

Structural studies of vacuum evaporated Lead Iodide Thin Films

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ABSTRACT

The single crystals of Lead Iodide were grown by gel method. Thermally evaporated Lead Iodide thin films, of gel grown Lead Iodide crystals deposited on glass substrate with constant temperature (353 K). Then, the structural characterizations of these films were done by XRD, Epignost Microscope and EDAX. The XRD shows, the films were polycrystalline in nature having hexagonal structure. The lattice parameters are almost matching with the ASTM data of the Lead Iodide. The most preferential orientation is along [0 0 4] for all the deposited films together with the abundant plane [0 0 3] and [0 0 2]. The surface topography of these films inferred that the growth of these films takes place by two-dimensional nucleation process. EDAX performed on these films indicates that there is proper proportion of the Lead and Iodine. The lattice parameters, grain size and microstrain in the films are calculated and correlated.

Keywords: Gel grown PbI_2 ; thin films of PbI_2 ; XRD; optical studies.

INTRODUCTION

Lead Iodide has attracted the attention of many researches due to its potential applications in the areas of radiation detectors, photo-optical devices and solar cell technology (1-6). Several theoretical and experimental investigation have been carried out on its single crystals and polycrystalline powder compacts to probe into its optical, electrical and physical properties (7-15)

There are various methods to grow the Lead Iodide crystals. However, the sizes of the grown crystals are very small. These crystals cannot be used properly for the characterizations. Hence, it has been decided in the work paper to prepare the thin films of synthesized Lead Iodide crystals. The thin films of synthesized Lead Iodide are transparent over the range of visible spectrum. It is well known that photoelectronic and other properties of compound thin films are highly structure sensitive which in turn can severely influence the device performance. The structure parameters viz., the crystallinity, crystal phase, lattice parameters, average stress and strain, grain size, orientation etc are dependent on deposition parameters. The structure of evaporated Lead Iodide thin films are likely to be governed by the rate of deposition, substrate

temperature, composition and film thickness. Few reports on Lead Iodide thin films are available, it is felt that less attention is given in the structural characterization and their correlation to other properties. Keeping in view all these aspects, an experimental study on the structural characterization of thermally evaporated thin films of synthesized Lead Iodide crystals have been under taken. A correlation between thickness and different structural properties along with the surface topography has been high lighted in this paper.

MATERIALS AND METHODS

Lead Iodide single crystals were grown by the gel method. These crystals are crushed in a uniform size (150 mesh). Then the thin films, of gel grown Lead Iodide, were deposited on highly cleaned glass substrate in a vacuum of 10^{-5} torr by using thermally evaporated method at the substrate temperature of 353 K. The rate of deposition was 1.1 to 1.3 Å/sec. The thickness of these films was measured by quartz crystal monitor make of HindHivac model no.101. The X-ray diffraction patterns of the deposited films were recorded with the help of X-ray diffractometer (Philips PW XL-1730) using $\text{CuK}\alpha$ radiation Ni filter (1.5418 Å). The XRD patterns of all the films were taken from 20 to 90° (2θ). The peaks of the patterns were searched by computer programming method. The surface topography of all these thin films was observed by Carl-Zeiss Epignost 2HD Microscope and the structural and elemental analysis of all thin films were recorded by Philips XL-30.

RESULTS AND DISCUSSION

Fig. 1 represents XRD pattern of all the thin films of Lead Iodide. It can be seen that the height of the peak increases significantly upto 2000 Å, but it goes on decreasing for 3000 and 4000 Å thickness of the samples respectively. The vacuum evaporated thin films are polycrystalline having hexagonal structure irrespective of their substrate temperature and thickness. It is confirmed by comparing the peak positions (2θ) of the XRD pattern of the films with the standard X-ray powder diffraction data file (ASTM data card 7-235). The XRD pattern of these films was taken from 20 to 90° (2θ). The lattice parameters 'a' and 'c' of all the films have been computed from the observed 'd' values by the method of successive refinement. Mean values of lattice parameters are given in Table 1.

The microstrain and degree of preferred orientation are correlated with thickness, which is given in Fig.2 and Fig.3. The lattice constant 'a' retains its values but the values of 'c' goes on increasing, decreases and then remains constant. It might be due to the growth of the films has been taken place by two-dimensional nucleation, which is confirmed by the surface topography. The change in lattice constant for the deposited thin film over the bulk clearly indicates that the film grains are strained and that may be owing to the change of nature and the concentrations of native imperfections. The change of grain size with thickness is not very prominent.

The degree of preferred orientation in the Lead Iodide thin films can be assessed by the ratio of $[0\ 0\ 4]$ to that of $[0\ 0\ 3]$ reflection on the same scale. It is observed that the XRD pattern of all the Lead Iodide thin films shows most preferred orientation along $[0\ 0\ 4]$ plane. The various structure parameters for synthesized Lead Iodide thin films deposited at substrate temperature 352 K with various thicknesses are calculated using the relevant formulas are systematically depicted in Table 1.

The origin of the strain is related to the lattice misfit, which in turn depends upon the deposition conditions. The microstrain (ϵ) developed in the Lead Iodide thin films is calculated by the relation

$$\epsilon = (\beta_{2\theta} \cos \theta) / 4,$$

where 2θ is the full width half at half maximum of [0 0 4] peak.

The grain size of the deposited films is estimated using Scherrer formula (Warren 1969),

$$D = K\lambda / \beta_{2\theta} \cos \theta$$

Here K is taken as 0.94, λ is the wavelength of the X-ray used and $\beta_{2\theta}$ is the full width half at half maximum of [0 0 4] peak of XRD pattern.

Fig.4 represents the small needles, disordered, not oriented in the particular direction. It is fibrous growth may be due to the rapid growth of the thin films.

Some voids are seen on the deposited thin films. The interesting thing is about these voids is that deposition of the voids have clustered at a point to produce regular shaped deposition. Such, regular, triangular and hexagonal, shaped deposition are seen in Fig.7 and Fig.8 respectively. So, the production of voids and clustering of atoms in voids to form regular structure is quite general phenomena. In fact these Figures, confirms the growth of the thin films has been taken place by two-dimensional nucleation. The triangular spiral, triangular and hexagonal growth hillocks on the surface of the Lead Iodide crystal were reported (16-17). However, the triangular growth spiral is not observed on the evaporated thin films.

Fig.5 depicts, interestingly, some large number of voids of different shapes gathered together to produce dendritic growth like structure. In fact, it is not dendritic growth but the voids gathered together in such a way that it seems to be dendritic growth. Fig.6 is the enlarge copy of Fig.5.

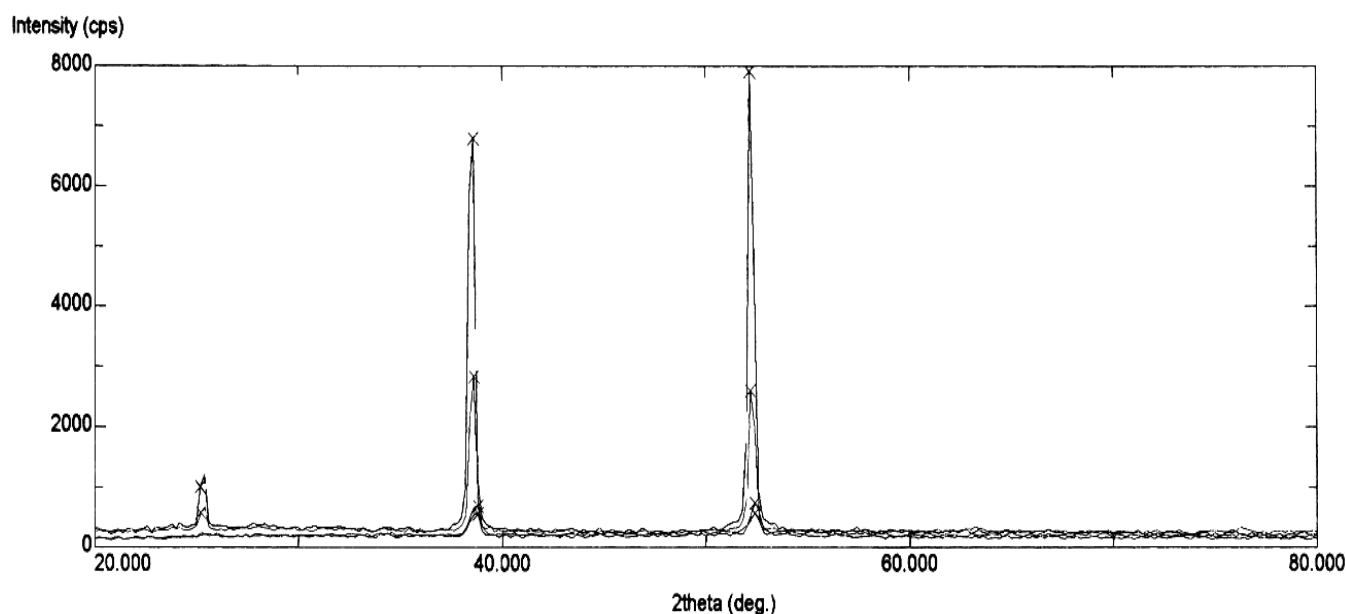


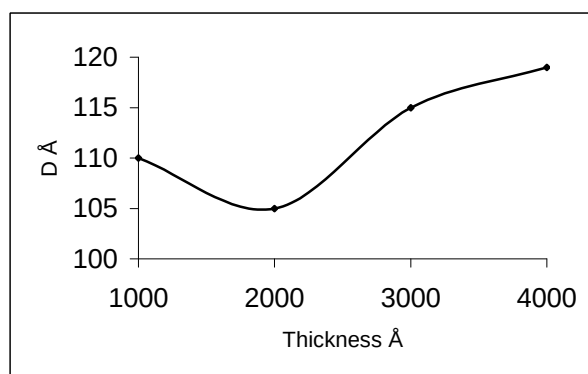
Fig. 1 X-ray diffractograms of PbI₂ thin films with various thicknesses.
(From top, 2000, 1000, 3000 and 4000 Å respectively)

Fig.9 represents hexagonal growth hillocks, which looks like hexagonal growth spirals. Similar observations for triangular spirals for Lead Iodide single crystals recently reported [16-17]. Frank predicted from theoretical considerations that crystal growth might proceed owing to the presence of screw dislocations [18]. The boundaries of the crystals at the center is not clearly resolved as the hexagonal structure, but as it proceed, from the center it takes regular form of hexagonal structure as seen from Fig.9

Electron Microscope Analysis of these films along with the elemental analysis is shown in Fig.10. A similar result was reported [19].

Table 1 Structural parameters of evaporated thin films

Thickness (in Å)	Lattice parameters		Grain size (in Å)	Microstrain $\epsilon \times 10^{-3}$
	'a' (in Å)	'c' (in Å)		
1000	4.557	7.0030	110	2.015
2000	4.557	7.0264	105	2.179
3000	4.557	7.0030	115	1.957
4000	4.557	7.0030	119	1.856



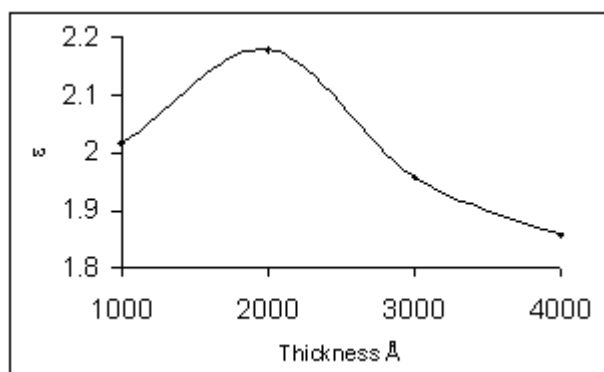


Fig. 2 and Fig. 3. Variation of D and ϵ vs. thickness.

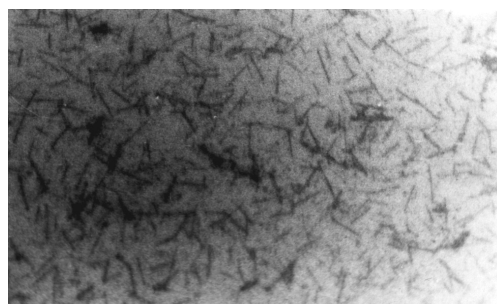


Fig.4 represents the small needles like structure

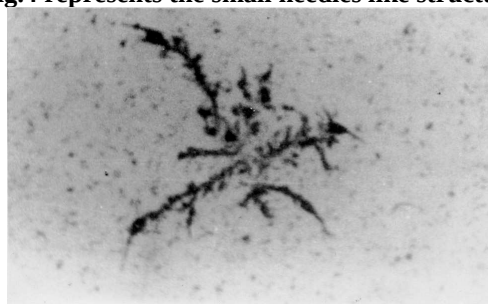


Fig. 5 represents the voids seems to be dendritic

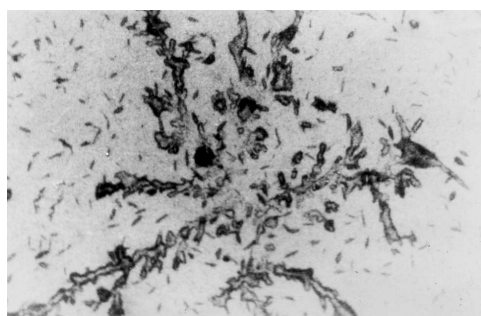


Fig.6 illustrates the enlarge copy of Fig.2

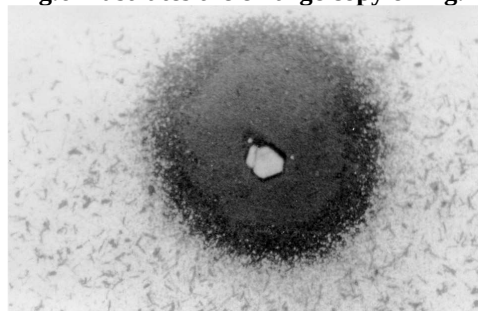


Fig.7 represents void with pentagon structure

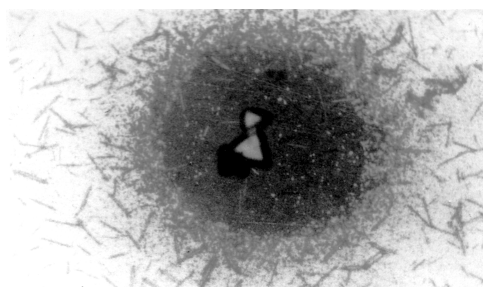


Fig.8 represents void with triangular structure

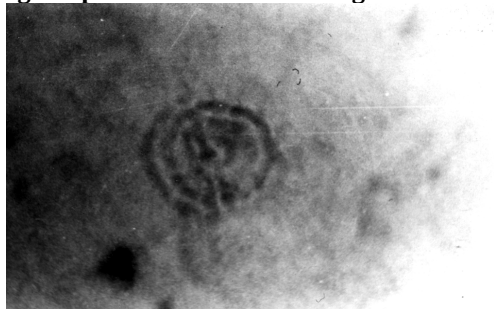


Fig.9 represents the hexagonal spiral structure

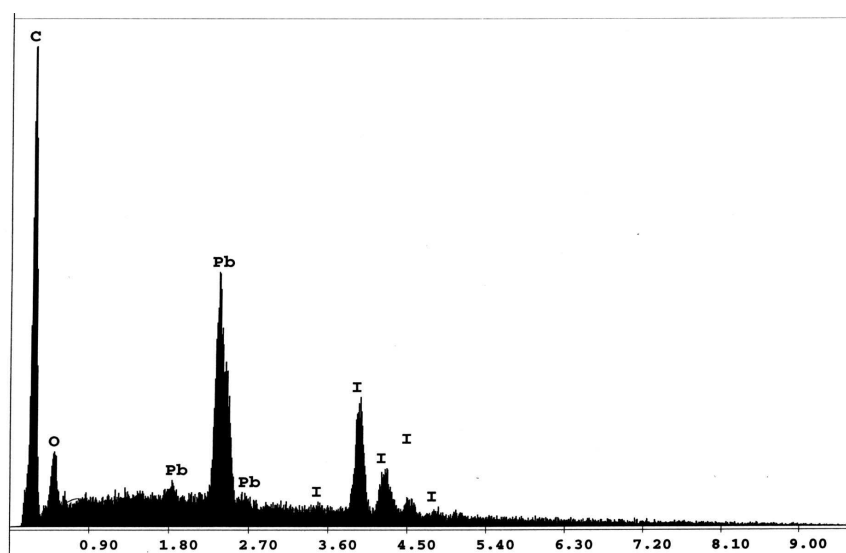


Fig. 10 depicts the EDAX for gel grown Lead Iodide thin film

CONCLUSION

All thermally evaporated thin films of Lead Iodide were polycrystalline having hexagonal type structure. Each films shows a preferred orientation along $[0\ 0\ 4]$ plane in addition to other two prominent plane $[0\ 0\ 3]$ and $[0\ 0\ 2]$. The grain size of the deposited films does not have significant dependence on the thickness of the thin films. However the degree of preferred orientation is expected to play a dominant role over the crystallite size in Lead Iodide thin films. The growth of the Lead Iodide thin films has been taken place by two- dimensional nucleation.

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REFERENCES

- [1] D.Z. Edwards, J.Z. Gier, Z.e. Nelson, and R.D. Roddick, *J.Solar Energy* 6 (1962) 1.
- [2] C. Manfredotti, R. Murri, A. Qurini, and L. Vasanelli, *IEEE Trans. Nucl.Sci.* 24 (1977) 126.
- [3] A.M. Salau, *Solar Energy Mat* 2 (1980) 327.
- [4] J. Schoonman, A. Wolfert, and D.F. Untereker, *Solid State Ionics* 11 (1983) 187.
- [5] J.C. Lund, K.S. Shah, M.R. Squillante, and F. Sinclair, *IEEE Trans.Nucl.Sci.* 35 (1988) 89.
- [6] J. Eckstein, B. Erler, and K.W. Benz, *Mat.Res.Bull.* 27 (1992) 537.
- [7] R.I. Dawood, and A.J. Froty, *Phil Mag.* 8 (1963) 1003.
- [8] A.E. Dugan, and H.K. Henish, *J.Phys.Chem.Solids* 28 (1967) 1885.
- [9] S. Baidyaroy, W.R. Bottoms, and P. Mark, *J.Phys.Chem.Solids* 33 (1972) 357.
- [10] J. Schoonman, *Solid State Commun.* 13 (1973) 673.
- [11] A.P. Lingras, and G. Simkovich, *J.Phys.Chem.Solids* 39 (1978) 1225.
- [12] J.F. Verway, *J. Phys.Chem.Solids* 31 (1970) 163.
- [13] J. Malinowsky, *Photo.Sci.Engg.* 15 (1971) 175.
- [14] H.K. Henish, and Srinivasgopalan, *Solid State Commun.* 4 (1966) 415.
- [15] N.L. Dmitruk, V.M. Shari, M.T. Kostyshin, and E.V. Mikhailovskaya, *Sov. Phys. Semiconductor* 14 (1980) 350.
- [16] D.S. Bhavsar, K.B. Saraf, *Cry.Res.Tech.* 37 (1) (2002) 51-55.
- [17] D.S. Bhavsar, K.B. Saraf, Tanay Seth, *Cry.Res.Tech.* 37 (2) (2002) 219-224.
- [18] F.C. Frank *Phil.Mag.* 42 (1951) 1014
- [19] S.C. Kuiry, S.K. Roy and S.K. Bose *Mate. Res. Bulletin* 31 (3) (1996) 317-327.