



# Structural and micro structural parameter studies on $Pb_{1-x}Zn_xS$ semiconductor compounds prepared by co-precipitation method

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## Abstract:

$Pb_{1-x}Zn_xS$  ( $x=0$  to  $0.4$  in steps of  $0.1$ ) ternary semiconductor compounds were synthesized by co-precipitation technique. XRD studies revealed that the compounds are polycrystalline in nature with cubic structure. Variation in density and porosity percentage, dislocation density, lattice strain and average grain size of all samples, with respect to change in Zinc concentration, were calculated.

**Keywords:**  $Pb_{1-x}Zn_xS$  semiconductor; co-precipitation technique; XRD; Grain size; Density

## 1. Introduction:

Over the past few years rapid advancements in electronic industry expects smarter and energy efficient semiconductor materials from researchers. Doping of a semiconductor is a strategic technic to improve the optical and electrical properties, so that they can applicable to various fields [1-5].  $PbZnS$  is a II-IV-VI ternary semiconductor having wider bandgap compared to  $PbS$  and less window absorption loss it is potentially used as a window material in the fabrication of p-n junctions without lattice mismatch in devices based on quaternary materials like  $CuIn_xGa_{1-x}Se_2$  [6], and  $CuIn(S_xSe_{1-x})_2$ [7].

## 2. Sample preparation:

$Pb_{1-x}Zn_xS$  bulk compounds with  $x=0$  to  $0.4$ , varied in steps of  $0.1$ , were prepared by co-precipitation method [8-12]. In this method, equimolar solutions of Lead acetate, Zinc acetate and Thiourea were taken in specific volumes so as to get the desired composition. The solution mixture was made alkaline by adding ammonium hydroxide (25%) under constant stirring process. The preparation process is based on the slow release of  $Pb^{2+}/Zn^{2+}$  and  $S^{2-}$  ions in solution. The ions condensed on ion-ion basis in the solution. The slow release of

$Pb^{2+}/Zn^{2+}$  ions is achieved by dissociation of complex species of Pb/Zn such as tetra amine lead(II)/tetra amine zinc(II) complex ions  $[(Pb(NH_3)_4)^{2+}/(Zn(NH_3)_4)^{2+}]$ .  $S^{2-}$  ions are supplied by decomposition of thiourea. The  $S^{2-}$  ions react with  $Pb^{2+}$  and  $Zn^{2+}$  ions in alkaline medium so that  $Pb_{1-x}Zn_xS$  precipitate is formed.

The solution mixture was heated at  $80^\circ C$  with constant stirring process for one hour. The color of the solution changed from pale yellow to grey indicating the formation of precipitation. The bath was further heated for 3 hours to complete reaction. The precipitate was filtered by using Whatman filter paper. 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 was placed in a quartz tube of diameter 3 cm and length 100 cm, arranged in a high temperature ( $RT-1000^\circ C$ ) 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  $300^\circ C$  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 10mm diameter. The thickness of pellets thus prepared was about 1.5mm. The pellets were heated at  $800^\circ C$  for 2 hours in nitrogen gas atmosphere. The samples were cooled slowly to room temperature and the pellets are used for further studies.

### 3. Results:

**3.1 X-ray diffraction:** Crystal structure of  $Pb_{1-x}Zn_xS$  semiconductor compounds was studied by X-Ray diffraction. Fig.1 shows X-ray diffraction patterns of all samples. The observed diffraction peak positions of  $Pb_{1-x}Zn_xS$  compounds are compared with those peak positions of Cubic PbS (JCPDS 05-0592) published in literature[13] and found that, the crystal structure of  $Pb_{1-x}Zn_xS$  is Cubic (PbS type). All the observed diffraction peak positions were compared with the JCPDS data and assigned hkl values for all the peaks. No secondary peaks related to ZnS are observed in the diffractograms, indicating the single phase of the prepared compound. This is evident that  $Zn^{2+}$  ions are incorporated in the PbS matrix and confirms the formation of ternary  $Pb_{1-x}Zn_xS$  compound. The presence of cubic phase in  $Pb_{1-x}Zn_xS$  may be due to the insertion of smaller number of Zinc atoms whose atomic radius is less than Lead atoms. Substitution of some Pb sites with Zn in PbS compound may not cause deviation in the crystal structure of PbS i.e. Cubic. However, it may cause slight alteration in the lattice parameter.

**3.2 Microstructural parameters:** The average crystallite size (D) of all  $Pb_{1-x}Zn_xS$  compounds is calculated using Debye Scherer formula [14].

$$D = \frac{0.94\lambda}{\beta \cos\theta} \dots\dots\dots (1)$$

The dislocation density ( $\delta$ ) and micro strain values of all  $Pb_{1-x}Zn_xS$  samples are calculated using the formulae

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

$$\epsilon = \frac{\beta \cos\theta}{4} \dots\dots\dots (3)$$

where  $\beta$  is FWHM of an X-ray diffraction peak at the angular position  $\theta$ .

Micro structural parameters like crystallite size, dislocation density and average micro strain of all  $Pb_{1-x}Zn_xS$  samples are summarized in Table 1. From the variations of these values with Zn concentration, one may notice that (i) the crystallite size decreases (ii) dislocation density and micro strain increase with the composition 'x'. A similar result was also observed in CdZnS by Awodugba et.al [15]. The increase in strain in the bulk samples studied may be due to the difference in the ionic radius between  $Zn^{2+}$  and  $Pb^{2+}$ . Obviously, the change in strain causes proportionate change in dislocation density.

**3.3. Density measurements:** Bulk densities of all  $Pb_{1-x}Zn_xS$  samples are calculated from XRD results and measured by Archimedes principle. From these density values, density and porosity percentages are also calculated using the following relations [16].

$$\text{Density} = \frac{\text{Weight of the sample in air} \times 0.861}{\text{Weight of the sample in air} - \text{Weight of the sample in Xylene}} \dots\dots\dots (4)$$

$$\text{Density from XRD} = \frac{ZXM.W.}{N_A V} \dots\dots\dots (5)$$

$$\text{Porosity (\%)} = \frac{(\text{Density from XRD} - \text{Experimental Density})}{\text{Density from XRD}} \times 100\% \dots\dots\dots (6)$$

$$\text{Density (\%)} = 100 - \text{Porosity\%} \dots\dots\dots (7)$$

where, Z represents the 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 porosity percentage is calculated by taking the density of ideal sample (taken from literature) as 100%. The density and porosity percentages of  $Pb_{1-x}Zn_xS$  compounds are in the range of 97-95% and 2.5-5% respectively. The values obtained for all the samples are given in Table2. It is observed from the data presented in Table 2 that the density of samples decreases with increase in the concentration of Zinc and this may be due to the heavier Pb ion being replaced by the lighter Zn ion.

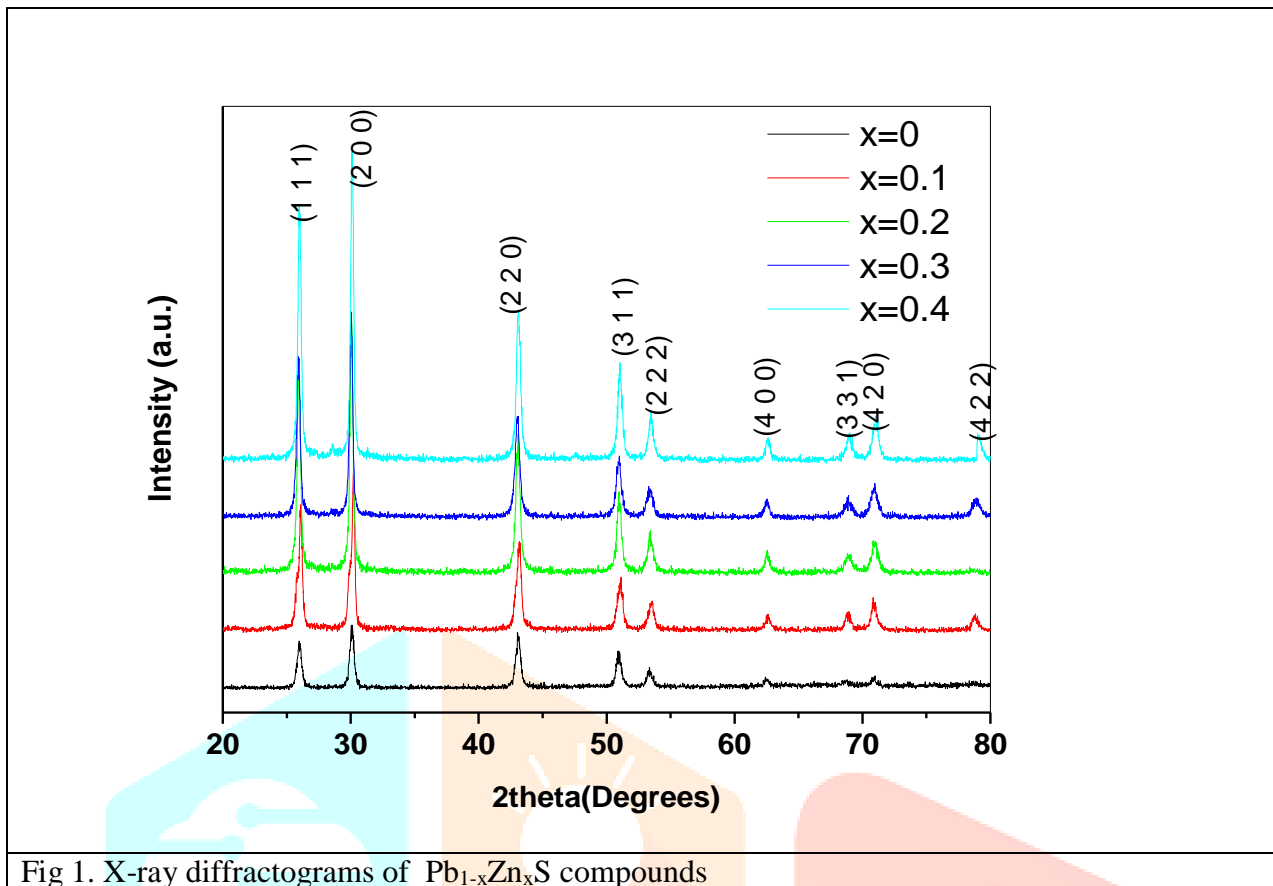


Fig 1. X-ray diffractograms of  $Pb_{1-x}Zn_xS$  compounds

S No	Sample $Pb_{1-x}Zn_xS$	Lattice parameter $a$ (Å)	FWHM	Crystallite size (D) (nm)	$\delta \times 10^{-4}$ ( $m^{-2}$ )	$\epsilon \times 10^{-2}$ ( $line^{-2}m^{-2}$ )
1	x=0	5.926	0.33	42.7	5.5	7.9
2	x=0.1	5.933	0.34	41.5	5.8	8.2
3	x=0.2	5.939	0.35	40.2	6.2	8.4
4	x=0.3	5.946	0.37	38.1	6.9	8.9
5	x=0.4	5.955	0.39	36.1	7.7	9.4

Table 1. Lattice parameter, Crystallite size, Dislocation density of  $Pb_{1-x}Zn_xS$  compounds

S.No.	Sample $Pb_{1-x}Zn_xS$	Density from Experiment	Density from XRD	Density%	Porosity %
1	x=0	7.68	7.88	97.46	2.54
2	x=0.1	7.23	7.48	96.66	3.34
3	x=0.2	6.88	7.19	95.69	4.31
4	x=0.3	6.29	6.59	95.45	4.55
5	x=0.4	5.73	6.02	95.18	4.82

Table 2. Density and porosity of  $Pb_{1-x}Zn_xS$  compounds

#### 4. Conclusions:

1.  $Pb_{1-x}Zn_xS$  ternary compounds have been synthesized by co-precipitation method.
2.  $Pb_{1-x}Zn_xS$  compounds are poly crystalline in nature with cubic structure.
3. The average crystallite size of the prepared compounds decreases with Zinc concentration and varies between 42.7 nm – 36 nm.
4. Dislocation density and Micro strain of the samples increase with increase in Zn concentration.

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