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Effects of Cobalt Doping on the Structural and Optical Properties of Gel Grown $Pb(IO_3)_2$ Crystals

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ABSTRACT

In this research, the growth of the cobalt 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 Co^{2+}. Influence of doping, on the crystallite structure and band gap energy has been investigated using XRD and UV-Vis. XRD analysis reveals that average grain size of the crystal decreased with increasing the doping concentration of Co^{2+} ions. The study of UV absorption spectra reveals that the % of transmission and value of band gap decreased slightly as the concentration of cobalt increased.

Keywords: Gel method, doping, XRD, band gap.

INTRODUCTION

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 Co^{+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 [1].

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 [2]. The gel growth technique has gained considerable importance due to its simplicity and effectiveness in growing single crystals of certain compounds [3-6]. Gel growth is an alternative technique to solution-growth with controlled diffusion and the growth process is free from convection [7]. We have reported the growth and XRD study of lead iodate crystals in silica gel [8].

In this paper, we report the effect of doping on the structural and optical properties of $Pb(IO_3)_2$ crystals obtained by gel method at various doping concentrations of Co^{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

2.1 Experimental Details

The solutions of three suitable compounds give rise to the required insoluble crystalline substances by mere chemical reaction between them. They are allowed to diffuse into the gel medium and to react chemically as follows:

AX + BX + CY → AY: B + CX.

Where, AX, BX, and CY are the solutions of three reactants, which on reaction give rise to the B doped insoluble substances AY and also the waste product CX being highly soluble in water [9-11].

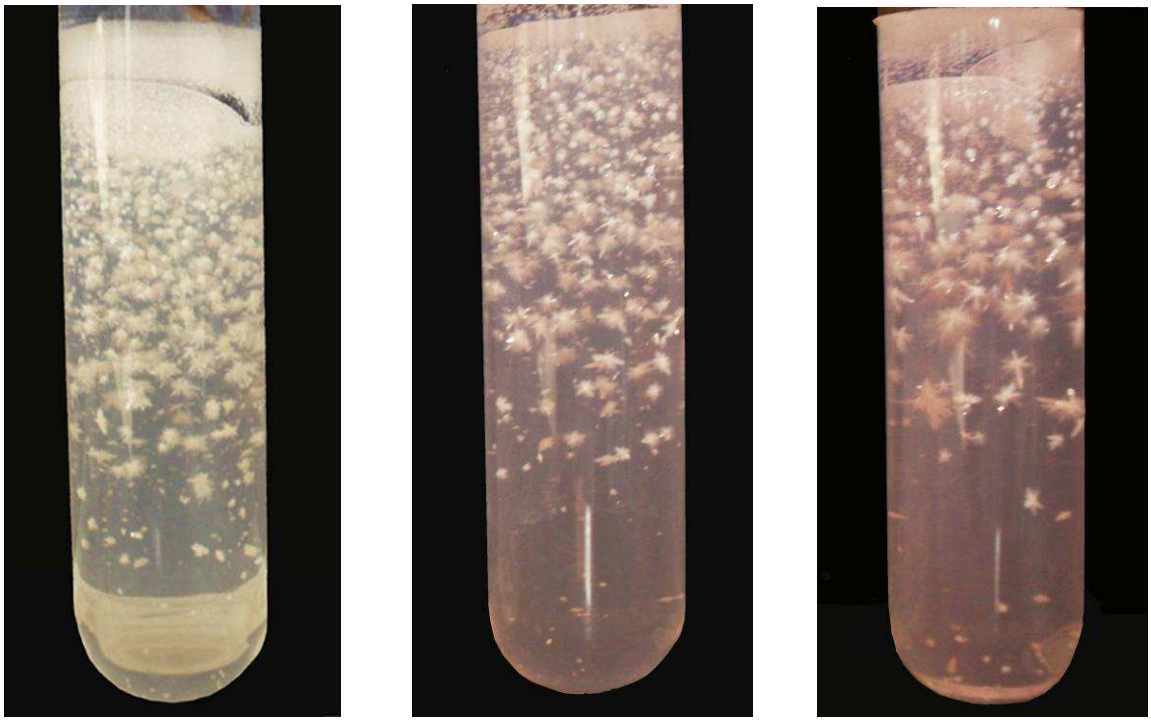
The reaction taken is

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

2.2 Growth of $Pb(IO_3)_2$: Co^{2+} Crystals by Single Diffusion Method

The gel is a two-component system with highly viscous, semi-solid in nature and having the fine pores through which diffusion takes place. The gelling process takes a definite amount of time that varies from minutes to days depending upon the nature of material and its temperature. The gelling time is always approximate in case of silica gel and the mechanical properties of fully developed gels are found to vary widely depending on the density and prescribed conditions during the gelling process. Silica gel 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 $Pb(NO_3)_2$ and 0.01M $Co(NO_3)_2$ 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. The gel was usually set within 4 to 8 days. 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.

Same experiments were carried out to grow the 0.04M and 0.07M Co^{2+} doped lead iodate crystals. Figure 1 shows (i) growth of Co^{2+} doped lead iodate crystals for different concentrations of Co^{2+} and (ii) the size of the doped lead iodate crystals increases as the doping concentration increases.



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

Fig. 1 xCo^{2+} doped crystals of lead iodate. (a) x = 0.01M, (b) x = 0.04M, and (c) x = 0.07M.

RESULTS AND DISCUSSION

3.1 X-RAY diffraction analysis

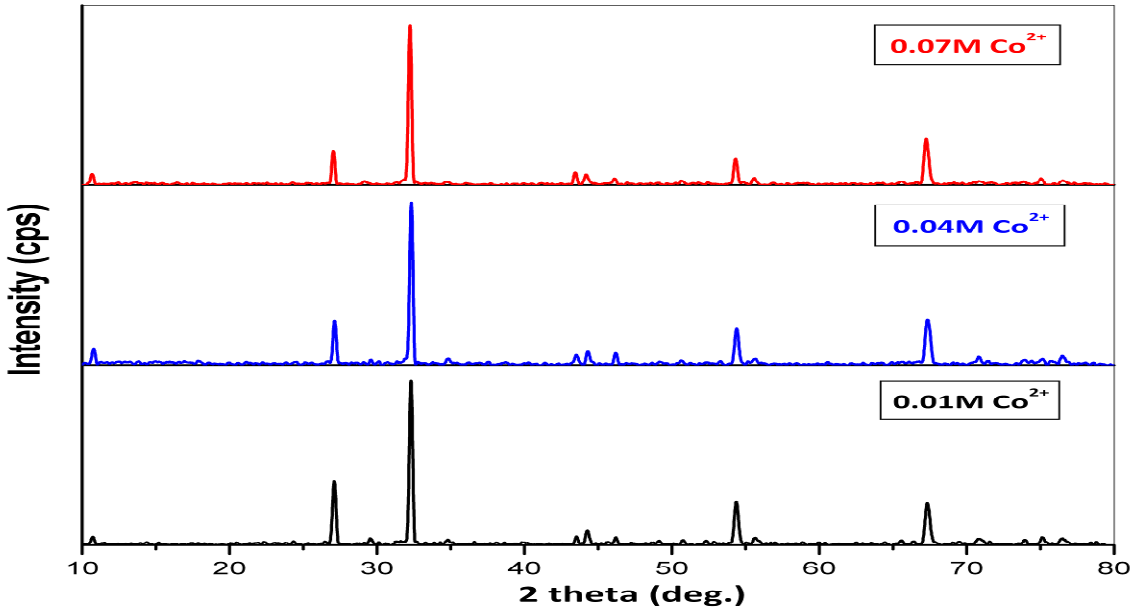


Fig. 2 XRD pattern of the crystals of $Pb(IO_3)_2$: Co^{2+}(for 0.01M, 0.04M, and 0.07M).

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. Results are shown in Fig. 2 for the Co^{2+} doped lead iodate crystals. All diffraction patterns were obtained using CuKα radiation (λ = 1.54051 A°), at 30 kV and 15 mA. Measurements were made from 2θ = 10° to 80° with steps of 0.02°. 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 given in the 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 Co^{2+} doped lead iodate crystal

Peak	d-spacing A°.		FWHM	Int.	Indices	Theta (Deg.)	
	Obs.	Cal.	β	I	h k l	Obs.	Cal.
1	8.2304	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
22	1.2442	1.2445	0.071	71	0 13 1	76.50	76.48
23	1.2135	1.2136	0.141	35	5 1 0	78.80	78.80

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

Peak	d-spacing A°.		FWHM	Int.	Indices	Theta (Deg.)	
	Obs.	Cal.	β	I	h k l	Obs.	Cal.
1	8.1848	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

The crystal structure of Co doped lead iodate is determined to be orthorhombic. It is evident from the XRD data that there are no extra peaks due to cobalt dopant, indicating that the as-

grown crystals are single phase [13]. The Co ion was understood to have substituted the Pb site without changing the orthorhombic structure of the parent crystal [14].

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 3 XRD data of 0.07M Co^{2+} doped lead iodate crystal

Peak	d-spacing A°.		FWHM β	Int. I	Indices h k l	Theta (Deg.)	
	Obs.	Cal.				Obs.	Cal.
1	8.2610	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

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 Co^{2+} doped lead iodate	6.0841	16.5968	5.5791	53.5930
0.04M Co^{2+} doped lead iodate	6.0911	16.5969	5.5755	45.6832
0.07M Co^{2+} doped lead iodate	6.0892	16.6093	5.5809	44.2353

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

Crystal	λ (nm)	Band gap Energy (eV)
Lead iodate	296	4.1892
0.01M Co^{2+} doped lead iodate	300	4.1333
0.04M Co^{2+} doped lead iodate	302	4.1060
0.07M Co^{2+} doped lead iodate	304	4.0789

3.2 UV Absorption Spectroscopy

Absorption spectra of undoped and Co^{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.

Figure 3 shows UV absorption spectra of undoped and Co^{2+} doped (for 0.01M, 0.04M, and 0.07M Co) lead iodate crystals. From the spectrum, it has been inferred that undoped and Co^{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 [15-18].

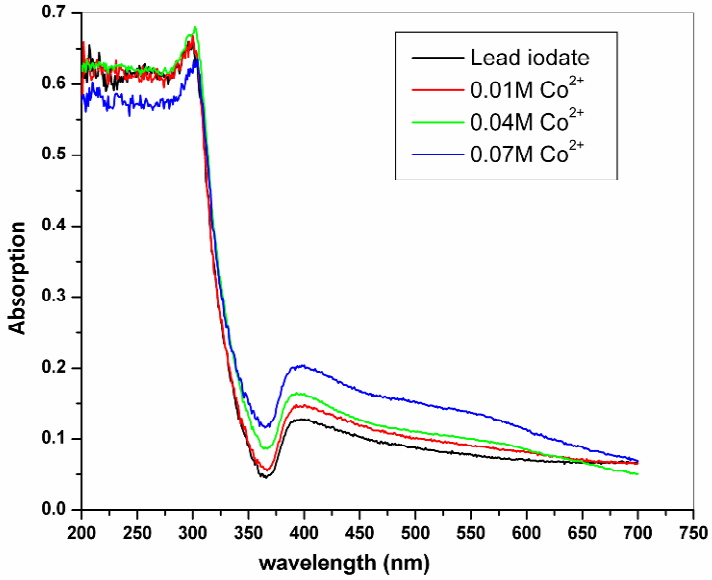


Fig. 3 Optical absorption spectra of undoped and xCo doped lead iodate, x = 0.01M, 0.04M, and 0.07M.

It was observed that doping by Cobalt does not affect the perfection of crystals. In addition, the percentage of transmittance of the lead iodate crystals decreases with increase in the doping concentration.

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;
Band gap energy (eV) = 1240/wavelength (nm).

Band gap Energy is presented in the table 5. It was observed that band gap energy of Co^{2+} doped lead iodate crystals decreases with the increasing doping concentration [19].

CONCLUSION

In conclusion, gel growth technique is suitable for growing the crystals of Co^{2+} doped lead iodate crystals. The size of the Co^{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 Co 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 and transparency of the lead iodate crystals decreases with increase in Co doping concentration.

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REFERENCES

[1] S Saliminan, S. Farjami Shayesteh, *Chalcogenide Letters*, **2010**, 7, No. 1, 59.
[2] K Sangwal and AR Patel, *J. Cryst. Growth*, **1974**, 23, 282.
[3] MS Joshi and SG Trivedi, *Indian J. Pure & Appl. Physics*, **1983**, 21, 435.
[4] SJ Shitole and KB Saraf, *Bull. Mater. Sci*., **2001**, 22, 461.
[5] SL Garud, KB Saraf, *Bull. Mater. Sci.*, **2008**, 31, No. 4, 639.
[6] SL Garud, NK Mahajan, KB Saraf, *Bull. Mater. Sci*., **2009**, 32, No. 2, 187.
[7] N Ajeetha, *Bulg. J. Phys.*, **2007**, 34, 108.
[8] KD Girase, ND Girase, TK Patil, DS Bhavsar, *Asian Journal of Chemical and Environmental research*, **2010**, 3, No.4, 59.
[9] EJ Kock, H Hopp, *Phys. Status Solidi*, **1980**, 57, 569.
[10] CC Desai, JL Rai, *J. Cryst. Growth*, **1980**, 50, 562.
[11] AR Patel, A. Venkateswara Rao, *J. Cryst. Growth*, **1980**, 49, 589.
[12] JCPDS data card no. 31-685.
[13] S Senthilkumaara, K Rajendran, S Banerjee, TK Chini, V.Sengodan, *Materials Science in Semiconductor Processing*, **2008**, 11, 6.
[14] P Nisha Santha Kumaria and S Kalainathan, *Cryst. Res. Technol*., **2008**, 43, No. 4, 413.
[15] G Ramesh Kumar and S Gokul Raj, *Advances in Materials Science and Engineering*, **2009**, 2009, 40.
[16] K Ambujam, K Rajarajan, S Selvakumar, D Prem Anand, Preema C Thomas, and P Sagayaraj, *Indian Journal of Pure & Applied Physics*, **2006**, 44, 243.
[17] P Nisha Santha Kumaria and S Kalainathan, *Cryst. Res. Technol*., **2008**, 7, No. 4, 317.
[18] D Kalaiselvi, R Mohan Kumar, and R Jayavel, *Cryst. Res. Technol*., **2008**, 43, No. 8, 851.
[19] Mihir M. Vora, Aditya M. Vora, *Chalcogenide Letters*, **2008**, 5, No. 4, 65.