



Effect of Cu^{2+} Doping on the Growth and Band Gap Energy of Nano Crystals of Lead Iodate

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ABSTRACT

Copper doped crystals of lead iodate were successfully grown in silica gel medium. Influence of metal Cu^{2+} dopant on the structural and optical properties of the lead iodate crystals has been studied using XRD and UV-Vis. It was observed that, size of the crystal increased with increasing the doping concentration of Cu^{2+} ions. XRD analysis reveals that the grain size of the crystal decreased with increasing the doping concentration of Cu^{2+} ions. The study of UV absorption spectra reveals that band gap energy of Cu^{2+} doped lead iodate crystals increases with the increasing doping concentration.

Keywords: Gel growth, copper doping, XRD, UV spectrum.

INTRODUCTION

With the development of electronic devices much attention has been paid to role of foreign particles in the crystallization process, particularly in semiconductor industries [1]. The effect of doping on gel-grown crystals has been studied by Dishovsky and Boncheva-M Ladenova [2] and Dennis and Henisch [3]. With proper doping it is possible to grow crystals as per requirement and of desired properties. The interest in doping lead iodate crystals is to explore the possibility of tailoring its optical properties. Such crystals could be used in areas like electronics and optoelectronics.

Most of the iodate compounds are insoluble in water and decompose before melting. Hence, crystals of such type of compounds cannot be grown by either slow evaporation or melt techniques. In this situation, gel method is the appropriate one for their growth [4]. The gel growth technique has gained considerable importance due to its simplicity and effectiveness in growing single crystals of certain compounds [5-8]. Gel growth is an alternative technique to solution-growth with controlled diffusion and the growth process is free from convection [9]. No literatures are available on the study of Cu doped $\text{Pb}(\text{IO}_3)_2$ crystals. However, growth and XRD study of undoped lead iodate crystals in silica gel is reported [10].

In this paper we report a method of growing copper doped lead iodate crystals by controlled diffusion of chemical reaction in silica gel medium. The aim of the present work was to investigate the effect of Cu^{2+} ion presence during the crystallization of lead iodate crystals in gels by studying its XRD and optical property.

MATERIALS AND METHODS

Experimental Details

To grow the copper doped $\text{Pb}(\text{IO}_3)_2$ crystals, the required silica gel medium was prepared by adding the sodium metasilicate solution of specific gravity 1.04 gm/cc drop by drop with constant stirring by using magnetic stirrer into the 7 ml (2N) acetic acid till the pH value 4.2 was set for the mixture. To the above sodium meta silicate solution of pH 4.2, 5ml aqueous solution of 0.1M $\text{Pb}(\text{NO}_3)_2$ and 0.01M $\text{Cu}(\text{NO}_3)_2$ were added as inner reagents with constant stirring. This mixture was then transferred to the test tube of length 15 cm and 2.5 cm diameter. To keep the solution free from dust and impurities, care was taken to cover the test tube. It would take about 2 days for the gel to set in summer ($32\text{--}40^\circ\text{C}$), where as it would take even 4-5 days for the gel to set in winter ($20\text{--}25^\circ\text{C}$). It was left for two more days for ageing and then the outer reagent, the aqueous solution of 0.1M KIO_3 was added on to the top of the gel. The outer reagent was added down the sides of the test tube using a pipette and not directly on to the gel medium. Due to the diffusion of the outer reagent into the gel medium and its reaction with the inner reagents, crystals started growing. Nucleation was observed within 24 hours of addition of the outer reagent. Star shaped, opaque and brittle crystals were observed as shown in figure 1. All experiments leading to the growth of crystals were carried out at room temperature. The reaction between lead nitrate, copper nitrate, and potassium iodate in gel medium resulted in the growth of star shaped Cu^{2+} doped lead iodate crystals.

The reaction that takes place in the gel medium is given below.

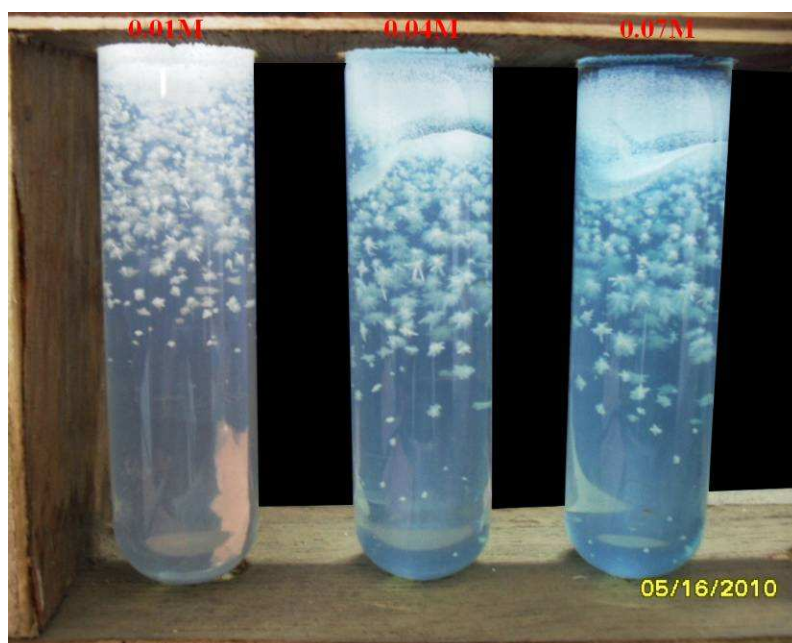


Figure 1 Cu^{2+} (0.01M, 0.04M, and 0.07M) doped crystals of lead iodate.

Same experiments were carried out to grow the 0.04M and 0.07M Cu²⁺ doped lead iodate crystals.

Figure 1 shows (i) growth of Cu²⁺ doped Lead iodate crystals for different concentrations of Cu²⁺ and (ii) the size of the doped Lead iodate crystals increased with increasing doping concentration of Cu²⁺ ions.

RESULTS AND DISCUSSION

3.1 X-RAY diffraction analysis

Cu²⁺ lead iodate crystals were powdered and X-ray powder diffraction (XRD) data were collected at room temperature on a Rigaku, Minislex model at NCL Pune. All diffraction patterns were obtained using CuK α radiation ($\lambda = 1.54051 \text{ \AA}$), at 30 kV and 15 mA. Measurements were made from $2\theta = 10^\circ$ to 80° with steps of 0.02° . Figure 2 shows the XRD patterns of crystals of lead iodate doped by different concentrations of Cu²⁺ ion. It shows very sharp peaks having high intensity, which leads to perfect crystallization [11]. The computer program POWD (an Interactive Powder Diffraction Data Interpretation and Indexing Program, Version 2.2) was used to calculate hkl and 'd' values. Calculated hkl and 'd' values are presented in table 1, 2, and 3 which are found to be in good agreement with the JCPDS values [12].

Table 1 XRD data of 0.01M Cu²⁺ doped lead iodate crystal

Peak	d-spacing \AA .		FWHM β	Intensity I	Indices h k l	Theta (Deg.)	
	Obs.	Cal.				Obs.	Cal.
1	8.2610	8.3450	0.282	94	0 2 0	10.70	10.59
2	3.2923	3.3079	0.306	539	1 3 1	27.06	26.93
3	3.0153	2.9956	0.165	77	2 1 0	29.60	29.80
4	2.7742	2.7817	0.306	1736	0 6 0	32.24	32.15
5	2.5786	2.5921	0.141	75	1 5 1	34.76	34.57
6	2.0805	2.0863	0.282	85	0 8 0	43.46	43.33
7	2.0464	2.0416	0.235	141	2 1 2	44.22	44.33
8	1.9665	1.9699	0.306	168	0 6 2	46.12	46.04
9	1.8004	1.8045	--	54	3 3 1	50.66	50.53
10	1.6874	1.6906	0.306	455	1 9 1	54.32	54.21
11	1.6526	1.6540	0.071	80	2 6 2	55.56	55.51
12	1.4219	1.4236	0.071	61	1 11 1	65.60	65.51
13	1.3915	1.3908	0.329	242	0 12 0	67.22	67.26
14	1.3571	1.3580	0.094	48	2 11 0	69.16	69.11
15	1.3547	1.3553	0.141	39	1 1 4	69.30	69.27
16	1.3483	1.3495	0.141	46	0 12 1	69.68	69.61
17	1.2841	1.2838	0.071	54	0 13 0	73.72	73.73
18	1.2644	1.2646	0.094	71	2 1 4	75.06	75.05
19	1.2458	1.2447	0.141	90	0 12 2	76.38	76.46

The crystal structure of Cu doped lead iodate is determined to be orthorhombic revealing that the incorporation of the dopant has not changed the structure of the parent crystal [13]. Lattice parameters are presented in table 4.

The variations in intensity of peaks and lattice parameters attribute to the incorporation of the dopant in the crystal. The grain size of the particles of powder samples were calculated using Scherrer formula $D = 0.9\lambda / \beta \cos\theta$, where β represents the full width at half maximum (FWHM) of XRD lines. The average grain size of the particles is given in table 4. It is found that the average grain size of the lead iodate crystal decreased with increasing the doping concentration of Cu²⁺ ions.

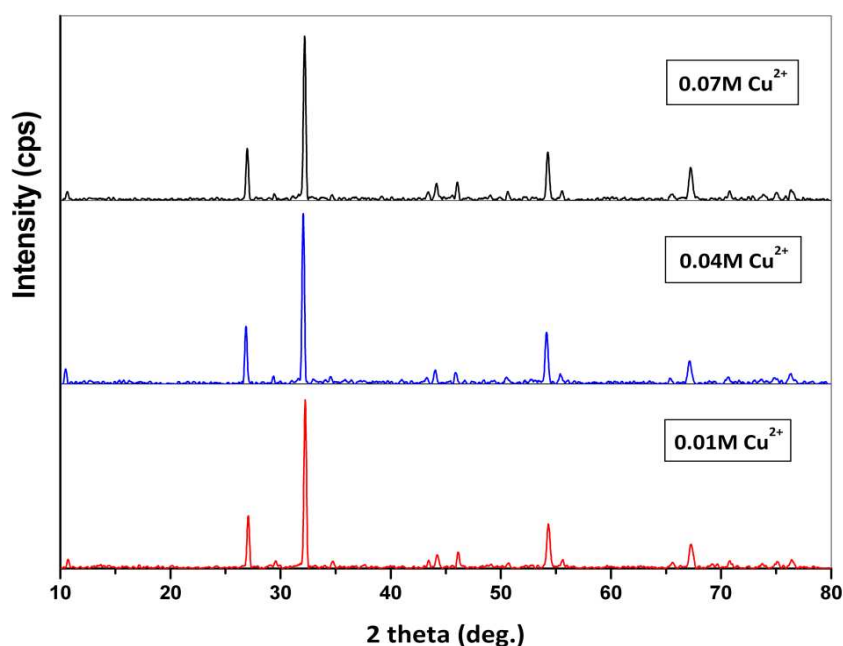


Figure 2 XRD pattern of the crystals of $\text{Pb}(\text{IO}_3)_2 : \text{Cu}^{2+}$ (for 0.01M, 0.04M, and 0.07M).

Table 2 XRD data of 0.04M Cu^{2+} doped lead iodate crystal

Peak	d-spacing \AA°		FWHM β	Intensity I	Indices h k l	Theta (Deg.)	
	Obs.	Cal.				Obs.	Cal.
1	8.4340	8.3924	0.259	130	0 2 0	10.48	10.53
2	3.3164	3.3126	0.282	500	1 3 1	26.86	26.89
3	3.0394	3.0421	0.212	70	2 0 0	29.36	29.33
4	2.7894	2.7877	0.259	1486	0 0 2	32.06	32.08
5	2.7152	2.7501	0.118	44	0 1 2	32.96	32.53
6	2.5916	2.6001	0.094	64	1 5 1	34.58	34.46
7	2.2015	2.2028	0.118	37	0 7 1	40.96	40.94
8	2.0887	2.0898	0.118	57	2 5 1	43.28	43.25
9	2.0535	2.0553	0.329	122	2 0 2	44.06	44.02
10	1.9770	1.9747	0.165	100	0 6 2	45.86	45.92
11	1.8044	1.8041	0.118	59	3 3 1	50.54	50.55
12	1.6926	1.6940	0.282	448	1 3 3	54.14	54.09
13	1.6576	1.6574	0.071	91	3 5 1	55.38	55.39
14	1.4269	1.4279	0.165	50	1 7 3	65.34	65.29
15	1.3926	1.3939	0.306	201	0 0 4	67.16	67.09
16	1.3310	1.3310	0.141	56	4 1 2	70.72	70.72
17	1.2461	1.2457	0.094	91	0 10 3	76.36	76.39

3.2 UV

Absorption Spectroscopy

Absorption spectra of undoped and Cu^{2+} doped Lead iodate crystals were recorded using a SHIMADZU UV-2450 UV-Vis spectrophotometer over the wavelength range 200 – 700 nm at Nano Research Laboratory, Department of Physics, Pratap College, Amalner.

Table 3 XRD data of 0.07M Cu²⁺ doped lead iodate crystal

Peak	d-spacing A°		FWHM β	Intensity I	Indices h k l	Theta (Deg.)	
	Obs.	Cal.				Obs.	Cal.
1	8.3075	8.3450	0.306	82	0 2 0	10.64	10.59
2	3.3019	3.3079	0.329	481	1 3 1	26.98	26.93
3	3.0293	3.0450	0.282	60	2 0 0	29.46	29.31
4	2.7792	2.7817	0.329	1515	0 6 0	32.18	32.15
5	2.5844	2.5921	0.353	53	1 5 1	34.68	34.57
6	2.0823	2.0863	0.376	79	0 8 0	43.42	43.33
7	2.0491	2.0537	0.329	156	2 6 0	44.16	44.05
8	1.9689	1.9699	0.329	168	0 6 2	46.06	46.04
9	1.8560	1.8544	0.329	47	0 9 0	49.04	49.08
10	1.8010	1.8045	0.353	84	3 3 1	50.64	50.53
11	1.6891	1.6906	0.376	445	1 9 1	54.26	54.21
12	1.6526	1.6540	0.329	88	2 6 2	55.56	55.51
13	1.4234	1.4236	0.565	55	1 11 1	65.52	65.51
14	1.3911	1.3908	0.424	302	0 12 0	67.24	67.26
15	1.3300	1.3297	0.306	89	3 9 1	70.78	70.80
16	1.2965	1.2961	0.306	41	2 10 2	72.90	72.93
17	1.2817	1.2832	0.565	53	4 7 0	73.88	73.78
18	1.2647	1.2646	0.424	72	2 1 4	75.04	75.05
19	1.2461	1.2470	0.541	99	0 6 4	76.36	76.30

Table 4 Calculated lattice parameters and Average grain size

Crystal	Lattice parameters			α=β=γ	Average grain size in nm
	a	b	c		
JCPDS data of lead iodate	6.09	16.69	5.58	90°	--
0.01M Cu ²⁺ doped lead iodate	6.0841	16.6861	5.5755	90°	47.74
0.04M Cu ²⁺ doped lead iodate	6.0841	16.7048	5.5755	90°	45.29
0.07M Cu ²⁺ doped lead iodate	6.0841	16.6861	5.5755	90°	20.51

Figure 3 shows UV absorption spectra of undoped and Cu²⁺ doped (for 0.01M, 0.04M, and 0.07M Cu) lead iodate crystals. From the spectrum, it has been inferred that undoped and Cu²⁺ doped lead iodate crystals have sufficient transmission in the entire visible and IR region. The absorption coefficient is high at lower wavelength and the wide transparency from 340nm suggesting their suitability for second and third harmonic generations of the 1064 nm radiation [14-17].

It was observed that doping of copper does not affect the perfection of crystals. In addition, 0.01M Cu²⁺ slightly enhances the percentage of transmittance of the lead iodate crystals while with increase in the doping concentration, the transparency of the lead iodate crystals decreases.

Table 5 Band gap energy of Cu²⁺ doped and undoped lead iodate crystals.

Crystal	λ (nm)	Band gap Energy (eV)
Lead iodate (Undoped)	338.54	3.6628
0.01M Cu ²⁺ doped lead iodate	337.32	3.6760
0.04M Cu ²⁺ doped lead iodate	332.67	3.7274
0.07M Cu ²⁺ doped lead iodate	330.72	3.7494

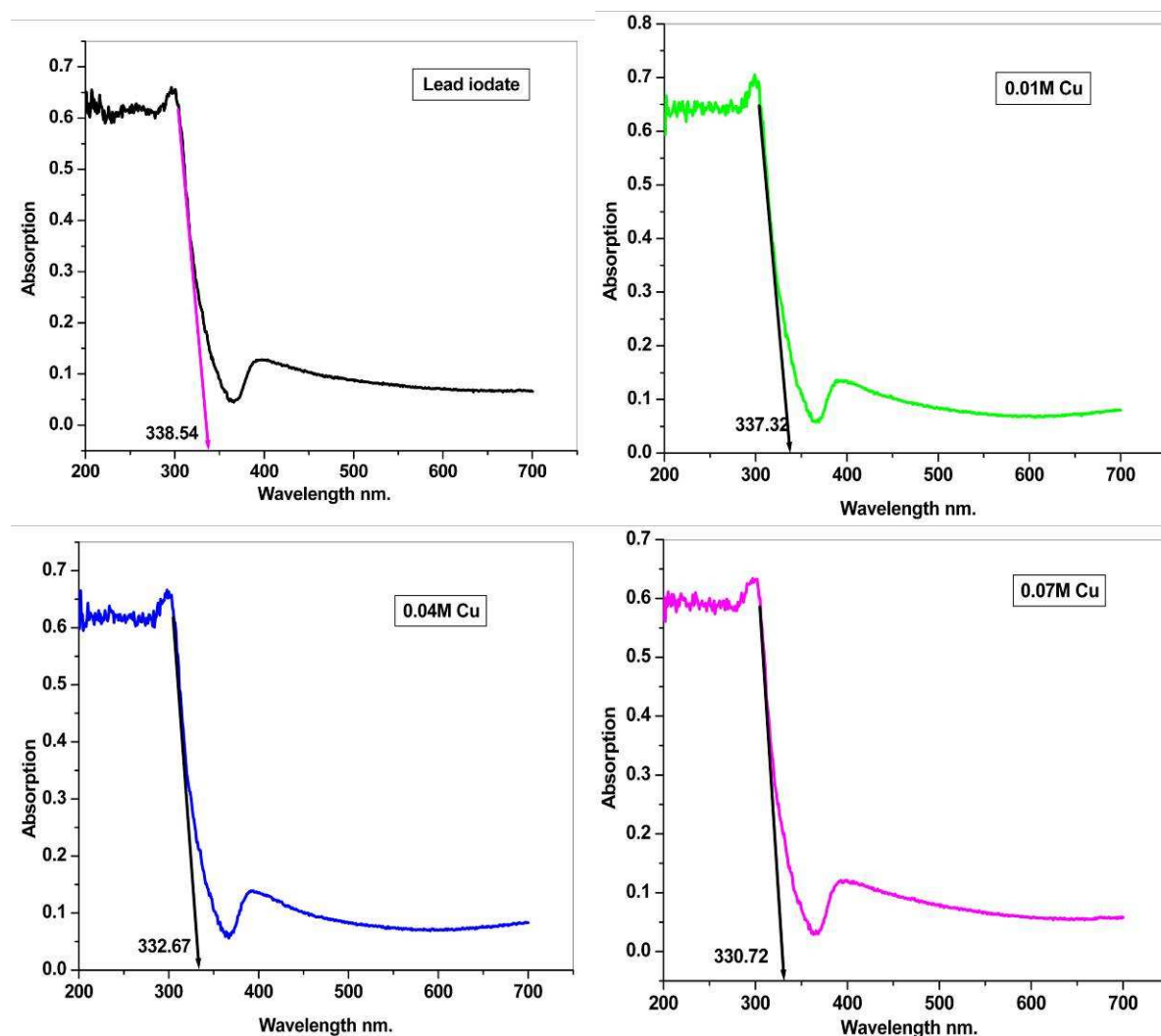


Figure 3 Absorption spectra of undoped and Cu^{2+} doped (for 0.01M, 0.04M, and 0.07M) lead iodate crystals.

The band gap energy of the Cu^{2+} doped and undoped lead iodate crystals with the obtained wavelength are calculated using the following simple conversion equation;

$$\text{Band gap energy (eV)} = 1240/\text{wavelength (nm)}.$$

Band gap energy is presented in the table 5. It was observed that band gap energy of Cu^{2+} doped lead iodate crystals increases with the increasing doping concentration [18].

CONCLUSION

From the above studies we conclude that:

1. Gel growth technique is suitable for growing the crystals of Cu^{2+} doped lead iodate crystals.
2. The size of the Cu^{2+} doped lead iodate crystals increases with increasing doping concentration.
3. XRD studies reveal that the crystalline perfection of the doped crystal is extremely good.
4. The incorporation of the dopant has not altered the structure of the parent lead iodate crystal.
5. Increase in dopant concentration leads to a smaller average grain size.

6 0.01M Cu²⁺ doping enhance the transparency of the lead iodate crystals.

7 The absorption spectra are influenced by the doping: in fact, band gap narrowing occurs with decreasing doping density.

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