 hours till a fine precipitate was formed.

The details of chemical reaction for the synthesis of $Pb_{1-x}Zn_xS$ bulkcompound are described in the following steps.

Ammonia ion formation:

$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

Sulfide ion formation from thiourea:

$(NH_2)_2CS + OH^- \rightarrow SH^- + CN_2H_2 + H_2O$

$SH^- + OH^- \rightarrow S^{2-} + H_2O$

When the ammonia is added to the Pb^{2+} salt solution $Pb(OH)_2$ starts precipitating

$Pb(CH_3COO)_2 + 2NH_4^+ \rightarrow Pb^{2+} + 2NH_4CH_3COO$

$Pb^{2+} + 2OH^- \rightarrow Pb(OH)_2$

The $Pb(OH)_2$ precipitate dissolves in excess ammonia solution to form the complex lead tetra-ammine ions.

$Pb^{2+} + 4NH_3 \rightarrow (Pb(NH_3)_4)^{2+}$

Similar reaction takes place with Zinc acetate salt solution in the presence of excess ammonia giving rise to $(Zn(NH_3)_4)^{2+}$.

Finally the two tetra ammine complexes combine in the reaction leading to the formation of $Zn_{1-x}Pb_xS$.

$$(x)\ (Pb(NH_3)_4)^{2+} + (1\text{-}x)\ (Zn(NH_3)_4)^{2+} + S^{2-} + NH_3 \rightarrow Zn_{1-x}Pb_xS.$$

The precipitate was filtered by using Whatmann filter paper no 41. The precipitate was then collected and dried at room temperature for 48 hours. The dried precipitate was transferred in to a clean and dry quartz boat. This boat is placed in a quartz tube of diameter 3 cm and length 140 cm, arranged in a high temperature ($0\text{-}1000^0$C) tubular furnace. Both the ends of the quartz tube were provided with two metal caps to pass inert gas through the tube. The precipitate was heated for 2 hours at 300^0C under nitrogen atmosphere and then cooled to room temperature. The dried precipitate was ground to fine powder to obtain uniform particle size. The powder was made in to pellets under pressure (10 tons per sq. Inch) by using a punch die of 1.5cm diameter. The thickness of pellets thus prepared is about 2mm. The pellets were then sintered at 800^0C for 2 hours in nitrogen gas atmosphere. The samples were cooled slowly to room temperature and the pellets are used for further studies.

Structural investigations are done by analytical X' pert powder X-ray diffractometer with Cu K_α radiation (λ=1.5405Å) in the angular range 20^0 to 80^0 at a scan speed of 0.02 degree/sec. Crystal structure, crystallite size, lattice parameter and density were obtained from X-RD data. Chemical analysis and morphological studies were carried out using Scanning Electron Microscopy (SEM) with Energy Dispersive Analysis of X-rays (EDAX) attachment (model ZEISSEVO-18). Densities of all samples were measured by Archimedes principle by taking Xylene as reference liquid.

III. RESULTS AND DISCUSSION

3.1 X-Ray diffraction

X-ray diffraction technique was used to investigate the crystallinity, the effect of Pb on the crystalline structure, the composition and different phases of $Zn_{1-x}Pb_xS$ compound. Fig.1 shows the X-ray diffraction patterns of all samples under present investigation. The presence of X-ray diffraction peaks (with some peak width) in the diffractograms of all samples shows that the compounds possess polycrystalline nature. These diffraction peak positions are compared with the peak positions of ZnS and PbS crystal structures and found that they correspond to those of Hexagonal ZnS structure (JCPDS 892347). All the observed peaks were compared with the reported peaks (standard data) and indexed with (hkl) values. Furthermore, any other phase corresponding to PbS /ZnS / clusters could not be detected from XRD. Therefore, this evidences to understand the formation of $Zn_{1-x}Pb_xS$ compound, the prepared samples are of polycrystalline and $Zn_{1-x}Pb_xS$ compound has hexagonal structure.

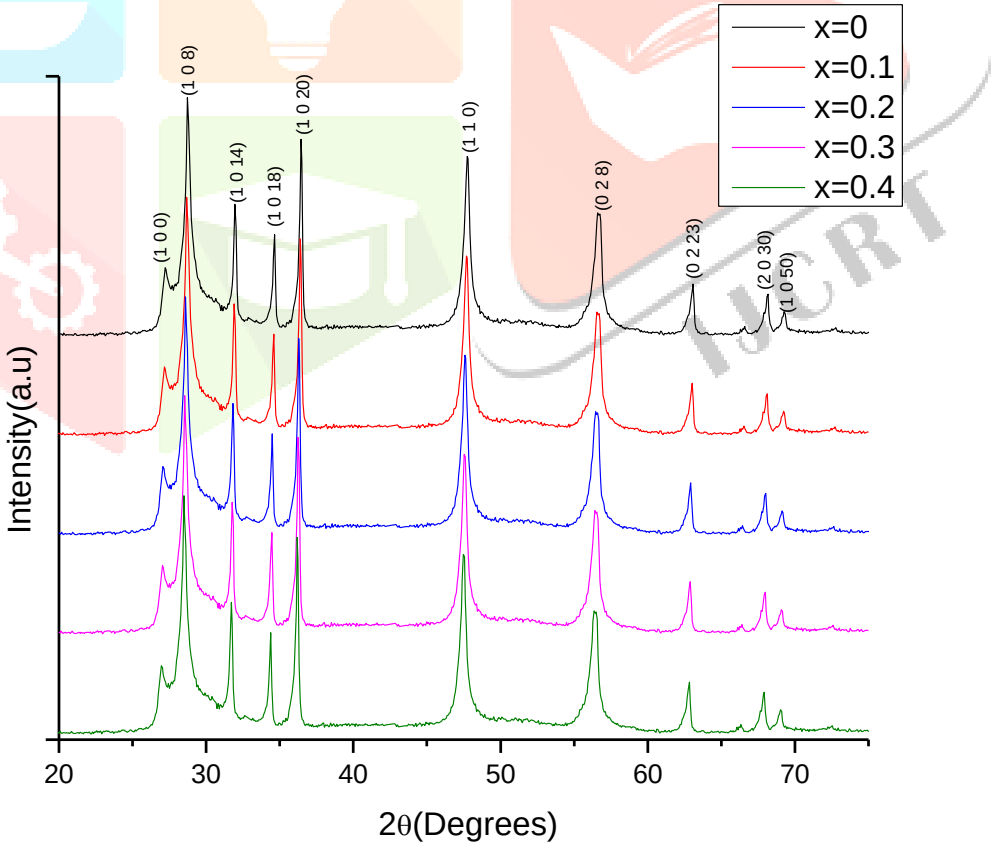

Fig1. X-ray diffractograms of $Zn_{1-x}Pb_xS$ compounds

3.2. Lattice parameters

The lattice parameters 'a' and 'c' for hexagonal structure were calculated according to the relation [25].

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2} \qquad (1)$$

Estimated lattice parameters of $Zn_{1-x}Pb_xS$ are given in Table 1. Graphical variation of these lattice parameters with Pb concentration is also shown in Fig.2a and Fig.2b. The graph shows clearly that the variation of lattice parameter with Pb concentration is linear and obeys Vegards law [26, 27]. A similar variation was also observed by Hasan [20] in $Zn_{1-x}Pb_xS$ thin films. The increase in the value of ***a*** may be due to the occupation of larger ionic radii Pb^{2+}ion in place of Zn^{2+}ion.

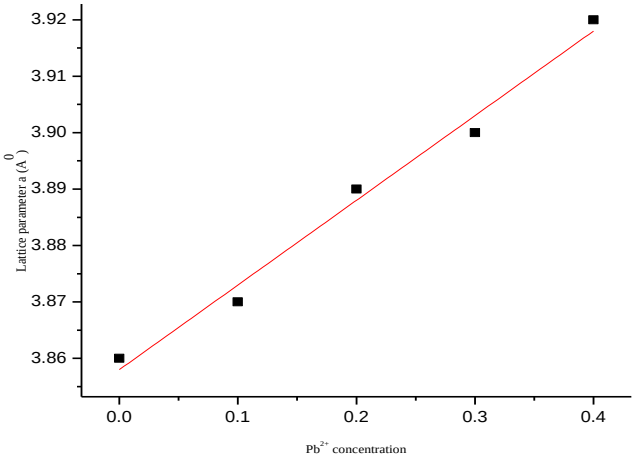

Fig2a. Variation of lattice parameter ***a*** with Pb^{2+} concentration

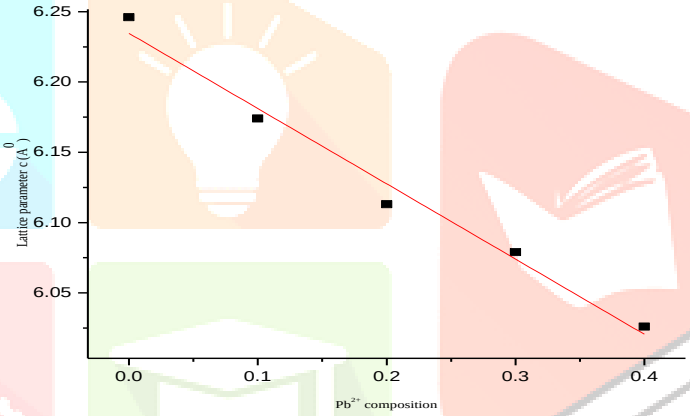

Fig2b. Variation of lattice parameter ***c*** with Pb^{2+} concentration

3.3 Microstructural parameters

The Average crystallite size (D) of $Zn_{1-x}Pb_xS$ compounds is calculated using Debye Scherer's formula [30].

$$D = \frac{0.94\lambda}{\beta cos\theta} \quad (2)$$

The Dislocation density (δ) and Average micro strain of all $Zn_{1-x}Pb_xS$ samples were calculated using the formulae.

$$\delta = \frac{1}{D^2} \quad (3)$$

$$\varepsilon = \frac{\beta cos\theta}{4} \quad (4)$$

where β is full width half maximum (FWHM) of an X-ray diffraction peak at the angular position θ.

All microstructural parameters (D, δ and ε) of all $Zn_{1-x}Pb_xS$ samples are summarized in Table 1. From the table it is observed that FWHM decreases with Pb concentration and results in the increase in grain size. Due to the increase of grain size, density of the compound increases as the pore size decreases.

Table 1: Variation of Lattice parameters *a* & *c*, Crystallite size, Dislocation density, Lattice strain and Density with Pb^{2+} concentration.

S No	Sample $Zn_{1-x}Pb_xS$	Lattice parameters (Hexagonal)		FWHM (β)	Crystallite size (D) (nm)	δ x10^{-4} $(nm)^{-2}$	ε x10^{-2}	Density from XRD	Density from experiment
		a(A°)	*c*(A°)						
1	x=0	3.86	6.246	0.49	28.9	11.9	11.7	4.09	3.97
2	x=0.1	3.87	6.174	0..47	30.2	10.9	11.3	4.69	4.28
3	x=0.2	3.89	6.113	0.44	32.1	9.7	10.5	4.98	4.59
4	x=0.3	3.90	6.079	0.42	33.7	8.8	10	5.16	4.77

3.4	5	x=0.4	3.92	6.026	0.41	34.5	8.4	9.9	5.33	4.98

Scanning electron micrographs and EDAX:

Fig. 3 shows the SEM images of all $Zn_{1-x}Pb_xS$ samples, taken at the same magnification. It is observed from these micrographs that the morphology of crystallites changes with increasing Pb concentration and grain size also increases. XRD studies have also revealed that the crystallite size increases with the increase in Pb concentration and corroborate the results from SEM. Chemical composition analysis of prepared compounds was done by EDAX technique. Fig. 4 shows typical EDAX spectra of $Zn_{1-x}Pb_xS$ (x=0–0.4) samples. The spectra indicates the presence of Zn and S in $Zn_{1-x}Pb_xS$ compound with x=0 and presence of Zn, Pb and S in all other compounds. The analysis revealed that peaks corresponding to all the elements in the compounds along with their percentages match with which they were mixed at the time of preparation.

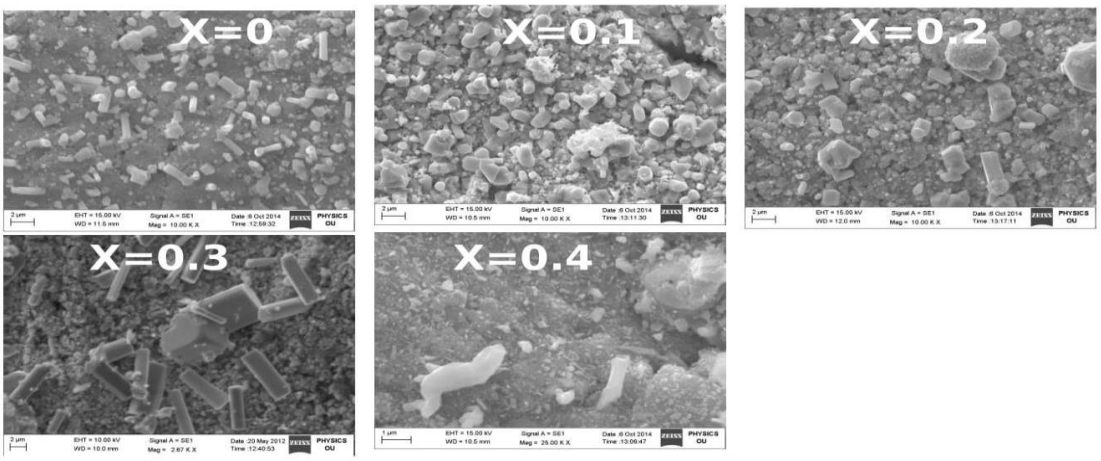

Fig3. SEM micrographs of $Zn_{1-x}Pb_xS$ compounds

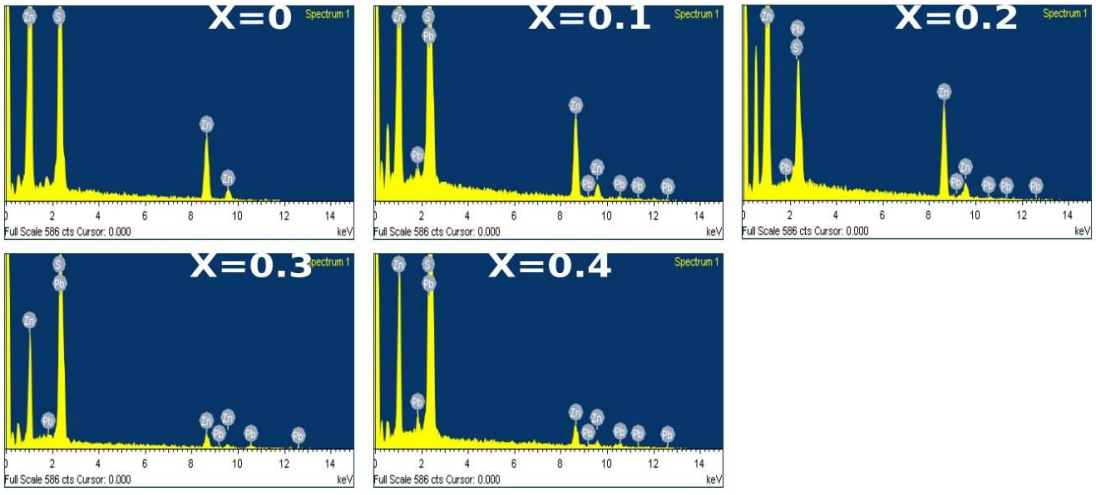

Fig.4. EDAX spectra of $Zn_{1-x}Pb_xS$ compounds with x=0, 0.1, 0.2, 0.3 and 0.4.

3.5 Density Measurements

Bulk densities of all $Zn_{1-x}Pb_xS$ samples are calculated from XRD results and measured by Archimedes principle.

$$\text{Density}=\frac{Weight\ of\ the\ sample\ in\ air\times 0.861}{Weight\ of\ the\ sample\ in\ air-Weight\ of\ the\ sample\ in\ Xylene} \quad (5)$$

$$\text{Density from XRD} = \frac{Z\times M.W.}{NA\times V} \quad (6)$$

where, Z is number of atoms per unit cell, N_A is Avogadro number; V is the volume of the unit cell and 0.861 is the density of Xylene solution in which the loss of weight of the sample is accounted. The values obtained for all the samples are given in Table 1. It is observed from the data presented in Table 1 that the density of samples increases with increase in the concentration of Pb and this may be due to the heavier Pb ion occupying the lighter Zn ion. Bulk density variation is also similar to the variation observed from XRD results.

IV. CONCLUSION

1. $Zn_{1-x}Pb_xS$ semiconductor compounds were synthesized by co-precipitation method at room temperature.
2. $Zn_{1-x}Pb_xS$ compounds are polycrystalline in nature and exhibited hexagonal structure.
3. The variation of lattice parameters of the compounds obey Vegard's law.

4. Lattice parameters, crystallite size and density values increase with Pb concentration in $Zn_{1-x}Pb_xS$ compounds.
5. Structural analysis and SEM micrographs confirmed the formation of $Zn_{1-x}Pb_xS$ ternary semiconductor compound.

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