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Studies of L-Alanine Crystals Admixtured with Potassium Hydroxide (LAPH)

KEYWORDS: L-alanine; crystal growth; XRD; NLO; SHG; microhardness; band gap ; impedance

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ABSTRACT *Single crystals of L-alanine admixtured with potassium hydroxide (LAPH) were grown by solution method with slow evaporation technique. The grown crystals were colorless, hygroscopic and transparent. The lattice parameters of the grown crystals were determined by X-ray diffraction technique. UV-visible transmittance spectrum of the sample was recorded to find the cut-off wavelength of the grown crystal. The nonlinear optical (NLO) property of the grown crystal was confirmed by Kurtz-Perry powder technique. The hardness of LAPH crystal was determined for different loads and the impedance analysis for the grown crystal was carried out to understand the electrical phenomena that are taking place in the sample.*

Introduction
Nowadays, there is a considerable interest in the synthesis of new nonlinear optical (NLO) materials because they have a significant impact on laser technology, optical communication and optical storage technology etc. Amino acids and their complexes are the second-order or third-order nonlinear optical (NLO) materials and these compounds contain amino groups and carboxylic acid groups. In a zwitteionic form, an amino acid contains positively charged ammonium ion (NH_3^+) and negatively charged carboxylate ion (COO^-) [1,2]. L-alanine is a non-centrosymmetric amino acid and it was first crystallized by Bernal and later by Simpson and Destro et al and its second harmonic generation (SHG) efficiency of about one-third of that of KDP crystal [3-5]. L-alanine can be considered as the fundamental building block of more complex amino acids which shows strong nonlinear behaviour and anomalous phonon coupling and is a system exhibiting vibrational solitons [6]. Crystals of L-alanine complexes have been studied by many researchers and reported in the literature [7-11]. If L-alanine is mixed with acids or bases to form novel materials, it is expected to get improved physical properties. In this work, L-alanine is mixed with potassium hydroxide to obtain LAPH crystals and the studies on growth, NLO activity, structural, optical properties, mechanical properties and impedance analysis are discussed.

Solubility and growth
High purity chemicals (AR grade) of L-alanine and potassium hydroxide were taken in 2:1 molar ratio and dissolved in double distilled water. The solution was stirred for about 3 hours using a hot plate magnetic stirrer at 50 °C. Then it was cooled to room temperature and was filtered using a fine quality Whatmann filter paper. The filtered solution was allowed for slow evaporation to get seed crystalline samples. The solubility in water was determined at different temperatures by gravimetrical method. The variation of solubility with temperature is displayed in the figure 1. From the data, it is observed that the solubility of the sample in water increases linearly with temperature, exhibiting a high solubility gradient and it has positive temperature coefficient. The bulk crystals of L-alanine admixtured with potassium hydroxide were grown by seed immersion technique. Using the solubility data, saturated solution was prepared at room temperature (30 °C) and it was allowed for slow evaporation for two or three days to get supersaturated solution. Then good quality seed crystals were placed at the bottom of the beaker containing the supersaturated solution. By slow evaporation method, bulk crystals were harvested after a growth period of 20 days. A typical grown crystal is shown in the figure 1.

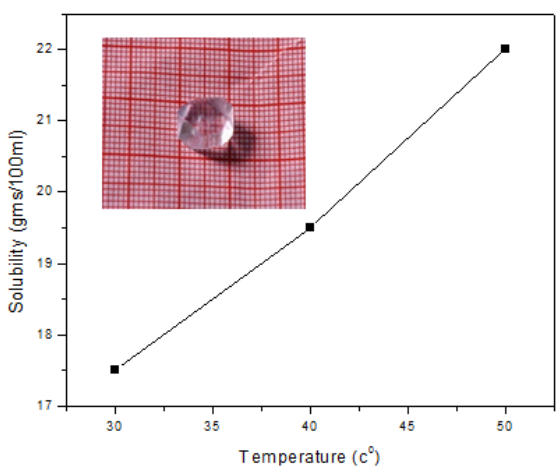

Fig.1: Solubility curve for potassium hydroxide admixtured L-alanine sample. (Inset: The grown crystal of LAPH).

3. Identification of crystal structure
The structure of the grown LAPH crystal was identified by single crystal XRD studies. To confirm the crystallinity and also to estimate the lattice parameters, a Bruker-Nonious MACH3/CAD4 single X-ray diffractometer was employed. From single crystal X-ray diffraction data, it is observed that the LAPH crystal belongs to orthorhombic structure with the lattice parameters a=5.765(2) Å, b=6.035(5) Å, c=12.323(3) Å, $\alpha=\beta=\gamma=90°$ and V =428.74(4) Å^3. The grown LAPH crystal has been crushed to a uniform fine powder and subjected to powder X-ray diffraction to identify the reflection planes. The well-defined peaks at specific 2-theta values show high crystallinity of the Fig.2. X-ray diffraction pattern of the grown crystal

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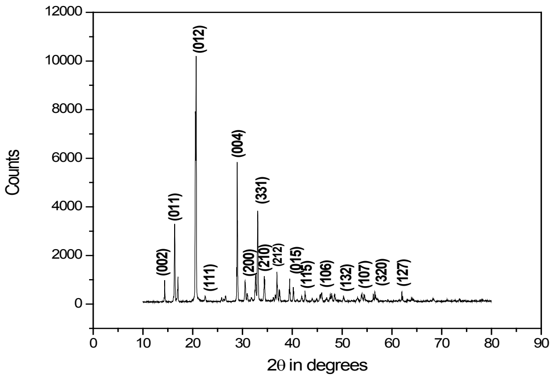


Fig.2. X-ray diffraction pattern of the grown crystal

grown crystal. The reflection peaks of the of powder XRD pattern of grown crystal were indexed using the INDEXING and TREOR software packages. The indexed powder X-ray diffraction pattern of the grown crystal is given in figure 2. Using the UNITCELL software package, the unit cell parameters for the sample from powder XRD data are obtained and these data are found to be well coinciding with those of single crystal XRD data.

4. Optical transmission studies

The recorded transmittance spectra of LAPH crystals in the wavelength range of 190-1100 nm are shown in Fig.3. At about 247 nm, a sharp fall to zero in the transmittance is observed for LAPH sample and the crystals have sufficient transmittance in the entire visible and near IR region. The sharp fall at 247 nm for the sample corresponds to the fundamental absorption edge, which is essential in connection with the theory of electronic structure.

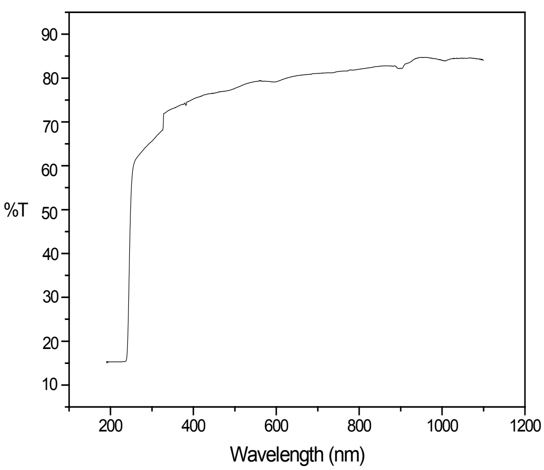


Fig.3:Optical transmittance curve for LAPH crystal.

5. Second-order NLO activity

A high intensity Nd:YAG laser (λ = 1064 nm) with a pulse duration of 6 ns was passed through the powdered sample of LAPH. The second-order NLO activity (SHG) was confirmed from the output of the laser beam having the green emission λ= 532 nm). It is observed that the SHG efficiency of the grown single crystal is 0.93 times that of the standard KDP crystal.

6. Impedance analysis

The electrical properties have been studied by complex impedance spectroscopy over a range of frequencies and temperatures. The method ensures an insight into the electrical processes that are taking place within the sample. The frequency dependent properties of a material are represented in terms of complex impedance Z^* and it is given by $Z^* = Z' - jZ''$ where Z' is the real part of impedance, Z'' is the imaginary part of impedance and j = square root of (-1). The frequency dependence of Z' for LAPH crystal is plotted at different temperatures and is shown in Fig.4(a). It is observed from the results that the values of Z' decrease with frequency upto a certain frequency and then become frequency independent. The higher values of Z' at lower frequencies and low temperatures means the polarization is larger. Debye-type dielectric dispersion is noticed in the frequency dependence curves [12]. The frequency dependence of Z'' is plotted for different temperatures and shown in Fig. 4 (b). The variation of Z'' with frequency is observed to be as same as that of variation of Z'. The values of Z' and Z'' are observed to be increasing with increase in temperature and this indicates the expansion and introduction of defects inside the crystal of LAPH.

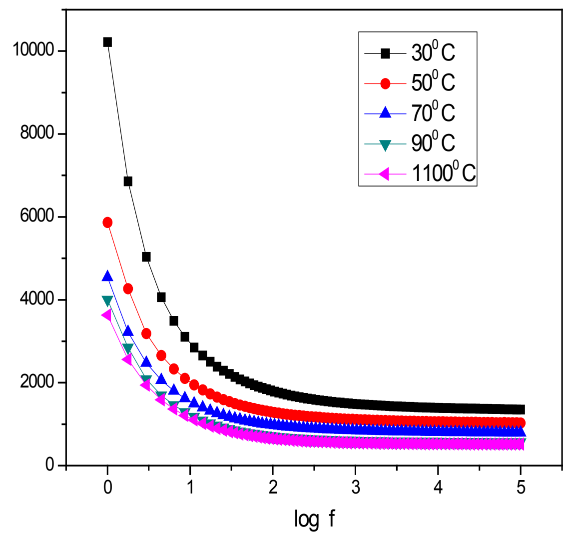
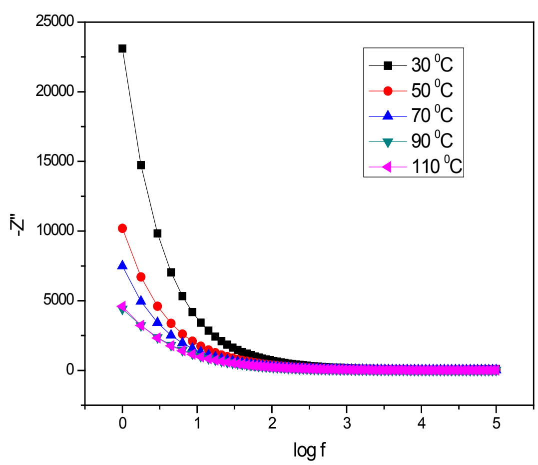


Fig. 4: Variations of (a) real part of impedance



(b) imaginary part of impedance with frequency at different temperatures

7. Microhardness

The mechanical strength of crystals was tested by carrying out microhardness studies by applying different low loads. The hardness of a solid is defined as its resistance to local plastic/permanent deformation and the simplest way to obtain it is to press a hard indenter of known geometry and to divide the applied load (P) by the area (A) of the indentation produced, i.e. hardness = P/A. The mean diagonal length of the indentation or impression was measured using a LEITZ microhardness tester, fitted with a Vickers diamond pyramidal indenter. Vickers microhardness values were calculated by using the formula $H_v = 1.8544\ P/d^2$ kg/mm^2 where P is the applied load in kg, d is the mean diagonal length of the indentation in mm and 1.8544 is a constant. The determined values of hardness for LAPH crystal are 56.12, 69.74, 81.36 and 105.48 kg/mm^2 for the applied loads 25 g, 50 g, 75 g and 100 g respectively. It is observed from the results that the hardness number is found to increase with increase in the applied load showing the reverse indentation size effect [13,14].

8.Conclusions

Good quality single crystals of LAPA (potassium hydroxide admixtured L-alanine) have been grown by slow evaporation technique. The solubility of LAPA sample was estimated for water solvent at different temperatures. The X-ray diffraction studies confirm the orthorhombic structure of the grown crystal. The optical cut-off wavelength for the LAPH crystal was found to be 247 nm. SHG studies reveal that LAPH crystal is a promising candidate for NLO applications. Real part and imaginary part of impedance of the sample was measured at different frequencies and temperatures and the results show the dielectric behavior of the sample. The hardness of LAPH crystal was measured at different loads which reveal the mechanical strength of the sample.

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REFERENCE

1. L.Misoguti , A.T. Varela , F.D.Nunes,V.S.Bagnato ,F.F.A. Melo, J. Mendes | Filho, S.C. Zilio, Opt.Mater. 6 (1996) 147. | 2. P. Selvarajan, J. Glorium Arul Raj and S. Perumal, J.Crystal Growth 311 (2009) | 3835. | 3. J.D. Bernal, Z. Kristallogr 78(1931)363. | 4.H.J. Simpson Jr., R.E. Marsh, ActaCryst. 8(1966)550. | 5.R. Destro, R.E. Marsh, R. Bianchi, J.Phys.Chem. 92(1988)966. | 6. Marder. S. R, Sohn J. E, Stucky. G. D, Materials for Nonlinear Optics; | American Chemical Society: Washington, DC (1991). | 7. D. Rajan Babu, D. Jayaraman, R. Mohan Kumar, R. Jayavel, J. Crystal Growth, | 245 (2002) 121. . | 8. C. Justin Raj, S. Jerome Das, J. Crystal Growth 304 (2007) 191. | 9. A.S.J. Lucia Rose, P. Selvarajan, S. Perumal, Mater. Chem. Phys., 30(2011)950. | 10. C. Razzetti, M. Ardoino, L. Zanotti, M. Zha, C. Parorici, Cryst. Res. Technol. | 37 (2002) 456. | 11. C. Ramachandra Raja, G. Gokila, A. Antony Joseph, Spectrochimica Acta Part A | 72 (2009) 753. | 12. Banarji Behera, P. Nayaka, R.N.P. Choudhary,J. Alloys and Compounds 436 | (2007) 226. | 13. K. Sangwal, Cryst. Res. Technol. 44 (2009) 1019. | 14. M.Krishnasamy, S.Subramanian, P.Selvarajan, D.Shanthi, Int. J. Adv.Sci. Tech. | Res. 4 (2013) 98. | |