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Research Article

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Infrared, raman spectra and thermal studies of lead iodate crystals doped with Zinc (II)

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ABSTRACT

The influence of doping the transition metal Zn (II) on thermal property of gel grown lead iodate crystals was studied using the thermo analytical techniques, which included TG, DTA, and DTG. It was found that, decomposition temperature of lead iodate crystal is shifted to higher value by 18°C. A close observation of FT-IR and Raman profiles of samples reveals presence of iodate group. It appears that the crystal undergoes considerable lattice stress as a result of doping the bivalent zinc. The absence of water of hydration in the grown crystals was confirmed by FT-IR and thermal analysis.

Key words: Inorganic compound, FTIR, Raman spectroscopy, Thermal analysis.

INTRODUCTION

The properties of crystals that make them most useful may easily be modified by introducing impurities into their crystal lattice. In the case of crystalline substances, the atoms of the dopant very commonly take the place of elements that were in the crystal lattice of the material.

In recent times much attention has been paid to the role of foreign element in the crystallization process in industrial crystallization [1] and in semiconductor industries [2]. Sometimes the addition of impurities to the crystals changes their physical properties in specific ways. Because of this, a lot of research is carried out to determine the influence of impurities on the crystal growth.

Lead iodate crystals possesses non-linear optical (NLO) property. NLO materials have been in great demand over the last few decades due to technological importance in the fields of optical communication. These materials must have good thermal stability. The purpose of zinc (II) doping is to improve the thermal stability of lead iodate crystals.

A detailed investigation highlighting the effect of doping of 0.04M Zn^{2+} on the thermal properties of $Pb(IO_3)_2$ single crystals by silica gel technique reported in this paper.

EXPERIMENTAL SECTION

The growth of mixed crystals of 0.04M zinc doped lead iodate crystals were carried out with simple gel method. The AR grade lead nitrate, zinc nitrate and potassium iodate were used to grow the crystal. The growth procedure and XRD analysis of zinc doped lead iodate crystal is already published [3].

In the present work, to study the chemical bonding of zinc doped lead iodate crystal, the FTIR spectra of finely crushed powder of the sample was recorded in the KBr phase in the frequency region 400-4000 cm^{-1} using spectrophotometer make SHIMADZU model IRAffinity-1 at Department of Organic Chemistry, N.M.U. Jalgaon and FT Raman spectrum were recorded using 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 TG, DTG and DTA thermal studies of zinc-doped lead iodate crystals were carried out by Diamond TG/DTA Thermal analyzer at NCL Pune. Sample of 45.595 mg was taken for TGA process. Thermal analysis was performed in nitrogen atmosphere from room temperature to 1000ºC with heating rate of 10°C/min, with α-Al_2O_3 standard reference.

DSC 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 18.50 mg and heating rate was maintained at 10°C/min.

FT-IR and Raman Spectrum analysis:

The FTIR and Raman spectra of zinc-doped lead iodate crystals are given in figure 1 and figure 2 respectively. The spectra are interpreted comparing with the pure lead iodate crystal [4]. The proposed assignments are tabulated in Table 1.

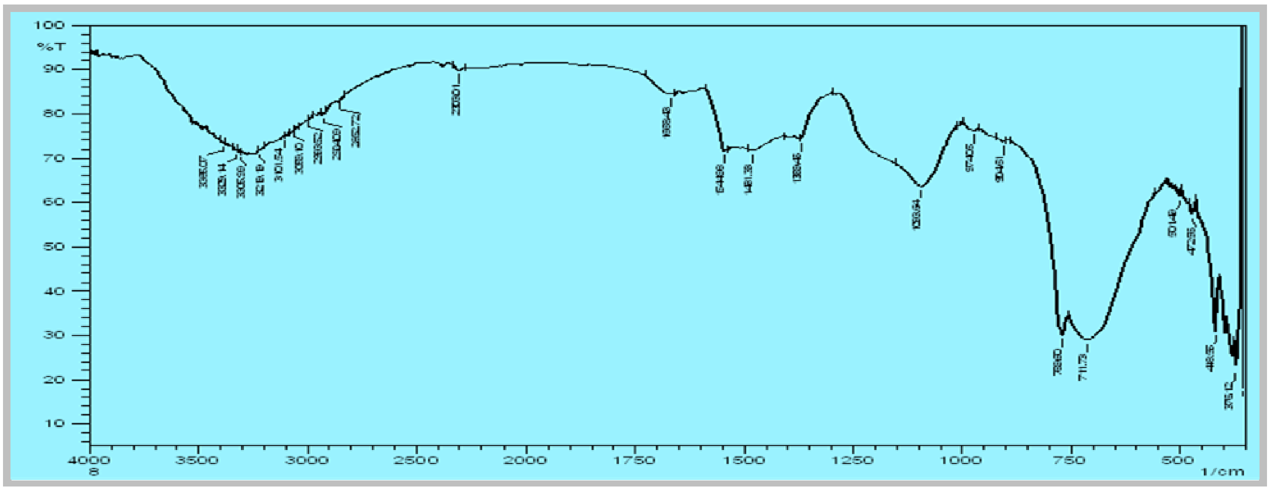

Figure 1: The FTIR spectrum of Zn doped lead iodate.

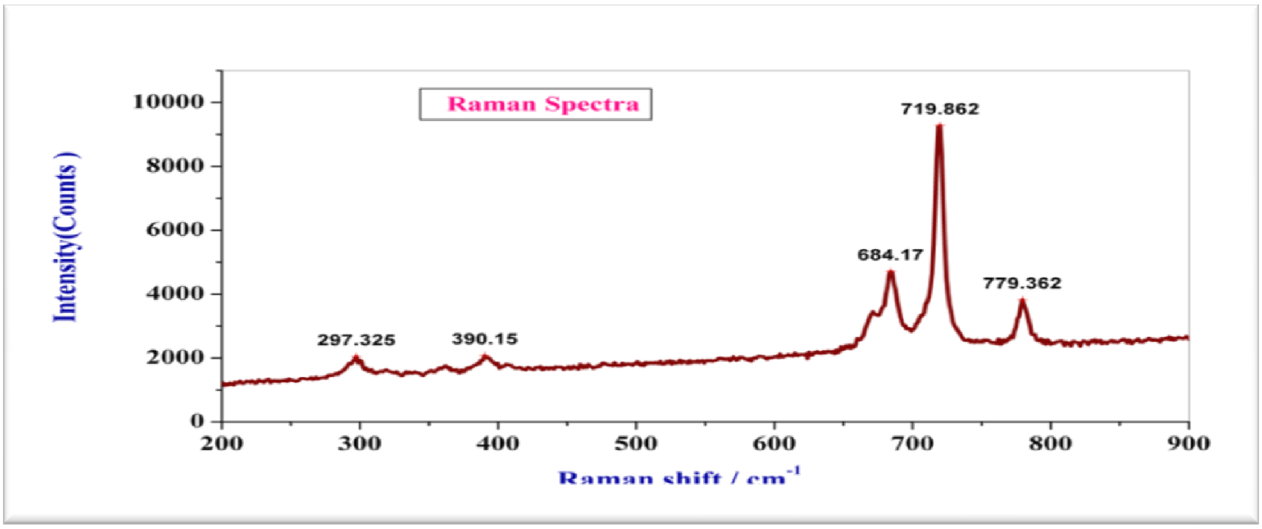

Figure 2: The Raman spectrum of Zn doped lead iodate

The FTIR and Raman spectrum shows 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 297.33 cm^{-1} is assigned to asymmetric bending ν_4 of iodate. The weak and low frequency band in Raman spectrum at 390 cm^{-1} is observed that might be attribute to O-Pb-O asymmetric bending, which coincide well with the IR features [8, 9]. The IR bands at 363.48 cm^{-1}, 711.73 cm^{-1}, 769.60 cm^{-1} and Raman lines at 362.19 cm^{-1}, 719.86 cm^{-1}, 779.36 cm^{-1} are due to iodate group.

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

Table 1 FTIR and Raman spectral analysis of Zn:Pb(IO_3)$_2$ crystals

Sr. No.	FTIR spectra Wave number cm^{-1}	Raman spectra Wave number cm^{-1}	Band assignments
1	---	297.33	ν_4- Asymmetric bending (I-O)
2	363.48	362.19	ν_2- Symmetric bending (I-O)
3	378.05	390.15	Asymmetric Bending (O-Pb-O)
4	---	684.17	ν3- Symmetric stretching (I-O)
5	711.73	719.86	
6	769.60	779.36	ν1- Asymmetric stretching (I-O)

Thermal studies:

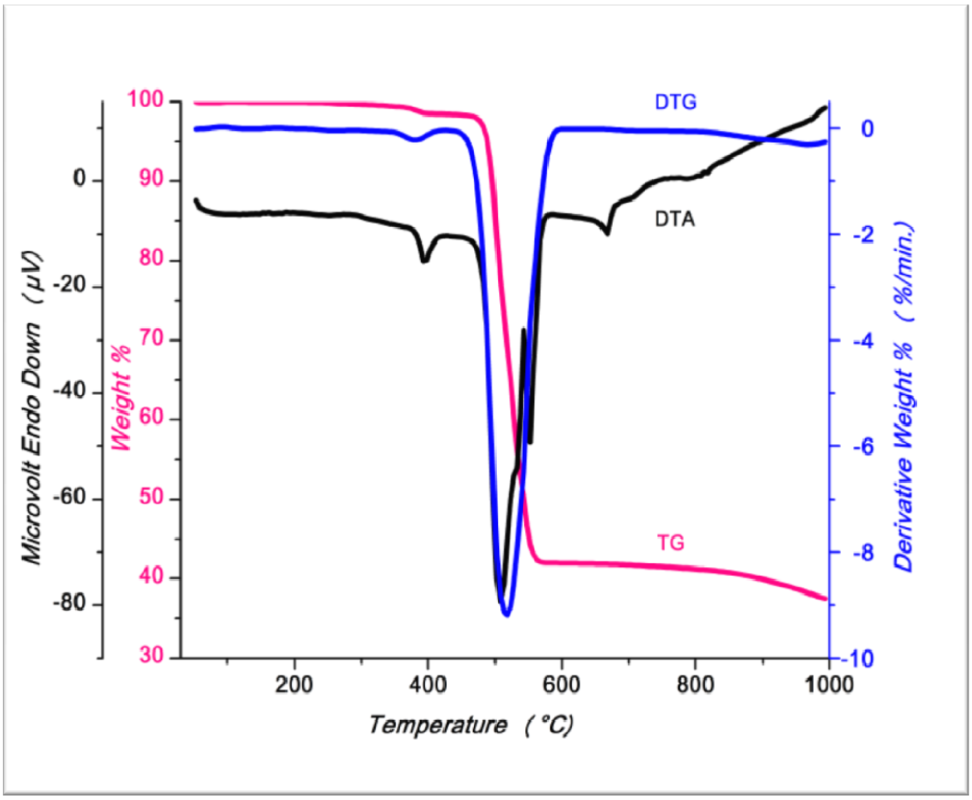

Figure 3: TG, DTG and DTA curves of Zn doped lead iodate crystals

The thermogram and differential thermogram are shown in Fig. 3. TG curve shows that there is no loss of weight observed around 100°C showing the absence of any absorbed water molecules in the sample. Major weight loss 57.73% occurs in the first stage between 318°C to 643°C. The weight loss in this range is due to the decomposition of 2O2 and I2 and it is in good agreement with the calculated value 57.10%. The major peak at 516.81°C in the DTG curve and major endothermic peak appears at 510°C DTA curve are corresponds to the first stage of TG curve.

The second stage of decomposition occurs in the temperature range from 728°C to 963°C. In this stage, 3.21% weight loss corresponds to the loss of ½O2 and it is in good agreement with the calculated value 2.87%. The minor peak at 983°C in the DTG curve corresponds to the second stage of TG curve. Beyond the temperature 983°C, the reaction proceeds and finally stable residue Zn:PbO remains up to the end of analysis.

CONCLUSION

From the above results, we conclude that, FTIR and Raman spectrum indicate the presence of I-O bond. The crystal is thermally stable up to 318°C and decomposes through two stages into lead oxide form at 983°C. The FTIR, TG, DTG, and DTA analysis, confirmed that no water molecule is associated with the crystal.

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