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Synthesis, Unidirectional Growth, Optical and Conductivity Studies of Single Crystals of L-Tartaric Acid

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Oriented organic crystals along prerequisite direction are very important in terms of reducing loss of material and cost during nonlinear optical device fabrication. The L-tartaric acid single crystal was successfully grown by unidirectional modified Sankaranarayanan-Ramasamy method at ambient temperature for the first time and the growth conditions are optimized. The grown single crystal has been subjected to different characterization analyses in order to find out its suitability for device fabrication. The optical properties of the Sankaranarayanan-Ramasamy method grown crystal are found to be better than the crystal grown by the conventional slow solvent evaporation technique. The AC conductivity and dielectric studies are carried out for the grown crystal.

Key Words: Organic nonlinear optical material, UV-Vis-NIR, AC Conductivity, Amino Acid, Dielectric constant.

INTRODUCTION

Organic nonlinear optical (NLO) crystals are gaining more attention due to their high nonlinearities and rapid response in the electro-optic effect compared to inorganic organic nonlinear optical counterparts. High quality phase matched second harmonic generation (SHG) single crystal is the current interest in the field of organic nonlinear optical materials. Various methods have been employed to grow bulk organic single crystals at selected orientation towards a phase matched direction.

A novel unidirectional crystal growth method has been recently developed and reported by Sankaranarayanan and Ramasamy[1,2]. The Sankaranarayanan and Ramasamy method, which was originally designed to grow large size organic crystals, is now turning out to be the best method not only for the organic crystals but also for the inorganic and semiorganic crystals. Its success has been now demonstrated by several research groups with the growth of high quality unidirectional bulk size crystals such as KDP[3], ADP[4], BTZC[5], L-MHCl[6], benzophenone[7], KAP[8] and TGS[9].

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The orientation of the growing crystal is imposed by means of a seed fixed at the bottom of ampoule. The effectiveness of Sankaranarayanan and Ramasamy method[1,2] lies on the fact that the entire quantity of the solute gets converted into crystal and thus remarkable 100 % solute-crystal conversion efficiency is achieved. The growth direction is imposed by suitably mounting the seed and minimum thermal stresses on the crystal during growth and also the growth rate at different planes can be measured. In addition, to the growth of bulk size crystals in preferred orientation, the method is proven to be economically more viable and simple in comparison to the existing techniques. By virtue of Sankaranarayanan and Ramasamy method[1,2], the usually observed microbial growth in amino-acid based solution can be suppressed. Further, in solution growth method, many of the commonly observed characteristic growth-induced defect structure comprising growth sectors and boundaries, growth banding, solvent inclusions, dislocations, twins and stacking faults can be attributed to impurities[10]. Besides, the relatively low growth efficiency, the common problem to all the above methods is that it is difficult to control the growth of crystal along a given direction. In other words, the grown crystals must be cut and polished to obtain the specific crystal faces before they are applied as a nonlinear optical device. Many methods have been developed for cutting cylindrical crystals[11,12]. Unfortunately, the cutting and polishing in a desired direction as phase matching angle are difficult for organic NLO crystals because of their poor chemical stability and brittleness. Cutting and machine working of single crystals result in the appearance of structural defects and what is most important, in these processes the expensive material ends up as scraps. To minimize the above problems, in the present case L-tartaric acid (LTA) crystals were grown with specific orientation in a growth vessel at room temperature employing the modified Sankaranarayanan and Ramasamy method[1,2]. Since L-tartaric acid has higher solubility in water it could be crystallized into bigger size and another added advantage is the low cost of the material when compared to the other amino-acid NLO materials. The growth conditions and experimental details are presented.

On the search of new NLO materials with better mechanical properties, many researchers have focused on the small organic molecules having a large dipole moment and a chiral structure. These molecules are usually linked through the hydrogen bond. The tartaric acid forms a broad family of hydrogen-bonded crystals. Because of the ability of enhancing the macroscopic nonlinearity in a synergistic mode and initiating multidirectional hydrogen bonds, tartaric acid was chosen to synthesize nonlinear materials. Tartaric acid belongs to monoclinic crystal system having the lattice dimensions a = 6.203 Å, b = 6.018 Å and c = 7.720 Å[13]. It has good thermal stability (m.p. *ca.* 170 °C). The crystal has a SHG efficiency which is nearly equal to that of KDP and a relatively high laser damage threshold of 5.4 GW/cm^2 and thus making it a potentially useful material in nonlinear optics[13].

Though the growth of tartaric acid has been reported in the past, the previous works were confined to conventional techniques and for the first time the unidirectional growth of bulk size L-tartaric acid crystal employing the Sankaranarayanan and Ramasamy method is reported in this article. Similarly, the earlier studies are limited to selected optical properties[13,14]. Hence, an attempt has been made in this work to further improve the growth of L-tartaric acid crystal and investigate its optical and electrical properties. The Sankaranarayanan and Ramasamy method grown crystals of L-tartaric acid are subjected to the optical absorption studies to estimate the band gap and to identify the optical transmission window. The AC conductivity and dielectric studies are carried out as a function of frequency/temperature.

EXPERIMENTAL

The most essential feature of the growth of high optical quality crystal is the purification of the raw material[15]. To improve the purity of the material, recrystallization is one of the best methods. In the present study, the commercially available salt of L-tartaric acid with purity (SD Fine chemicals, 99 %) was dissolved in double distilled water and purified by the recrystallization processes and the recrystallized salt was used as the charge material for preparing the saturated solution. Three times recrystallized material was used for the growth. The seed crystals were prepared from the slow evaporation solution growth technique. The defect free, good quality single crystal was used as seed for the growth purpose.

The Sankaranarayanan and Ramasamy method[1,2] setup used in the present study is shown in Fig. 1. The ampoule or container used in this method is made up of an ordinary hollow glass tube with a tapered V-shaped bottom to mount the seed crystal and U-shaped top portion to a fill a good amount of supersaturated solution to grow a relatively good size crystal. The ring heater was connected to temperature controller and it provides the necessary temperature. Prior to crystal growth experiment, the growth ampoule was cleaned and pre-annealed to avoid any surface contamination from the wall of the ampoule. For controlled evaporation, the top portion was closed with some opening at the center. The seed was carefully mounted in the bottom of the glass tube, by choosing the < 110 > direction of the seed crystal parallel to the length of the glass tube. Before the saturated solution was prepared, the L-tartaric acid material was purified by repeated recrystallization processes. The recrystallized salt was used to prepare the supersaturated solution using double distilled water as the solvent. Then, the solution was filtered using Whatman filter paper. The filtered solution was taken in a beaker and then carefully decanted into the glass tube without disturbing the specimen seed. The top portion of the tube was covered by a plastic sheet with a hole at the center to limit the evaporation. Then, the whole tube was housed in a constant temperature bath with a setting temperature of 25 ºC, which is the optimized growth temperature. The experimental conditions were closely monitored and we found the seed crystal growing after 5 days. In a time span of 60 days, a good quality single crystal of L-tartaric acid 42 mm length 12 mm diameter was harvested from the glass tube. The as grown and the cut and polished sections of L-tartaric acid crystals are shown in Fig. 2. This is achieved by periodically feeding

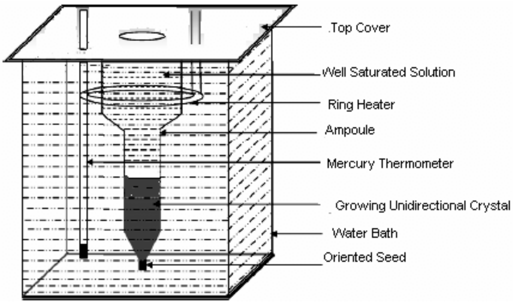

Fig. 1. Sankaranarayan and Ramasamy method growth setup

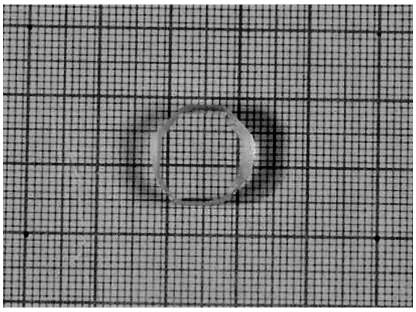

Fig. 2. Cut and polished ingots of L-tartaric acid single crystal grown by Sankaranarayan and Ramasamy method

the freshly prepared solution during the growth process to suppress the microbial growth, if any. In order to estimate the crystalline quality and the properties of the grown sample, various characterization studies have been carried out.

RESULTS AND DISCUSSION

Single crystal XRD analysis: The grown crystal was subjected to single crystal X-ray diffraction studies using Enraf Nonius CAD-4 single crystal X-ray diffractometer with MoK$_\alpha$ radiation ($\alpha = 0.7170$ Å) to solve the three dimensional structure. The calculated lattice parameters of L-tartaric acid are a = 6.202(5) Å, b = 6.016(3) Å and c = 7.715(6) Å, $\beta = 100.10°(2)$. The XRD data prove that the crystal is monoclinic in structure with the noncentrosymmetric space group P2$_1$. The XRD data almost fits well with the earlier work[16].

Optical absorption spectral study: The UV-vis -NIR spectrum of LTA crystal was recorded in the wavelength range between of 190-1100 nm, using Lamda 35 UV-Vis spectrophotometer (Fig. 3). UV-vis-NIR spectrum gives information about the structure of the molecule and the absorption of UV and visible light involves promotion of the electron in the σ and π orbital from the ground state to higher states[17]. The Sankaranarayanan and Ramasamy method grown L-tartaric acid crystal has excellent transmission in the entire visible region and the lower cut off wavelength is 220.15 nm. Thus the cut-off wavelength of L-tartaric acid is lower than some of the well known LAP family of crystals like LHB (290 nm)[18], LHPC (310 nm)[19] and LHFB (270 nm)[20].

Thus, the large transmittance window in the entire visible-NIR region enables very good optical transmission of the second harmonic frequencies of Nd:YAG laser. The low value of cut-off wavelength and the large transmittance window are the most desirable properties of the crystals used for NLO applications.

The direct band gap value of L-tartaric acid crystal has been calculated from $(\alpha h\nu)^{1/2}$ *versus* $h\nu$ (Fig. 4) plots. The direct band gap energy (E_{gd}) of L-tartaric acid is found to be 4.81 eV. From the absorbance spectra it is suggested that there is no remarkable absorption in the entire region of the spectra. It is an important requirement for the materials having nonlinear optical properties[21].

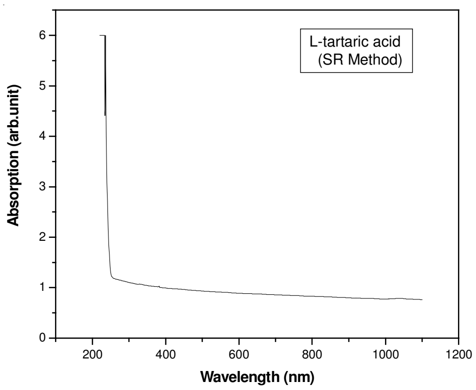

Fig. 3. UV-Vis and NIR absorption spectrum of L-tartaric acid

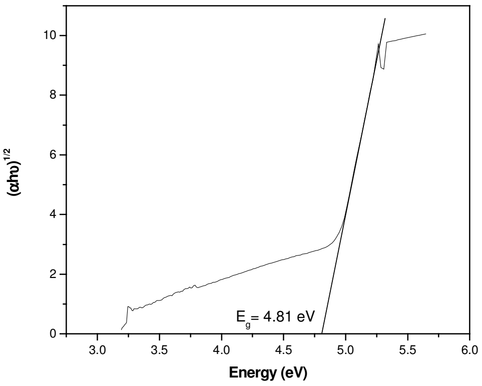

Fig. 4. Tauc's plot of L-tartaric acid

Dielectric measurements: Dielectric characteristics of the materials are carried out to study the lattice dynamics of the crystals[22]. It is an important tool to understand the nature of defects on the grown crystal[23]. The sample was prepared from the large crystal by thinning it to the appropriate thickness. Silver coating was applied on opposite faces to establish Ohmic contact, to make a capacitor with the crystal as the medium. The dielectric constant is calculated using the equation,

$$\varepsilon_r = Cd/\varepsilon_o A$$

where, A is the area of the sample, C is the capacitance and d is the thickness of the sample. The dielectric constant (ε_r) and the dielectric loss (tan δ) of the L-tartaric acid sample were measured at different temperatures using HIOKI 3532-50 LCR Hitester in the frequency region 100 Hz to 1 MHz. Figs. 5 and 6 show the variations of dielectric constant and dielectric loss with log frequency. The decrease is rapid in the low frequency region and then it starts decreasing very slowly. In high frequency region, both dielectric constant and dielectric loss are fairly remaining constant. The high dielectric constant at low frequency is due to the presence of all types of polarizations *viz*., electronic, ionic, orientation, space charge polarization, *etc*. The space charge polarization depends on the purity and perfection of the sample. Its influence is large at high temperature and is noticeable in the low frequency region. The larger values of ε_r and tan δ at lower frequencies may be attributed to space charge polarization due to charged lattice defects.

AC Conductivity study: Small signal AC impedance analysis is a powerful technique for the electrical characterization of materials. The AC conductivity measurements were taken using HIOKI 3532-50 LCR Hitester in the frequency range 100 Hz to 1 MHz. The sample was subjected to a temperature variation from 303-384 K. The AC conductivity was calculated using the formula; $\sigma = \omega\varepsilon_r \tan \delta\varepsilon_o$ (where, ε_o is the vacuum dielectric constant) at different temperatures[23,24]. The Arrhenius plot of log σT *versus* 1000/T is shown in Fig. 7. It is evident from the graph that the conductivity increases with temperature. The value of activation energy for ionic migration was estimated from the graph.

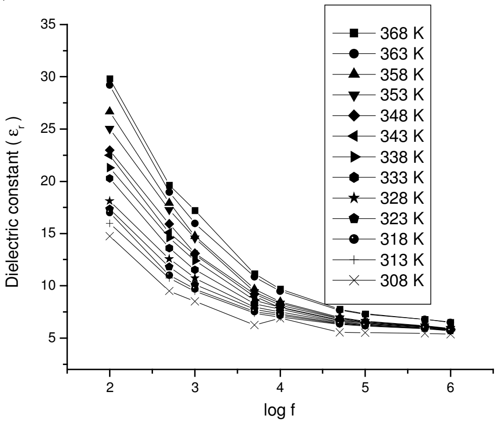

Fig. 5. Variation of dielectric constant of L-tartaric acid with frequency at different temperatures

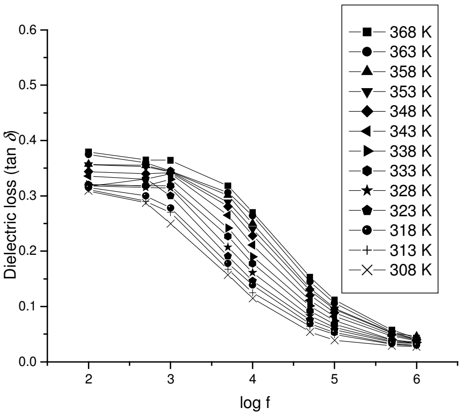

Fig. 6. Variation of dielectric loss of L-tartaric acid with frequency at different temperatures

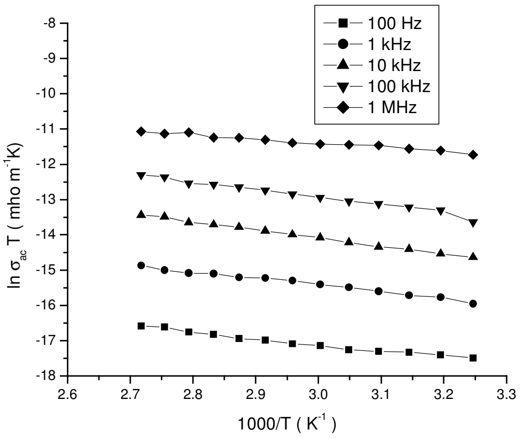

Fig. 7. AC Conductivity plot for L-tartaric acid crystal

The line of best fit for the plot of ln σT *versus* 1/T obeys Arrhenius relationship, $\sigma T = \sigma_o \exp(-E_a/kT)$ where, σ_o is the pre-exponent factor, E_a the activation energy for the conduction process and k is the Boltzman's constant. Therefore, the sample exhibits Arrhenius type conductivity behaviour in the temperature range of investigation. From the conduction process, the activation energy of L-tartaric acid is found to be 0.21 eV.

Conclusion

The growth of L-tartaric acid crystal has been achieved with success by unidirectional solution growth Sankaranarayanan and Ramasamy method for the first time. The grown crystal is transparent and the microbial growth has been avoided by optimizing the growth condition. From the optical absorption study the good optical grade of the L-tartaric acid crystal is confirmed. The relative lower cut off wavelength of L-tartaric acid is an important criterion for utilizing its NLO properties. The dielectric studies prove that the sample has low dielectric constant and dielectric loss values at high frequency. The AC conductivity study confirms that the sample exhibits Arrhenius type conductivity and the corresponding activation energy is found to be 0.21 eV.

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REFERENCES

1. K. Sankaranarayan and P. Ramasamy, *J. Cryst. Growth*, **280**, 467 (2005).
2. K. Sankaranarayan and P. Ramasamy, *J. Cryst. Growth*, **284**, 203 (2005).
3. N. Balmurugan and P. Ramasamy, *Cryst. Growth Design*., **6**, 1642 (2006).
4. K. Sethuraman, R. Ramesh Babu, R. Gopalakrishnan and P. Ramasamy, *J. Cryst. Growth*, **294**, 349 (2006).
5. S.K. Kushwaha, N. Vijayan and G. Bhagavannarayana, *Mater. Lett*., **62**, 3931 (2008).
6. R.R. Babu, K. Sethuraman, R. Gopalakrishan and P. Ramasamy, *J. Cryst. Growth*, **297**, 356 (2006).
7. P. Ramasamy, *J. Cryst. Growth*, **310**, 1501 (2008).
8. N. Balamurugan, M. Lenin and P. Ramasamy, *Mater. Lett*., **61**, 1896 (2007).
9. N. Balamurugan, M. Lenin, G. Bhagavannarayana and P. Ramasamy, *Cryst. Res. Technol*., **42**, 151 (2006).
10. H.G. Gallagher, R.M. Vrcelj and J.N. Sherwood, *J. Cryst. Growth*, **250**, 486 (2003).
11. F. Barbieri and J. Durand, *Rev. Sci. Instrum*., **27**, 871 (1956).
12. R. Pepinsky, *Rev. Sci. Instrum*., **24**, 403 (1956).
13. S.A. Martin Britto Dhass, M. Suresh, G. Bhagavannarayana and S. Natarajan, *J. Cryst. Growth*, **309**, 48 (2007).
14. S. Debrus, M.K. Marchewka, J. Baran, M. Drozd, R. Czopnik, A. Pietraszko and H. Ratajczak, *J. Solid State Chem*., **178**, 2880 (2005).
15. C.G.C. Catesby, *Acta Cryst*., **16**, 392 (1963).
16. Y. Okaya and N.R. Stemple, *Acta Cryst*., **21**, 237 (1966).
17. R. Sankar, C.M. Raghavan, M. Balaji, R.M. Kumar and R. Jayavel, *Cryst. Growth Design*, **7**, 348 (2007).
18. R. Ittyachan and P. Sagayaraj, *J. Cryst. Growth*, **249**, 557 (2003).
19. R. Ittyachan, S.X. J. Raja, S.A. Rajasekar and P. Sagayaraj, *Mater. Chem. Phys.*, **90**, 10 (2005).
20. S. Dhanuskodi and J. Ramajothi, *Cryst. Res. Tech*., **39**, 592 (2004).
21. N. Vijayan, R.R. Babu, R. Gopalakrishnan, S. Dhanuskodi and P. Ramasamy, *J. Cryst. Growth*, **236**, 407 (2002).
22. R.R. Babu, K. Sethuraman, N. Vijayan, G. Bhagavannarayana, R. Gopalakrishnan and P. Ramasamy, *Cryst. Res. Technol*., **41**, 906 (2006).
23. B.S. Acharya and M.L. Mukherjee, *Indian J. Pure Appl. Phys*., **22**, 252 (1984).
24. R. Reddy, V.R. Kumar and V. Veeraiah, *Indian J. Pure Appl. Phys*., **33**, 48 (1995).

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