Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Applied Science Research, 2010, 2 (4): 26-32

(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

Synthesis, growth and characterization of L-alaninium oxalate a promising nonlinear optical single crystal

S. Alfred Devaprasad and J. Madhavan

Department of Physics, Loyola College, Chennai, India

ABSTRACT

Single crystals of L-alaninium oxalate (LAO), a promising semiorganic nonlinear optical (NLO) material have been successfully grown by slow evaporation technique. The grown crystals have been subjected to powder X-ray diffraction analysis to identify the cell parameters and morphology. The Second Harmonic Generation (SHG) efficiency of the crystal has been determined by the Kurtz test. The hardness studies confirm the normal indentation size effect. The dielectric constant and dielectric loss of the crystal at different temperatures was studied as a function of frequency and the results are discussed.

INTRODUCTION

New molecular organic compounds with one or more aromatic systems in conjugated positions, leading to highly efficient charge transfer systems have been actively studied. Most of the organic crystals are composed of aromatic molecules that are substituted with π-electron donors and acceptors which exhibit intermolecular charge transfer resulting in high SHG efficiency. These compounds must crystallize in a noncentrosymmetric class in view of applications making use of quadratic optically nonlinear effects. Organic compounds are formed by weak Van der Waal's and hydrogen bonds and possess high degree of delocalization [1]. Hence they are optically more nonlinear than inorganic materials. Some of the advantages of organic materials include flexibility in the methods of synthesis, scope for altering the properties by functional substitution, inherently high nonlinearity, high damage resistance etc [2]. Organic materials with delocalized π-electrons usually display a large NLO response which makes it most resourceful for various application including optical communication, optical computing, optical information processing, optical disk data storage, laser fusion reactions and laser remote sensing [3]. Further investigations on organic NLO materials have subsequently produced very good materials with highly attractive characteristics. L-alaninium oxalate (LAO) is one such recently developed organic NLO crystals and its growth and structure had been reported [4]. In L-alaninium oxalate $C_3H_8NO_2^+.C_2HO_4^-$, the alanine molecule exists in the cationic form and the oxalic acid in the mono-ionized state. The alaninium and semi oxalate ions from alternate columns leading to a layered arrangement parallel to the *ac* plane and each such layer is interconnected to the other through N–H···O hydrogen bonds. The earlier works on LAO were restricted to structure solving, thermal, optical and photoacoustic studies. Hence, attempts were made in the present work to investigate more detailed physicochemical properties of LAO.

The present investigation deals with the growth of LAO single crystal by slow solvent evaporation technique. The grown crystal was subjected to powder XRD, FT-IR, UV-Vis-NIR, microhardness and dielectric studies.

MATERIALS AND METHODS

SYNTHESIS

Equimolar amounts of L-alanine and oxalic acid were dissolved in double distilled water to prepare the aqueous solution of LAO. The synthesized salt of LAO was obtained by evaporating the solvent.

2.1 Solubility and growth

The solubility of LAO was measured at different temperatures and the variation of solubility (g LAO / 100 ml H_2O) with temperature is shown in Fig. 1. The solution was saturated at 40 °C and seed crystals were formed due to spontaneous nucleation. Transparent good quality seed crystals free from macro defects were used for growth experiments. Single crystals up to size 7 x 4 x 6 mm^3 were grown in 50 days and the photographs of the as grown crystals of LAO were shown in Fig. 2.

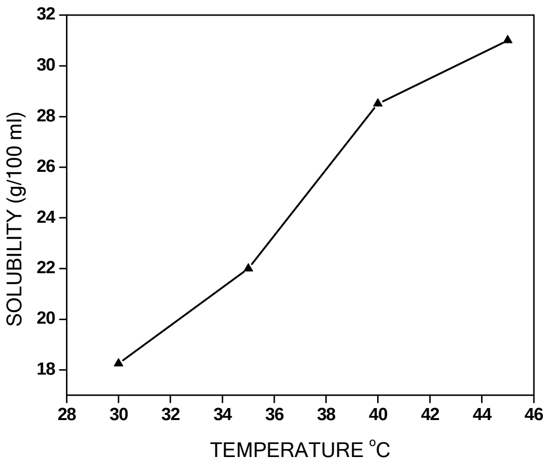

Figure 1 Solubility curve of LAO

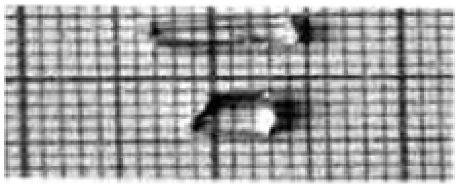

Figure 2 Photograph of as grown LAO single crystals

Characterization

3.1 Powder XRD studies

The structural property of the single crystals of LAO was studied by X-ray powder diffraction technique. Powder X-ray diffraction studies of LAO crystal was carried out, using Siemens D500 X-ray diffractometer with Cu K_α (λ = 1.5418 Å) radiation. The sample was scanned for 2θ values from 10˚ to 50˚ at a rate of 2˚ /min. Figure 3 shows the Powder XRD pattern of the pure LAO crystal. The diffraction patterns of LAO crystal have been indexed by least square fit method. The lattice parameter values of LAO crystal were calculated and are matched with the reported literature [4]. The lattice parameters are shown in Table 1.

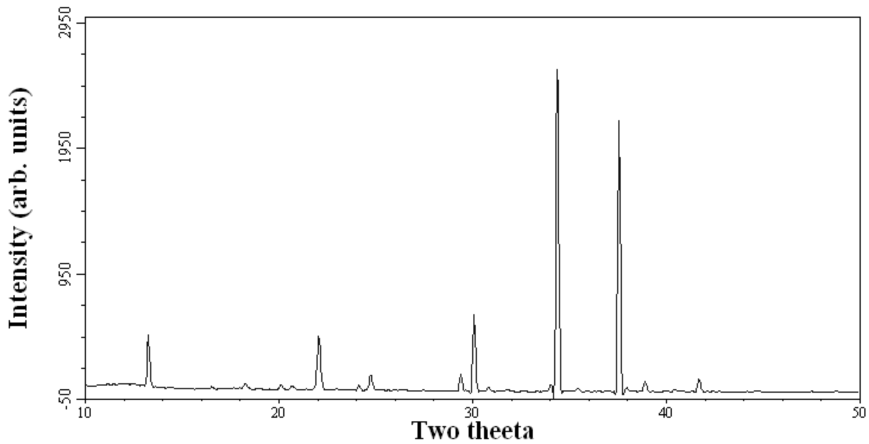

Figure 3 Powder X-ray diffraction pattern of LOA

Table 1: Lattice parameter values of LAO

Empirical formula	$C_5H_9NO_6$
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a	5.54 (3) Å
b	7.30 (2) Å
c	19.41 (1) Å
Volume	784.98 Å^3

3.2 FT-IR analysis

Figure 4 shows the FT-IR spectrum of LAO. The sample was prepared by mixing it with KBr. It can be noted from the spectrum that the broad envelope in the higher energy region consists of peaks due to NH vibrations at 3330 and 3170 cm^{-1}. The broad envelope contains peak at 3100 cm^{-1} due to CH vibration. This broadening is further widened due to the presence of N – H ··· O hydrogen bonding. The – NH_3^+ absorption, characteristic of amino acids, occurring in the range

3130- 3100 cm^{-1} is more often shifted to lower wavenumber side due to the formation of amino salts, and in LAO, it occurs at 3083 cm^{-1}. The C=O vibration of the carboxyl group is observed at 1670 cm^{-1}. The symmetrical NH_3^+ vibration is positioned at 1495 cm^{-1}. The CH_2 bending modes produce peak at 1365 cm^{-1}. The C-N vibrations produce a group of peaks between 1260 and 1090 cm^{-1}.

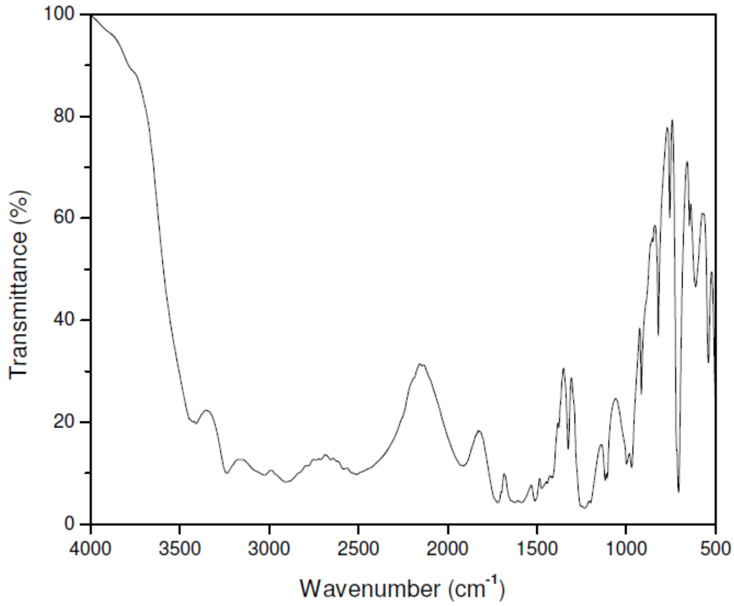

Figure 4 FT-IR spectrum of LAO

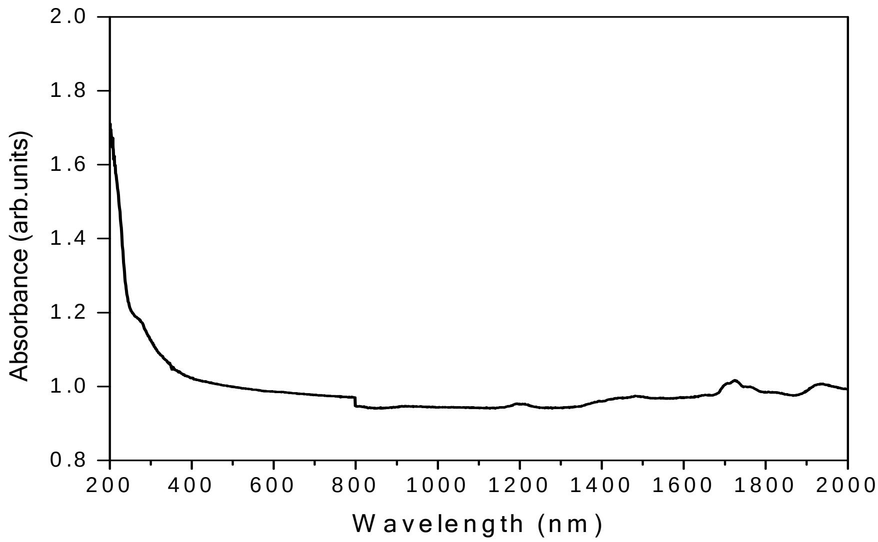

Figure 5 Optical absorption spectrum of LAO

3.3 UV-Vis-NIR spectral analysis

Figure 5 shows the UV-Vis-NIR optical absorption and spectra of LAO crystal. The cut-off wavelength as observed from the absorption spectrum (Figure 5) is 250 nm. Interestingly, in the entire region starting from 250 nm to 2000 nm, the crystal has almost less than one unit of absorption. The wide optical transmission window is an encouraging optical property seen in LAO crystal and is of vital importance for NLO materials.

3.4 NLO Test

Second harmonic generation test was done on the LAO sample [5]. The source used was Q-switched, mode-locked Nd^{3+}: YAG laser emitting 1.06 μm fundamental radiations. The input laser beam was passed through IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of diameter 0.154 mm. For the SHG efficiency measurements, microcrystalline material of KDP was used for comparison. When a laser input of 6.2 mJ was passed through LAO, second harmonic signal of 149 mV is produced and the experiment confirms a second harmonic efficiency of nearly 1.2 times that of KDP(124 mV). Thus SHG efficiency of LAO sample is comparable with other promising amino acid based NLO crystals [6, 7].

3.5 Microhardness test

Hardness of the material is a measure of resistance, it offers to deformation. The pure and doped crystals which are free from cracks and transparent were selected for microhardness measurements. Micro hardness studies were carried out for the pure and doped crystals using Leitz Wetzlar Vickers micro hardness tester by varying the applied load from 10 g to 50 g. The indentation time was kept as 5s for all the loads. Figure 6 shows the variations of Vickers hardness number with applied load for (010) plane of the pure and doped crystals. The value of work hardening coefficient of the crystal was found to be 1.61. According to Onitsch, n lies between 1 and 1.6 for hard materials, and n is greater than 1.6 for soft materials [6]. Hence, it is concluded that LAO is a soft material.

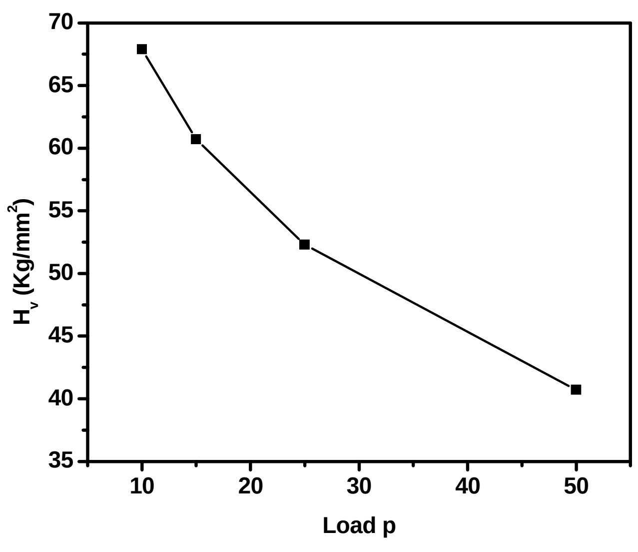

Figure 6 Variation of hardness with applied load for the plane (010)

3.6 Dielectric study

Figures 7 and 8 show the variations of dielectric constant and dielectric loss with log frequency. The dielectric constant of the sample was measured for different frequencies under various temperature slots from 308 K to 388 K. It is observed from the plot (Figure 7) that the dielectric constant decreases exponentially with increasing frequency and then attains almost a constant value in the high frequency region starting from 3 KHz to 5 MHz. It is observed that at all temperatures, both the dielectric constant and dielectric loss decrease with increasing frequency. It is further observed that as the temperature increases, the value of dielectric constant increases to a considerable value (Figure 7). A similar trend is observed in the case of dielectric loss also (Figure 8).

At relatively lower frequency, the higher the temperature the larger is the dielectric constant. Such variations at high temperature may be attributed to the blocking of charge carriers at the electrodes. Because of the impedance to their motion at the electrodes, space charge and macroscopic distortion result, which might cause the observed larger values of dielectric constant at lower frequencies. With increasing temperature, a high degree of dispersion in the permittivity begins to occur at lower frequency. This could be again due to the thermally generated charge carriers from the onset of space charge limited to dc conduction. It is in fact the space charge effect that leads to the dispersion of dielectric constant at low frequencies. 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 nonlinear optical materials and their applications.

CONCLUSION

Single crystals of LAO of appreciable size were grown by slow evaporation technique at room temperature. Powder XRD confirmed the grown crystal. It is observed FT-IR analysis that the –NH_3^+ absorption, characteristic of amino acids, occurring in the range 3130-3100 cm^{-1} is more often shifted to lower wavenumber side due to the formation of amino salts. The optical absorption spectrum reveals the very low absorption in the entire visible and infrared region of the crystal.

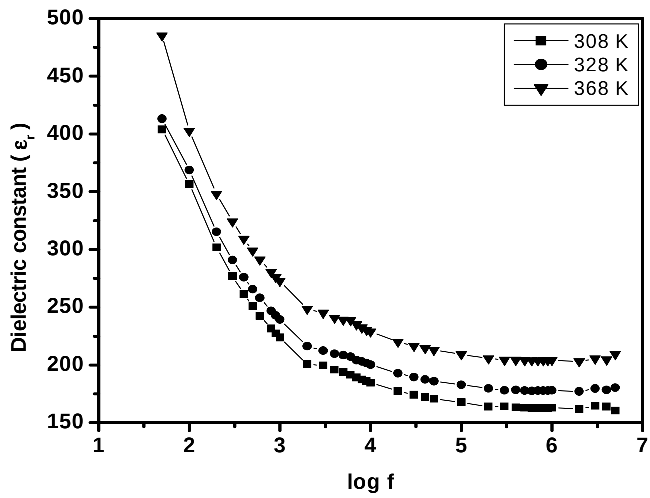

Figure 7 Variation of dielectric constant with log frequency at different temperatures for LAO single crystal

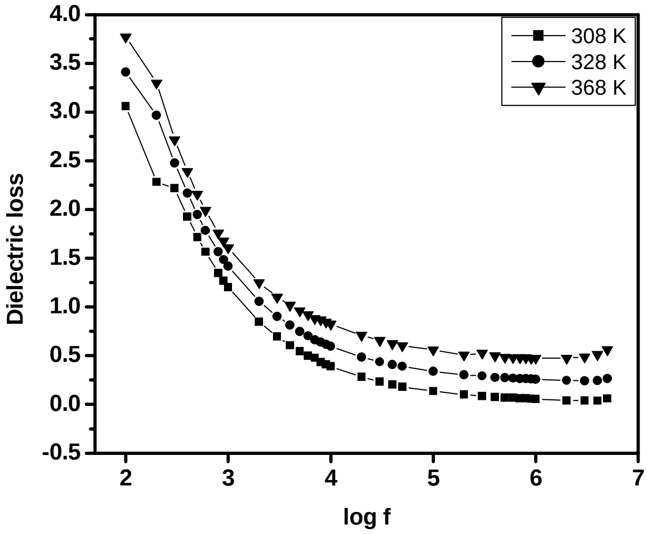

Figure 8 Variation of dielectric loss with log frequency at different temperatures for LAO single crystal

The lower UV cut-off wavelength of the sample abserved at 250 nm is a desirable parameter for NLO crystals. The NLO property was confirmed using Nd : YAG laser of wavelength 1064 nm and the efficiency was estimated to be 1.2 times higher than that of KDP. The microhardness study indicates that the crystal belongs to the class of soft materials. The dielectric studies prove the low values of dielectric constant and dielectric loss in the sample at high frequency. The promising crystal growth characteristics and properties of LAO crystal indicate it as a potential material for photonic, electro-optic and SHG device application.

Acknowledgements

The authors acknowledge University Grants Commission (UGC), India for funding this research project - F.No. 33-11/2007 (SR).

REFERENCES

[1] M. Narayan Bhat, S.M. Dharmaprakash, *Journal of Crystal Growth*, **2002**, 235, 511–516.
[2] B. Narayana Moolya , S.M. Dharmaprakash, *J. Crystal Growth*, **2006**, 290, 498–503.
[3] Tanusri Pal., Tanusree Kar., Gabriele Bocelli., Lara Rigi., *Crystal Growth & Design*, **2003**, 3, 13–16.
[4] M. Subha Nandhini, R.V. Krishnakumar, S. Natarajan , *Acta Cryst*., **2001** E57, 633–o635.
[5] S.K. Kurtz, T. T. Perry, *J. Appl. Phys*., **1968**, 39, 3798–3813.
[6] S. Dhanuskodi, K. Vasantha, *Cryst. Res. Tech*., **2004**, 39, 259–265.
[7] M. Sivabarathy, S. Natarajan , S.K. Ramakrishnan, K. Ramachandran, *Bull. Mater. Sci*., **2004**, 27, 403–407.