Investigation of 2nd Order Nonlinear Optical Property Semi organic L-Tyrosine Barium Chloride Single Crystal for Photonic applications

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Abstract

New bulk size single crystals of L-Tyrosine Barium Chloride LTBC have been synthesized from the solution prepared from the blend of tyrosine and barium chloride using slow evaporation solution growth method. Single crystal X-ray diffraction analysis shows the grown crystal crystallized in orthorhombic system with non-centrosymmetric space group P. Fourier transform infrared spectral studies revealed the orientation of discrete functional group in the grown crystal. The optical absorption studies show the material has largish optical transparency in the total visible region. The band gap energy values were also determined by using the optical studies. SHG efficiency was confirmed by Kurtz Perry powder technique. The thermal stability of LTBC crystals was analyzed by DSC technique. The electrical behavior of the crystal was studied by dielectric method. The SEM image expelled the surface morphology of the grown crystal. The hardness values of crystal were estimated by Vickers micro hardness tester and other such properties show the suitability of the LTBC crystal for photonic and optoelectronic applications.

1. Introduction

In the arena of device fabrication, the growth of bulk size single crystals is crucial. Especially, for fabrication of Opto-electronic and photonic devices and in Laser processing the semi organic nonlinear optical single crystals are fundamental. Exactly due to this reason, sweeping research were initiated focusing onto formulate highly efficient new nonlinear optical (NLO) crystal material that operate on less cutoff wavelengths [1-5]. The development the semi organic NLO crystals and its subsequent applications in photonic and optoelectronic integrated chip manufacturing have to be attributed to lot of specific reaserch in them [6-13]. Consequently, in the current scenario, it is imperative to grow semi organic bulk size single crystals with consistent organic and inorganic properties.

This paper is a report of high-quality L-Tyrosine Barium Chloride single crystals synthesized by slow evaporation solution growth technique. The results of various analyses done on LTBC irrefutably suggest this crystal to be advantageous in the engineering of optoelectronic and photonic devices.

1.1. Materials

A premium quality of L-Tyrosine ($C_9H_{11}NO_3$) and Barium Chloride ($BaCl_2$) procured from Merch Company has been used in the synthesis of the crystal by using deionized water as a solvent.

1.2. Crystal growth

It is common to use the slow evaporation solution growth technique to develop the organic, inorganic and semi organic crystals under normal room temperature. The equimolar ratio of title compounds L-Tyrosine and barium chloride were dissolved using aqueous solution as solvent. The resultant solution was incessantly stirred using a magnetic stirrer for 12 hours. After ascertaining the whole disbanding of parent compound, a homogenous clear keen solution was filtered off in to a crystal growth vessel, which is then tightly packed in perforated filter sheet. This solution was left for slow evaporation without any

disturbance at normal temperature. A virtuous quality single crystal has been made within 35 days. The grown crystal is indicated in figure 1.

2. Discussion

2.1. Single crystal X-Ray diffraction

To measure the lattice parameters of the single crystal, the optical good quality LTBC was subjected to single crystal X-ray diffraction analysis by BRUKER KAPPA APEX II CCD. The title compound was crystallized in orthorhombic system with non-centrosymmetric space group P_2 . The lattice parameters are $a=6.78\text{\AA}$, $b=7.16\text{\AA}$, $c=10.95\text{\AA}$, $\alpha=90^\circ$, $\beta=90^\circ$, $\gamma=90^\circ$ and $V=532\text{\AA}^3$.

2.2. FTIR analysis

A PERKIN ELMER Fourier transform infrared spectrometer with KBr pellet technique has been employed to analyse the different functional groups present in the LTBC. Fourier transform infrared (FTIR) spectrum was recorded in the range of 4000 to 400 cm^{-1} as shown in Fig. 2. The far-reaching peaks about 2000 and 3500 cm^{-1} contains overlap of absorption peaks due to O-H stretch of -COOH and phenolic O-H, and N-H stretch of NH_3^+ . The CH_2 vibration group lies under 3000 cm^{-1} . The widening of peak in this region is owing to hydrogen bonding. Overtones and combination bands with protruding peaks near 2200 and 2000 cm^{-1} are attributed to barium chlorides in FTIR spectrum. In the finger print region of FTIR spectrum, the C=O vibration of -COOH lies at 1715 cm^{-1} . The bending modes of NH_3^+ befalls approximately at 1636 and 1601 cm^{-1} . The CH_2 bending modes can be seen at 1365 cm^{-1} . The para substitution in the aromatic ring is established by the peak at 696 cm^{-1} . The peaks detected at 525 cm^{-1} is due to C-C-C out of plane bending C1-H bending + C-C-C out of plane bending.

2.3. Optical absorption studies

To discover the utility of LTBC single crystal in optical applications, it is endorsed that to subject them to optical absorption studies. The spectrum was recorded using Varian carry 5E India spectrophotometer in the range of 200 - 1000 nm . Fig. 3 illustrates the noted spectrum of the LTBC crystal. The cutoff wavelength, 212 nm , falls in the ultra violet region and there is no transparency ensues in the entire visible region. These characters demonstrate that the LTBC crystal can be more active in the second harmonic generation applications [14].

2.3.1. Energy band gap

The Touch's relation helps to deduce the optical absorption coefficient (α) of LTBC crystal [15].

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

Fig. 4. displays the Tauc's plot of $(\alpha h\nu)^2$ vs $h\nu$ that has been plotted to estimate the energy band gap value, where α is the absorption coefficient, $h\nu$ is the photon energy(eV) and E_g is the optical band gap energy. The inference of linear portion of the graph gives the optical band gap E_g of LTBC crystal. The value of E_g is found to be as 6.34eV. There is direct proportional rise in the optical energy band gap with more defect's concentration in grown crystal. For optoelectronic applications, wide optical band gap energy and less crystal defects, in the grown LTBC crystal are desired.

2.4. SHG analysis

The Kurtz-Perry powder setup has been employed to analyze the LTBC crystal's second harmonic generation efficiency. A 1064 nm, fundamental wavelength, Q-switched Nd-YAG laser with a pulse width of 8 ns and repetition rate of 10 Hz was used. The grained grown crystals were filled in a uniform micro-capillary tube and exposed to laser radiations. A monochromatic, high intensity of 532 nm beam was emitted by the sample [16]. The SHG efficiency, 1.7 times greater than that of KDP crystal was detected by the emission of green light radiation.

2.5. Thermal analysis

The grown LTBC crystal was subjected to the thermal stability study in a Differential scanning calorimeter (DSC) using NETZSCH STA 409C instrument in the temperature range of 50-300°C at a heating rate of 10°C/min in a nitrogen atmosphere and the samples were placed in the aluminum crucible. The Fig.5 shows the DSC curve of LTBC crystal. The exothermic peak at 102°C predicts that the material will be thermally stable and should be absent of any heat losses. The lack of water while synthesizing the structure is distinguished with the absence of the weight loss and there is no decomposition near the melting point. This property of the grown crystal is apt for applications at high temperature like laser heat treatment. Almost nil phase transition till the crystal melts enhances the temperature range ability of the crystal. The phase transition here refers to common phase transitions like, solid-to-liquid, liquid-to-gas etc.

2.6. Dielectric studies

The HIOKI 3532-50 LCR HITESTER meter measured the dielectric constant and dielectric loss. The graph is shown in Fig 6 (a) and (b). In the temperature range of 313, 333, 353, and 373 K the dielectric constant of the crystal is inversely proportional to frequency. The space charge polarization could be the reason for the large value of ϵ_r at lower frequency [17]. It is apparently seen in Fig. 6 (a) that the crystal has very less dielectric loss at the higher frequency region, indicating the number of imperfections in the crystal are at a low. The direct dependence of both dielectric constant and dielectric loss with temperature can be noticed. A low dielectric loss at large frequency is an appreciable optical quality of the crystal with lesser impurities and also the common property required for all NLO applications. The grown crystal with its low dielectric constant is a competent NLO material to be used as substrate for opto-electronic modulators and in microelectronic foundaries.

2.7. Scanning Electron Microscope analysis

The surface morphology and imperfections in the LTBC crystal are observed using Scanning electron microscope (SEM) technique, a HITACHI S4800 instrument [15] shown in Fig.7 has been used. The rift of layer over the surface of the crystal at 5µm scale is expressed. It is evident that the LTBC crystal has stepped growth due to the ceaseless rate of evaporation of solvent at normal temperature.

2.8. Micro hardness studies

To discover the mechanical strength of the LTBC crystal, the micro hardness testing is indispensable. Lattice energy, Debye temperature, interatomic spacing and formation of heat are the parameters which determine the hardness of the crystal. The study, with applied loads of 20, 40, 60, 80 and 100 g has been done using HMT 2 T, Vickers's micro hardness instrument at normal temperature. No less than four well distinct impressions were found and the average of all the diagonals (d) was measured. The hardness specifies the function of applied load and the diagonal of the indent [18]. The Vickers micro hardness value was calculated using the standard relation

$$H_v = 1.8544(P/d^2) \text{ kg/mm}^2 \quad (4)$$

Here P is the applied load in g and d is the conservative diagonal length of the indentation in mm, and 1.8544 is a constant of geometrical factor. The Fig. 8 (a) shows the graph plotted between the variation of hardness number (Hv) and applied load range from 20 g to 100 g for grown LTBC crystal. It can be seen that the value of Hv rises with increase in the load which underscores the reverse indentation size effect [RISE]. The hardness of the crystal begins to decrease due to the release of internal stress by the load applied at different indent [19].

Mayer Index (n)

The Meyer's coefficient was determined by using Meyer's law, this relates the applied load P and indentation diagonal strength d is given by,

$$P = k_1 d^n \quad (5)$$

(or)

$$\log P = \log k_1 + n \log d \quad (6)$$

To determine the work hardening coefficient value 'n', a graph is plotted between log P vs log d as shown in Fig. 8 (b). The straight line obtained from the slope expels the value of 'n' and it is found to be 4.1405. For standard ISE virtue, we have $n < 2$. When $n > 2$, there is a reverse ISE virtue. This is well related to the experimental data and thus confirms the reverse ISE. The work hardening coefficient 'n' occurs between 1 and 1.6 for harder materials and above 1.6 for softer materials as given by Onitsch [20]. The grown LTBC

crystal with work hardening coefficient 'n' of 1.8460 shows that the LTBC crystal is under soft material category. Thus, the grown crystal can be considered as fit material for laser based applications.

3. Conclusions

Semi organic, NLO quality, transparent single crystals of LTBC were synthesized from aqueous solution through slow evaporation method. The lattice parameters of the crystal were determined by single crystal XRD, the crystal can crystallize in orthorhombic system with space group P. The presence of barium chloride in the crystal lattice of tyrosine was identified by FTIR spectral analyses. Optical studies show the material has lower cut-off wavelength at 212 nm. Using optical study, the band gap energy values were calculated. The SHG efficiency of LTBC is 1.7 times that of KDP crystal which was performed by non-linear optical studies. The thermal studies show that the materials possess optimum thermal stability. Dielectric constant decreases with increase in frequency and very low value of dielectric loss infer very high purity of the crystal. The SEM study shows the surface morphology of the crystal. The mechanical properties of the grown crystal were studied using Vickers micro hardness tester and suggest that the material belongs to soft material category. The present characterization report adverts that the grown crystal is suitable for the upcoming modulation, switching and optoelectronic device applications.

Declarations

Competing interests: The authors declare no competing interests.

References

- [1] C. Zhang, Z. Li, H. Cong, J. Wang, H. Zhang, R.I. Boughton, Journal of Alloys and Compounds. 507, 335–340 (2010)
- [2] S.A. Oliver, App. Phys. Lett. 76, 3612 (2000)
- [3] Mohd Shakir, B. Riscob, K.K. Maurya, V. Ganesh M.A. Wahab, G. Bhagavannarayana, Journal of Crystal Growth. 312, 3171-3177 (2010)
- [4] V. Chithambaram, S. Krishnan, Synthesis, optical and thermal studies on novel semi organic nonlinear optical Urea Zinc Acetate crystals by solution growth technique for the applications of optoelectronic devices. Optics and Laser Tech. 55, 18-20 (2014)
- [5] D. Sonal, S. Gupta Ranjith, A. Pardhan, D. Maeano, Nouredine Melikechi, Desai CF, J. Appl. Physics. 91 (5), 3125-3128 (2002)
- [6] R. Uthrakumar, C. Vesta, G. Bhagavannarayana, R. Robert, S. Jerome Das, Journal of Alloys and Compounds. 509, 2343–2347 (2011)

- [7] P.V. Dhanaraj, N.P. Rajesh, G. Bhagavannarayana, *Physica B, Condensed Matter*. 405, 3441–3445 (2010)
- [8] Dennis J & Henisch H K, *J. Electrochem. Soc. USA*, 114, 263 (1967)
- [9] S. Arjunan, A. Bhaskaran, R. Mohan Kumar, R. Mohan, R. Jayavel, *Journal of Alloys and Compounds*. 506, 784–787 (2010)
- [10] M.H. Jiang, Q. Fang, *Advanced materials*. 11, 1147-1151 (1999)
- [11] J.M. Linet, S. Dinakaran, S.J. Das, *Journal of Alloys and compounds*, in press.
- [12] S. Aripnammal, S. Radhika, R. Selva, N. Victor Jeya, *Crystal Research Technology*. 40, 786-788 (2005)
- [13] J. Ramajothi, S. Dhanuskodi, K. Nagarajan, *Crystal Research Technology*. 39, 414-420 (2004)
- [14] V. Chithambaram, S. Jerome Das, R. Arivudai Nambi, K. Srinivasan, S. Krishnan. Effect of metallic dopants on potassium acid phthalate (KAP) single crystal,. *Physica B*. 405, 2605-2609 (2010)
- [15] N. Saravanan, S. Santhanakrishnan, S. Suresh, S. Sahaya Jude Dhas, P. Jayaprakash, V. Chithambaram, Crystal growth and investigation of novel semiorganic single crystal: L-malic acid sodium nitrate for photonic applications. *J. Material Science*. (2018)
- [16] Kurtz. SK, Perry TT, *J App Phy*, 39, 3798 (1968)
- [17] V. Chithambaram, S. Jerome Das, S. Krishnan, Synthesis, Optical and dielectric studies on novel semi organic nonlinear optical crystal by solution growth technique., *J. Alloys and Compounds*. 509, 4543-4546 (2011)
- [18] R. Vivekanandhan, K. Raju, V. Ravisankar, V. Chithambaram, Growth and characterization of novel nonlinear optical L-Valine zinc chloride single crystal grown by slow evaporation technique, *J. Pure and Applied mathematics*, 115, 281-285 (2017)
- [19] N. Saravanan, V. Chithambaram, V. Ravisankar, Growth and characterization of novel semi organic nonlinear optical urea lead acetate single crystal by solution growth technique. *J. material science*. 29, 5009-5013 (2018)
- [20] E.M. Onitsch, *Mikroscopia*. 2, 131-151 (1947)

Figures

Figure 1

Photograph of grown LTBC crystal.

Figure 2

FT-IR Spectrum of LTBC crystal.

Figure 3

UV-vis spectrum.

Figure 4

Tauc's plot of LTBC.

Figure 5

DSC Thermal Analysis.

Figure 6

(a). Plot of log frequency vs dielectric loss of LTBC. (b). Plot of log frequency vs dielectric constant of LTBC.

Figure 7

SEM image of grown crystal.

Figure 8

(a) Variation of (Hv) with load P. (b) Plot of log P with log d for LTBC.