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Original Article

XRD, UV-VIS, PL and Thermal Studies of Lead Iodate Crystals

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Abstract *- The lead iodate crystals have been grown in sodium meta-silicate gel using the single diffusion method at room temperature. The grown crystals were characterized by X-ray powder diffraction (XRD), UV, PL, and TGA/DSC. The crystal system is confirmed to be orthorhombic, having lattice parameters a= 16.70Å, b= 5.578Å and c= 6.083Å by powder X-ray diffraction analysis. The crystal's optical properties were characterized using UV-visible and Photoluminescence (PL) spectroscopy. TGA and DTA/DSC analysis show remarkable thermal stability.*

Keywords *- Gel method, Lead iodate, XRD, UV-vis, TGA.*

I. Introduction

A versatile and highly efficient Nonlinear Optical (NLO) frequency conversion material is of vital importance for many applications in the field of photonics and optoelectronics [1]. Most of the iodate compounds are not soluble in water and decompose before melting. Hence, crystals of such types of compounds cannot be grown by either slow evaporation or melt techniques. In this situation, the gel method is appropriate for their growth [2-3]. Crystal of the iodate family has aroused much interest recently because of high effective nonlinear coefficients, high laser damage threshold, excellent optical quality in large single crystals, high thermal stability etc. [4]. These compounds are rare in nature [5]. This paper presents the growth of lead iodate single crystals in sodium Metasilicate gel. The grown crystals were characterized by X-ray powder diffraction (XRD), UV-vis spectroscopy, Photoluminescence spectroscopy, Thermo Gravimetry Analysis (TGA), and Differential Thermal Calorimetry.

2. Literature Review

In the literature, very few attempts have been made to study the growth and characterization of iodate crystals [19]. Nonlinear optical materials have evolved as one of the most interesting research fields for various applications such as amplitude modulation, phase modulation, optical communication, optical electronics, optical data storage, laser frequency shifting, optical limiting etc. [18]. Iodates are compounds with pyramidal or umbrella-like $(IO_3)^-$ structural groups formed by pentavalent I atoms [5].

3. Materials and Methods

Crystals of Lead iodate were grown using a single diffusion technique at room temperature. The materials used for the synthesis were of A.R. grade. The silica gel medium required to grow lead iodate crystals was prepared by adding the sodium meta silicate solution of specific gravity 1.04 g/cc drop by drop to 2N 7ml acetic acid. The mixture was stirred constantly till a pH of 4.3 was obtained. To the sodium meta silicate solution above, 5 ml aqueous solution of 0.4 M $Pb(NO_3)_2$ was added as an inner reagent with constant stirring. The mixture was then transferred into a test tube with a 15 cm length and 2.5 cm diameter. Care was taken to cover the test tube to keep the solution free from dust and impurities. The gel was usually set within 4-8 days. It was left for a few days for gel aging, and then the outer reagent, the aqueous solution of 0.4 M KIO3, was added to the top of the gel. The supernatant was added down the sides of the test tube using a pipette and not directly on the gel medium's top. Crystals started growing due to the diffusion of the outer reagent into the gel medium and its reaction with the inner reagent. Nucleation was observed within 24 hours of the addition of the outer reagent. Star-shaped, opaque and brittle crystals were observed. The experiments were carried out at about room temperature. The grown crystals are shown in Fig.1.

Lead iodate crystals in the shape of stars were formed as a result of the interaction between lead nitrate and potassium iodate in gel media is given below.

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

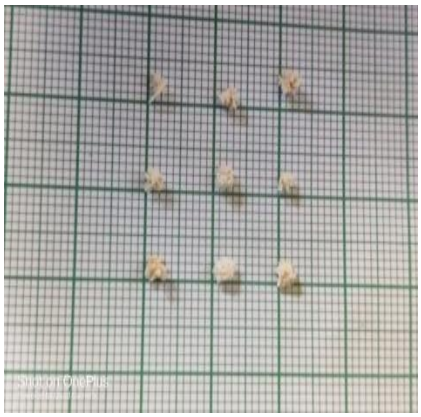

Fig. 1 Lead iodate crystal

4. Characterization of Gel-Grown Crystals of Lead Iodate

The crystalline structure of these crystals was analyzed using an X-ray diffractometer (Rigaku, Miniflex model) using CuKα radiation (λ =1.54051Å) at 40KV and 15mA. UV-vis spectrum was recorded employing Shimadzu, Japan spectrophotometer in order to understand optical characteristics. Thermal stability and decomposition behavior are studied using a thermogravimetric analysis simultaneous thermal analyzer (STA 6000) instrument for temperatures in the range of 0 to 900 ^{0}C, with a heating range of 3^{0}C/min.

5. Results and Discussion

5.1. X-Ray Diffractometry (XRD)

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 (λ =1.54051Å) at 40KV and 15mA over the 2θ range of 10^0-80^0. The observed peaks of the grown crystal match well with the standard data file (JCPDS: 820477) and indicate the orthorhombic structure of lead iodate having lattice parameters a= 16.70Å, b= 5.578Å and c= 6.083Å and more interplane distance (d) is 2.83Å. The average grain size was determined using the Scherrer formula and was estimated at 28.14nm.

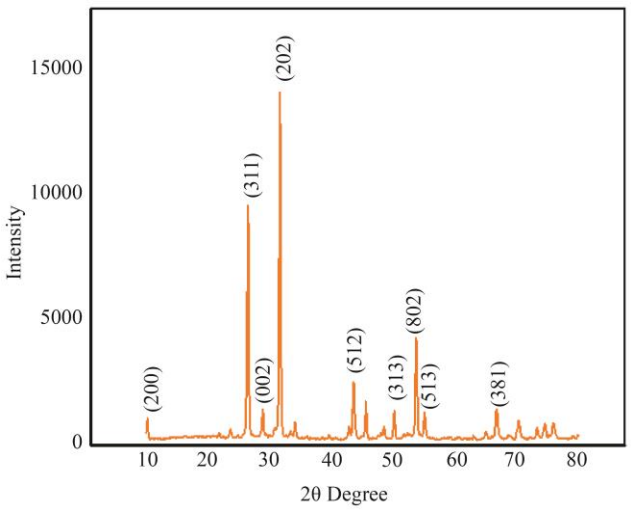

Fig. 2 X-ray diffractogram of lead iodate single crystal

5.2. UV-VIS Spectroscopy

The optical properties of lead iodate can be studied using UV-VIS spectroscopy. A fine powdered form of lead iodate crystals was used as a sample. The absorption spectra of lead iodate crystals have been recorded over the wavelength range of 200 to 800 nm. The linear extrapolation of this curve to the energy axis gives the band gap value of lead iodate as 2.24 eV.

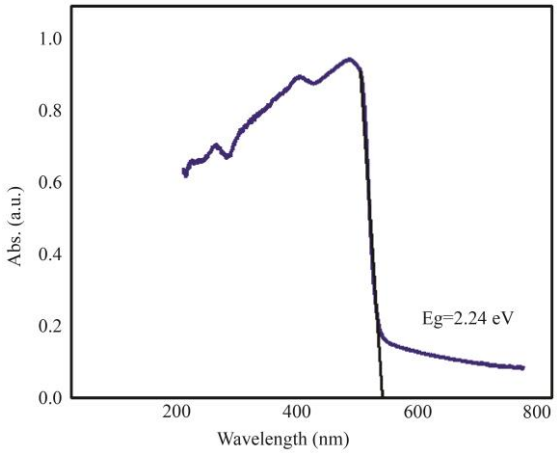

Fig. 3 UV-Vis spectroscopy of lead iodate

5.3. Thermal Analysis

The present work completed thermal analysis (TGA, DTA) of gel-grown lead iodate crystals. The TGA curve of lead iodate crystals, fig 4, was recorded as a function of temperature and % weight of the loss of substance. The DTA of lead iodate crystals were recorded and given in fig. 5, respectively. The initial weight of the sample taken for recording the TG/DSC curves was 29.458 mg, and the heating rate was maintained at 50 ^{0}C min^{-1}.

Thermograms of lead iodate crystals show that there is no loss in weight up to 283^{0}C. Hence the material is thermally stable, which indicates no possibility of co-ordinate water molecules or any water of crystallization. Lead iodate crystals melt at around 310^{0}C, and slow and gradual weight loss is observed. Then after, slow decomposition is observed from 310^{0}C to 460^{0}C, and then sudden loss in weight is observed up to 550^{0}C. The DSC curve of lead iodate crystal is represented in fig.5, and there is an endothermic peak at 400 ^{0}C and 520.48 ^{0}C. These peaks are caused due to phase transformation.

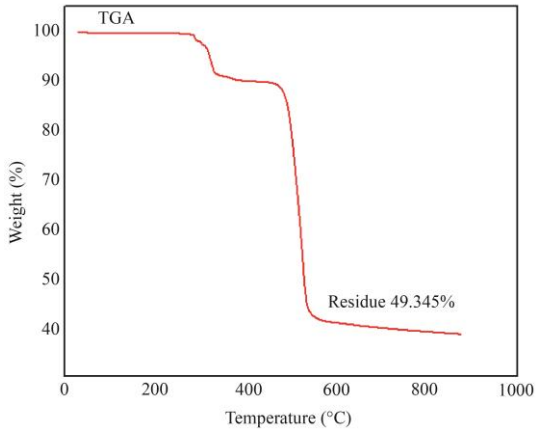

Fig. 4 TGA for Lead iodate

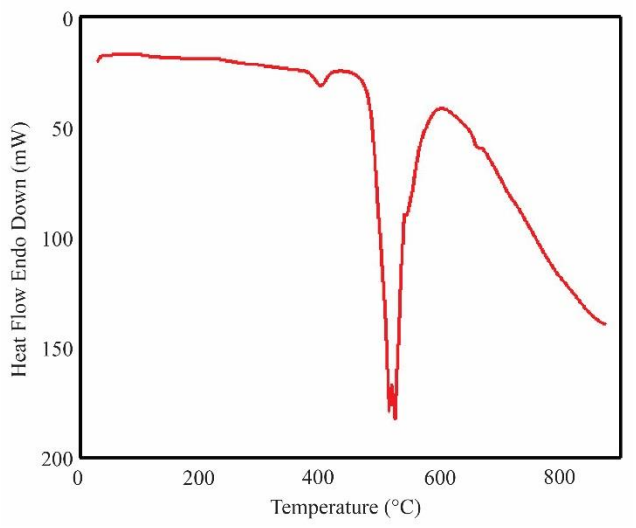

Fig. 5 DSC for lead iodate

5.4. Photoluminescence Spectroscopy

To measure the surface defect of the lead iodate at room temperature, Photoluminescence spectra were carried out shown in the figure. The calculated energies for the emission spectra with wavelengths 482nm and 532nm were found to be more than the energy gap found using UV absorption spectra. So, these peaks are due to point defects in the prepared sample. The violet emission occurs at different wavelengths. This is attributed to the generation of new energy band gap structures as a result of various defects in lead iodate.

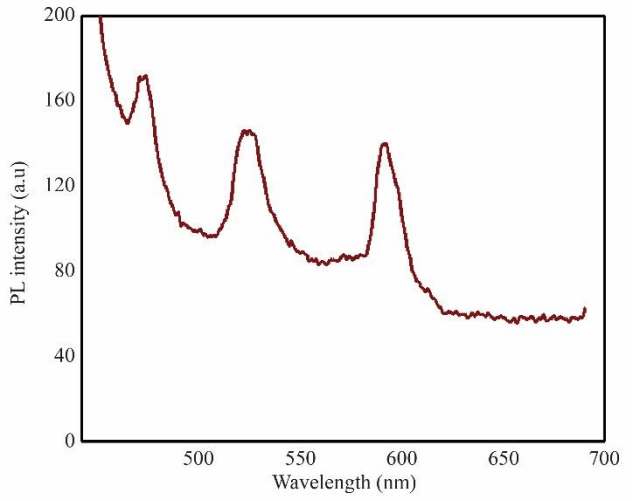

Fig. 6 Photoluminescence (PL) emission spectra (Exc.400)

6. Conclusion

The present study provides detailed information on the structural and optical properties of lead iodate. The XRD patterns confirmed the orthorhombic structure of the prepared crystals. The band gap energy value calculated from UV-VIS spectra was found to be 2.24 eV. According to the PL measurements, the excitation-emission line from the lead iodate crystal is crisp and intense. Thermal analysis reveals that lead iodate crystals grown in silica gel using the single diffusion method are structurally stable up to 283 ^{0}c and above this temperature; it decomposes with the evaluation of oxygen and iodine.

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