

Study of Structural, FT-IR and Nonlinear optical properties of Lithium iodate

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Abstract

Crystals of lithium iodate were grown by simple evaporation method. Crystals having prism and prismatic pyramidal shapes were obtained. These crystals were characterized by XRD powder diffraction method. . These crystals belong to hexagonal system with $a = b \neq c$ and $\alpha = 120^\circ$, $\beta = \gamma = 90^\circ$. The calculated values of a , b , c are in good agreement with the reported ones. FT-IR analysis was carried out. The bands due to vibrations involving metal, iodine and oxygen atoms are found predominantly in the range $700 - 800 \text{ cm}^{-1}$. These frequencies match very well with the reported values. Non-linear optical properties were studied using powder SHG measurements. Value of the nonlinear coefficient (d) of LiIO_3 is higher than that of KDP, but still smaller than that of reported one.

Key-words

Lithium iodate, XRD , FT-IR , Non-linear optical properties.

1. INTRODUCTION

Crystals of hexagonal modification of lithium iodate are of great practical importance in nonlinear optics [1]. High efficiency acousto-optic and acousto-electronic instruments are devised in which LiIO_3 crystals are widely used [2]. They have good nonlinear optical, electro-optical [3], photoelectric, and piezoelectric properties [4]. These crystals are of interest in second harmonic generation within the range $0.53 - 1.06 \mu\text{m}$ [5]. The crystals used in second harmonic generation belong to the point group 6 and have a prismatic form, which is hexagonal in cross section. They are uni-axial and optically negative [5, 6]. Various methods have been adopted by researchers [7 - 11] to grow these crystals.

2. Experimental

Single crystals of lithium iodate were grown by solvent evaporation method in the following manner:

Stoichiometric quantities of iodic acid and lithium carbonate were dissolved in double distilled water by using magnetic stirrer. Measured pH of the solution was always in the range of 1.9 – 2.0. The medium of growth was thus acidic. The solution was then warmed to remove any remaining

carbon dioxide. The solution was allowed to evaporate at room temperature until crystals began to nucleate within 15 days. Small prismatic pyramidal crystals began to form. All the crystals were removed only after complete dehydration of the solution.

2.1. Results and discussion

The crystals obtained were pseudo-prisms upto 4 mm long and 3 mm in diameter. Fig. 1 shows few prism shaped crystals. Variety of crystals having prismatic pyramidal shape was observed. Careful examination reveals that the apparent prisms are actually portions of extremely steep hexagonal pyramids.

2.2. Observations

Crystals obtained are illustrated in magnified form in Figs. 2 - 6. Fig. 2 shows needle shaped crystal, having well-developed prism and pyramidal faces on it. It is long along c-direction. Its prism faces are transparent, while pyramidal faces are translucent. Fig. 3 shows prismatic pyramidal crystal having good transparency and edges of faces are sharp and well defined. One of them shows etching while growth on prism faces of it. Its growth is nearly same along all the directions. Fig. 4 shows the same feature as that of Fig.3, but here growth takes elongated form along c-direction. Well developed, transparent prism face along with steep pyramidal faces can be seen in Fig.5. Fig. 6 also shows transparent prism face, along with distorted pyramidal faces.



Fig. 1 Few crystals of lithium iodate

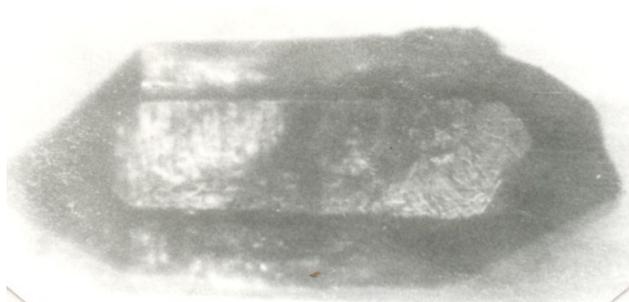


Fig. 2 (x 40)



Fig. 3 (x 20)

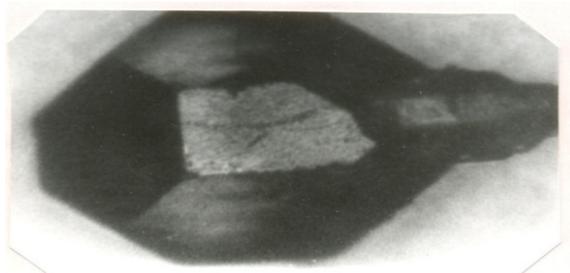


Fig. 4 (x 50)

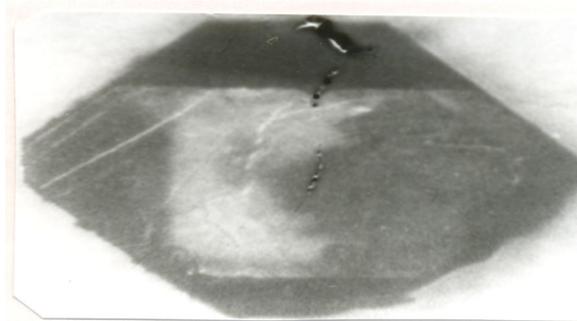


Fig. 5 (x 50)

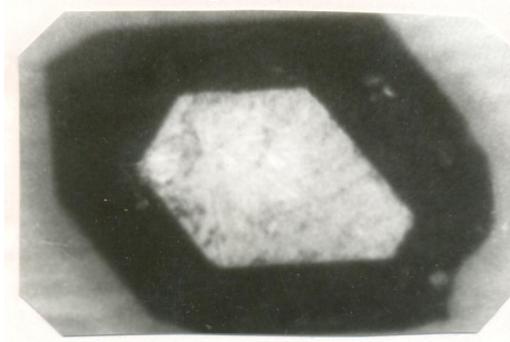


Fig. 6 (x 50)

Fig. 2 - 6 Variety of crystals obtained, represented in magnified form

3. Characterization

3.1 X-ray diffractometry

In the present investigation, X-ray powder diffraction method is used to determine 'd' value, hkl parameters, and unit cell parameters of lithium iodate crystals.

The X-ray diffractogram of lithium iodate crystals is shown in Fig.7. From this diffractogram, intensity ratios I / I_0 , 'd' values, and hkl were computed. 'd' values are in good agreement with the reported values [12]. These crystals belong to hexagonal system with $a = b \neq c$ and $\alpha = 120^\circ$, $\beta = \gamma = 90^\circ$. The calculated values of a, b, c are in good agreement with the reported ones, are represented in Table 1.

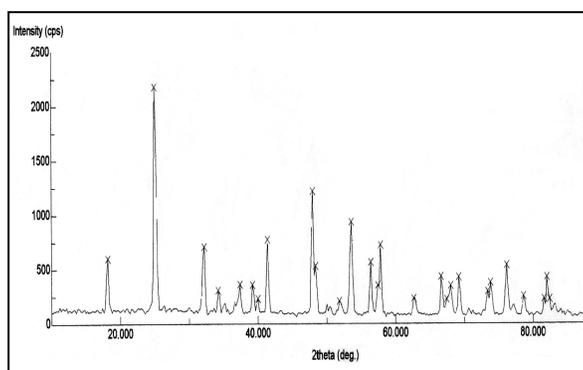


Fig. 7 X-ray diffractogram of lithium iodate

Table 1 - Lattice parameters of lithium iodate crystals

Lattice parameters	Reported	Observed
$a \text{ \AA}^0$	5.481	5.4815 (5)
$b \text{ \AA}^0$	5.481	5.4815 (5)
$c \text{ \AA}^0$	5.172	5.1689 (7)
β°	90.00	90.00
$V (\text{ \AA}^0)^3$	-	134.502

3.2 FT-IR analysis

The IR spectrum serves as compound's fingerprint and provides specific information about chemical bonding and molecular structure. IR spectrum is a fingerprint for identification of a substance [13]. Fourier Transform infrared spectroscopy (FT-IR) is more advanced and powerful analytical tool for characterization and identification of molecules.

In the present work, the FT-IR spectrum of lithium iodate was scanned by using FT-IR spectrophotometer, Spectrum-2000, Perkin-Elmer model by placing sample KBr pellet in sample

beam in two ranges, $4000 - 400 \text{ cm}^{-1}$ and $710-300 \text{ cm}^{-1}$. These spectra are represented in Figs. 8 (a), and (b).

Rocchiccioli [14] has reported the observations of IR spectrum of LiIO_3 . The study suggests a symmetrical pyramidal structure of the IO_3^- anions. The band due to vibrations between metal, iodine and oxygen at 784 cm^{-1} is reported. In the present work, this band has been observed at 782.95 cm^{-1} . The various bands observed are as follows

I.The bands due to vibrations involving metal, iodine and oxygen atoms are found predominantly in the range 700

$- 800 \text{ cm}^{-1}$.

II.The observed fundamental frequencies are,

- a. Symmetric stretching γ_1 at 702.35 cm^{-1}
- b. Symmetric bending γ_2 at 381.07 cm^{-1}
- c. asymmetric stretching γ_3 at 782.95 cm^{-1}
- d asymmetric bending γ_4 at 335.21 cm^{-1}

The extra bands observed at 410.98 and 437.13 cm^{-1} may be due to metal- oxygen vibration. From above, γ_1 and γ_3 lay between $700 - 800 \text{ cm}^{-1}$. The highest frequency 782.95 cm^{-1} has been assigned to γ_3 .

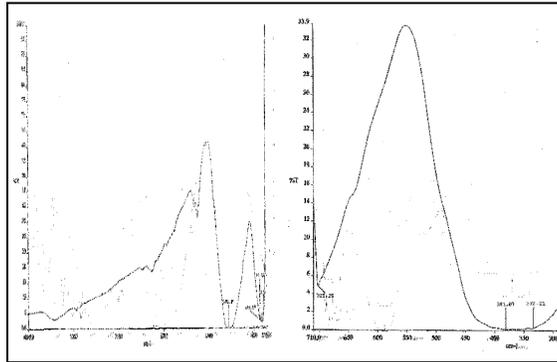


Fig. 8 FT-IR spectra of lithium iodate in the range (a) $4000-400 \text{ cm}^{-1}$ (b) $710-300 \text{ cm}^{-1}$

3.2 Powder SHG measurements

For performing experiments, sample plates were prepared from powder samples of KDP and lithium iodate. These samples were sieved by a $75\mu\text{m}$ sieve. Conversion efficiency and nonlinear coefficient were calculated by exposing the sample plates to Nd:YAG laser and measuring $V(\omega)$ and $V(2\omega)$ of reference and SHG signal, respectively.

Values of conversion efficiency for corresponding arc lamp voltage of samples of KDP and lithium iodate are given in Table 2. Table 2 gives the results of calculations of nonlinear coefficients (d 's). From Table 2, it can be seen that value of conversion efficiency of lithium iodate is higher than that of KDP, but it is still less than reported one [6]. The reason might be the impurities in the chemicals used to grow the crystals, limitations of the instrument, manual

handling of the instrument, etc.

Table 2

Substance	Nonlinear coefficient (d's) pm/v
KDP	0.44
LiIO ₃	0.4568

4. CONCLUSION

The following conclusions are drawn from the above discussion:

1. Crystals of Lithium iodate can be grown by solvent evaporation method
2. XRD analysis suggests that grown crystals are lithium iodate. The 'd' values and unit cell parameters are in good agreement with reported values of standard JCPDS data.
3. FT-IR analysis shows that bands due to vibration between metal, iodine, and oxygen are present.
4. Powder second harmonic generation experiment verifies the nonlinear optical property of the crystals. Its value of nonlinear coefficient is higher than KDP, but less than reported one. Reason may be the impurities included in the sample

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