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Effect of Cobalt Doping on FT-IR, Raman Spectra and Thermal Stability of Lead Iodate Crystals

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Gel grown lead iodate crystals doped by 0.04 M cobalt were characterized by Raman, Fourier transform infrared (FT-IR) spectroscopy and thermo analytical techniques (thermogravimetric and differential thermal analyses). The Fourier transforms infrared and Raman spectrum reveals various vibrational modes characterizing particular functional group. The investigation confirms the existence of iodate group. Thermal analysis shows that thermal stability of lead iodate crystals decreases slightly due to cobalt doping. The effect of doping is reported and discussed in detailed.

Keywords: Doping, FT-IR, Raman spectra, Thermal analysis.

PACS numbers: 81.70.Pg, 82.80.Gk

1. INTRODUCTION

Single crystals are the backbone of the modern technological revolution. The impact of single crystals is clearly visible in industries like semiconductor, optics, etc. With the invention of lasers, the field of nonlinear optics touched new heights and practical implementation was possible with the application of nonlinear optical crystals. Now-a-days great attention has been devoted to the growth and characterization of pure and doped crystals with the aim of identifying new materials for practical purposes. The effect of dopant on various properties of single crystals is of great interest from both solid-state science as well as technological points of view [1, 2].

Cobalt doped lead iodate crystals exhibits SHG property [3]. Nonlinear optical (NLO) crystals find wide range of applications in the field of telecommunication for efficient signal processing and optical information storage devices. SHG materials must possess good thermal stability. In view of this requirement, it is decided to study the thermal property of Cobalt doped lead iodate crystals.

Report on the growth and a characteristic of doped lead iodate crystals in particular is scanty in the literature. Moreover, information on doping of pure lead iodate crystals by cobalt is completely lacking. To the best of my knowledge, this paper is first to report the doping by foreign element cobalt in lead iodate crystal.

2. MATERALS AND METHODS

Cobalt doped lead iodate crystals were grown in silica gel using single diffusion technique. Its growth and XRD analysis is already reported [3, 4].

The FTIR spectra of cobalt-doped lead iodate crystals were recorded on SHIMADZU IRAffinity-1 spectrophotometer with KBr pellet method over the wave number range 350-4000 cm^{-1} at Department of Organic Chemistry, N.M.U. Jalgaon and Raman spectra were obtained with Renishaw Invia Raman Microscope at Gemological Institute of India, Mumbai. Samples were excited by the 325 nm (UV) laser and power of the laser spot on the surface was 5 mW.

The thermal decomposition behavior of the 0.04 M cobalt-doped lead iodate crystals was studied by thermogravimetry (TG) and differential thermal analysis (DTA). Diamond TG/DTA thermal analyzer was used for obtaining the TG and DTA curves at NCL Pune. Experiments were carried out in static nitrogen atmosphere. The initial weight of sample taken for recording the TG/DTA curves was 55.059 mg and heating rate was maintained at 10 °C/min.

The Differential scanning calorimetric analysis of the grown crystals was recorded between 30 °C to 400 °C in the nitrogen atmosphere using Metlar TA 4000 Instrument at NCL Pune. The initial weight of sample taken for recording the DSC curves was 11.00 mg and heating rate was maintained at 10 °C/min.

3. RESULTS AND DISCUSSION

3.1 FT-IR and Raman Spectrum Analysis

Fig. 1 and 2 respectively shows the FT-IR and Raman spectrum of 0.04 M cobalt doped lead iodate crystals. Several sharp peaks in the region 600-800 cm^{-1} and 300-500 cm^{-1} are owing to the stretching vibrations (ν_1 and ν_3) and bending vibrations ν_2 of iodate respectively [5-7]. In addition, Raman spectrum shows the band near to 296 cm^{-1} is assigned to asymmetric bending ν_4 of iodate. The weak and low frequency band in Raman spectrum around 390 cm^{-1} is observed that might be attribute to O-Pb-O asymmetric bending, which coincide well with the IR features [8, 9]. A comparison of the bands and peaks of FT-IR and Raman spectra is given in Table 1 and it shows that all bands in FT-IR coincide with the corresponding bands in Raman spectra. A close observation of FT-IR and Raman profiles of doped and undoped samples reveals some minor structural variations. These studies indicate that the crystal undergoes considerable lattice stress because of doping. The minor shift in a wave number may be due to the difference in mass number of Co (58.9332) and Pb (207.2) ions. The difference in mass of ions leads to a change in the molecular geometry and mechanical vibrations, which results in a shift in bands [10-12].

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The FTIR spectrum does not give any proof of the presence of combined water molecule in the cobalt doped lead iodate crystals.

The doubly degenerate ν_3 (E) around 700 cm^{-1} is found to split into two bands at 684.1 and 718.7 cm^{-1}. This suggests that cobalt doped lead iodate crystal belongs to orthorhombic crystal system.

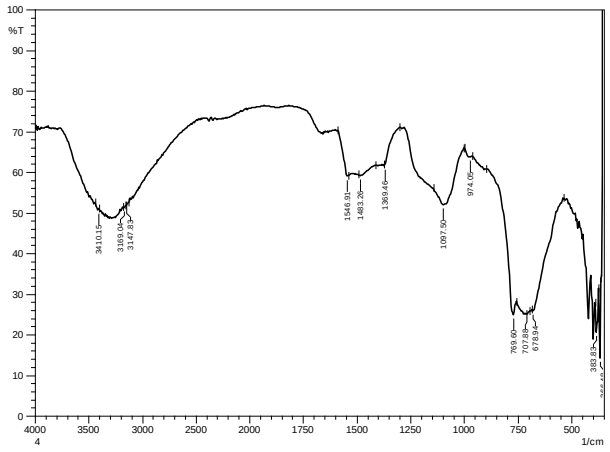

Fig. 1- FT-IR spectrum of 0.04 M Co doped lead iodate crystal

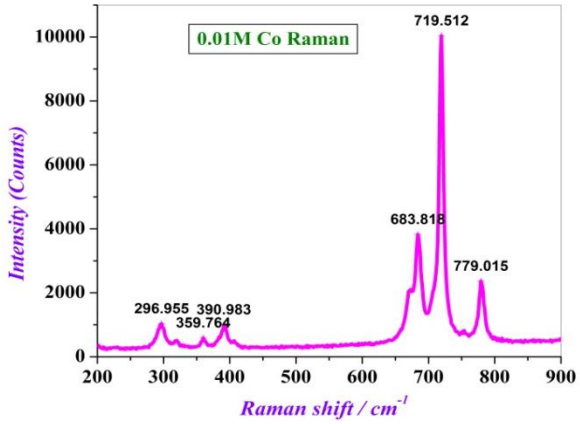

Fig. 2 – Raman spectra of 0.04 M Co doped lead iodate crystal

3.2 Thermogravimetric Analysis (TGA)

Fig. 3 shows TG, DTA and DTG curves of 0.04 M Co doped lead iodate crystal. TG curve shows that, the Co^{2+} doped lead iodate crystals show same features as that of undoped lead iodate crystals [13], but there is a distinct shift in the decomposition temperatures. As a result of Co^{2+} doping, decomposition temperature is shifted to lower value by 2 °C.

Co doped lead iodate crystal is thermally stable up to 298 °C temperature. Above this temperature, weight loss occurs in two stages. The weight loss in first stage is due to the evolution of oxygen and iodine [14]. Two decomposition stages were found during the heating. The following chemical reactions are expected to occur during two decomposition stages.

$$Co : Pb(IO_3)_2 \rightarrow Co : PbO_2 + 2O_2 \uparrow + I_2 \uparrow \text{ and}$$

$$Co : PbO_2 \rightarrow Co : PbO + \tfrac{1}{2}\, O_2 \uparrow$$

The first stage of decomposition occurs in the temperature range from 298 °C to 724 °C. In this range, the major weight loss 56.99 % of the sample corresponds to the evolution of $2O_2$ and I_2 and it is in good agreement with the calculated value 57.10 % ($2O_2$ = 11.50 % and I_2 = 45.60 %). It is supported by the

Table 1 – Comparison of the bands and peaks of FTIR and Raman spectra of $Pb(IO_3)_2$:Co crystals

Sr. No.	FTIR spectra Wave number / cm^{-1}		Raman spectra Wave number / cm^{-1}		Band assignments
	Undoped	Co doped	Undoped	Co doped	
1	–	–	296.98	296.11	ν_4 – Asymmetric bending
2	362.62	368.40	362.19	360.13	ν_2 – Symmetric bending
3	387.69	387.69	393.40	392.55	Asymmetric Bending (O-Pb-O)
4	–	677.01	684.99	684.17	ν_3 – Symmetric stretching
5	709.80	711.73	719.54	718.71	
6	769.60	769.60	780.18	779.36	ν_1 – Asymmetric stretching

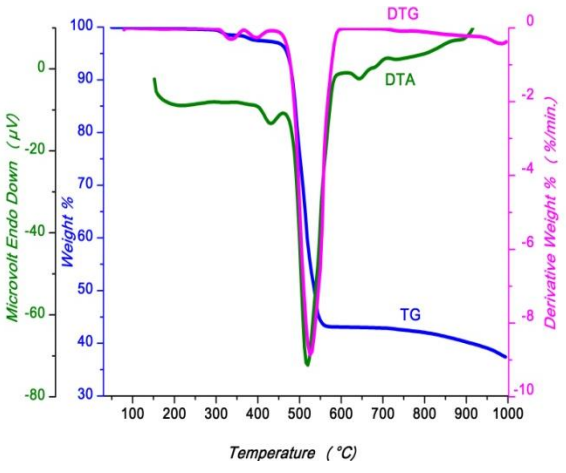

Fig. 3 – TG, DTA and DTG curves of 0.04 M Cu doped lead iodate crystal

first major peak in DTG and DTA curves. The step inflection point in this stage occurs at 517.77 °C and onset temperature is 482.89 °C. The second stage of decomposition occurs in the temperature range from 779 °C to 949 °C. In this stage, 3.15 % weight loss cor-

responds to the loss of ½O_2 and it is in good agreement with the calculated value 2.87 % and the stable residual weight 37.42 % corresponds to PbO (calculated value 38.68 %). The TGA data collected from the TG curve are listed in a Table 2.

TG curve indicates that there is no water of crystallization in the crystal as there is no major peak up to 400 °C temperature. DTG, DTA, DSC and FTIR also confirmed it.

Table 2 – TGA data of undoped and 0.04 M Co doped lead iodate crystals

Stage	Lead iodate crystal	Sample	Onset (°C)	Observed weight loss (%)	Calculated weight loss (%)	Probable loss
1	Undope	$Pb(IO_3)_2$	492.12	57.31	57.10	$2O_2$ and I_2
	Co dope	Co: $Pb(IO_3)_2$	482.89	56.99	57.10	
2	Undope	PbO_2	778.70	2.91	2.87	½O_2
	Co dope	Co:PbO_2	779.00	3.15	2.87	
Co:PbO - stable residual weight				37.42	38.68	-----

3.3 Derivative Thermogravimetric Analysis (DTG)

The DTG curve for 0.04 M cobalt-doped lead iodate gel grown crystals is as shown in the Fig. 3 by pink color.

1. In the first stage of decomposition, major peak (at 509 °C) is shifted to lower value by 1 °C due to the Co^{2+} doping and it is attributed to the loss of $2O_2$ and I_2. The peak observed in the DTG curve corresponds to the weight loss in the TG curve.

2. The minor peak at 983 °C in the second stage of decomposition is attributed to the loss of ½O_2. The peak observed in the DTG curve corresponds to the weight loss in the TG curve.

Beyond the temperature 949 °C, the reaction proceeds and finally stable residue Co : PbO remains up to the end of analysis.

3.4 Differential Thermal Analysis (DTA)

The DTA curve for 0.04 M Co doped lead iodate gel grown crystals is as shown in the Fig. 3 by green color. This curve indicates that the decomposition process is endothermic and the major endothermic peak (at 503 °C) is shifted by 7 °C due to the Co^{2+} doping. This peak corresponds to the major weight loss due to the decomposition of the crystal with the evolution of oxygen and iodine. The endothermic peak at 963.86 °C is due to the decomposition of compound and this peak in the second stage of decomposition is attributed to the loss of ½O_2. This endothermic coincides to the peak 983 °C that is observed in the DTG to the weight loss of ½O_2 in the TG curve.

The minor endothermic peaks appearing at 493 °C and 659 °C occurs only in the DTA curve, are may be due to weak solid to solid phase transition as there is no loss in weight at these temperatures in the TG curve [15-17]. Beyond the temperature 949 °C, the reaction proceeds and finally stable residue Co : PbO remains up to the end of analysis. However, an exothermic peak was not noticed in the DTA graph.

3.5 Differential Scanning Calorimetry (DSC)

The DSC curve for Co doped lead iodate gel grown crystals is shown in the Fig. 4. Since the instrument cannot go beyond 400 °C, complete endotherm could not be recorded. DSC curve shows that there is no water of crystallization in the crystal as there is no major peak up to 400 °C temperature.

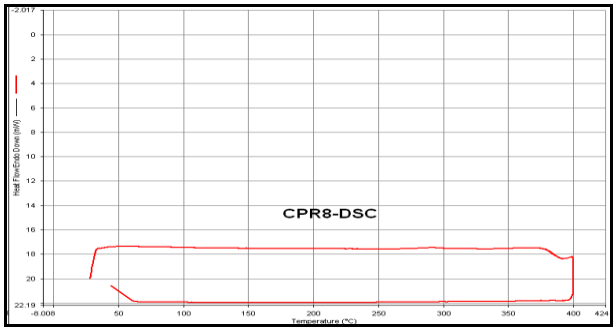

Fig. 4 – DSC curve of 0.04 M Co doped lead iodate crystal

4. CONCLUSIONS

From the above results, we conclude that Raman spectral studies reveal that lead iodate crystal belongs to orthorhombic crystal system. FTIR and Raman spectrum reveals some minor structural variations. From the thermogram it is concluded that the thermal stability of lead iodate crystal decreases by 2 °C due to cobalt doping. The FTIR, TG, DTG, DTA and DSC analysis, confirmed the absence of water molecules.

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