Linear and nonlinear optical properties of unidirectionally grown L-Threonine acetate single crystals

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Abstract. Unidirectional <1 1 0> L-Threonine acetate (LTA) single crystal was grown and reported. The grown crystal was characterized by powder X-ray diffraction (XRD) studies to confirm the crystal structure. The optical band gap (Eg) value of the grown crystal is obtained from the tauc’s plot of (αhν)² vs hν which was determined by extrapolating the linear region of the curve to the hν axis where (αhν)² = 0. Other linear optical parameters such as Extinction coefficient, Reflectance, Refractive index, Complex dielectric constant, and Optical conductivity are calculated for the grown crystal and its variation with incident photon energy is analysed. Second Harmonic Generating (SHG) efficiency of the candidate material was determined by Nd:YAG Q-switched laser Kurtz powder technique.

1. Introduction
Engineering of new nonlinear optical (NLO) materials, both organic and inorganic, structures and devices with enhanced figures of merit over the past two decades has become a major force to drive nonlinear optics from the laboratory to real applications [1]. The optical behavior of materials is an essential parameter to determine its usage in optoelectronic devices [2]. Knowledge of optical constants of a material such as optical band gap and extinction coefficient is vital to scrutinize the materials’ potential for optoelectronic applications [3]. The crystal with specific orientation can be grown from solution by Sankaranarayanan–Ramasamy (SR) method [4]. By this method the entire solute can be converted into crystal so that 100% solute–crystal efficiency can be achieved. In this paper we discuss the growth of Unidirectionally grown bulk L-Threonine acetate (LTA) single crystal along with linear and nonlinear optical properties and its variation with incident Photon energy.

2. Experimental Procedure
The experimental setup of SR method consists of growth ampoule made-up of glass with seed mounting pad [4]. The seed crystal from the conventional slow solvent evaporation technique was used for the current study. <110> plane of the seed crystal of LTA was chosen and it was transferred to the saturated solution of LTA. The chemical reaction involved for the grown L-Threonine acetate is given below:

\[ \text{C}_4\text{H}_9\text{NO}_3 + \text{CH}_3\text{COOH} \rightarrow \text{C}_4\text{H}_{10}\text{O}_3 + \text{CH}_3\text{COO}^- \]

Growth of highly transparent single crystal of LTA of 10mm diameter and 44 mm length was harvested (Figure 1.) in a period of 27 days and reported for the first time.
3. Characterization

3.1 Powder XRD studies
To identify the crystal structure of the grown crystal powder X-ray diffraction studies of LTA crystals were carried out using Siemens D500 X-ray diffractometer with Cu Kα (λ = 1.5418Å) radiation. The samples were scanned for 20 values from 10° to 70° at a rate of 2°/min. Powder XRD pattern LTA crystals are shown in Figure 2. The diffraction patterns of the LTA crystal are indexed by least square fit method. The lattice parameter values of the LTA crystal have been calculated and were found to be well matched with the reported literature [5]. LTA crystal crystallizes in to the orthorhombic crystal system with the space group of P2₁2₁2₁ and unit cell dimensions were found to be a = 5.542Å, b =8.131Å, c = 13.912Å. The volume of the system is V=626.903Å³.

3. Optical Properties of LTA
The optical absorption spectrum of LTA single crystal is shown in Figure 3. The spectra indicate that LTA crystal has minimum absorption in the entire visible and near infrared region. This data was further used for analyzing optical band gap energy (E_g) using the formula for optical absorption of

\[(\alpha h\nu) = k (h\nu-E_g)^{n/2}\]

n is an integer equal to 1 for a direct band gap and 4 for an indirect band gap. The values of the direct optical band gap E_g were obtained from the intercept of (αhν)² versus hν curve plotted in Figure 4. The intercept obtained by the extrapolation of the linear portion of the plot to energy axis gives the band gap energy of the crystal. The band gap is found to be 4.5 eV. The other optical constants were calculated using the theoretical formulae reported elsewhere [6,7]. Figure 5 and Figure 6 shows the plot of extinction coefficient and reflectance against incident photon energy.
Figure 3. Optical absorption spectrum of LTA

Figure 4. Energy band gap of LTA

Figure 5. Extinction coefficient Vs Incident Photon Energy of LTA

Figure 6. Reflectance Vs Incident photon energy of LTA

Figure 7. Refractive index Vs Incident photon energy of LTA

Figure 8. Complex dielectric constant Vs Incident photon energy of LTA
It’s found that extinction coefficient remains constant for incident photon energy of 1.2 eV to 5.5 eV and reflectance increases linearly with photon energy Figure 7 depicts the variation of refractive index with incident photon energy. Initially the refractive index decreases with increasing photon energy then becomes constant. Variation of complex dielectric constant and optical conductivity of the material with incident photon energy is analysed from Figure 8 and Figure 9. The high optical conductivity (10^9) confirms the high photo response nature of the material.

4. SHG Efficiency Studies
The quantitative work was done on powdered single crystal of LTA and they were graded by the use of standard sieves to desire the range of particle sizes. A relevant comparison was made on KDP with LTA. The reference material was also powdered and used for further studies [8]. The experimental samples reported an input pulse of 6.2 mJ, the second harmonic signal (532 nm) of 89.52 mW for KDP and 268.56 mW for LTA. It is thus elucidated that the SHG efficiency of LTA is 3.0 times higher than that of KDP.

5. Conclusion
Good quality single crystal of L-Threonine acetate has been grown successfully by the unidirectional solution growth SR method. It is understood from the present work that the SR technique was found to be suitable method to grow high quality and large-size single crystal of L-Threonine acetate. Optical absorption spectrum was recorded for the given crystal and it is found that it has minimum absorption between 240 -1000 nm. The optical band gap of the material is found as 4.5 eV. Various linear optical constants like extinction coefficient, reflectance, refractive index, complex dielectric constant and optical conductivity are calculated and related with incident photon energy. This optical analysis reveals the NLO behavior of the material.

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