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Growth and thermal behavior of lead Iodate crystals grown in silica gel

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Abstract The $Pb(IO_3)_2$ crystals have been grown in sodium meta silicate gel using the single diffusion method at room temperature. The grown crystals were characterized by thermo analytical techniques (TG, DTA, and DTG), X-ray powder diffraction (XRD), and FTIR spectroscopy. The crystal system is confirmed to be orthorhombic having lattice parameters a = 6.09 Å, b = 16.68 Å, and c = 5.58 Å by powder X-ray diffraction analysis. FTIR study reveals that lead iodate crystal is anhydrous. TG, DTA, and DTG analysis shows a remarkable thermal stability.

Keywords Lead Iodate · XRD · Thermal properties

Introduction

Very few literatures are available on the study of $Pb(IO_3)_2$ crystals. Most of the iodates exhibit prominent non-linear optics (NLO) behavior. Iodates have important electro-optical properties [1, 2] because of the un-bond electron pair of iodine atoms in $(IO_3)^-$anions [3]. A lot of related compounds containing $(IO_3)^-$anions have been synthesized since 70 s [4–7]. Hence, it has been decided to grow and study the lead iodate crystals in view of crystallographic, optical, and thermal properties.

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. The gel growth technique has gained considerable importance due to its simplicity and effectiveness in growing single crystals of certain compounds. Gel growth is an alternative technique to solution-growth with controlled diffusion and the growth process is free from convection [8]. The growth of single crystals in gel is a self-purifying process, free from thermal strains, which is common in crystals grown from melt [9].

In this investigation, $Pb(IO_3)_2$ crystals were grown by single diffusion gel technique using the AR grade lead nitrate and potassium iodate. The grown crystals have been subjected to different characterizations. To the best of the knowledge, there is no literature is available on the study of FTIR and thermal analysis of gel-grown $Pb(IO_3)_2$ crystals.

Experimental

To grow the $Pb(IO_3)_2$ crystals, the required silica gel medium was prepared by adding the sodium Metasilicate solution of specific gravity 1.04 g/cc drop by drop with constant stirring by using magnetic stirrer into the 7 mL (2 N) acetic acid till the pH value 4.2 was set for the mixture. To the above sodium meta silicate solution of pH 4.2, 5 mL aqueous solution of 0.1 M $Pb(NO_3)_2$ was added as inner reagent with constant stirring. This mixture was then transferred to the test tube of length 15 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 4–8 days. It was left for two more days for gel ageing and then the outer reagent, the aqueous solution of 0.1 M KIO_3 was added on to the top of the gel. The outer reagent was added down the sides of the test tube

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using a pipette and not directly on to the gel medium. Owing to the diffusion of the outer reagent into the gel medium and its reaction with the inner reagent, crystals started growing. Nucleation was observed within 24 h of addition of the outer reagent. Star shaped, opaque and brittle crystals were observed. The experiment was carried out at an ambient temperature of about 30 °C.

The reaction between lead nitrate and potassium iodate in gel medium resulted in the growth of star shaped $Pb(IO_3)_2$ crystals. The reaction that takes place in the gel medium is given below.

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

Figures 1 and 2 show photographs of lead iodate crystals, inside and outside the gel medium, respectively. The physical dimension of lead iodate crystal is found to be around 7 × 7×4 mm. This size is sufficient for different characterizations.

Results and discussion

X-ray diffraction

Lead iodate crystals were powdered and X-ray powder diffraction (XRD) data were collected at room temperature on a Rigaku, Minislex model. All diffraction patterns were obtained using CuKα radiation ($\lambda = 1.54051$ Å), at 30 kV and 15 mA. Measurements were made from $2\theta = 10$–$80°$ and is shown in Fig. 3. It shows very sharp peaks having high intensity, which leads to perfect crystallization and larger particles. 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 were found to be in good agreement with the JCPDS values [10] and indicating orthorhombic structure of lead iodate having lattice parameters a = 6.089 Å, b = 16.68 Å, c = 5.58 Å, and $\alpha = \beta = \gamma = 90°$. Comparison of standard and observed XRD data is given in Table 1. The grain size of the particles of powder sample 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 and $\lambda = 1.54051$ Å. The average grain size of the particles is around 35 nm.

Fig. 1 *Star shaped* lead iodate crystals inside the gel medium

Fig. 2 *Star shaped* lead iodate crystals outside the gel medium

FT–IR spectrum analysis

The FTIR spectrum of lead iodate crystals is shown in Fig. 4. The FT–IR spectrum shows strong band in the region 500–830 cm^{-1} indicating the presence of iodate and metal oxide [11, 12]. Fundamental infrared frequencies, observed in all iodate compounds in general, are also found in present FT–IR analysis, which confirm the iodate group of grown crystals. The bands at 376.12 and 387.69 cm^{-1} are due to iodate group [13]. Fundamental frequencies that have been observed are ν_1 at 709.8 cm^{-1} is due to O–Pb–O symmetric stretching and ν_3 at 769.6 cm^{-1} is due to the O–Pb–O asymmetric stretching. The dominant absorption bands are found at 700–800 cm^{-1} in all iodate compounds

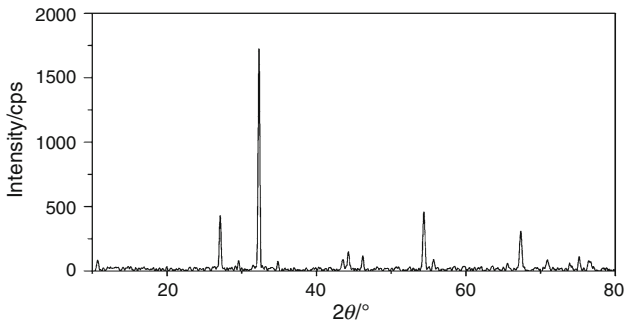

Fig. 3 XRD pattern of lead iodate crystal

Table 1 Comparison of standard and observed XRD data

Peak	d-spacing/Å		FWHM	Intensity	Indices	Theta/°	
	Obs.	Cal.	β	I	h k l	Obs.	Cal.
1	8.2457	8.3450	0.188	84	0 2 0	10.72	10.59
2	3.2876	3.3079	0.282	430	1 3 1	27.10	26.93
3	3.0193	2.9956	0.235	79	2 1 0	29.56	29.80
4	2.7675	2.7817	0.282	172	0 6 0	32.32	32.15
5	2.5729	2.5921	0.165	76	1 5 1	34.84	34.57
6	2.0741	2.0629	0.141	90	1 7 1	43.60	43.85
7	2.0456	2.0416	0.259	146	2 1 2	44.24	44.33
8	1.9624	1.9699	0.306	117	0 6 2	46.22	46.04
9	1.6857	1.6906	0.306	460	1 9 1	54.38	54.21
10	1.6494	1.6540	0.118	92	2 6 2	55.68	55.51
11	1.4223	1.4236	0.165	60	1 11 1	65.58	65.51
12	1.3890	1.3883	0.353	309	0 8 3	67.36	67.39
13	1.3280	1.3297	0.188	85	3 9 1	70.90	70.80
14	1.2817	1.2832	0.188	63	4 7 0	73.88	73.78
15	1.2627	1.2632	0.165	112	2 8 3	75.18	75.14
16	1.2436	1.2447	0.071	73	0 12 2	76.54	76.46

[14], and can be expected to contain v_1 and v_3 as well as possible splitting of v_3. The band at 1103.28 cm^{-1} may be due to the symmetric and asymmetric stretching of Pb–O bond in the compound [11]. The FT–IR spectrum does not give any proof of the presence of combined water molecule in the lead iodate crystals.

Thermal analysis

The thermal decomposition behavior of the grown 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 41.140 mg and heating rate was maintained at 50 °C min^{-1}.

Figure 5 shows the TG/DTA/DTG curve of lead iodate crystal. TG curves shows that, lead iodate crystal is thermally stable up to 300 °C temperature [15]. The slow but continuous weight loss from room temperature to 290 °C, which the authors assign to the loss of bound surface water. Above this temperature, it decomposes with the evolution of Oxygen and Iodine [16]. Two decomposition stages were found during the heating.

Decomposition reaction of first stage:

$$Pb(IO_3)_2 \rightarrow PbO_2 + 2O_2 \uparrow + I_2 \uparrow$$

and the decomposition reaction second stage:

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

The first stage of decomposition occurs in the temperature range from 300 to 715 °C. In this range, 57.31% of the weight is lost, which corresponds to the loss 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%). The step inflection point in this stage occurs at 509.96 °C. The second stage of decomposition occurs in the temperature range from 750 to 995 °C. In this range, 2.91% of weight is lost very slowly [17], which corresponds to the loss of $\frac{1}{2}O_2$ and it is in good agreement with the calculated value 2.87% and the stable residual weight 38.30% corresponds to PbO (calculated value 38.68%), The DTA curve of lead iodate crystal shows three endothermic peaks. The minor endothermic peak appearing at 401 °C, where no weight loss occurs, can be attributed to phase transitions. The major endothermic peak appearing at 510.28 °C corresponds to the major weight loss due to the decomposition of the crystal with the evolution of Oxygen and Iodine. The third minor endothermic peaks appearing at 980 °C corresponds to the loss of $\frac{1}{2}O_2$.

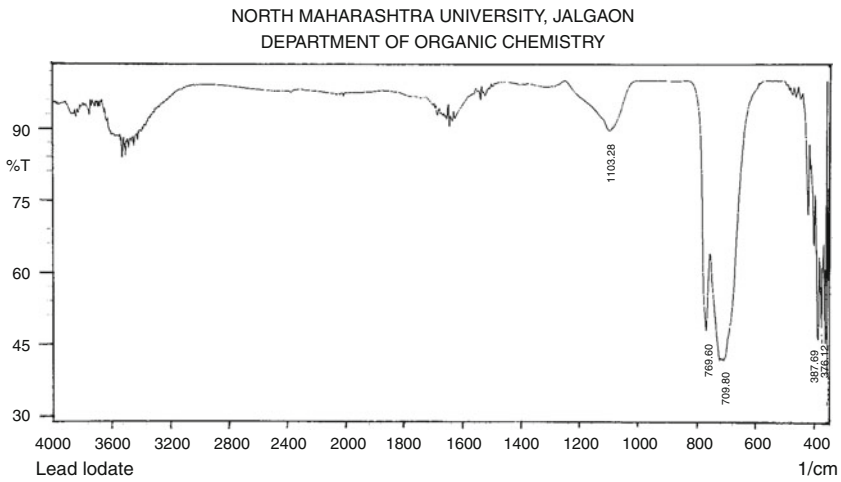

Fig. 4 FT–IR spectrum of lead iodate crystal

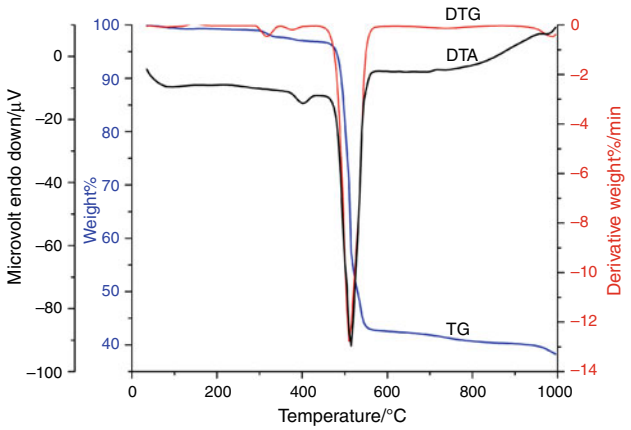

Fig. 5 TG/DTA/DTG curve of lead iodate crystal

The DTG curve of lead iodate crystal shows Peaks at 510 and 980 °C, which coincides with the DTA endothermic peaks appearing at 510.28 and 980 °C. TG, DTA, and DTG curve also shows that there is no water of crystallization in the crystal as there is no major weight loss up to 300 °C temperature.

Conclusions

Thermal analysis reveals that lead iodate crystals grown in silica gel using the single diffusion method are structurally stable up to 300 °C and above this temperature; it decomposes with the evolution of Oxygen and Iodine. The presence of iodate group in the grown crystals was identified by FTIR studies. The absence of water molecules into the lead iodate crystals was confirmed by the FT–IR and thermal analysis.

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