

Scholars Research Library

Archives of Applied Science Research, 2014, 6 (2):90-98 (http://scholarsresearchlibrary.com/archive.html)



Thermal and electrical behavior of organic nonlinear optical single crystals: L-Leucinium oxalate (LLO)

P. Baskaran^a, S. Rajasekar^b, M. Kumar^c, M. Vimalan^{d*} and K. Selvaraju^{a**}

^aPG & Research Department of Physics, Government Arts College, Ariyalur, Tamil Nadu, India ^bDepartment of Physics, Syed Ammal Engineering College, Ramanathapuram, Tamil Nadu, India ^cDepartment of Physics, Arignar Anna Government Arts College, Cheyyar, Tamil Nadu, India ^dDepartment of Physics, Thirumalai Engineering College, Kancheepuram, Tamil Nadu, India

ABSTRACT

Single crystals of L-Leucinium Oxalate (LLO), an organic nonlinear optical (NLO) material have been successfully grown by slow solvent evaporation technique. The grown crystal was characterized by single crystal X-ray diffraction analysis. The optical properties of the grown crystals have been investigated by using UV-Vis-NIR spectrum. The thermal stability of the grown crystal has been investigated using thermo gravimetric analysis. The field dependence of dark and photo current of LLO were reported. The response of dielectric constant in the frequency region of 50 Hz to 5 MHz has been investigated. The second harmonic generation (SHG) in the sample was confirmed and compared with KDP by Kurtz powder technique.

INTRODUCTION

In the last several decades, Non-Linear Optical (NLO) materials have attracted much attention due to their potential uses in many fields of photonics, such as optical modulation, optical switching, optical logic gates, frequency shifting, color displays and optical data storage for the developing technologies in telecommunication and in efficient signal processing [1-3]. In these respect amino acids based crystals are playing vital role in photonic applications. Most of the natural amino acids show potential nonlinear optical effect. In amino acid, the tetrahedral array of four different groups about α-carbon atom confers its optical activity. In solid state, amino acid contains a deprotonated carboxyl acid group (COO⁻) and protonated amino group (NH₃⁺). This zwitter ionic nature favours crystal hardness, thus making them ideal candidates for NLO devices. But amino acids are organic materials so they can have very large nonlinear susceptibilities relative to inorganic crystals but exhibit low damage threshold and poor processibility [4-8]. Recently, single crystals of amino acid family have gained importance due to the fact that the amino acids form complexes with simple organic salts and show interesting properties from the application point of view. In the well-known amino acid salts of L-arginine trifluoroacetate crystal, L-arginine bis (trifluoroacetate) crystal, glycinium oxalate and L-alanine oxalate were successfully met these requirements [9-13]. In the same way, recent studies suggested that many oxalates of amino acid family are also predominant Second Harmonic Generation (SHG) active [14]. L-Leucinium Oxalate (LLO) is one such an organic nonlinear optical (NLO) crystal with molecular formula C₈H₁₅NO₆, its structure has been solved by Rajagopal et al. [15]. The present investigation deals with the growth of LLO single crystal by slow solvent evaporation technique. The grown crystal has been subjected to XRD, UV-Vis-NIR, SHG, thermal, dielectric, photoconductivity and ac/dc conductivity studies. The results of these investigations are reported and discussed.

MATERIALS AND METHODS

The starting materials of high purity L-Leucine and oxalic acid were taken in the ratio 1:1 was dissolved in double distilled water to prepare the aqueous solution of LLO. The solution was continuously stirred and heated slightly above the room temperature. The expected chemical reaction is as follows,

$C_{6}H_{13}NO_{2} + C_{2}H_{2}O_{4} + H_{2}O \longrightarrow C_{6}H_{14}NO_{2}^{+}.C_{2}HO_{4}^{-}$

The prepared solution was allowed to evaporate at room temperature, which yield the salt of L-Leucinium oxalate. The synthesized salt was purified by the repeated crystallization process. In order to prevent microbial contamination a few drops of H_2O_2 were added to the mother solution and transparent colourless crystals were harvested with the dimension of 23 mm x 6 mm x 4 mm after a period of 45–50 days. Fig. 1 shows the photograph of LLO single crystal grown from its aqueous solution by slow solvent evaporation technique.



Fig. 1 Photograph of LLO single crystal

1. Characterization

Single crystal XRD data are recorded using ENRAF NONIUS CAD4 single crystal X-RAY diffractometer with MoK_{α} (λ = 0.71073). The UV-Vis-NIR optical spectrum of sample was recorded in the region between 190 and 1100 nm covering the ultraviolet, visible and near infrared regions using the Shimadzu UV-2400 PC Spectrophotometer. The SHG efficiencies of the crystals were studied using Nd:YAG Q-switched laser. Thermal stability is studied using NETSZCH STA 409C and PERKIN ELMER Thermal Analyzer. The *ac* conductivity, dielectric constant and dielectric loss of the sample were measured at different temperatures using HIOKI 3532-50 LCR HITESTER instrument from 50 Hz to 5 MHz. The measurements of *dc* electrical conductivity were done using the conventional two-probe technique for temperatures ranging from 308 K to 368 K. The measurements of photo current and dark current were done using a picoammeter (Keithley 485).

RESULTS AND DISCUSSION

4.1. Single crystal X-ray diffraction studies

The LLO grown crystal was characterized by single crystal X-ray diffraction and the cell dimensions were obtained as a = 5.66 Å, b = 9.76 Å, c = 9.89 Å and V = 546.34 Å³. These values confirmed that the crystal belongs to triclinic system with the space group P1. It is found that the single crystal XRD results are in good agreement with the reported values [15].

4.2. UV-Vis-NIR spectral analysis

The optical properties of a material are important, as they provide information on the electronic band structures, localized states and types of optical transitions. For optical applications, especially for SHG, the crystal should be highly transparent in the considerable region of wavelength. The transmission spectrum of LLO is shown in Fig. 2. The cut-off wavelength as observed from the transmission spectrum is 215 nm. LLO has a wide transmission window between 215 and 1100 nm. The transmittance of LLO crystal is about 85 % and this transparent nature of grown crystal in the visible region is a desirable property for NLO applications.



4.3. NLO Test

The second harmonic generation efficiency of the powdered material was tested using Kurtz and Perry method [16]. A Q-switched, mode locked Nd:YAG laser operating at the fundamental wavelength of 1064 nm was used. In the present investigation, the laser pulse of 8 ns with spot radius of 1 mm was employed. The emission of green radiation from the crystal confirms the second harmonic generation in the crystal. Microcrystalline material of KDP was used for comparison with LLO for second harmonic generation experiment. The input laser beam was passed through the IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube. When a laser beam of 10.8 mJ was passed through the sample, second harmonic signal of 532 nm was generated and output voltages of 53 and 35 mV were obtained from KDP and LLO respectively. The experiment confirms and shows that the second harmonic efficiency of the LLO crystal is nearly 0.7 times that of KDP.



4.4. Thermal analysis

TG-DTA was carried out on the grown LLO sample for qualitative analysis and the respective gravimetric plots are shown in Fig. 3. From the DTA curve, it is observed that endothermic peak at about 171°C corresponds to the melting point of the compound which is exactly coinciding with the stability of the material shown by TGA trace. This is attributed to utilization of the thermal energy to overcome the valence bonding between the L-Leucine cation and oxalate anion, which happens in the initial stage of decomposition. The two broad endothermic peaks at 171 and 205 °C represent the decomposition of molecular fragments in two stages. This weight loss is followed by a major weight loss pattern between 173 and 357 °C occurring in three stages, first stage decomposition in the temperature

range from 173 to 205 °C with the mass change 5 %, second stage decomposition starts from 205 to 235 °C and third stage goes up to 357 °C, the total weight loss of these stages correspond to 65 % of the substance due to release of CO_2 and CO molecules in oxalic acid. The reactions of simplest amino acids induced by heating include the condensation reactions of carboxyl and amino groups leading to the formation of peptide bonds. The total weight loss nearly equals to 90% and the resulting 10 % residue is stable up to 800 °C. From this study it is concluded that the melting and decomposition occur in successive steps but the process appear to occur closely. This analysis indicates the possible NLO application of the material up to 171 °C.



Fig.4 Variation of dielectric constant with log frequency at different temperatures for LLO single crystal



Fig.5 Variation of dielectric loss with log frequency at different temperatures for LLO single crystal

4.5. Electrical studies

The dielectric studies on grown LLO crystals were carried out. The capacitance and dielectric loss of the grown crystal as a function of frequency were observed. The observations were made in the frequency range 50 Hz - 5 MHz in the temperature range 308 - 368 K. Figs. 4 and 5 show the plot of dielectric constant and dielectric loss of LLO as a function of log frequency for different temperatures. Both dielectric constant and dielectric loss of LLO crystal decrease gradually with increasing frequency as shown in Figs. 4 and 5. The decrease of dielectric constant with increasing frequency is a normal dielectric behavior and can be explained on the basis of polarization mechanism. There are four primary mechanisms of polarization exists in dielectric materials, i.e., electronic, ionic or atomic, dipolar or orientational and space charge or interfacial polarization. At low frequencies, all the mechanisms of polarization contribute to the dielectric constant and with the increase in frequency, the contributions from different polarizations start decreasing. For example, at very high frequencies (10¹⁵ Hz) only electronic polarization contributes to the dielectric constant, while ionic polarization takes place at IR frequencies (10^{13} Hz) [17]. The large value of dielectric constant at low frequency is due to the presence of space charge polarization. The space charge contribution depends on the purity and perfection of the material. Its influence is mainly noticeable in the low frequency region [18]. From Fig. 5, it can be noticed that as the frequency increases the dielectric loss decreases. This behavior is similar to that of the dielectric constant. At low frequencies the dipoles can easily switch alignment with the changing field. As the frequency increases the dipoles are less capable of rotating and maintaining phase with the field; thus they reduce their contribution to the polarization field, and hence the observed reduction in dielectric constant and dielectric loss. The characteristic of low dielectric loss with high frequency for a given sample suggests that the sample possesses enhanced optical quality with lesser defects and this parameter is of vital importance for nonlinear optical materials in their application [19]. The variation of dielectric constant and dielectric loss with temperature is shown in Figs. 6 and 7. From the Figures, it is observed that both the dielectric constant and dielectric loss increase with increase in temperature. The increase in dielectric constant with temperature is essentially due to the temperature variation of ionic polarizability. The characteristic of low dielectric constant and dielectric loss with high frequency for a given sample suggests that the sample possesses enhanced optical quality with lesser defects and this parameter is of vital importance for various microelectronic materials and nonlinear optical materials and their applications [20].



Fig. 6 Temperature dependence of dielectric constant for LLO single crystal



Fig. 7 Temperature dependence of dielectric loss for LLO single crystal

AC conductivity is one of the studies done on solids in order to characterize the resistance of the crystalline sample. It also gives information of electrical properties and their interface with electronically conducting electrodes. The variation of *ac* conductivity with temperature is shown in Fig. 8. From the graph, it is observed that conductivity increases as the temperature increases. The Arrhenius plot of $ln\sigma_{ac}$ versus 1000/T is shown in Fig. 9. The sample exhibits Arrhenius type conductivity behavior in the temperature range of investigation. The activation energy of LLO, for the conduction process, calculated from the plot for LLO (Fig. 10).



Fig. 8 The AC electrical conductivities for LLO single crystal



Fig.9 Plot of $ln(\sigma_{ac})$ versus 1000/T for LLO single crystal



Fig. 10 Frequency dependence of AC activation energy for LLO single crystal

The dc electrical conductivity measurements were carried out for the LLO crystal using the conventional two-probe technique in the temperature range 308 – 368 K. Fig. 11 shows the variation of dc conductivity with temperature. It

is evident from the graph that the conductivity increases with temperature. The plot of $ln\sigma_{dc}$ versus 1000/T as obtained for the crystal is shown in Fig.12. The SPH (small polaron hopping theory) model is based on a strong coupling of electron with the lattice by a single phonon. According to this model the *dc* conductivity is given by $\sigma = \sigma_0 \exp(-E_d/kT)$, where σ_0 is a pre exponential factor, E_d is the activation energy, k is Boltzmann constant and T is temperature in K. Activation energy of the sample is found to be 0.018 eV from the Fig. 12.



Fig. 11 The DC electrical conductivities for LLO single crystal



Fig. 12 Plot of $ln(\sigma_{dc})$ versus 1000/T for LLO single crystal

4.6. Photoconductivity studies

Field dependence of dark and photo current of LLO crystal is shown in Fig. 13. The experiment was performed at room temperature. Electrical contacts were made at a spacing of about 0.5 cm on the samples using silver paint. The DC input was increased and the corresponding dark currents were noted from the electrometer. The photo current of the sample was measured by illuminating with a halogen lamp (100 W) containing iodine vapour by focusing a spot of light on the sample with the help of a convex lens. The same field variation was applied and the corresponding photo current was recorded. A plot has been drawn for the photo current and dark current as a function of the applied field and presented in Fig. 13. It is observed from the plot that the dark current is always higher than the photo current, hence it is concluded that the sample exhibits negative photoconductivity. The above study reveals the negative photoconducting nature of the grown crystal, which may be due to the loss of water molecules, can also lead to decrease in conductivity. The same phenomenon was successfully explained with specific reference to semiconducting crystals by the Stockmann model [21].



Fig. 13 Field dependent photoconductivity of LLO single crystal

CONCLUSION

Single crystals of LLO were successfully grown by slow solvent evaporation technique at room temperature. The grown crystal was confirmed by single crystal XRD analysis. The optical studies reveal that the crystal has very high transmission in the entire visible and infrared region, with the lower UV cut off around 215 nm, which is an essential consideration for NLO crystals. The Kurtz SHG test shows that the grown crystal has its SHG efficiency comparable to KDP. The LLO is stable up to 171 °C. Dielectric studies imply that there is a decrease of dielectric constant and dielectric loss with increase of temperature at all frequencies. The *ac/dc* conductivity studies are carried out and the activation energy is also determined. The negative photoconducting nature of the sample is confirmed by photoconductivity study. The above investigations made on the grown crystal shows that LLO is a potential candidate for photonic applications.

Acknowledgements

One of the authors (M. Vimalan) thanks the management, Dr. P. Thamil Selvi (Principal) and Dr. R. Sendhil Kumar (Administrative Officer), Thirumalai Engineering College, Kilambi, Kancheepuram, Tamil Nadu, India, for their encouragement, support, valuable suggestions and useful discussion.

REFERENCES

[1]P.N. Prasad, D.J. Williams, Introduction to Nonlinear Optical Effects in Organic Molecules and Polymers, Wiley Inter science, New York, **1991**.

[2] R.A. Hann, D. Bloor (Eds.), The Royal Society of Chemistry Spec, London, 1989, 176.

[3]D.S. Chemla, J. Zyss (Eds.), *Non-linear Optical Properties of Organic Molecules and Crystals*, Academic Press, Orlando, New York, **1987**.

[4]S.B. Monaco, L.E. Davis, S.P. Velsko, F.T. Wang, D. Eimerl, A. Zalkin, J. Cryst. Growth, 1987, 85, 252.

[5]T. Pal, T. Kar, X.Q. Wang, G.Y. Zhou, D. Wang, X.F. Chen, Z.H. Yang, J. Cryst. Growth, 2002, 235, 523.

[6]T. Pal, T. Kar, G. Bocelli, L. Rigi, Cryst. Growth Des., 2003, 3, 13.

[7] R.M. Kumar, D. Rajanbabu, D. Jayaraman, R. Jayavel, K.J. Kitamura, J. Cryst. Growth, 2005, 275, 1935.

[8]N.M. Bhat, S.M. Dharmaprakash, J. Cryst. Growth, 2002, 235, 511.

[9] D. Xu, M.H. Jiang, Z.K. Tan, Acta Chim. Sin., Chinese, 1983, 41, 570.

[10] D. Xu, X.Q. Wang, W.T. Yu, S.X. Xu, G.H. Zhang, J. Cryst. Growth, 2003, 253, 481.

[11] P. Mythili, T. Kanagasekaran, R. Gopalakrishnan, Mater.Lett., 2008, 62, 185.

[12] M. Vimalan, A. Ramanand, and P. Sagayaraj, Cryst. Res. Technol., 2007, 42, 1091.

[13] D. Eimerl, S. Velsko, L. Davis, F. Wang, G. Loiacono, and G. Kennedy, *IEEE J. Quant. Electron.*, 1989, 25, 179.

- [14] H. L. Bhat, Bull. Mater. Sci., 1994, 17, 1233.
- [15] K. Rajagopal, R. V. Krishnakumar, M. Subha Nandhini, R. Malthi, S. S. Rajan, S. Natarajan, Acta Cryst. E, 2003, 59, 0878.
- [16] S.K. Kurtz, T. T. Perry, J. Appl. Phys., 1968, 39, 3798.
- [17] I.G. Austin, N.F. Mott, Adv. Phys., 1969, 18, 41.
- [18] K.V Rao and A. Samakula, J. Appl. Phys., 1965, 36, 2031.
- [19] C. Balarew and R. Duhlew, J. Solid state Chemistry, 1984, 55, 1.
- [20] S. Goma, C.M. Padma and C.K. Mahadevan, Mater. Lett., 2006, 60, 3701.
- [21] V.N. Joshi, *Photoconductivity*, Marcel Dekker, New York, 1990.