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Synthesis of undoped and X (Cu, Al & Zn)-doped lead iodide crystals by gel technique and preparation & characterization of thin films of gel grown crystals

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ABSTRACT

Undoped and X-(Cu, Al & Zn) doped lead iodide crystals have been grown by gel technique. Interestingly, thin films of these gel grown crystals have been prepared of various thicknesses by vacuum thermal evaporation technique on glass substrates (80^0 C). These films are smooth, uniform, adhesive and reflecting. Optical and structural investigations of these thin films were carried out. Measurements of absorption coefficients have been carried out and reported. As expected, the optical energy gap decreases with increasing dopant concentration, but in case of Al-doped thin films optical energy gap increases in the present investigation. The thin films are polycrystalline in nature and crystallinity increases after doping but decreases when the thickness increased (above 3000Ǻ). The absorption edge shifts towards the higher wavelength side and becomes broader as the doping concentrations were increased. X-ray diffractograms and Scanning Electron Microscopy were employed on these thin films. The lattice parameters and the [h, k, l] values almost matching with the ASTM data for lead iodide.

Keywords: gel technique, thin films, XRD, SEM, transmittance

INTRODUCTION

Lead iodide has been the subject of many investigations in view of its potential as a device material. Among the semiconductor, a challenging material is lead iodide, which has direct band gap semiconductor (2.55 eV), having the same crystals structure as CdI2 (point group D3d). The atomic arrangement is in the form of layers of lead and iodine atoms oriented perpendicularly to C-axis. Lead iodide is a layered structured of different polytypes that are generally hexagonal in shape. The bulk lead iodide crystal is featured by a strong interlayer chemical bonding and a weak layer van der Waal's interaction [1]. Lead iodide is highly insulating material with a resistivity of about 1012 ohm-cm. The high atomic number of Pb and I (Z=82 and 57 respectively) yield superior power for high energy x-ray and gamma rays [2].

Single crystals of lead iodide have been grown form aqueous solutions, gel, sublimation, chemical vapour transport, melt grown and a combination of gel and melt growth has been carried out [3]. The 2H polytype has been reported to the most predominant polytype in melt and sublimation growth crystals [4].

In the present course of investigation it has been decided to grow the undoped and doped crystal of Lead Iodide by gel technique. The thin films of gel grown crystals have been prepared by thermal evaporation technique. Such reports are not available in the literature/journal. Characterization of these thin films, to study the optical and structural properties, has been undertaken. The purpose of this paper is to study the effect of doping with respect to absorption coefficient, band gap energy and dielectric constant.

MATERIALS AND METHODS

2.1 Growth of crystals by gel technique

Single crystals of lead iodide can be grown by gel technique in a variety of ways by varying the parameters. Good crystals can be obtained by this simple technique. In the due course of investigation analar grade chemicals were used. X-(Cu, Al and Zn) doped and undoped lead iodide crystals have been successively grown by this technique in our research laboratory. A solution of acetic acid & lead acetate (each 5ml) was poured in test tube. Then, sodium metasilicate (sp.gr. 1.04 g cm^{-3}) was poured drop by drop, with constant stirring, in to the test tube, till 4pH of the solution was obtained. The mouth of the test tube was covered by cotton, so that foreign particles should not enter inside the test tube & kept in constant temperature bath (30^0C). After 8/10 days, gel was set. Thereafter, potassium iodide poured slowly over the set gel. Precaution should be taken that the gel should not be punchered. To get the X-(Cu, Al & Zn) doped lead iodide crystals, in the mixture of acetic acid & lead acetate, X-acetate was poured (1 ml). The above procedure was repeated to get the doped lead iodide crystals.

2.2 Preparation of Thin Films by Thermal Evaporation Technique

Thin films of gel grown doped and undoped lead iodide crystals have been prepared by thermal evaporation technique in our research laboratory. Gel grown crystals were crushed to a uniform size (150 mesh). Then, thin films of these gel grown crystals were deposited onto glass substrates, which were chemomechanically and ultrasonically cleaned, by thermal evaporation technique. The evaporation was carried out in a conventional vacuum coating unit of 1.3 to $5x10^{-3}$ pd, with a constant substrate temperature of 353 K (with different thicknesses). The thickness was measured by a quartz crystal thickness monitor, HindHivac DTM model no.101. Care should be taken to avoid the overheating of lead iodide during sublimation, otherwise thermal decomposition gives rise to non-stoichiometry in the films, apart from this, no special precautions are necessary.

2.3.1 X-ray diffractogram

X-ray diffractograms on Lead Iodide thin films of, undoped and doped (Cu^{+2}, $Al^{+3}$and Zn^{+2}), gel grown lead iodide crystals, were recorded using powder rotation photographs method. For this purpose Philips X-ray difractometer (Model PW-1730) using CuKα radiation with Ni filter (λ=1.5418Å) was used. The sample was rotated in the range 20^0-90^0.

2.3.2 Scanning electron microscope (SEM)

The thin films of doped and undoped gel grown lead iodide crystals were studied under scanning electron microscope, applying beforehand a thin coating of gold (silver) on the two sides of the cut slides. This characterization was carried out at C-MET, Pune by Philips XL-30.

2.3.3 Optical Properties of gel grown doped and undoped Lead Iodide crystals

The transmittance and reflectance spectra were recorded for all the films on Hitachi (model 330) spectrophotometer at normal and near normal incidence respectively at Cosist Lab. University of Pune, Pune.

RESULTS AND DISCUSSION

It is well known that the properties of thin films are greatly affected by deposition environment. Deposition parameters includes, temperature of substrate, substrate nature, pressure, thickness etc. for the meaningful measurements and reproducible results, the prepared films should as stable as possible. To achieve these, necessary precautions should be taken in preparing the films.

3.1 X-ray diffractogram

Preparation of X-(Cu, Al & Zn) doped Lead Iodide thin films suitable for use in photoconductors, photodetectors and photovoltaic applications including photochemical cell has been the attraction for the researchers. The films were prepared by thermal evaporation technique that is simple, easy and entirely reproducible, and the adjustment of semiconducting properties by band gap variation, doping, control over stoichiometry etc.can be accomplished by effectively with great accuracy [3-6].

Records of X-ray powder diffraction of thin films of gel grown doped and undoped Lead Iodide crystals under identical conditions signifies that the samples belongs to hexagonal system and are crystalline in nature. Fig. 1 &

Fig. 2 represent an X-ray diffractogram of Cu-doped lead iodide thin films of thickness 2000 Å & 4000Å respectively. Fig. 3 infers X-ray diffractogram of Al-doped lead iodide thin films having various concentrations. [7] X-ray diffractogram of Zn-doped lead iodide crystals are already reported [8]. The observed and calculated 'd' values of thin films of gel grown doped lead iodide are given in Table 1 and Table 2 respectively. While effect of preparative conditions on lattice parameters given in Table 3. It can be seen from the observed and ASTM data that, the strongest peak is observed at d = 2.3385 and corresponds to the plane (0 0 4). Similar observations were already reported in our previous paper for undoped and doped thin films of Lead Iodide crystals [5].

XRDs of different thin film samples reveal the existence of hexagonal structure. It is clearly seen that the addition of dopant into lead iodide decreases the height of the peaks as the thickness of the sample increases while the height of the peaks tends to increase as the thickness of the sample increases. The lattice parameters 'a' and 'c' of all the samples are well matching with the ASTM data of Lead Iodide (Table 3). It may be seen from this table that the unit cell volume is sensitively affected by doping and thickness of the samples.

3.2 Scanning electron microscope (SEM)

The crystalline nature of these films has been examined by scanning electron microscopy. The scanning electron micrographs for these thin films are shown in fig. 7, 8. & 9. The crystallinity of the thin film of all the samples turns to amorphous as the thicknesses of the samples are increased. For lower thickness of the samples the thin films are almost uniform. Moreover the grain size of the samples tends to increase as the thickness of the sample increases. In our previous paper similar results were reported for thin films of Zn-doped Lead Iodide crystals. (7).Similar results were given for antimony-doped CdS films [9]. As seen from SEM micrographs of the thin films of all the samples, the surface consists of wide range of grains and voids. Grains vary from 40 to 400 nm.

3.3Transmittance& Reflectance Measurements

3.3.1 Film thickness 2000Å (Cu doped PbI_2)

For this sample, transmittance is constant over the wavelength 1900 to 2500nm then slowly increases from 46% at the wavelength 2500nm to 64% 1500nm, then slowly decreases as the wavelength decreases to 1% at the wavelength 300nm. In this curve there is noise over wavelength range 2040 to 2100nm and 670 to 850nm.

3.3.2 Film thickness 4000Å (Cu doped PbI_2)

For this sample, transmittance increases from 59% at the wavelength 2500nm to 72% 2100nm, then slowly decreases as the wavelength decreases to 1% at the wavelength 300nm. In this curve there is noise over wavelength range 2105 to 2045nm and 690 to 875nm.

3.3.3 Film thickness 2000Å (Al doped PbI_2)

For this sample, transmittance increases from 58% at the wavelength 2500nm to 73% 2100nm, then slowly decreases as the wavelength decreases to 2% at the wavelength 300nm. In this curve there is noise over wavelength range 2050 to 2110nm and 750 to 950nm.

3.3.4 Film thickness 4000Å (Al doped PbI_2)

For this sample, transmittance increases from 45% at the wavelength 2500nm to 68% 2100nm, then slowly decreases as the wavelength decreases to 3% at the wavelength 300nm. In this curve there is noise over wavelength range 2000 to 2110nm and 700 to 805nm.

3.3.5 Film thickness 2000Å (Zn doped PbI_2)

For this sample, transmittance increases from 46% at the wavelength 2500nm to 65% 1700nm, then slowly decreases as the wavelength decreases to 1% at the wavelength 300nm. In this curve there is noise over wavelength range 2050 to 2110nm and 700 to 950nm.

3.3.6 Film thickness 2000Å (Zn doped PbI_2)

For this sample, transmittance increases from 59% at the wavelength 2500nm to 75% 2100nm, then slowly decreases as the wavelength decreases to 3% at the wavelength 300nm. In this curve there is noise over wavelength range 2050 to 2110nm and 700 to 875nm.

From these observations, it is obvious that the film material is highly absorbing. It is also observed from these curves that transmittance variation is function of thickness of the sample. That is maximum transmittance is for the lower thickness samples. This obviously expected for the absorbing material.

Table 1 X-ray powder diffraction data (Cu-doped Lead Iodide thin films, 2000Å & 4000Å).

'd' values		I/I_o	hkl plane
diffractogram	computer		
3.5036, 3.5310	3.5015	20, 13	0 0 2
2.3305, 2.3421	2.3343	100, 96	0 0 3
1.7508, 1.7508	1.7508	83, 100	0 0 4

Table 2 X-ray powder diffraction data (Al-doped Lead Iodide thin films, 2000Å & 4000Å)

'd' values		I/I_o	hkl plane
diffractogram	computer		
3.5036	3.5015	20	0 0 2
2.3305	2.3343	100	0 0 3
1.7508	1.7508	75	0 0 4

Table 3 Effect of preparative conditions on lattice parameters

Compound	Thickness in (Å)	Lattice parameters a (Å)	c (Å)	c/a	V(Å)^3
Cu-doped PbI_2	2000	4.557	7.0264	1.5419	126.36
	4000	4.557	7.003	1.5360	125.94
Al-doped PbI_2	2000	4.557	7.0264	1.5419	126.36
	4000	4.557	7.0264	1.5419	126.36
Zn-doped PbI_2	2000	4.557	7.0264	1.5419	126.36
	4000	4.557	7.0264	1.5419	126.36

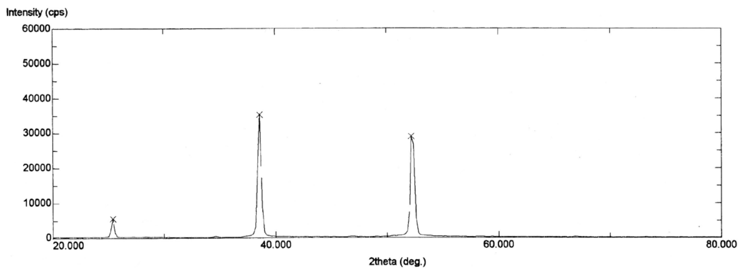

Fig. 1 X-ray diffractogram for Cu-doped PbI_2 thin film (2000Å)

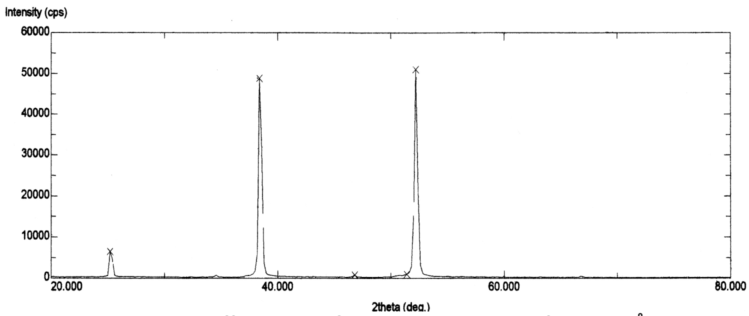

Fig. 2 X-ray diffractogram for Cu-doped PbI_2 thin film (4000Å)

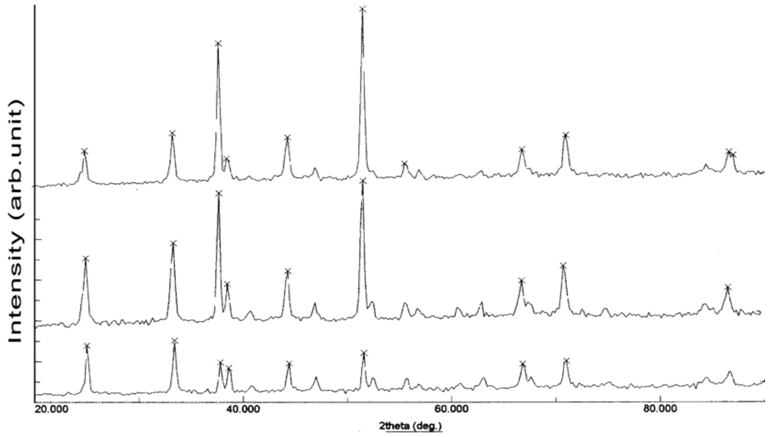

Fig. 3 X-ray diffractogram of Al-doped PbI_2 (From top 0.1M, 0.5M & 1M respectively)

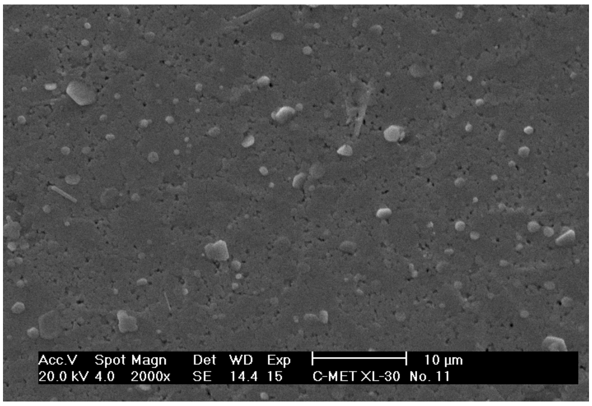

Fig. 4 SEM micrograph thin film of Cu-doped PbI_2 (2000Å)

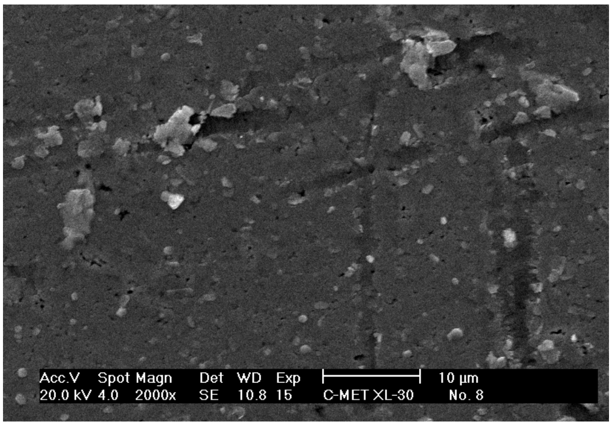

Fig. 5 SEM micrograph thin film of Cu-doped PbI_2 (4000Å)

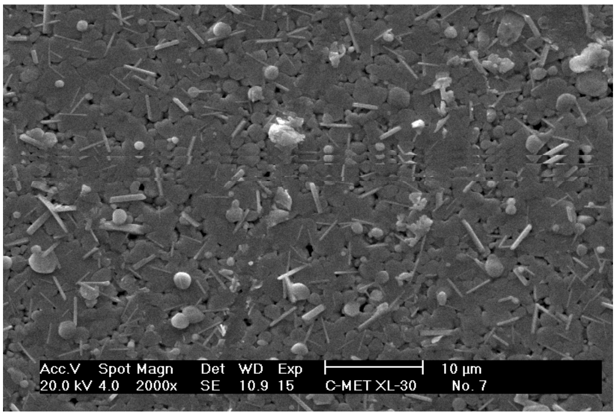

Fig. 6 SEM micrograph thin film of Al-doped PbI_2 (2000Å)

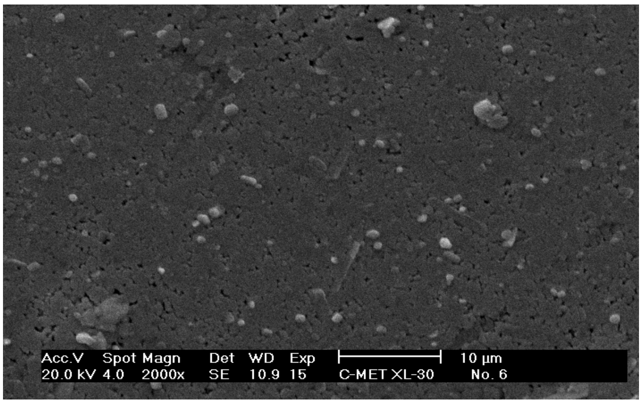

Fig. 7 SEM micrograph thin film of Zn-doped PbI_2 (2000Å)

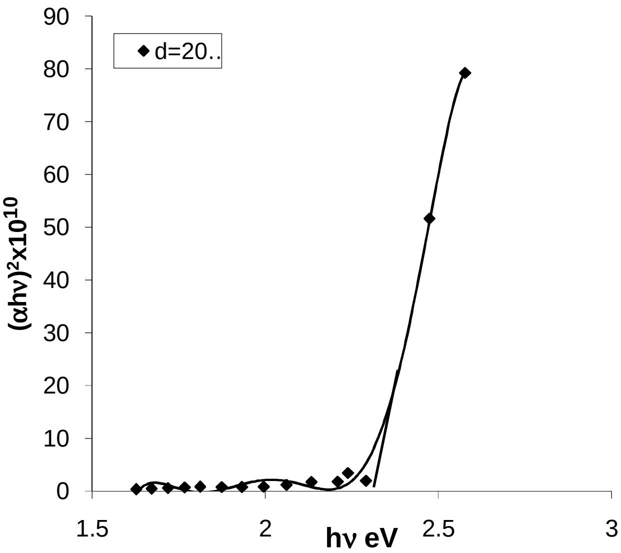

Fig. 8 Plot of $(\alpha h\nu)^2$ versus hν (Al-doped)

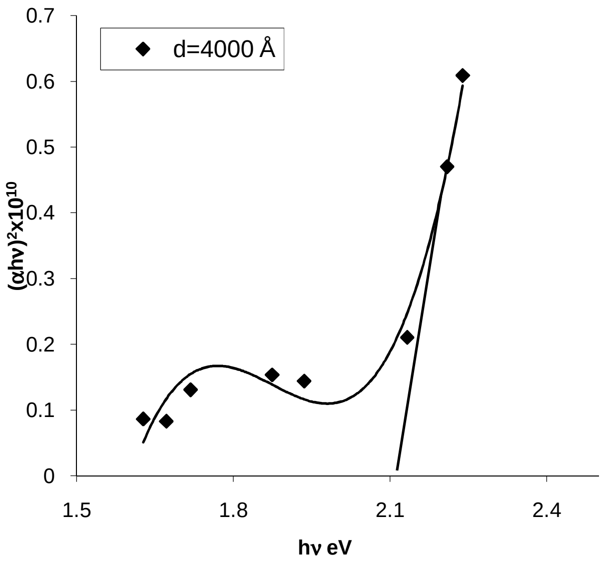

Fig. 9 (b) Plot of $(\alpha h\nu)^2$ versus hν (Al-doped)

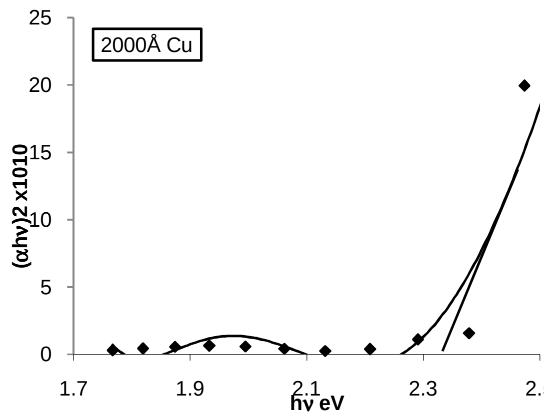

Fig. 10 Plot of $(\alpha h\nu)^2$ versus hν (Cu-doped)

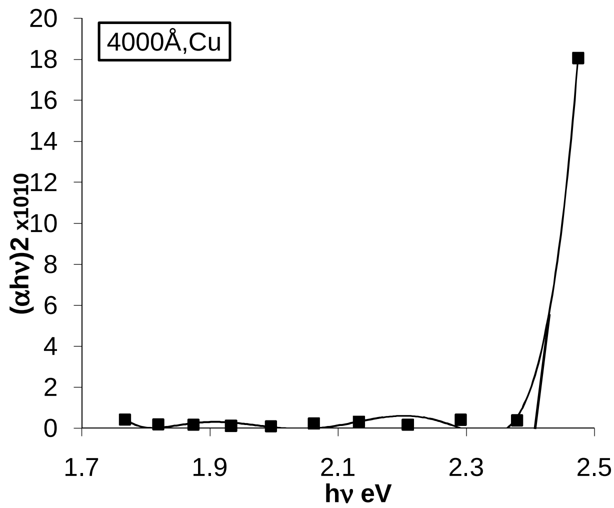

Fig. 11 Plot of $(\alpha h\nu)^2$ versus hν (Cu-doped)

CONCLUSION

1. Single crystals of X-(Cu, Al and Zn) doped and undoped lead iodide crystals have been successively grown by gel technique.
2. Different shape of crystals has been obtained like hexagonal, triangular, tree shaped, needle, layered etc.
3. Interestingly, thin films of these as gel grown crystals have been successively prepared by thermal evaporation technique.
4. From SEM study it is observed that deposited CdS film was homogenous and granular structure with nanocrystalline in nature.
5. Band gap of doped thin films increases slightly.

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