Sciencia Acta Xaveriana
An International Science Journal
ISSN. 0976-1152

Volume 4
No. 2
pp. 41-50
September 2013

Linear and Non Linear Optical Properties of L- Alaninium Malate (LAM) Single Crystal an Efficient Organic NLO Material.

M.Victor Antony Raj[a],D.Prem Anand[b] and J.Madhavan[a]*

[a] Department of Physics, Loyola College, Chennai-34

[b] Department of Physics,St.Xavier's College,Palayamkotti-627002.

*jmadhavang@yahoo.com

Abstract : Amino acid family of materials is suitable for Non Linear Optical applications due to Zwitter ionic and chiral nature of its molecules. L alanine family of crystals has high optical transmittance in the whole visible range. The optical band gap (Eg) value of the grown crystal is obtained from the tauc's plot of $(\alpha h\nu)^2$ vs hν which was determined by extrapolating the linear region of the curve to the hν axis where $(\alpha h\nu)^2=0$ and its found that 4.67eV. Other linear optical parameters such as Extinction coefficient, Reflectance, Refractive index, Complex dielectric constant, and Optical conductivity are calculated for the grown crystal and its variation with incident photon energy is analyzed. Second Harmonic Generating (SHG) efficiency of the candidate material was determined by Nd:YAG Q-switched laser Kurtz powder technique and its 1.1 times greater than KDP.

(Received July 2013, Accepted September 2013)

Introduction

The search of new materials with large nonlinearity is motivated by the development of nonlinear optical devices such as ultrafast optical switches, power limiters, real time holography, self-focusing white-light continuum generation and photonic applications.[1] Advance in developing new physical principles of optical measurements has been achieved by extensive works and intensive efforts of a great number of scientists and researchers. Band gap tailoring at the ultraviolet end and visible region of the visible spectrum is of considerable interest for large area optical device fabrications. The optical band gap of Non Linear Optical (NLO) materials can be controlled via the modification of their chemical structures. The chemical structure can be improved by enhancing π-orbital overlap and by introducing electron donor and acceptor moieties into a conjugated molecule which can directly affect ionization potential (IP) and electron affinity (EA) of the crystal.[2]The fast developments in the field of optoelectronics and photonics necessitates the search for new and efficient nonlinear optical(NLO) materials that can be utilized for optical computing, optical communications , electro-optic, frequency shifting and optical data storage for developing technologies in telecommunications, and signal processing [3]. The present study is aimed at measuring directly the band gap energies of LAM single crystal using UV-NIR Spectroscopy which is particularly suitable for the determination of absorption edges of powdered materials. The optical constants (a, n, K, R) of the candidate material are calculated and related with incident photon energy. Second harmonic generating efficiency (SHG) of the LAM single crystal is found and its greater than the KDP.

2. Synthesis and Growth of L-Alaninium Maleate (LAM) Single Crystals

Analytical grade L-alanine (AR grade) and maleic acid was dissolved in double deionized water. In order to grow good quality crystals, it is essential to increase purity up to a respectable level. In the present study, the commercially available salt was dissolved in water and purified by the repeated recrystallisation process and the recrystallised material was used to prepare the saturated solution. The solubility of LAM was measured at different temperatures and the drawn solubility curves are shown in Figure 1. It is seen that the solubility of LAM increases with temperature. The resulting aqueous solution was filtered and allowed to evaporate under optimized conditions to grow crystals by slow evaporation method at room temperature (30°C). The reaction that takes place between L-alanine and maleic acid in water medium is as follows:

$$C_3H_7NO_2 + C_4H_3O_4 + H_2O \longrightarrow C_3H_8NO_2^{+}.C_4H_3O_4^{-}$$

In a period of thirty days a good transparent single crystal of size 30 x 10 x 8 mm was harvested. The as grown single crystal of LAM is shown in Figure 2.

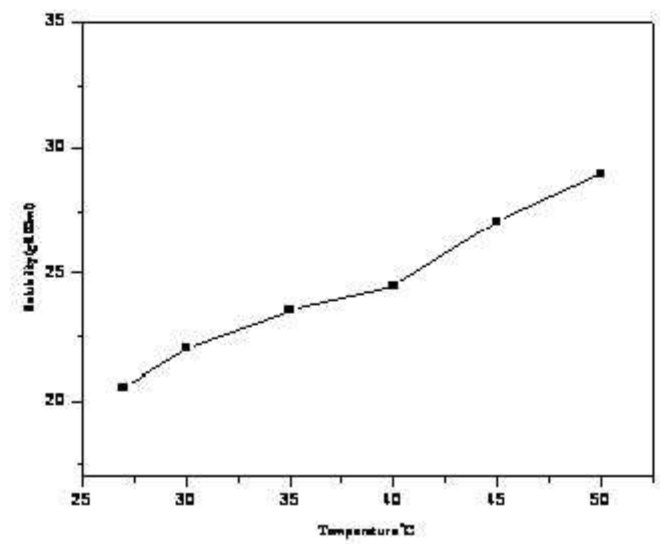

Figure 1. Solubility of LAM

Figure 2. Photograph of as grown LAM single crystal

3. Results and Discussions

3.1 Powder Crystal XRD

The purified samples of the grown crystals have been crushed to a uniform fine powder and subjected to powder X-ray diffraction using a Rich Seifert powder X-ray diffractometer. The K_α radiations ($\lambda = 1.5406$ A°) from a copper target were used. The specimen was scanned in the reflection mode in the 2θ range 10–50^0. Figure 3 represents the powder diffractogram for the grown LAM crystal.

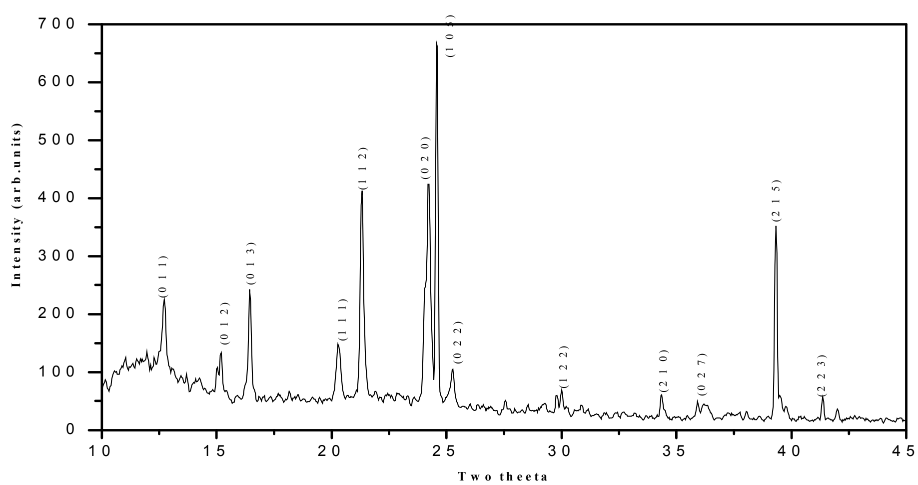

Figure3. Powder XRD pattern of LAM

3.2 Optical Properties of LAM

The optical absorption spectrum of LAM single crystal is shown in Figure 4. The spectra indicates that LAM crystal has minimum absorption in the region between 250–1200 nm. A good optical transmittance is very desirable in an NLO crystal since the absorptions, if any, in an NLO material near the fundamental of the second harmonic will lead to less conversion efficiency in those wavelengths. When absorption is monitored from shorter wavelength to longer wavelength, the enhanced transmission is observed between 300 and 1100 nm.

As the entire region does not bear any absorption band it can be used for NLO applications. The absorption coefficient (α) of a crystalline solid obeys the following relationship [4]

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

n is an integer equal to 1 for a direct band gap and 4 for an indirect band gap. The values of the direct optical band gap Eg were obtained from the intercept of $(\alpha h\nu)^2$ versus hν curve plotted in Figure 5. Energy gap (E_g) was evaluated by extrapolating the linear part of the curve to energy axis.The band gap is found to be 4.67 eV. This value of optical band gap shows blue shift, which is useful for gas sensing applications As a consequence of wide band gap, the crystal under study has a large transmittance window. The band gap width E_g of crystalline materials depends on their anisotropy, temperature, pressure on effect of external electric and magnetic field forces. The other optical constants were calculated using the following theoretical formulae [5,6].

The extinction coefficient in terms of absorption coefficient is obtained as

$$K = \frac{\alpha\lambda}{4\pi} \quad (2)$$

The Reflectance is derived as a function of absorption coefficient as

$$R=(1 \pm \sqrt{(1-\exp(-\alpha d)+\exp(-\alpha d))}/(1+\exp(-\alpha d)) \quad (3)$$

And the linear refractive index is given by

$$n= ((-(R+1) \pm \sqrt{(-3R^2+10R-3)})/((2(R-1))) \quad (4)$$

Then the complex dielectric constant is related to refractive index and the extinction coefficient

$$\text{as } \varepsilon_c=\varepsilon_r+\varepsilon_i \quad (5)$$

Where the real and imaginary and part of dielectric constant is $\varepsilon_r=n^2\text{-}K^2$ (6)

$$\varepsilon_i=2nK \quad (7)$$

The optical conductivity as a function of frequency response of the material when irradiated with light is calculated as

$$\sigma_{op} = \alpha nc / 4\pi \quad (8)$$

where c is the velocity of light. The electrical conductivity can also be estimated by optical method using the relation

$$\sigma_e = \frac{2\lambda\alpha op}{\alpha} \quad (9)$$

Extinction coefficient Vs photon energy is shown in Figure.6and variation of reflectance with incident photon energy is depicted in Figure.7.Refractive index, complex dielectric constants and optical conductivity as a function of incident photon energy for the grown single crystal are illustrated in Figures 8, 9 and 10. It is shown that the refractive index and extinction coefficient of LAM changes with increasing Photon energy. The high transmission or low absorption in the region 300-1900nm makes the material to obtain low reflectance and refractive index which is a suitable property for antireflection coating solar thermal devices and nonlinear optical applications. The low extinction coefficient (10^{-5}) and high optical conductivity (10^{9}) confirms the high photo response nature of the material [7].

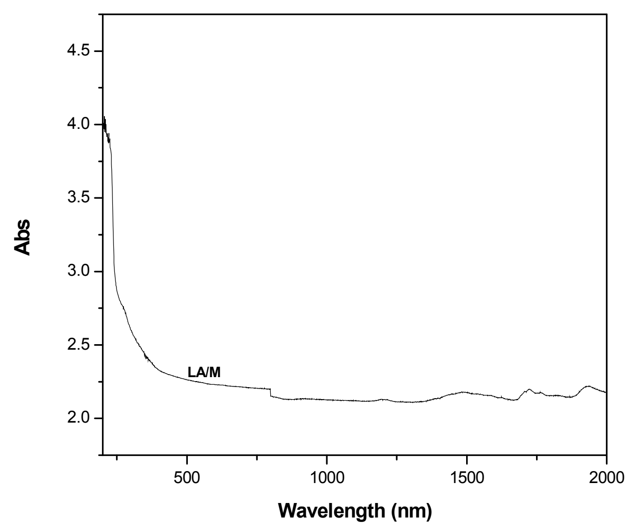

Figure 5. Optical absorption spectrum of LAM

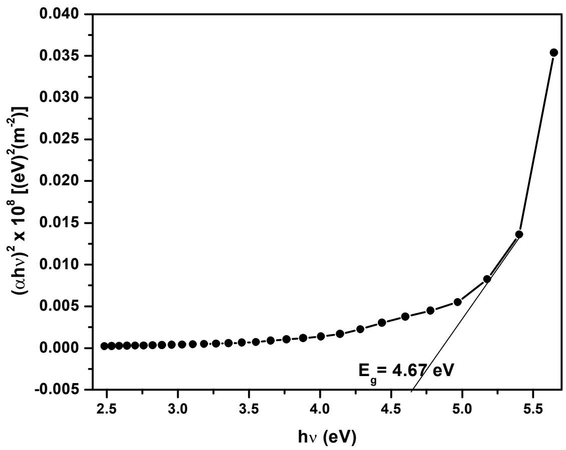

Figure 6. Energy band gap

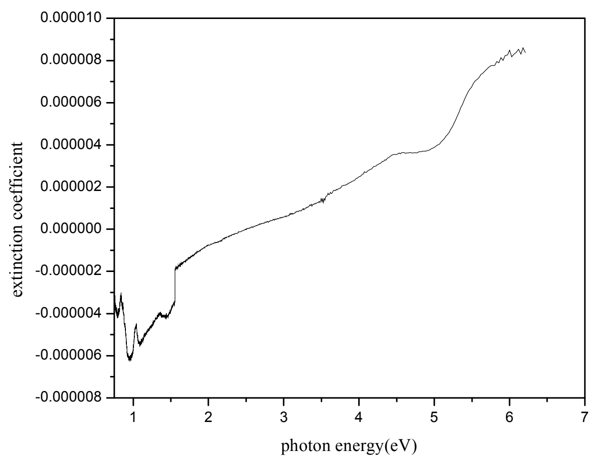

Figure 7. Extinction coefficient Vs Incident Photon Energy

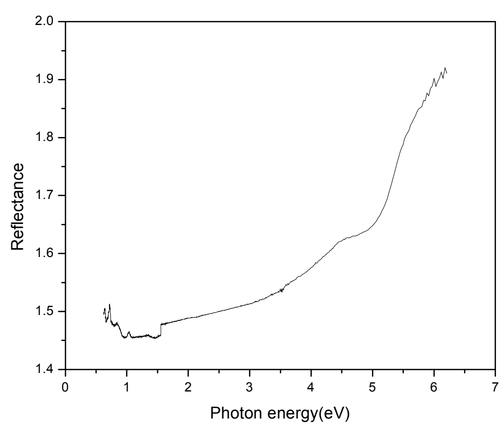

Figure 8. Reflectence Vs Incident photon energy

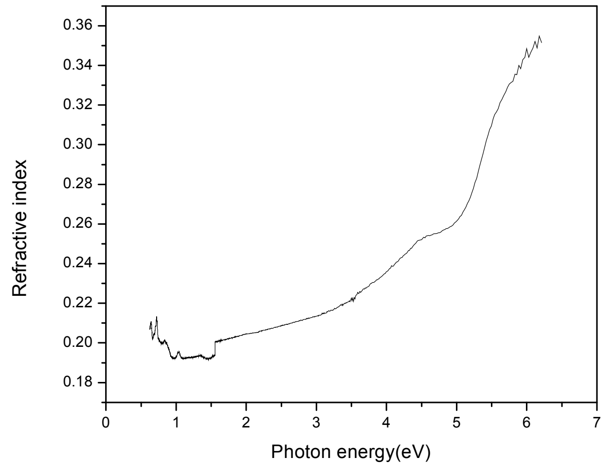

Figure 9. Refractive index Vs Incidient photon energy

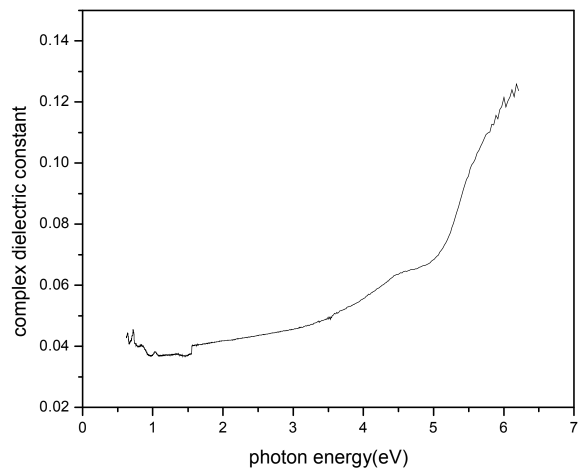

Figure 10. Complex dielectric constant Vs Incident photon energy

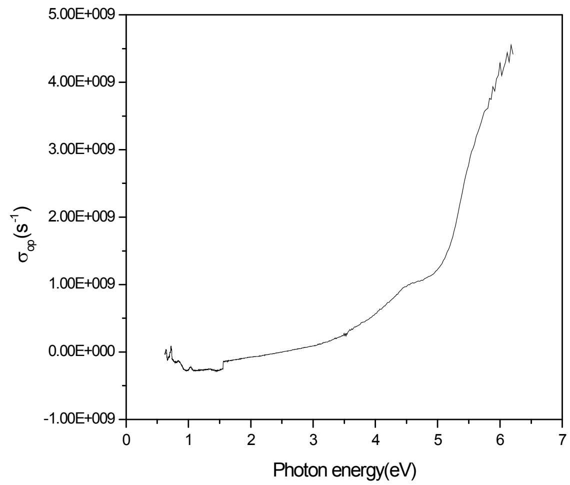

Figure 11. Opticalconductivity Vs Incident photon energy

3.3 NLO Studies

Second harmonic generation (SHG) efficiency was measured to get an idea how much efficient the material is in transferring energy from fundamental laser beam to second harmonic beam. The grown crystal LAM were subjected to Kurtz[8] Second Harmonic Generation (SHG) test using the Nd:YAG Q-switched laser beam for the nonlinear optical (NLO) property. The second harmonic signal of 301 mW was obtained for LAM single crystal with reference to KDP (275 mW). Thus, the SHG efficiency of LAM single crystal is nearly 1.1 times greater than KDP. So the candidate material can be used for frequency conversion in NLO devices.

4. Conclusion

Good quality single crystals of L-Alaninium Maleate (LAM) were grown successfully by slow evaporation technique. Powder XRD studies was carried out for the grown crystal and it was observed that the crystal belongs to orthorhombic crystal system with $P2_12_12$ space group. Calculation of Other linear optical parameters such as Extinction coefficient, Reflectence, Refractive index, Complex dielectric constant, and Optical conductivity reveals the photonic property of the grown crystal and its variation with incident photon energy is analysed.SHG efficiency of the LAM single crystal is 1.1 times greater than KDP.

References

[1] P. Praveen Kumar , V. Manivannan , S. Tamilselvan , S. Senthil, M. Victor Antony Raj, P. Sagayaraj , J. Madhavan, Optics Communications, May 2008.

[2] M. Victor Antony Raj1 J.Madhavan1 M. Gulam Mohamed, J. Comput. Method. Mol. Design, 2011, 1 (4):57-64

[3] J. Madhavan, S. Aruna, K. Prabha, J. Packiam Julius, Ginson P. Joseph, S.Selvakumar, P. Sagayaraj., Journal of crystal growth 293(2006) 409.

[4] Sirohi S and Sharma T P, Opt. Materials, 13, 267 (1999)

[5] P.A. Henikhena, African Phys. Rev. 2, 68 (2008).

[6] J.I. Pankove, Optical Processes in semiconductors (Pentice Hall, New York, 1971).

[7] T.C.Sabari Girisun and S. Dhanuskodi, Cryst. Res. Technol. 44,No.12, (2009).

[8] Kurtz S.K. and Perry T.T. (1968), J. Appl. Phys., Vol. 39, pp. 3798–38l3.