Optical and Dielectric Studies on Semiorganic Nonlinear Optical Crystal by Solution Growth Technique

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Abstract

The field of nonlinear optics became practically a reality after the invention of laser. High performance electro-optic switching elements for telecommunication and optical information processing are based on materials with high nonlinear optical (NLO) properties. Single crystals of nonlinear optical material L-lysine sulphate (LLS) are grown by slow evaporation technique. The crystal structure and lattice parameters are determined for the grown crystal by single X-ray diffraction studies. The wide transparency range of the crystals in the visible region of the electromagnetic spectrum is identified by the UV-Vis-NIR technique. The mechanical property of the grown crystal is determined by Vicker’s microhardness test. It is observed from the microhardness studies of the grown crystals that the hardness increases with increase in load. Meyer’s index n is calculated which proves that the material belongs to soft material category. The dielectric constant and dielectric loss are calculated by varying the frequencies at room temperature. The emission of green light on passing the Nd: YAG laser confirms the second harmonic generation (SHG) property of the crystals. The SHG efficiency of the crystals are found to be better than that of Potassium Dihydrogen Phosphate (KDP)

Keywords:

Single crystal, NLO, Single crystal XRD, Microhardness, Dielectric constant and Dielectric loss.

1 Introduction

Crystal growth is an important area of science and technology, especially in the field of photonics. The single crystals with advanced properties play a significant role in the growth of modern scientific world of advanced technology. Crystal growth is a significant field of materials science, which involves controlled phase transformation. In the current decades, there has been a growing interest in crystal growth process, particularly in view of the development of materials for technological applications [1]. Materials can be classified as single crystals, poly crystals and amorphous materials depending upon the arrangement of constituent molecules, atoms or ions. If the surroundings of an atom are exactly the same as the surroundings of every similar atom then that crystal is said to be ideal. The real crystals are finite and they contain defects. The single
crystals are solids in the most uniform condition that forms the basis for most of the applications of crystals. The uniformity of single crystals can allow the transmission of electromagnetic waves, without scattering. There are many methods for growing crystals and mainly dictated by the characteristics of the material and its size [2]. The semi-organic crystals attract great attention in the field of nonlinear optics due to their optical nonlinearity, chemical flexibility, thermal stability and excellent transmittance in the UV–visible region [3, 4]. The semi-organic crystals possess properties such as high damage threshold, wide transparency region and high nonlinear coefficient which have various applications and they need NLO require single crystals in the bulk form. This is achieved with the crystals, which exhibit wide transparency, large and bulky crystal morphologies. The contribution from the delocalized $\pi$-electrons belonging to the organic ligand results in wide optical transmittance and high nonlinear electro-optic coefficients. L – Lysine sulphate is a semi-organic NLO material possessing large value of hyperpolarizability. The LL S possesses good stability and do not show any hygroscopic effect for a long time. It has been found that there is a network of hydrogen bonds in crystal that stabilizes its structure. From the optical assessment, LLS is a promising new nonlinear-optical crystal for frequency up conversion in the UV region of high-power laser sources.

Hence, in the present investigation, report the single X-ray diffraction, optical, mechanical, dielectric and SHG characterization of the L-lysine sulphate single crystal for NLO applications. Single crystal X-ray diffraction analysis confirmed the lattice parameters and crystal structure of the grown crystals. Microhardness studies of the crystal have been determined using Vicker’s indentation test. Dielectric constant and dielectric loss studies were carried out at room temperature. The SHG test proves that the LLS crystal was one of the potential nonlinear optical materials.

2 EXPERIMENTAL PROCEDURE

Slow evaporation of L-Lysine and sulphuric acid taken in equimolar ratio in aqueous solution was used to grow single crystals of L-lysine sulphate. The solution was stirred continuously and the solution was filtered. The solution is kept undisturbed at room temperature. Defect free tiny seed crystals with good transparency formed due to spontaneous nucleation was selected and suspended in the mother solution. This solution which was allowed to evaporate at room temperature yields large size single transparent crystals due to collection of monomers at the seed crystal sites from the mother solution. Crystals of LLS were harvested by slow evaporation technique in a period of 30 days.

3 RESULTS AND DISCUSSIONS

3.1 Single Crystal X-ray diffraction Analysis

Single crystal X-ray diffraction provides detailed information about the molecular structure, atomic co-ordinates, band lengths, band angles, unit cell dimensions, molecular orientation and packing of molecules in single crystals which is a non-destructive analytical technique. ENRAF NONIUS CAD4 automatic X-ray diffractometer was used to identify the cell parameters. The crystals belongs to orthorhombic system and the lattice parameters were calculated to be $a = 5.73\text{Å}$, $b = 11.54\text{Å}$, $c = 16.58\text{Å}$, $\alpha = \beta = \gamma = 90^\circ$ with noncentrosymmetric space group P2$_1$2$_1$2$_1$. 
3.2 UV-VIS-NIR Spectral Analysis

The absorption of UV and visible light involves promotion of the electron in the $\sigma$ and $\pi$ orbital to higher states, the UV-VIS-NIR spectrum gives information about the structure of the molecules in the crystals. The optical absorption spectrum of LLS crystal shown in Fig. 1 was recorded between 200 and 1200 nm. The crystal exhibits excellent transmission in the entire visible region. The lower cutoff wavelength is 240 nm. Single crystals are mainly used in optical applications as optical transmittance windows. For the realization of SHG output in the range of (200nm-400nm), the transparency lower cut off (200 nm-400 nm) is very important.

This transparent nature of the crystals in the visible region is the property which makes the material important for NLO applications. The bandgap of the crystal ($E_g$) was estimated from the following relation

$$E_g = \frac{1.243 \times 10^3}{\lambda_{\max}}$$

(1)

Where $\lambda_{\max}$ is the maximum wavelength. This was found to be 5.17 eV, which is typical property of the dielectric materials.

This high value of bandgap shows the crystal possesses dielectric behavior to induce polarization when powerful radiation is incident on the material. The suitability of the grown crystals for photonic and optical applications is confirmed by the absence of absorption bands in the visible region. The large energy bandgap also confirms that the defect concentration in the grown crystal is very low.

Fig. 1 Absorption spectrum of LLS crystal
3.3 Refractive index measurements

Finely polished crystals of the as grown L-lysine sulphate (LLS) were used for refractive index measurements. The crystals which were cleaved and placed on a rotating mount at an angle varying from 0 to 90 degrees. The He-Ne laser of wavelength 632.8 nm was used as the source. Brewster’s angle ($\theta_p$) for LLS was measured to be 58.4 degrees. The refractive index has been calculated using the following relation

$$n = \tan \theta_p$$  \hspace{1cm} (2)

where $\theta_p$ is the polarizing angle and it is found to be 1.625.

3.4 Microhardness Studies

The resistance offered by a material to the motion of dislocation, deformation or damage under an applied stress is measured by the hardness of the crystal. During the making of NLO crystals mechanical stress is applied on the crystal while cutting and polishing. So it is necessary to know the mechanical stress the crystals can withstand without any crack. The ratio of the applied load to the projected area indentation gives the hardness. To find the surface hardness of the grown L-lysine sulphate microhardness was measured for a load of 5-50 gms using SHIMADZU HMV – 2000 microhardness tester with diamond pyramid indenter attached to an optical microscope. Several indentations were made on the sample with a dwell time of 10 seconds for the accuracy of the obtained results. The Vickers hardness number (Hv) was calculated using the standard formula,

$$H_v = 1.8544 \left( \frac{P}{d^2} \right) \text{kg} / \text{mm}^2$$  \hspace{1cm} (3)

where $P$ is the applied load and $d$ is the mean diagonal length of the indentation. The increase of the hardness with load up to 50g is represented in Fig.2 which proves the use of grown crystals in which can withstand thermal local stresses. The Mayer’s index number was calculated from Mayer’s law, which relates the load and the indentation diagonal length as

$$P = k_i d^n$$  \hspace{1cm} (4)

where ‘$n$’ is called Mayer’s index or work hardening index. In order to find work hardening index (n), a graph is plotted with log P against log d which gives a straight line. From the slope of the line, the Mayer’s index number was found to be 3.65. According to Onitsch, if the value of $n$ is greater than 2, the microhardness will increase with increase of load. From the hardness study, the grown LLS crystal is found to be relatively soft material.
3.5 Dielectric Studies

Dielectric properties are related with the electric field distribution within solid materials. One of the widely used parameters is the relative dielectric constant or relative permittivity and the dielectric constant of a material gives an insight into the nature of bonding. The dielectric property of the LLS crystals was studied at room temperature using HIOKI 3532 LCR HITESTER in the frequency region 50Hz - 5MHz. The variation of dielectric constant with frequency is shown by Fig.4. The dielectric constant is higher in the region from 50Hz - 5MHz.
and gradually decreases with increase in frequency and continues up to 5MHz. After this, it almost remains constant at all other higher frequencies. The presence of electronic, ionic, dipolar and space charge polarizations in the material are the reasons for the high value of dielectric constant at low frequency [5]. In accordance with Miller rule, the lower value of dielectric constant at higher frequency is a suitable parameter for the enhancement of SHG coefficient [6]. Fig. 5 shows the variation of dielectric loss with frequency. The crystal possesses enhanced optical quality with lesser defects and this parameter plays a vital role for the fabrication of nonlinear optical devices because of low dielectric loss with high frequency for the samples [7].

Fig. 3 Variation of dielectric constant of LLS single crystal with frequency

Fig. 4 Variation of dielectric loss of LLS single crystal as a function of frequency
3.6 NLO Test – Kurtz Powder SHG Method

The Kurtz powder technique is used to identify the materials with non-centrosymmetric crystal structures and is the most widely used technique for confirming the SHG efficiency of NLO materials. In order to confirm the NLO behavior of these material, powdered samples were subjected to Kurtz and Perry powder technique. The NLO property of the sample was tested using a Q-switched Nd: YAG laser beam of wavelength 1064nm and 10ns pulse width with an input rate of 10Hz. The output of the grown crystal was measured as 8mV while the KDP gave an SHG signal of 16mV for input beam energy of 6.5mJ/Pulse. The green radiation generated confirms the second harmonic signal generated in the crystalline sample. The standard NLO inorganic KDP was used as the reference material. The emission of green light (λ=532 nm) from the LLS crystals confirmed their noncentrosymmetric crystal structure. The SHG efficiency is decreased due to lower polarizing ability of the material.

4. CONCLUSION

L-lysine sulphate (LLS) single crystal was grown by slow evaporation technique. From the single crystal XRD data obtained, it is proved that the crystals belong to orthorhombic structure and non-centrosymmetric space group P2₁2₁2₁. The presence of a wide transparency window lying between 200 nm and 1200 nm with λ_{max} =240 nm is represented by the UV spectrum. The bandgap was estimated to be of 5.17 eV which is typical of dielectric material. The wide energy band gap confirms that the defect concentration in the grown crystal is very low and large transmittance in the visible region. The crystal possesses moderate mechanical stability which is confirmed by the Vickers microhardness analysis. By Meyer’s law, the value of Meyer’s index n estimated to be 3.65 indicates that the crystal belongs to soft material category and the dielectric property studied at room temperature indicates that the dielectric constant and dielectric loss decreases with the increase in frequency which is the normal behavior of nonlinear optical materials. The low dielectric constant and dielectric loss of the crystal in the high frequency region represent good optical quality. The nonlinear optical nature of the crystal was confirmed by Kurtz-Perry powder technique. The transmission near the Nd:YAG laser fundamental (1064 nm) and second harmonic wavelength (532 nm) is reduced. This reduction contributes to the resistance of the material to laser damage threshold. This transmission range of the crystal makes it valuable for applications that require blue green light. High frequency shift and good NLO property and other physicochemical properties make this material a good laser converter.

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References


