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Growth, optical, mechanical and electrical studies of nonlinear optical crystal: L-Valinium oxalate

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ABSTRACT

L-Valinium oxalate (LVO) single crystal has been grown by solution growth technique at room temperature. The crystal structure and lattice parameters were determined for the grown crystal by single crystal X-ray diffraction studies. Optical constants like band gap, refractive index, reflectance, extinction coefficient and electric susceptibility were determined from UV–vis–NIR spectrum. The microhardness studies reveal the mechanical strength of the grown crystal. The dielectric constant, dielectric loss and AC conductivity of the compound were calculated at different temperatures and frequencies to analyze the electrical properties. Nonlinear optical property was discussed to confirm the SHG efficiency of the grown crystal.

1. Introduction

Crystal growth is a frontier area of science and technology, which plays a major role in the technology of photonics. The field of nonlinear optics has been in the hands of materials scientists for the past five decades for which organic materials are attracting a great deal of attention, as they have large optical susceptibilities, inherent ultrafast response time and good optical properties as compared to that of inorganic crystals. Research on organic and inorganic functionalized nonlinear optical materials plays a crucial role because of their molecular interactions, bond strength, high molecular polarizability, easy incorporation of ions in the lattice, etc. The organic NLO materials are attracted by many scientists due to their frequency conversion efficiency, piezoelectric, pyro-electric properties and their wide applications in the recent technologies like lasers, optical communications and data storage [1]. New materials with higher optical nonlinearities are quite important due to their extensive applications in harmonic generation, amplitude and phase modulation, switching and other signal processing devices [2–4]. The main goal to design the molecules with the third order nonlinearities is to incorporate them into the devices used in all types of optical signal processing [5,6]. Nonlinear optical (NLO) materials have shown potential applications in optical information storage, optical logic gates, laser radiation protection and phase locked laser mode. Hence the interest in searching for NLO materials has increased gradually [7]. In the present investigation, the growth aspects of the L-valinium oxalate single crystals have been carried out by slow evaporation technique. The grown crystal is subjected to different characterizations such as single crystal X-ray analysis, optical analysis, NLO test, microhardness test, dielectric and AC electrical conductivity measurements. The results of these studies have been discussed in this paper in detail manner.

2. Experimental procedure

Single crystals of L-valinium oxalate (LVO) were grown, by slow evaporation technique. The solution was prepared by dissolving equimolar amounts of oxalic acid and L-valine in deionized water at room temperature and stirred well to yield a homogenous mixture of solution. The solution was then filtered. The filtered solution was taken in a beaker which was closed with a tissue paper and few pin holes were made on the tissue paper. The solution was then allowed to evaporate slowly which resulted gradually in supersaturation. L-Valinium oxalate crystal was harvested in a growth period of twenty days by slow evaporation of the solvent. The photograph of the grown L-valinium oxalate crystal is shown in Fig. 1.

3. Results and discussion

3.1. Single-crystal X-ray diffraction

Single crystal X-ray diffraction analysis for the grown crystals has been carried out to identify the cell parameters using an ENRAF NONIUS CAD 4 automatic X-ray Diffractometer. Single crystal XRD

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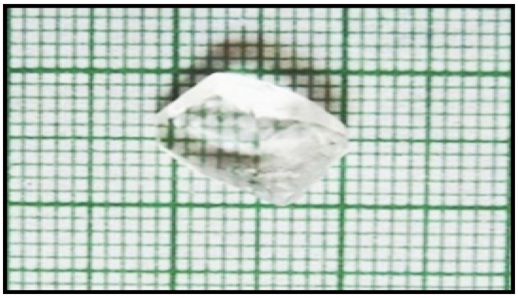

Fig. 1. Photograph of as-grown L-valinium oxalate crystal.

data confirms that the crystal belongs to monoclinic crystal system and the calculated lattice parameters are $a = 21.304$ Å, $b = 7.02$ Å, $c = 5.532$ Å, $\alpha = \gamma = 90^\circ$ and $\beta = 92.40^\circ$ and which agree well with the available reported literature values [8].

3.2. UV–vis–NIR spectral analysis

The optical transmittance spectrum of L-valinium oxalate was recorded in the range 100–1100 nm with a crystal of thickness 2 mm. Fig. 2 shows that the crystal has a wide transmission of above 70% in the entire range without any absorption peak. The lower cutoff wavelength of L-valinium oxalate was found to be at 290 nm. The crystal has good optical transmission in the visible region. The transparency in the visible region for this crystal suggests its suitability for second harmonic generation. The measured transmittance (T) was used to calculate the absorption coefficient (α) using the formula

$$\alpha = \frac{2.3026\ \log(1/T)}{t} \tag{1}$$

where t is the thickness of the sample. The optical band gap (E_g) is related to optical absorption coefficient (α) and energy ($h\nu$) of the incident photon as given by [9]

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \tag{2}$$

where A is a constant, h is the Planck constant and ν is the frequency of the incident photons. The band gap of L-valinium oxalate crystal was estimated by plotting $(\alpha h\nu)^2$ versus $h\nu$ as shown in Fig. 3. From the figure, the value of band gap was found to be 4.30 eV. The extinction coefficient (K) can be obtained from the following equation,

$$K = \frac{\lambda\alpha}{4\pi} \tag{3}$$

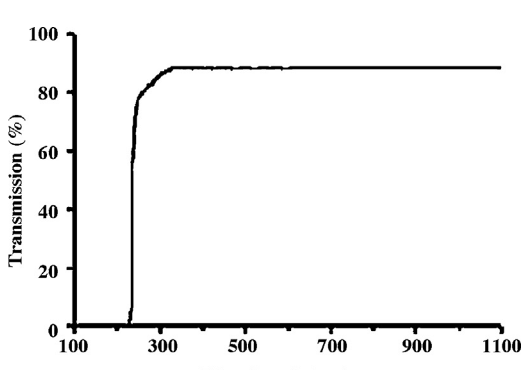

Fig. 2. UV transmission spectrum of L-valinium oxalate single crystal.

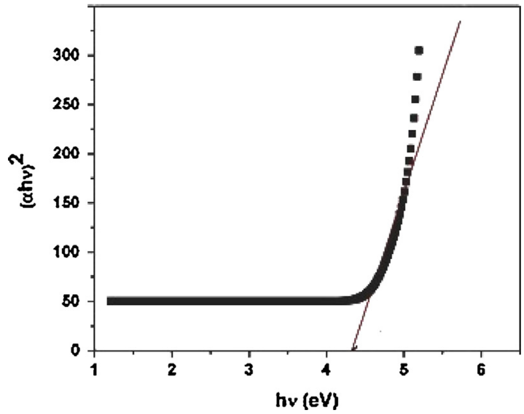

Fig. 3. Plot of $(\alpha h\nu)^2$ versus photon energy of the title crystal.

The transmittance (T) is given by

$$T = \frac{(1-R)^2\exp(-\alpha t)}{1 - R^2\exp(-2\alpha t)} \tag{4}$$

Reflectance (R) in terms of absorption coefficient can be obtained from the above equation.

Hence,

$$R = \frac{1 \pm \sqrt{1 - \exp(-\alpha t + \exp(\alpha t)}}{1 + \exp(-\alpha t)} \tag{5}$$

Refractive index (n) can be determined from reflectance data using the following equation,

$$n = -\frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \tag{6}$$

The refractive index (n) was found to be 1.71 at $\lambda = 1100$ nm. From the optical constants, electric susceptibility (χ_C) can be calculated according to the following relation [10]

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_C = n^2 - k^2 \tag{7}$$

Hence,

$$\chi_C = \frac{n^2 - k^2 - \varepsilon_0}{4\pi} \tag{8}$$

where ε_0 is the permittivity of free space. The value of electric susceptibility χ_C is 0.193 at $\lambda = 1100$ nm. The real part dielectric constant ε_r and imaginary part dielectric constant ε_i can be calculated from the following relations [11]

$$\begin{aligned} \varepsilon_r &= n^2 - k^2 \\ \varepsilon_i &= 2nk \end{aligned} \tag{9}$$

The value of real ε_r and ε_i imaginary dielectric constants at $\lambda = 1100$ nm were estimated at 1.642 and 5.232×10^{-5}, respectively. The moderate values of refractive index and optical band gap suggest that the material has the required transmission range for NLO application. The lower value of dielectric constant and the positive value of the material are capable of producing induced polarization due to intense incident light radiation.

3.3. NLO test – Kurtz powder SHG method

In order to find NLO property, the grown L-valinium oxalate crystal was subjected to second harmonic generation studies by Kurtz powder technique. The sample was crushed into very fine powder and tightly packed in a microcapillary tube. Then, it was mounted in the path of Nd:YAG laser beam of 9.6 mJ/pulse energy