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Influence of Zn(II) Doping on the Structural and Optical Properties of Gel Grown Lead Iodate Crystals

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ABSTRACT

In this research, the growth of the zinc doped lead iodate crystals is reported. The crystals were grown in silica gel medium by single diffusion technique. It was observed that, size of the crystals increased with increasing the doping concentration of Zn^{2+}. The influence of doping of transition metal Zn on lead iodate crystals has been studied using XRD and UV-Vis. XRD analysis reveals that average grain size of the crystal decreased with increasing the doping concentration of Zn^{2+} ions. The study of UV absorption spectra reveals that value of band gap energy increased slightly as the concentration of zinc increased.

Keywords: Silica Gel, Zinc doping, XRD, Energy band gap.

INTRODUCTION

The effect of doping on gel-grown crystals has been extensively studied by Dishovsky and Boncheva-M Ladenova [1] and Dennis and Henisch [2]. The growth and characterization of doped nanocrystals (NCs) have attracted considerable attention in recent years. Dopants within nanocrystals have been used as probes of microscopic structural parameters. Our discussion focused on Zn^{+2} as dopant and lead iodate crystals as host. The structural and optical properties of NCs are different from those of the corresponding bulk material because in the nano-size regime solids are gradually losing their bulk behavior due to quantum confinement [3].

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]. In searching the literature no information was found regarding its crystallographic properties except our two papers on lead iodate crystals in silica gel [10, 11].

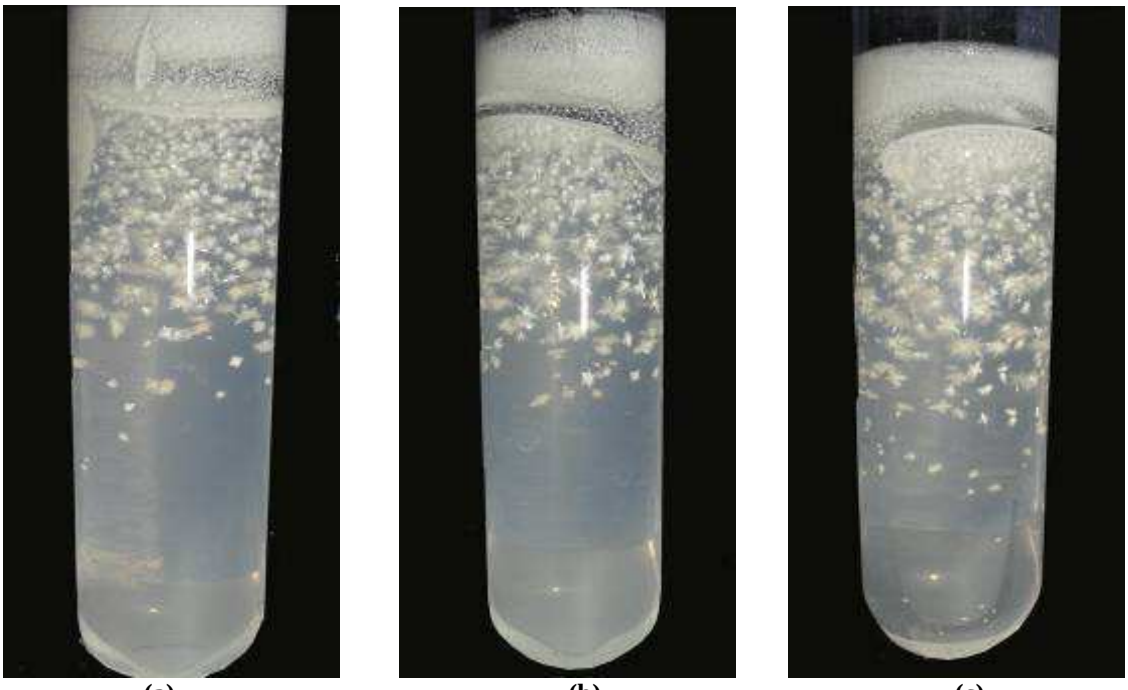
In this paper, we report the effect of doping on the structural and optical properties of $Pb(IO_3)_2$: Zn crystals obtained by gel method at various doping concentrations of Zn^{2+} ion. The samples have been characterized by X-Ray Diffraction for structure determination and UV-Visible Spectrophotometer for optical absorption properties study.

MATERIALS AND METHODS

2. Experimental details

Lead iodate shows poor solubility in water hence it was thought worthwhile to grow such a kind of material by chemical reaction at controlled rate using gel method [12, 13]. The experiments pertaining to the growth of zinc doped lead iodate crystals were conducted in borosilicate glass tubes of 2.5 cm diameter and 15 cm length. Gel was prepared by mixing sodium meta silicate solution of specific gravity 1.04 gcm^{-3} with the 5ml aqueous solution of 0.1M $Pb(NO_3)_2$ which acted as a lower reactant, 0.01M $Zn(NO_3)_2$, and 7ml (2N) acetic acid. The solution was continuously stirred to avoid local ion concentration, which may cause premature local gelling and make the final solution inhomogeneous. The pH of the gel medium was adjusted to 4.2. The solution was then transferred to several glass tubes. The glass tubes were sealed with cotton material to prevent fast evaporation and contamination of the exposed surface of the gel and left for gelling. The gel setting time was found to be strongly dependent on pH and environmental temperature. It would take about 24h for the gel to set in summer (32–40^oC), where as it would take even 3-4days for the gel to set in winter (20–25^oC). After confirming the gel setting, an aqueous solution of the aqueous solution of 0.1M KIO_3 was carefully poured along the walls of the tube with the help of pipette over the set gel, in order to avoid any gel breakage [14, 15]. 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. The following reaction is expected to take place in the gel medium.

$Pb(NO_3)_2 + Zn(NO_3)_2 + 2KIO_3 = Pb(IO_3)_2$: Zn + $2KNO_3$.



(a) **(b)** **(c)**

Figure 1 Zn^{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 Zn^{2+} doped lead iodate crystals. Figure 1 shows (i) growth of Zn^{2+} doped Lead iodate crystals for different concentrations of Zn^{2+} and (ii) the size of the doped Lead iodate crystals increased with increasing doping concentration of Zn^{2+} ions.

RESULTS AND DISCUSSION

3.1 X-RAY DIFFRACTION ANALYSIS:

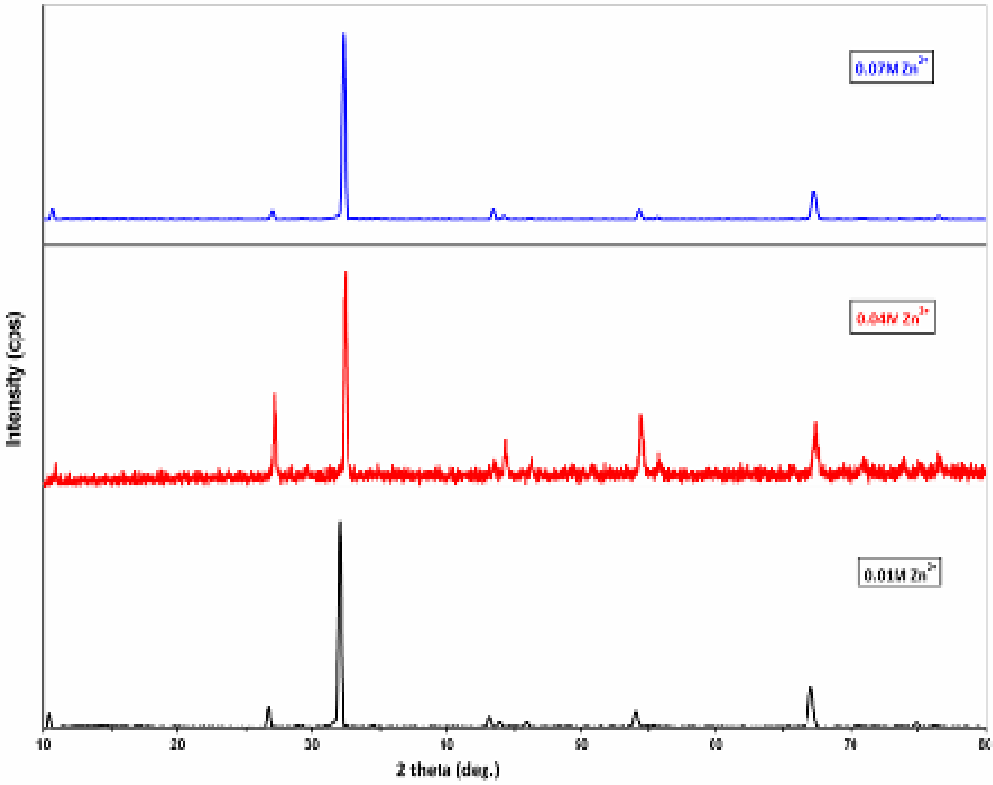


Figure 2 XRD pattern of the crystals of $Pb(IO_3)_2$: Zn(for 0.01M, 0.04M, and 0.07M Zn).

The structure and phase purity of the as-grown crystals were investigated by XRD. The XRD diffraction patterns were obtained using Rigaku, Minislex model at NCL Pune. Figure 2 shows the XRD patterns of crystals of lead iodate doped by different concentrations of Zn^{2+} ion. It shows very sharp peaks having high intensity, which leads to perfect crystallization [16]. The computer program POWD (an Interactive Powder Diffraction Data Interpretation and Indexing Program, Version 2.2) was used to calculate lattice parameters, 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 [17].

The crystal structure of Zn doped lead iodate is determined to be orthorhombic. It is evident from the XRD data that there are no extra peaks due to zinc dopant, indicating that the as- grown crystals are single phase [18]. The Zn ion was understood to have substituted the Pb site without changing the orthorhombic structure of the parent crystal [19]. The variations in intensity of peaks and lattice parameters attribute to the incorporation of the dopant in the crystal. The lattice parameters derived from the powder XRD data are listed in Table 4. The grain size of the particles of powder samples were calculated using Scherrer equation $D = 0.9\lambda / \beta\cos\theta$, where β represents the full width at half maximum (FWHM) of XRD lines. The average grain size of the particles is presented in table 5.

Table 1 XRD data of 0.01M Zn^{2+} doped Lead iodate crystal

Peak	d-spacing A°.		FWHM β	Int. I	Indices h k l	Theta (Deg.)	
	Obs.	Cal.				Obs.	Cal.
1	8.2304	8.2984	0.141	87	0 2 0	10.74	10.65
2	3.6567	3.6845	0.141	41	1 2 1	24.32	24.13
3	3.2876	3.3002	0.282	642	1 3 1	27.10	26.99
4	3.0213	3.0421	0.141	69	2 0 0	29.54	29.33
5	2.8167	2.7896	0.071	35	0 0 2	31.74	32.06
6	2.7692	2.7661	0.282	1643	0 6 0	32.30	32.34
7	2.5743	2.5828	0.188	58	1 5 1	34.82	34.70
8	2.4518	2.4533	0.094	36	2 4 0	36.62	36.60
9	2.0777	2.0809	0.212	91	2 5 1	43.52	43.45
10	2.0438	2.0466	0.306	146	2 6 0	44.28	44.22
11	1.9632	1.9636	0.165	82	1 8 0	46.20	46.19
12	1.8524	1.8522	0.165	48	1 8 1	49.14	49.15
13	1.7990	1.8021	0.212	48	3 3 1	50.70	50.61
14	1.7471	1.7479	0.165	47	2 5 2	52.32	52.29
15	1.6862	1.6826	0.329	432	1 9 1	54.36	54.49
16	1.6521	1.6529	0.141	72	3 5 1	55.58	55.55
17	1.4215	1.4227	0.071	50	1 7 3	65.62	65.56
18	1.3897	1.3899	0.400	421	0 1 4	67.32	67.31
19	1.3271	1.3271	0.094	60	0 11 2	70.96	70.96
20	1.2808	1.2802	0.071	56	4 7 0	73.94	73.98
21	1.2638	1.2642	0.071	81	2 1 4	75.10	75.08

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

Peak	d-spacing A°.		FWHM β	Int. I	Indices h k l	Theta (Deg.)	
	Obs.	Cal.				Obs.	Cal.
1	8.1848	8.2984	0.306	168	0 2 0	10.80	10.65
2	3.2852	3.3006	0.306	447	1 3 1	27.12	26.99
3	2.7675	2.7661	0.282	1629	0 6 0	32.32	32.34
4	2.5715	2.5830	0.118	67	1 5 1	34.86	34.70
5	2.0777	2.0746	0.141	104	0 8 0	43.52	43.59
6	2.0438	2.0407	0.282	134	2 1 2	44.28	44.35
7	1.9624	1.9635	0.306	116	0 6 2	46.22	46.19
8	1.6857	1.6827	0.259	359	1 9 1	54.38	54.48
9	1.6494	1.6503	0.165	64	2 6 2	55.68	55.65
10	1.3897	1.3890	0.282	458	0 1 4	67.32	67.36
11	1.3297	1.3307	0.071	83	3 3 3	70.80	70.74
12	1.3193	1.3194	---	42	4 2 2	71.44	71.44
13	1.2808	1.2813	0.141	54	4 7 0	73.94	73.91
14	1.2737	1.2720	0.071	45	4 4 2	74.42	74.53
15	1.2633	1.2638	0.071	64	2 1 4	75.14	75.11
16	1.2442	1.2445	0.188	93	0 13 1	76.50	76.48

3.2 UV ABSORPTION SPECTROSCOPY

Absorption spectra of undoped and Zn^{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 Zn^{2+} doped lead iodate crystal

Peak	d-spacing A°.		FWHM	Int.	Indices	Theta (Deg.)	
	Obs.	Cal.	β	I	h k l	Obs.	Cal.
1	8.2610	8.3046	0.306	138	0 2 0	10.70	10.64
2	3.2947	3.3023	0.282	429	1 3 1	27.04	26.98
3	3.0619	3.0446	0.212	55	2 0 0	29.14	29.31
4	2.7742	2.7682	0.282	1998	0 6 0	32.24	32.31
5	2.5829	2.5846	0.141	46	1 5 1	34.70	34.68
6	2.0805	2.0824	0.282	162	2 5 1	43.46	43.42
7	2.0482	2.0482	0.188	136	2 6 0	44.18	44.18
8	1.9689	1.9717	0.071	77	3 2 0	46.06	45.99
9	1.9665	1.9652	0.235	82	0 6 2	46.12	46.15
10	1.8017	1.8035	0.118	58	3 3 1	50.62	50.57
11	1.7640	1.7634	0.141	33	0 3 3	51.78	51.80
12	1.6880	1.6838	0.353	320	1 9 1	54.30	54.44
13	1.6515	1.6511	0.165	91	2 6 2	55.60	55.61
14	1.3911	1.3903	0.259	580	0 1 4	67.24	67.29
15	1.3297	1.3312	0.165	49	3 3 3	70.80	70.71
16	1.2823	1.2813	0.118	46	4 7 0	73.84	73.91
17	1.2808	1.2808	0.071	46	1 9 3	73.94	73.94
18	1.2650	1.2647	0.141	86	2 1 4	75.02	75.04
19	1.2439	1.2454	0.118	60	0 13 1	76.52	76.41

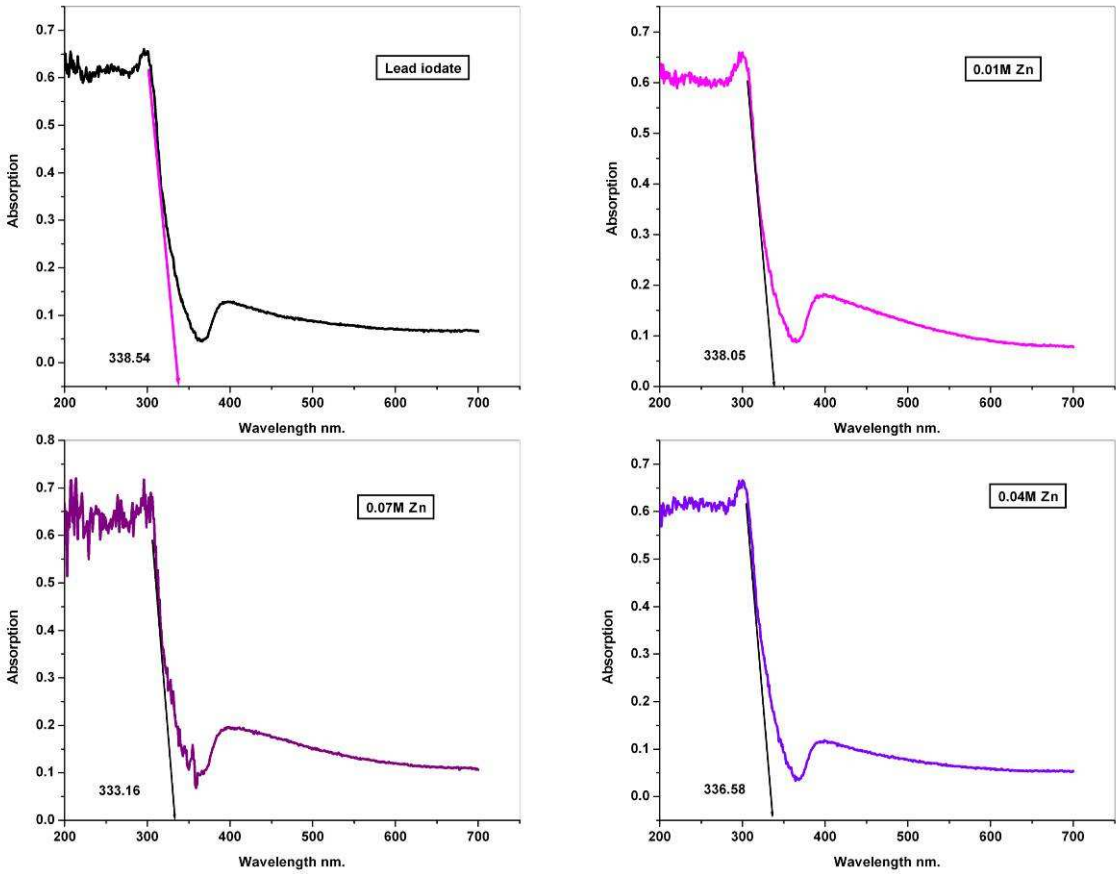


Figure 3 Optical absorption spectra of undoped and xZn doped lead iodate, x = 0.01M, 0.04M, and 0.07M.

Table 4 Calculated lattice parameters and Average grain size

Crystal	Lattice parameters			Average grain size in nm
	a	b	c	
JCPDS data of lead iodate	6.09	16.59	5.58	--
0.01M Zn^{2+} doped lead iodate	6.0841	16.5968	5.5791	53.5930
0.04M Zn^{2+} doped lead iodate	6.0911	16.5969	5.5755	45.6832
0.07M Zn^{2+} doped lead iodate	6.0892	16.6093	5.5809	44.2353

Figure 3 shows UV absorption spectra of undoped and Zn^{2+} doped (for 0.01M, 0.04M, and 0.07M Zn) lead iodate crystals. From the spectrum, it has been inferred that undoped and Zn^{2+} 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 340 nm suggesting their suitability for second and third harmonic generations of the 1064 nm radiation [20-23].

It was observed that doping by Zinc does not affect the perfection of crystals. In addition, 0.04M Zn^{2+} slightly enhances the percentage of transmittance of the lead iodate crystals while with the 0.01M and 0.07M doping concentration of zinc, the transparency of the lead iodate crystals decreases.

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

Band gap energy (eV) = 1240/wavelength (nm).
Band gap Energy is presented in the table 5. It was observed that band gap energy of Zn^{2+} doped lead iodate crystals increasing with the increasing doping concentration [24].

Table 5 Band gap energy of Zn^{2+} doped and undoped lead iodate crystals

Crystal	λ (nm)	Band gap Energy (eV)
Lead iodate	338.54	3.6628
0.01M Zn^{2+} doped lead iodate	338.05	3.6681
0.04M Zn^{2+} doped lead iodate	336.58	3.6841
0.07M Zn^{2+} doped lead iodate	333.16	3.7219

CONCLUSION

In conclusion, gel growth technique is suitable for growing the crystals of Zn^{2+} doped lead iodate crystals. The size of the Zn^{2+} doped lead iodate crystals increases with increasing doping concentration. XRD pattern shows very sharp peaks having high intensity, which leads to perfect crystallization. It also suggests that Zn atoms substitute Pb sites in the crystals without changing the orthorhombic structure, but the lattice parameters varying slightly with the doping. Increase in dopant concentration leads to a smaller average grain size. The UV–Vis measurements indicate the band gap energy of the lead iodate crystals increases with increase in Zn doping concentration.

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