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Der Pharma Chemica, 2010, 2(5):247-254
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X

Growth, Optical and Mechanical Properties of nonlinear optical alpha-Lithium Iodate Single Crystal

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ABSTRACT

The growth and characterization of a nonlinear inorganic crystal, alpha-lithium iodate is reported. The growth of single crystals of alpha-lithium iodate was accomplished by slow evaporation technique. The formation of alpha-lithium iodate compound has been confirmed by single crystal X-ray diffraction studies. The UV-Vis-NIR absorption spectrum has been recorded in the range 200-1200 nm. The Kurtz Perry SHG test confirms the NLO property of the grown crystal and the relative efficiency is 78 times greater than KDP. The compressive strength of the grown crystals was found using Tinius Olsen compression testing machine. Vickers microhardness study was carried out on the well developed face of the grown crystal.

Keywords: X-ray diffraction, Single crystal, Inorganic compounds, Nonlinear optic materials.

INTRODUCTION

Crystals of the iodate family have aroused much interest recently because of high effective nonlinear coefficients [1, 2], high laser damage threshold [3], excellent optical quality in large single crystals [4, 5], high thermal stability (T>200˚C) [6], low thermal expansion and above all a crystal structure which is acentric due to highly polarized iodate (IO_3^-) ions [7] as well as the development of SHG powder evaluation technique [8]. The alpha-lithium iodate crystals have been grown by various research groups [9, 10] and several investigations were carried out to understand the mechanism of thermal conductivity [11], electrical conductivity [12] dielectric property [13, 14] and optical activity [15]. Third order nonlinear optical materials with weak nonlinear absorption but strong nonlinear refraction have attracted considerable attention because of their potential uses in the optical signal processing devices. Due to its non-linear optical properties, alpha-lithium iodate is commonly used in optical devices. The importance of alpha-lithium iodate material for technological applications is emphasized by the fact that it was grown in scientific return satellites [16, 17]. Alpha-lithium iodate has a moderate solubility with negative temperature coefficient, therefore cannot be grown by the method of temperature reduction since accurate control over the rate of evaporation has always been a difficult task compare to reducing temperature at a particular rate. Nucleation of beta phase during the growth of alpha-lithium iodate is a major problem since it prevents the further growth of alpha-phase; this problem was controlled by controlling the supersaturation of the solution. The mechanical strength of the crystal is estimated by Vickers hardness test.

MATERIALS AND METHODS

2.1. Materials Synthesis

Aqueous solution of alpha-lithium iodate was prepared from lithium carbonate (Sigma-Aldrich, 99.99%) and Iodic acid (Sigma-Aldrich, 99.5%). The reactants were thoroughly dissolved in deionized water (resistivity 18.2MΩcm). The temperature of the solution was maintained at 55°C and it was stirred using magnetic stirrer for 12 hours to attain the homogeneity. Then the solution was allowed to evaporate at 55°C which yielded white crystalline salt of alpha-lithium iodate after 6 weeks. Synthesized salt was recrystallized twice prior to the growth.

2.2. Crystal growth

In order to get the good quality seed crystals, the concentrated solution was prepared using the synthesized salt and kept at 55°C for about two weeks. A transparent and inclusion free seed crystal was taken from the mother solution and then suspended by a nylon thread in the growth solution of 200 ml. After a time span of 45 days, perfectly faceted with hexagonal prismatic morphology of crystal was harvested from the above said solution. Fig. 1 shows the as grown (size 15mmx 7mmx7mm alpha-lithium iodate single crystal. The grown crystal was found to be stable and unaffected by the environment.

Fig.1 As grown crystal of alpha-lithium iodate

RESULTS AND DISCUSSION

3.1. X-ray diffraction analysis

Powder X-ray diffraction pattern of alpha-lithium iodate crystal and standard JCPDS pattern are shown in Fig. 2. The observed Powder X-ray diffraction pattern of alpha-lithium iodate crystal is in good agreement with the reported JCPDS data (card number-00-008-0465). The single crystal X- ray diffraction of the grown crystal was carried out using an *Oxford X'calibur Single Crystal X- ray Diffractometer*, From the single crystal X-ray analysis, the calculated lattice parameters are: a = 5.448 Å, b =5.460 Å, c = 5.1639 Å, α=90.09°, β= 90.02°, γ=119.90° and V = 133.15 $Å^3$.

The title compound crystallizes in hexagonal crystal system (space group: $P6_3$). The observed data are in good agreement with the reported literature values [18, 19].

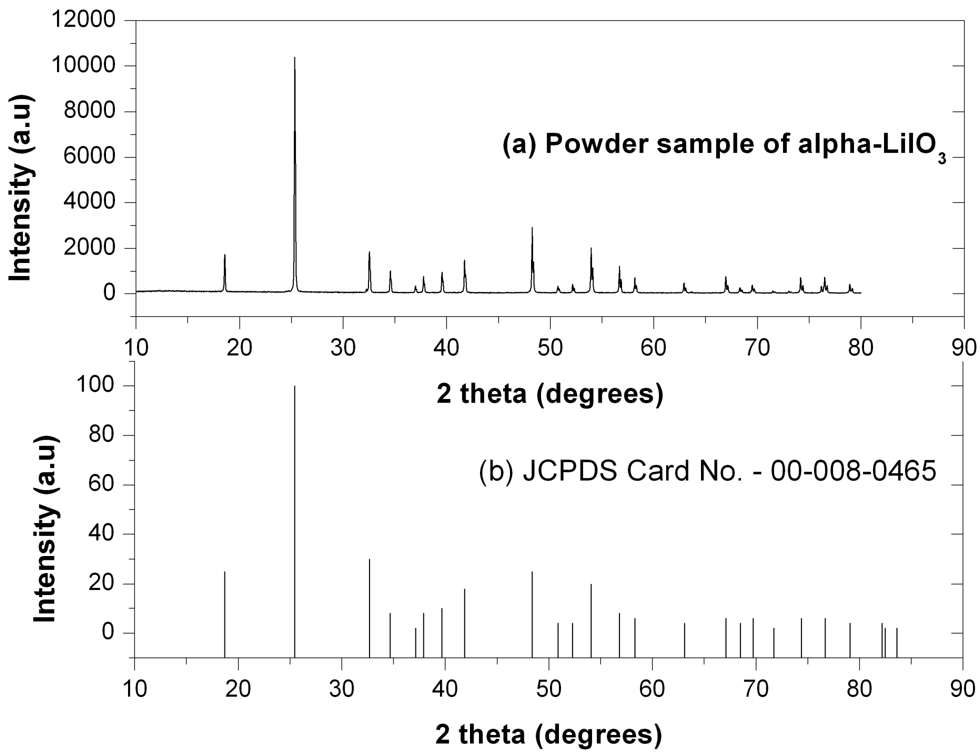

Fig. 2 The pattern of X-ray powder diffraction: (a) powder sample pattern, (b) the standard JCPDS pattern

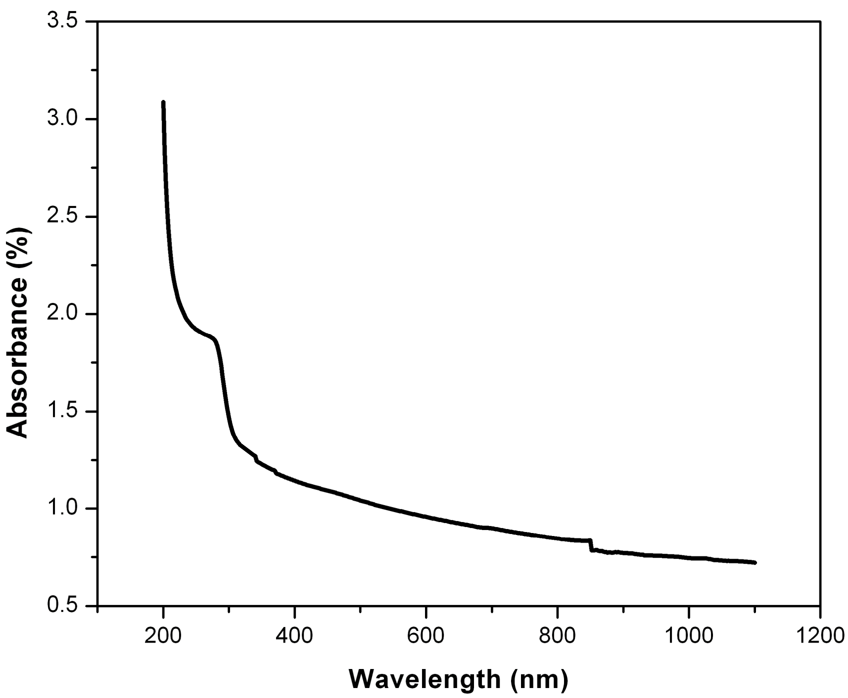

Fig.3 Absorbance spectrum of alpha-lithium iodate

3.2. Optical studies

The UV-VIS-NIR absorption spectrum of the crystal was recorded using JASCO V-570 UV-VIS-NIR spectrophotometer in the wavelength region of 200 – 1200 nm and it is shown in Fig. 3. The characteristic absorption band is observed at 300 nm and there is no absorption in the entire visible regions [4], hence the crystal is expected to be transparent to all the UV–VIS radiations in between these two wavelengths. This is the most favorable characteristics for a NLO material.

3.3. SHG studies

The second harmonic generation behaviour of the powdered alpha-lithium iodate was tested using the Kurtz and Perry method [8]. A high-intensity Nd: YAG laser (λ =1064 nm) with a pulse duration of 10 ns was passed through the powdered sample. The SHG behaviour was confirmed from the output of the laser beam having the bright green emission (λ = 532 nm). The second harmonic signal of 1.1 V/pulse was generated for alpha- lithium iodate for an input energy of 5.56 mJ/pulse. But the standard KDP crystalline powder gave a SHG signal of only 14 mV/pulse for the same input energy. Thus, it was observed that the relative SHG efficiency of alpha-lithium iodate is 78 times higher than that of the standard KDP crystal at this wavelength.

3.4. Compressive strength studies

Compressive strength studies were performed on alpha-lithium iodate and KDP single crystals using materials testing machine Tinius Olsen, Model H5KS, UK. For the present study 5 kN load cell was used for the compression test [20] with the standard grips provided with crosshead speed of 0.05 mm min^{-1}. The compressive strength was determined by the collapse of the material due to compression [21] by minimum of 10% force change in alpha-lithium iodate. The same study was carried out on standard KDP crystal. Compressive strengths for both the crystal samples were determined from the graph drawn (Fig. 4). The test result indicates that the compressive strength of KDP crystal was observed as 49.05MPa and alpha-lithium iodate crystal was 50.56 MPa. It reveals that the compressive strength of alpha-lithium iodate crystal is on par with KDP crystal.

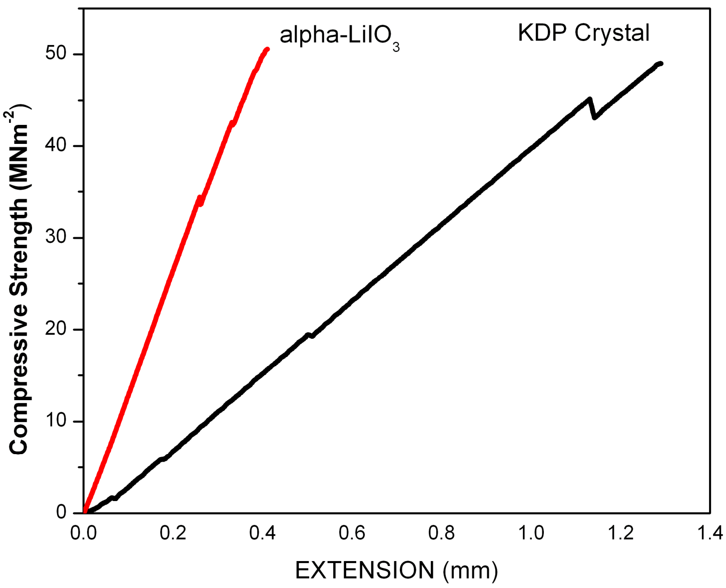

Fig.4 Compressive strength of alpha-lithium iodate and KDP crystal.

3.5. Microhardness studies

In order to understand the plasticity of the crystals, microhardness studies were carried out on the grown crystals, as the hardness of the crystals is dependent on the type of chemical bonding, which may differ along the crystallographic directions. Microhardness indentations were made on the well-developed grown crystal of alpha-lithium iodate crystals using Leitz-Wetzlar hardness tester fitted with a diamond pyramidal indenter. A diamond indenter is pressed into the surface of the alpha-lithium iodate crystal under the influence of a known load (10–100 g) and the size of the resulting indentation is measured. At lower loads the hardness decreases with load, which can attributed to the work hardening of the surface layers. At higher loads the hardness is increased which is essential requirement for device fabrication. Owing to the observed micro cracks at the corners of the impressions made on the crystals, the maximum indenter load applied was 100 g. This may be due to the release of internal stresses generated locally by indentation and further measurements are not possible. Vickers diamond pyramidal number, Hv was calculated from the following equation:

$$H_v = \frac{1.8544P}{d^2} kg/mm^2 \qquad (1)$$

where P is the applied load in kg and d is the diagonal length of indentation in mm. For each load P, an average of at least three impressions were recorded and the average of diagonal lengths (d) of the indentation mark after unloading was obtained .

The values of Hv vs. loads, calculated using Eq. (1) were plotted against loads (Fig.5). The relation between load and the size of indentation is given by Meyer's law [22] as

$$P = k_1 d^n \qquad (2)$$

where k_1 is a constant, n is the Meyer index (or work-hardening coefficient).
Using Eqs. (1) and (2), we have

$$H_v = bP^{\frac{n-2}{n}} \qquad (3)$$

$$H_v = 1.8544 k_1 d^{n-2} \qquad (4)$$

where b is a constant. The above relation indicates that H_v should increase with P if n > 2 and decrease with P when n < 2. We can determine n from the slope of a plot of log d versus log P. Fig. 6 shows the plot of log P versus log d fitting data before cracking (up to 100 g of load) using least-squares fit method and the value of n was found to be 2.12 which is greater than 2. The dependence of microhardness of a solid on the applied load at low level of testing load is known as Indentation Size Effect (ISE). When n = 2 for pyramidal indentors the hardness is independent of indentation size, when n < 2 there is a "normal" ISE and when n > 2 there is "reverse" ISE. The reverse effect is very uncommon and is usually due to softer superficial layers on the specimen surface [23]. On the basis of careful investigation on various substances, the value of n comes out to be 1–1.6 for hard materials and more than 1.6 for soft ones. Thus alpha-lithium iodate crystal belongs to the soft material category. The resistance pressure is defined as a minimum level of indentation load (w) below which there is no plastic deformation [24]. Hays and Kendall [25] proposed a relationship to calculate 'w' by the equation

$$d^n = \frac{w}{k_1} + \frac{k_2}{k_1} d^2 \qquad (5)$$

Fig. 7 reveals that the plot between d^n and d^2 gives a straight line having the slope k_2/k_1 and intercepts w/k_1. From these values the value of 'w' was calculated as 10.2g which shows that the mechanical property of the crystal is quite good.

The elastic stiffness constant (C_{11}) was calculated with Wooster's empirical relation [26]. The calculated stiffness constant for a load from 10 g to 100 g has been calculated and given in Table 1. Here we have a high value of C_{11}, which indicates that the binding forces between the ions are quite strong.

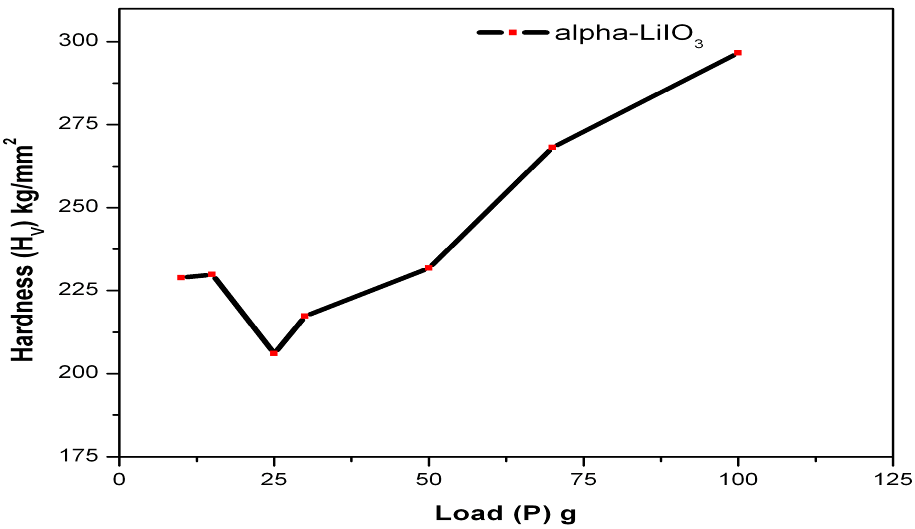

Fig. 5 Microhardness studies of alpha-lithium iodate

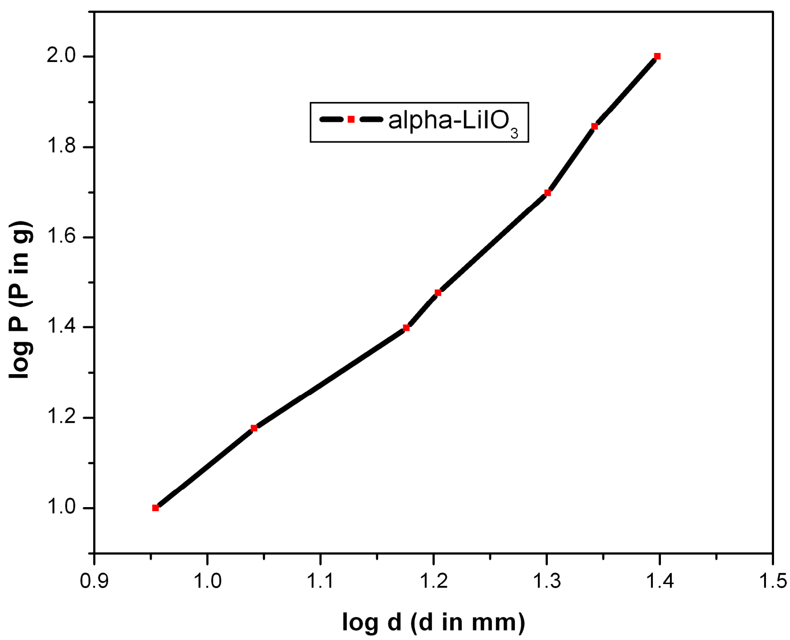

Fig. 6 Plot of log d versus log p

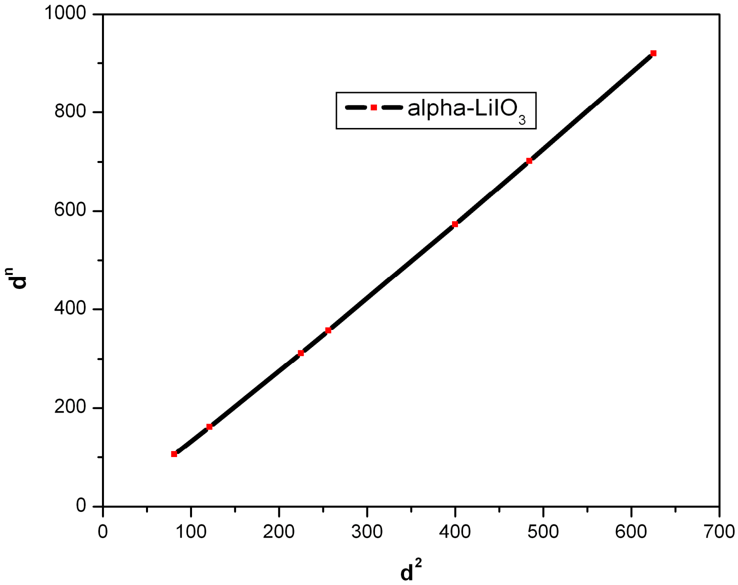

Fig. 7 Plot of d^2 versus d^n

Table 1 Stiffness constant of alpha-lithium iodate for various loads.

Load (P) in g	Hv (kg/mm^2)	C_{11} (10^{15}Pa)
10	228.888	4.1741
15	229.834	4.2043
25	206.000	3.4713
30	217.265	3.8102
50	231.750	4.2658
70	268.140	5.5062
100	296.640	6.5709

CONCLUSION

The Alpha-lithium iodate single crystals have been successfully grown by conventional slow evaporation method. It is a well known compound for nonlinear optical applications. Single crystal X-ray diffraction studies confirmed the structure of the grown crystals. UV-Visible studies confirmed that grown crystals may find useful optical window applications in the wavelength region 300-1200nm. Powder SHG measurement reveals that the relative efficiency of alpha-lithium iodate crystal is 78 times more when compared to KDP at 1.064 µm. We reported the compressive strength studies of alpha-lithium iodate crystal using material testing machine Tinius Olsen. The compressive strength of alpha-lithium iodate crystal is on par with KDP crystal. Vickers microhardness study on alpha-lithium iodate crystal reveals that the hardness number H_v decreases with increasing load for very small loads and then increases with increase in load. The value of Meyer's index, n was found to be greater than 1.6 for alpha-lithium iodate and the grown crystal falls under the soft material category. The value of C_{11} gives the idea of tightness of bonding between neighboring atoms. Here we have large value of elastic stiffness constant, which indicates that the binding force between Li^+ and IO_3^- ions is quite strong. Good mechanical properties, excellent optical quality, moderate compressive strength, SHG efficiency, confirm that alpha-lithium iodate is a good candidate for NLO device fabrication.

Acknowledgements
The authors thank DST, Government of India for funding this research project (SR/S2/LOP-07/2007). The authors are grateful to the management, VIT University, Vellore for their constant support and encouragement. The authors are grateful to Prof. P. K. Das, Dept. of Inorganic and Physical Chemistry, IISc, Bangalore for providing the SHG studies. The authors are expressing their sincere thanks to Prof. K. Kishan Rao, Department of Physics, Kakatiya University, Warangal for providing the micro- hardness test facilities.

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