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Effect of doping on Lead Iodide single crystals by gel technique

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ABSTRACT

The undoped and doped Lead Iodide single crystals have been grown by gel technique. These crystals were characterized by X-ray diffraction, SEM, EDAX, Thermal analysis (TGA and DSC), IR, and Magnetic Properties. The observation on XRD shows that the peaks of the intensities goes on increasing as dopant concentrations increases. The IR and Thermal analysis, leads to the conclusion that there is no water molecules present in the crystals and the crystals is thermally stable. The inclusion of Cu as an impurity in lead iodide confirmed by EDAX. Convertion of diamagnetic lead iodide crystals into paramagnetic Cu-doped lead iodide crystals confirmed by magnetic susceptibility. The probable role of this doped element into the Lead Iodide crystals is explained along with surface structure of these crystals with the SEM.

Keywords*:* Gel; XRD; SEM; EDAX; Magnetic properties; Thermal analysis; IR.

INTRODUCTION

Lead Iodide has wide spread applications in the field of electronics ranging from phosphors to photovoltaic cells due to its photoconducting nature. Single crystals of photoconductors are preferable because of relative case of defining the case of pertinent variables [1].

Survey of literature reveals that good amount of experimental and theoretical information is advocated by no. of authors. Lead Iodide is an important crystal for nuclear particle detectors [2,3], photoconductor [4,5], photodecomposition [6,7], its potential image recording capabilities [8], polyptism [9,10,11], photoluminescence [12,13] and many more. Recently morphology of Lead Iodide crystals has been studied [14]. Hence it has occupied a central position in the iodide group. So, it has been decided to grow the doped and undoped Lead Iodide single crystals and to study the effect of doping on it.

It has already been reported that a variety of single crystals suitable for solid-state experimentation can be grown in silica gel [2,15-19]. The method is especially used for substances, which because of their low solubilities or low dissociation temperature (or both) cannot be readily grown by other methods since the crystals in any one growth systems grow

competitively, control of nucleation process is in many cases a key to the practical utility of the method [2].

In the present course of investigation, we have observed that i) the lattice parameters 'a' and 'c' and hence the unit cell volume are sensitively affected by the dopant concentration ii) the surface structure of the doped structure is not much affected by the doping iii) the M.P.of the doped structure is shifted slightly to the lower temperature. The purpose of this communication is to present preliminary account of the doping effect on the Lead Iodide crystals.

MATERIALS AND METHODS

Analar grade chemicals and doubly distilled water used through out the experiment in the present work. Cu-doped and undoped Lead Iodide crystals were grown by gel method at constant temperature (30^0C). Then these crystals were characterized by X-ray diffractometer (Philips PW-1730) using CuKα radiation with Ni filter (1.5418Å), Scanning Electron Microscope (Philips PW XL-30), EDAX (Philips PW XL-30), Thermoanlytical Studies (Thermogravimetric Analysis and Differential Scanning Calorimeter Analysis) using a STA-409, Nelzsch Geratebau GmbH thermal analyzer, and IR (Hitachi 331).

RESULTS AND DISCUSSION

3.1. Structural and magnetic properties studies

Fig. 1 and Fig. 2 shows an X-ray diffractogram of undoped and doped Lead Iodide single crystals. The observed and calculated values are given in Table 1 (a). The lattice parameters 'a' and 'c' are well matching with ASTM data of Lead Iodide crystals as depicted in Table 1 (b). It may be seen from this Table that lattice constant 'c' and hence the unit cell volume is sensitively affected by the dopant concentrations. X-ray diffractogram studies of these crystals confirmed that grown crystals are of Lead Iodide having hexagonal structure. As seen from Fig. 2, the height of the peaks goes on increasing as the dopant concentration increases. For Cu-doped Lead Iodide crystals, marginal increase in the lattice cell volume is observed.

The lattice parameters 'a' and 'c' for the doped and undoped Lead Iodide crystals have been computed from the observed 'd' values by the method of successive refinement. Mean values of lattice parameters are given in Table 2. It may be seen from this Table that lattice constants 'a' and 'c' and hence the unit cell volume is sensitively affected by the dopant concentrations. With increase in dopant concentration, initially the lattice parameters 'a' and 'c' and the unit cell volume remain almost constant upto 0.1 M. However at higher concentrations, a marginal increase in the lattice cell volume is observed.

Electron Microprobe Analysis of these crystals along with the elemental analysis is shown in Fig. 6 and Fig. 7. Similar results were reported [20]. Considering the systematic deviation, the analysis results are identified that some impurities along with Cu are the host lattices.

The magnetic properties of Cu-doped and undoped Lead Iodide single crystals have been studied by Guoy method. The values of magnetic susceptibility of these samples have been tabulated in Table 2. The measurement of magnetic susceptibility found that, the doped and undoped Lead Iodide single crystals are paramagnetic and diamagnetic respectively. The Lead Iodide crystals convert from diamagnetic to paramagnetic by doping Cu into the Lead Iodide crystals, this is due to the fact that the Cu+2 (d^9) has one unpaired electron, which might be responsible for this

convertion. Also, as the dopant concentration increases Cu doped Lead Iodide single crystals turn to more paramagnetic in nature as seen from Table 2.

The elemental analysis of Cu-doped by EDAX and the magnetic properties of these crystals, both are well agree with for the conclusion that there is a proper doping of Cu into the Lead Iodide single crystals.

The effect of dopant concentration on the lattice parameters and elemental analysis could be assumed as follows: i) Cu doped in the form of $CuCl_2$ of various concentration (0.1 to 1 M) presumably dissociates into Cu^+ and Cl^- ions. Cu^+ (ionic radius= 0.96Å) might be replacing Pb^{+2} (ionic radius=1.21Å), where maintaining the overall charge neutrality. As the radii of the substituted and replaced ions are comparable, the lattice parameters and the unit cell volume remain almost unaltered at lower $CuCl_2$ concentration in Lead Iodide ii) at higher concentration (nearly above 0.5N), the non-isoelectronics substitution may result in the creation of vacancies. The substitution of Cu^+ ions at anion sites lead to the creation of anion vacancies. The vacancies so created in the lattice might be responsible for the increase in the values of lattice parameters. The ratio of lattice parameters 'c/a' given in Table 1(b) is almost constant for all the dopant concentrations studied, indicating that there is no dilation of the unit cell along 'a' or 'c' direction.

The surface exposure to air of doped and undoped Lead Iodide single crystals were examined by SEM. Fig. 4 represents the SEM photograph of undoped Lead Iodide crystals namely a smooth and continuous surface.

The corners and edges of the crystals serves as the initiation point for the growth layers [21]. An excellent example showing, the SEM photograph of Fig.5, the growth layers radiating out from the initiation centers located at the center. The corners in this Fig. 5 are the terminal points of the crystals.

Fig. 6 illustrates the hexagonal overgrowths on its surface. Similar results were also previously obtained [22]. Such overgrowth was not frequently observed. Few regular hexagons are seen on the surface; also the neighboring hexagons coalesce as seen at two places. The existence of such hexagonal overgrowth is clearly indicative of a two dimensional nucleation mechanism of crystal growth.

3.2 Thermal and IR studies

The thermal behavior (DSC and TGA) of doped and undoped Lead Iodide crystals were given in Fig.8 and Fig.9 respectively. Themograms of undoped Lead Iodide crystals shows that there is no loss in weight upto 390^0C, hence the material is thermally stable, which indicates no possibility of co-ordinated water molecules or any water of crystallization in Lead Iodide crystals. Lead Iodide crystals are found to be melted at around 400^0C and slow and gradual weight loss is observed. Such result was also obtained by Differential thermal analysis [21]. Then after, slow decomposition is observed from 420^0C to 480^0C, and then sudden loss in weight is observed from 600^0C. While the thermal behaviour of doped lead iodide crystals illustrates that there is a little shift of melting point. The DSC curve of undoped Lead Iodide crystals is represented in Fig., there is an endothermic peak at 405^0C and an exothermic peak at 423^0C. Hence, it is inferred that an endothermic peak must have been caused by a phase transformation.

Fig. 10 shows the IR spectrum of Lead Iodide crystals, there is no significant band from 4000 to 200 nm. Therefore, there is no possibility of presence of water of crystallization in the Lead Iodide crystals.

Thermal Analysis and IR, both are well agree for the conclusion that there is no co-ordinated nor water of crystallization present in the crystals.

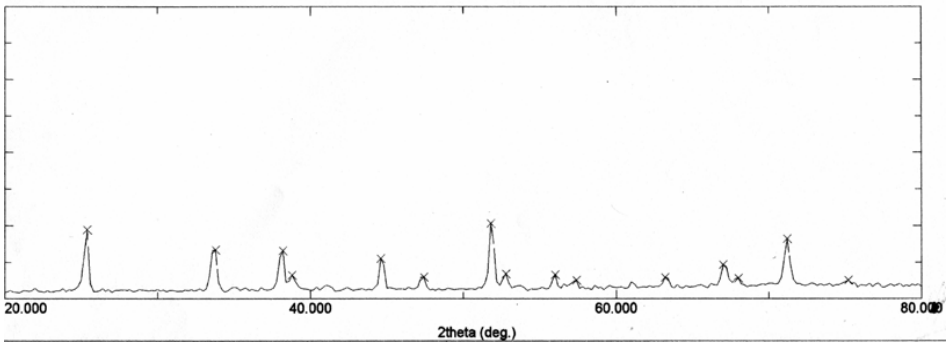

Fig. 1. X-ray diffractogram of undoped PbI_2

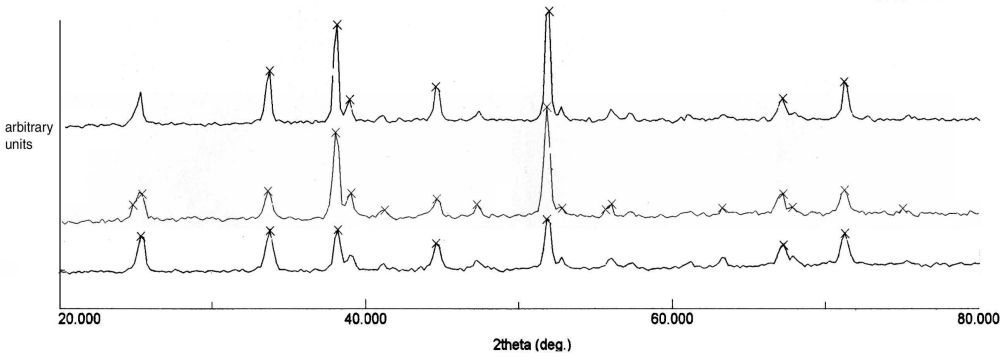

Fig. 2. X-ray diffractogram of Cu-doped PbI_2 (from bottom 0.1, 0.5 and 1N respectively)

Table 1(a) : XRD data of crystalline PbI_2

2-theta		d-value Å		Intensity	I/I_O	
observed	calculated	observed	calculated	observed		hkl
25.400	25.25	3.5036	3.5269	945	92	002
33.800	33.03	2.6496	2.6297	670	66	102
38.200	38.28	2.3540	2.3512	662	65	003
44.600	44.82	2.0299	2.0199	553	54	103
47.400	47.37	1.9163	1.9138	302	30	112
51.800	51.85	1.7634	1.7634	1030	100	004
52.800	53.19	1.7323	1.7220	340	33	202
56.000	56.22	1.6407	1.6363	332	33	113
57.400	57.22	1.6040	1.6100	258	26	104
63.200	63.51	1.4700	1.4594	295	29	211
67.000	67.01	1.3955	1.3946	467	46	114
68.000	68.01	1.3774	1.3738	285	67	212
71.200	70.42	1.3232	1.3284	823	80	300
75.200	75.23	1.2624	1.2595	258	26	213

Table 1. Effect of preparative conditionons lattice parameters

Compound	Dopant Concentration In Molar	Lattice Parameters a (Å)	c (Å)	c/a	V (Å)^3
Reported		4.575	6.989	1.5337	125.69
Undoped		4.575	7.0357	1.5479	128.85
Cu-doped	0.1	4.5757	7.1176	1.5555	129.06
Cu-doped	0.5	4.575	7.062	1.5436	128.01
Cu-doped	1.0	4.5757	7.1176	1.5555	129.06

Table 2 Susceptibility data
(undoped and Cu-doped Lead Iodide crystals)

Sample	Susceptibilty 10 x 10^{-6}	
Undoped PbI2	-0.03147	
Cu-doped PbI2	+0.531 (0.5M)	+(0.564)

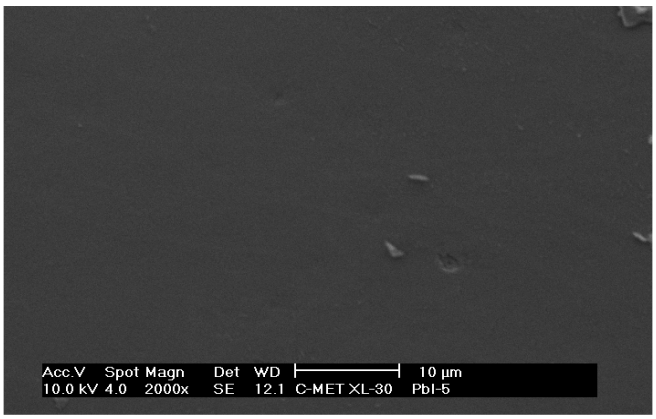

Fig. 3. illustrates SEM of PbI2 showing initiation of growth layer

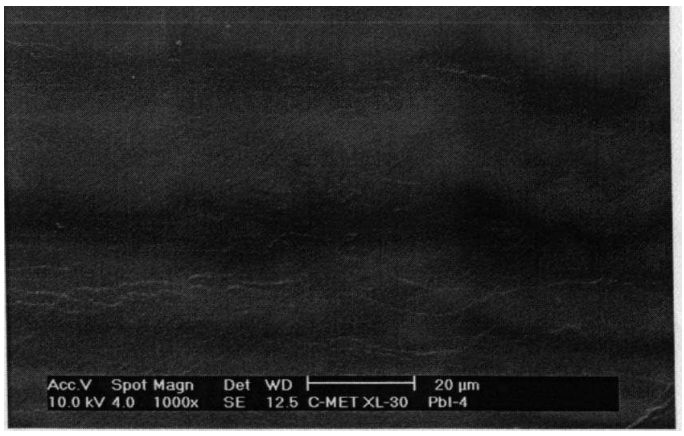

Fig. 4. illustrates SEM of PbI2 showing initiation of growth layer

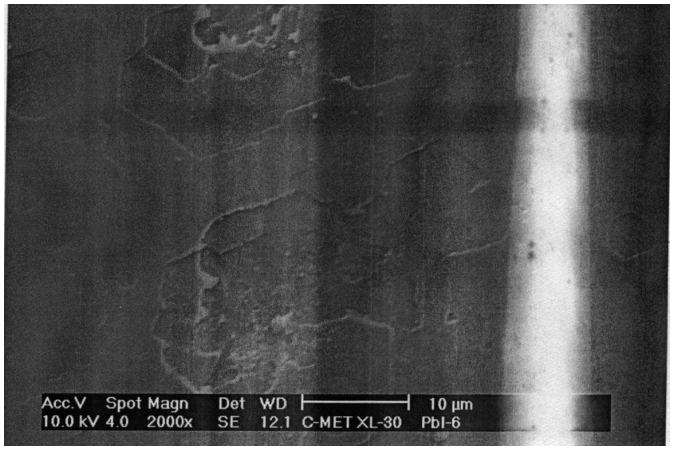

Fig. 5. represents SEM of PbI2 showing regular hexagonal and overgrowth of hexagonal

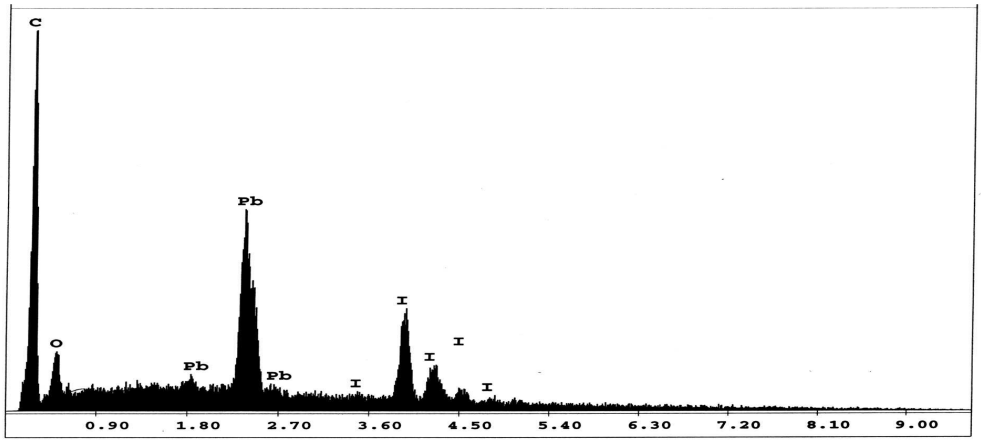

Fig. 6. represents the EDAX of undoped Lead Iodide crystals

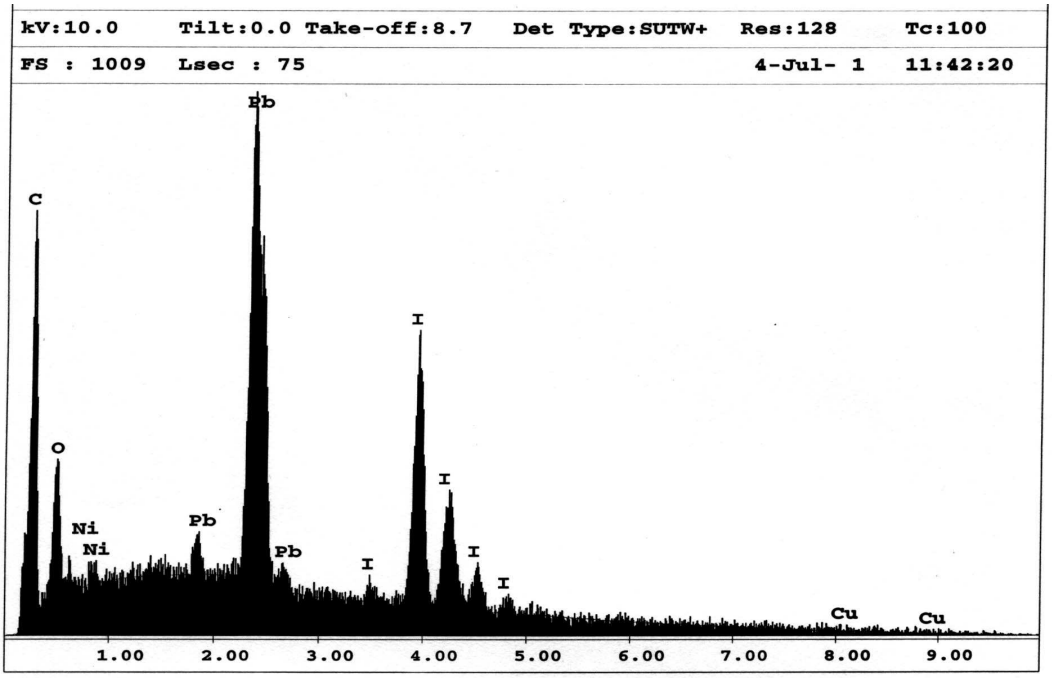

Fig. 7. illustrates the EDAX of Cu-doped Lead Iodide crystals

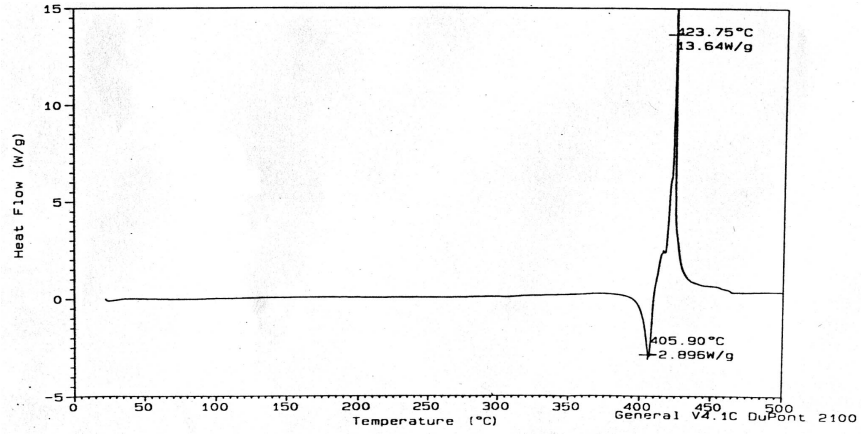

Fig. 8. shows DSC curve for Undoped Lead Iodide crystals

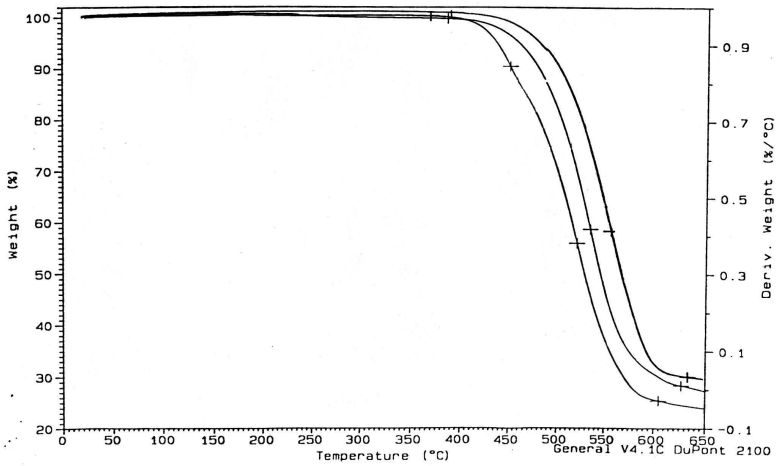

Fig. 9. represents TGA curve from top undoped and Cu-doped Lead Iodide crystals (0.5 and 1N respectively)

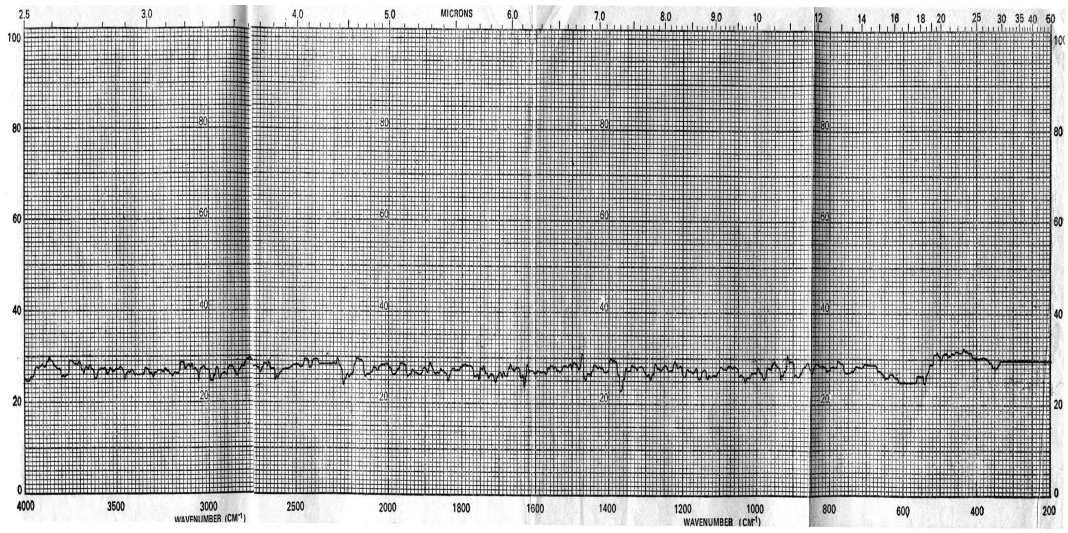

Fig. 10. depicts the IR spectrum for undoped Lead Iodide crystals

CONCLUSION

1) Lattice constants 'a' and 'c' and hence the unit cell volume are sensitively affected by the dopant concentrations
2) Unit cell volume tends to increase with dopant concentrations
3) There is no dilation of the unit cell along 'a' or 'c' direction as the ratio of 'c/a' is almost constant.
4) The addition of CuCl2 into PbI2 in the present case is considered to enhance the atomic rearrangement by creation of Pb vacancies.
5) Dimagnetic material can be converted into paramagnetic and depends upon the dopant concentrations.
6) The shifting of melting point is observed to lower temperature as seen from TGA curve in present investigation.

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