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Growth, Crystalline Perfection and Z-scan Studies of Nonlinear Optical alpha-Lithium Iodate Single Crystal

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ABSTRACT

Single crystal of an inorganic nonlinear optical (NLO) material, alpha-Lithium Iodate was grown by slow evaporation method. Solubility of α-$LiIO_3$ in water was determined for various temperatures. The crystalline perfection of the grown crystal was analyzed by high resolution X-ray diffraction (rocking curve) measurements. Defects of the grown crystal was studied by etch patterns. The third order optical nonlinearity of the alpha-lithium iodate crystal has been investigated by using Z-scan method with He-Ne laser pulses at the wavelength of 632.8 nm. The nonlinear refractive index n_2, nonlinear absorption coefficient β and the third order nonlinearity χ3 are found to be 5.46x10-7 cm^2/W, 3.95 cm/W and 1.63 x 10^{-3} esu respectively.

Keywords: Solution growth, Slow evaporation, Solubility, HRXRD, Etching studies, Z Scan Technique.

1. INTRODUCTION

Crystals of alpha-lithium iodate is one of the most useful optical materials for integrated optics. Optical waveguides using α-$LiIO_3$ crystal are of considerable practical interest for integrated optical devices such as optical modulators, optical switches and frequency converters where a quasi-phase-matching (QPM) technique is used[1,2]. A single crystal of α-$LiIO_3$ has been studied extensively because it has good non-linear optical, electro-optical, photoelastic and piezoelectric properties[3,4]. α-$LiIO_3$ has a moderate solubility with small negative temperature coefficient and it has been used for second harmonic generation and frequency mixing, new applications in the fields of solid state laser technology and optical data storage have been proposed by incorporating iron-group ions and rare earth elements in these crystals. The alpha-lithium iodate crystals have been grown by various research groups by the method of free evaporation and temperature gradient[5-7]. A structural, thermal and dielectric study has been investigated thoroughly[8-10]. 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. The Z-scan method has gained rapid acceptance by the nonlinear optics community as a standard technique for separately determining the nonlinear changes in index and changes in absorption[11-14]. In this paper, we report the moderate negative solubility with temperature, crystalline perfection of pure α-$LiIO_3$ with evidence from X-ray rocking curve measurement and the investigation of the third order nonlinear optical properties of the grown crystal by a single beam Z scan technique.

2. EXPERIMENTAL RESULTS

2.1. Solubility

The starting material was synthesized by adding equimolar ratios of lithium carbonate (Sigma-Aldrich, 99.99%) and Iodic acid (Sigma-Aldrich, 99.5%) and purified by repeated recrystallization from aqueous solution. The solubility of α-$LiIO_3$ in water was determined as a function of temperature in the temperature range of 35-60°C. The beaker containing the solution was maintained at a constant temperature having an accuracy of ±0.01°C and continuously stirred using a magnetic stirrer. The amount of α-$LiIO_3$ required saturating the solution at this temperature is estimated and this process was repeated for different temperatures. The solubility data obtained in this work are shown in fig.1 and it was found to be the moderate negative temperature coefficient material.

2.2. Crystal growth

According to the solubility data (67.05g/100ml) the saturation solution of α-$LiIO_3$ was prepared at 55˚C temperature using Millipore water of resistivity18.2MΩ cm and stirred well to yield a homogeneous solution. The saturation solution of α-$LiIO_3$ was prepared and transferred into a seed crystal mounted glass beaker. After one week, the seed crystal mounted at the bottom starts to grow. Under this condition the highly transparent crystal was seen and the growth system was kept constant for a long period for attaining continuous growth which at the end has yielded alpha-lithium iodate crystal of length 15 mm and diameter 7 mm within 50 days (Fig. 2). The average growth rate was nearly 0.3 mm/day.

2.3. High Resolution X-ray Diffraction Studies

The crystal specimen was first lapped and chemically etched in a non preferential etchant of water and acetone mixture in 1:2 volume ratio to remove the non- crystallized solute atoms remained on the surface of the crystal and also to ensure the surface planarity. The crystalline perfection of the grown single crystals was characterized by HRXRD by employing a multicrystal X-ray diffractometer (MCD) developed at National Physical Laboratory[15]. The well-collimated and monochromated Mo$K\alpha_1$ beam obtained from the three monochromator Si crystals set in dispersive (+,-,-) configuration has been used as the exploring X-ray beam. The specimen crystal is aligned in the (+,-,-,+) configuration. Due to dispersive configuration, though the lattice constant of the monochromator crystal(s) and the specimen are different, the unwanted dispersion broadening in the diffraction curve (DC) of the specimen crystal is insignificant. The specimen can be rotated about the vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.4 arc sec. The rocking or

diffraction curves were recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position θ_B (taken as zero for the sake of convenience) starting from a suitable arbitrary glancing angle and ending at a glancing angle after the peak so that all the meaningful scattered intensities on both sides of the peak include in the diffraction curve. The DC was recorded by the so-called ω scan wherein the detector was kept at the same angular position $2\theta_B$ with wide opening for its slit.

Fig.3 shows the high-resolution rocking/ diffraction curve (DC) recorded for a typical α-$LiIO_3$ single crystal specimen grown by slow evaporation solution growth technique using (100) diffracting plane in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer with MoKα_1 radiation. As seen in the fig.3, the DC contains a single peak and indicates that the specimen is free from structural grain boundaries. The full width at half maximum (FWHM) of these curve is 30 arc s which is somewhat more than that expected from the plane wave theory of dynamical X-ray diffraction, for an ideally perfect crystal but close to that expected for nearly perfect real life crystals. This much broadness with good scattered intensity along the wings of the DC indicates that the crystal contains point defects and their aggregates. Such defects are very common to observe in almost all real crystals including nature gifted crystals and are many times unavoidable due to thermodynamical conditions. It is worth to see the shape of the DC. As seen in the figure, the DC is not symmetric with respect to the Bragg peak position, which indicates that the density of vacancy and interstitial defects are not same. For a particular angular deviation ($\Delta\theta$) of glancing angle (θ) with respect to the Bragg peak position (taken as zero for the sake of convenience), the scattered intensity is much more in the positive direction in comparison to that of the negative direction. This feature clearly indicates that the crystal contains predominantly interstitial type of defects than that of vacancy defects. This can be well understood by the fact that due to interstitial defects (which may arise due to self interstitials due to fast growth or incorporation of impurities etc.), the lattice around these defects undergo compressive stress which was shown inset of the fig.3 and the lattice parameter d (interplanar spacing) decreases and leads to give more scattered (also known as diffuse X-ray scattering) intensity at slightly higher Bragg angles (θ_B) as d and sin θ_B are inversely proportional to each other in the Bragg equation. The inset in the curve shows the schematic to illustrate how the lattice around the defect core undergoes compressive stress. The converse explanation is true in case of vacancy defects which cause tensile stress in the lattice around the defect core leading to increase of lattice spacing and in turn results in more scattered intensity at the lower Bragg angles[16]. However, the single diffraction curve with reasonably low FWHM indicates that the crystalline perfection is fairly good. The density of such vacancy defects is however meager and in almost all real crystals including nature gifted crystals, such defects are commonly observed and are many times unavoidable due to thermodynamical conditions and hardly affect the device performance. It is worth to mention here that the observed scattering due to point defects is of short range order as the strain due to such minute defects is limited to the very defect core and the long range order could not be expected and hence the change in the lattice

parameter of the overall crystal is not expected. It may be mentioned here that the minute information like the asymmetry in the DC could be possible as in the present sample only because of the high-resolution of the multicrystal X-ray diffractometer used in the present investigation.

2.4. Etching Studies

The patterns of etch pits depend on the etchant, etching time and crystal planes. Etch pits are associated with dislocations and dislocation bundles and hence bring out the crystal quality. The etch pits in α-$LiIO_3$ single crystals were examined using normal incident light type microscope. Etching experiments were performed using water as etchant at room temperature for 10 s on (1 0 0) plane which was carefully oriented and polished before etching. Fig. 4(a) shows predominant rectangular etch pits on crystals. Some of them extend completely over the surface while others are partly extended. Fig. 4(b) shows the striations parallel to c-axis on its face for etching period of 20s.

2.5 Z- Scan studies

The Z-scan is a well known experimental technique to measure the intensity dependent third order nonlinear susceptibility of the materials[17,18]. The nonlinear optical measurements were carried out by using single beam Z-scan technique with a He-Ne laser operated at a repetition rate of 1 kHz and at the wavelength of 632nm.The open and closed aperture Z-scan configurations are used to investigate the nonlinear absorption coefficient β and nonlinear refractive index n_2 respectively. Fig. 5(a) shows the normalized transmittance T with closed aperture as a function of the distance z along the lens axis in the far field and Fig.5(b) shows the normalized transmittance T with open aperture as a function of the distance z along the lens axis in the far field. The nonlinear refractive index (n_2) of the crystal was calculated using the standard relations given below:

$$\Delta\Phi_0 = \frac{\Delta T_{p-v}}{0.406(1-s)^{0.25}} \qquad (1)$$

Where ΔT_{p-v} is the difference between the normalized peak and valley transmittance and S is the linear transmittance of the aperture. The nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) are given by,

$$n_2 = \frac{\Delta\Phi_0}{kI_0L_{eff}} \qquad (2)$$

and

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}} \qquad (3)$$

Where k is the wave number $k = \frac{2\pi}{\lambda}$ and

$L_{eff} = \frac{1-\exp(-\alpha L)}{\alpha}$ with $I_0 = \frac{P}{\pi\omega_0^2}$ defined

as the peak intensity within the sample, where L is the thickness of the sample, and α is the linear absorption coefficient. The real and imaginary parts of the third order nonlinear susceptibility χ3 are defined as

$$\mathrm{Re}\,\chi^3 = \frac{10^{-4}(\varepsilon_0 c^2 n_0^2 n_2)}{\pi} esu \qquad (4)$$

$$\mathrm{Im}\,\chi^3 = \frac{10^{-2}(\varepsilon_0 c^2 n_0^2 \lambda\beta)}{4\pi^2} esu \qquad (5)$$

Where ε_0 is the vacuum permittivity, n_0 is the linear refractive index of the sample and c is the velocity of light in vacuum.

Thus, we can easily obtain the absolute value of χ^3 by the following formula

$$\chi^3 = \sqrt{(\mathrm{Re}\,\chi^3)^2 + \mathrm{Im}(\chi^3)^2}\, esu \qquad (6)$$

As seen from the closed aperture Z-scan curve the prefocal transmittance valley is followed by the post focal peak which is the positive nonlinearity[19]. The calculated value of the nonlinear refractive index n_2 is 5.46×10^{-7} cm^2/W. As the material has a positive refractive index, it results in self focusing nature of the material, which is essential property for all optical switching devices[20]. The value of nonlinear absorption coefficient β estimated from the open aperture Z-scan curve is 3.95 cm/W. The third order susceptibility of α-$LiIO_3$ is 1.63×10^{-3} esu. Table 1 shows the experimental details and the results of the Z-scan technique for alpha-lithium iodate single crystal.

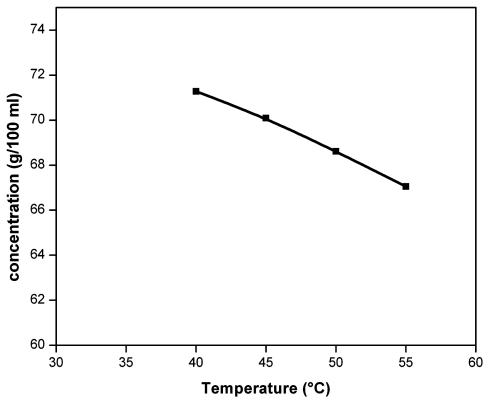


Fig.1. Solubility of α-$LiIO_3$ in aqueous solution.

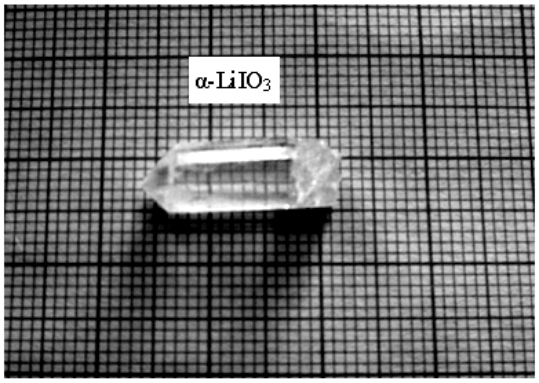


Fig. 2. As grown single crystal of α-$LiIO_3$

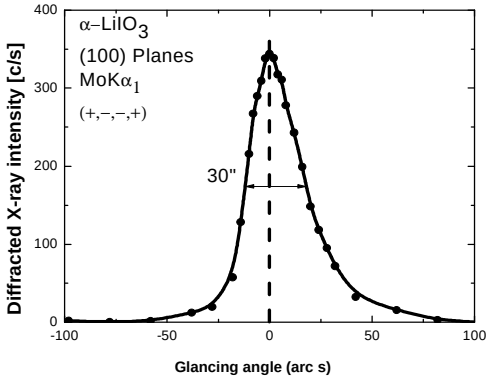
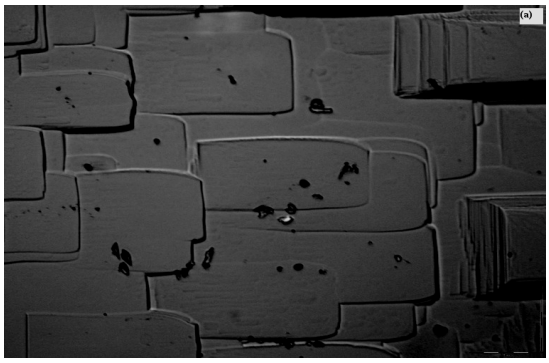


Fig.3. High-resolution X-ray diffraction curve recorded for α-$LiIO_3$ single crystal using (100) diffracting planes.



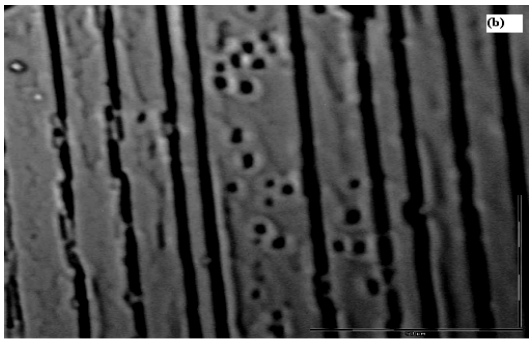


Fig.4. Etch patterns observed on (1 0 0) plane of α-$LiIO_3$ single crystal with water as an etchant for a period (a) 10 s and (b) 20 s.

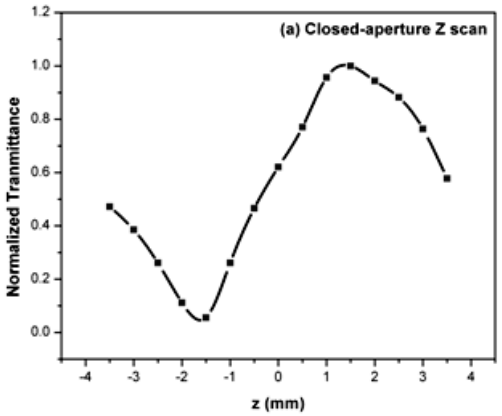


Fig. 5(a) shows the normalized transmittance with closed aperture as a function of the z position.

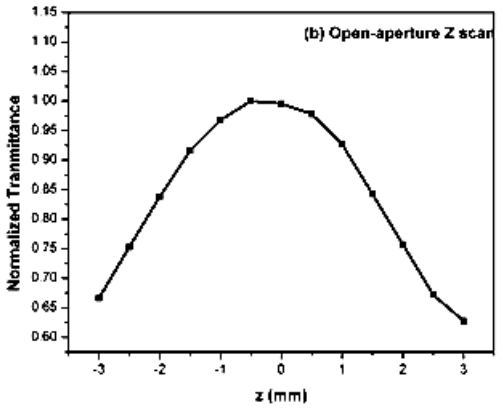


Fig. 5(b) shows the normalized transmittance with open aperture as a function of the z position.

Table 1 Measurement details and the results of the Z-scan technique

Laser beam wavelength (λ)	632.8 nm
Laser Power (P)	35 mW
Lens focal length (f)	24 cm
Optical path distance (Z)	175 cm
Beam radius of the aperture (ω_a)	4 mm
Sample thickness (L)	1mm
Aperture radius of detector (r_a) for closed	4 mm
Aperture radius of detector (r_a) for open	30 mm
Incident intensity at the focus (Z=0)	1.19mW/cm^2
Nonlinear refractive index (n_2)	5.46 x 10^{-7} cm^2/W
Nonlinear absorption coefficient(β)	3.95 cm/W
Third order susceptibility (χ^3)	1.63 x 10^{-3} esu

3. CONCLUSIONS

The solubility of the α-$LiIO_3$ material in water at different temperatures was determined. The solubility test of α-$LiIO_3$ indicates that it has moderate negative gradient solubility in water. Single crystal of size 15 x 7 x7 mm^3 was grown by slow evaporation solution growth technique. The high-resolution XRD measurement confirms the excellent quality of the crystal free from major defects like structural grain boundaries and inclusions. Etchants of water gives the rectangular shape etch pits which reveal the growth patterns of α-$LiIO_3$. The growth striations were observed from the etch pattern on (1 0 0) plane of the grown crystal for etching period of 20s. Surface defect was studied by etch patterns of the α-$LiIO_3$ crystal. The Z-scan measurements,

performed with 632 nm laser pulses, confirmed that alpha-lithium iodate possesses prominent third order nonlinearity.

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