

Linear and nonlinear optical properties of pure and doped L-alaninium maleate single crystals

M. Victor Antony Raj and J. Madhavan

Department of Physics, Loyola College, Chennai, India

ABSTRACT

Amino acid family crystals exhibit excellent nonlinear optical and electrooptical properties. Single crystals of pure, Cu^{2+} and Mg^{2+} doped L-alaninium maleate (LAIM) were grown successfully by slow evaporation technique. The growth conditions of the crystals are studied and the grown crystals are confirmed by powder X-ray diffraction studies. The Second Harmonic Generation in the samples are confirmed by the Kurtz powder technique. The crystals are characterized by FTIR, optical absorption and photoconductivity studies.

INTRODUCTION

In the modern world, the development of science in many areas has been achieved through the growth of single crystals. Nonlinear optical (NLO) materials are expected to play a major role in the technology of photonics including optical information processing [1, 2, 3]. Many research efforts are undertaken to synthesize and characterize new molecules for second-order nonlinear optical (NLO) applications such as high-speed information processing, optical communications, and optical data storage. These applications depend on the various properties of the materials, such as transparency, birefringence, refractive index, dielectric constant, thermal, photochemical and chemical stability. Among NLO materials, organic NLO materials are generally believed to be more versatile than their inorganic counterparts due to their more favorable nonlinear response. In the organic class, R-amino acids exhibit some specific features such as molecular chirality, weak Vander Waals and hydrogen bonds, the absence of strongly conjugated bonds, wide transparency ranges in the visible and UV spectral regions, and zwitter ionic nature of the molecule which favors crystal hardness. Other advantages of organic compounds apart from the above include, amenability for synthesis, multifunctional substitutions, higher resistance to optical damage and maneuverability for device applications, etc. The importance is due to the fact that amino acids contain chiral carbon atom and crystallize in the noncentrosymmetric space groups, therefore, they are potential candidates for optical second harmonic generation [4]. This paper deals with L-alaninium maleate (LAIM), an analog of L-alanine. The structure of L-alaninium maleate (LAIM) was solved by Alagar et al (2001) [5]. In the LAIM compound, the

alanine molecule exists in the cationic form and the maleic acid molecule in the mono-ionized state. LAIM is stable up to 180 °C and transparent from 300 to 1200 nm thus enabling the use of this material for SHG applications [6]. The growth, thermal, spectroscopic and optical studies of LAIM were carried out by Natarajan *et al* (2006) [7]. In the present investigation, a systematic study has been carried out on the growth of pure and metal (Cu^{2+} and Mg^{2+}) doped LAIM crystals. Powder X-ray diffraction studies were carried out and the lattice parameters were calculated by least square method for the grown pure and doped crystals. The content of Cu and Mg has been determined by Atomic absorption studies. Fourier transform infrared (FT-IR) and UV-Vis-NIR studies were carried out for the grown crystals. The SHG efficiency of the pure and doped LAIM crystals were also studied using Nd:YAG Q-switched laser. The results of these investigations are discussed in this paper.

MATERIALS AND METHODS

2 Experimental Procedure

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 the pure and doped LAIM was measured at different temperatures and the drawn solubility curves are shown in Figure 1. It is seen that the solubility of both pure and doped LAIM 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:

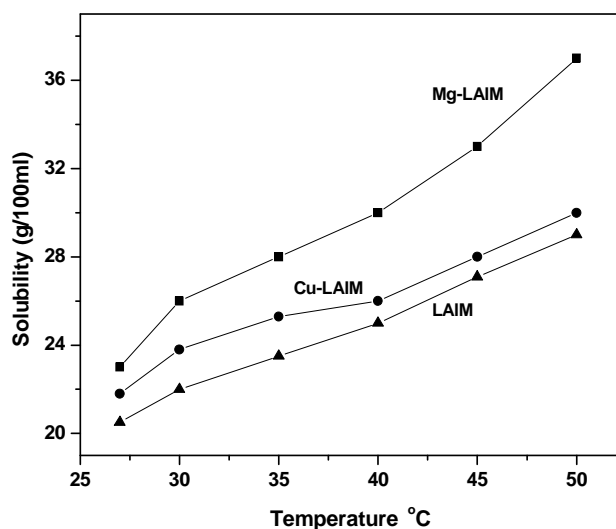


Figure 1 Solubility of LAIM, Cu- LAIM, Mg- LAIM

The same procedure was applied to grow the metal (Cu^{2+} and Mg^{2+}) doped crystals by adding 2 mol % of Cu^{2+} and Mg^{2+} to the respective LAIM solution. The growth and size of the doped crystals are respectively faster and better than the pure crystals. The incorporation of dopant into the parent solution has promoted the growth rate and improved the quality of the crystals. The pure and doped LAIM crystals were grown by slow evaporation technique at room temperature. The photographs of the as grown pure and doped crystals are shown in Figure 2. Bulk crystals

were grown by successive recrystallisation and purification and the crystals are found to be transparent and free from defects. The synthetic reaction is as follows:



Figure 2 Photograph of (a).LAIM (b) Cu- LAIM (c) Mg- LAIM

3 Characterization

3.1 Powder XRD studies

The structural properties of single crystals of pure and doped LAIM have been studied by X-ray powder diffraction technique. Powder X-ray diffraction studies of pure, Cu^{2+} and Mg^{2+} doped LAIM crystals were carried out, using Siemens D500 X-ray diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5406\text{\AA}$) radiation. The samples were scanned for 2θ values from 10° to 50° at a rate of $2^\circ/\text{min}$. Figure 3 (a) shows the Powder XRD pattern of the pure LAIM crystal. The powder XRD pattern of the Cu^{2+} and Mg^{2+} doped crystals are shown in Figure 3(b) and 3(c). The diffraction patterns of the pure and doped LAIM crystals have been indexed by least square fit method. The lattice parameter values of the pure LAIM crystal has been calculated and is well matched with the reported literature [5]. It is seen that both the pure and doped crystals crystallizes in orthorhombic $\text{P}2_12_12_1$ space group and the lattice parameters are shown in Table 1. There are slight variations in the lattice parameters and cell volume of the pure and doped crystals. These variations are due to the incorporation of Cu^{2+} and Mg^{2+} in the LAIM crystal lattice.

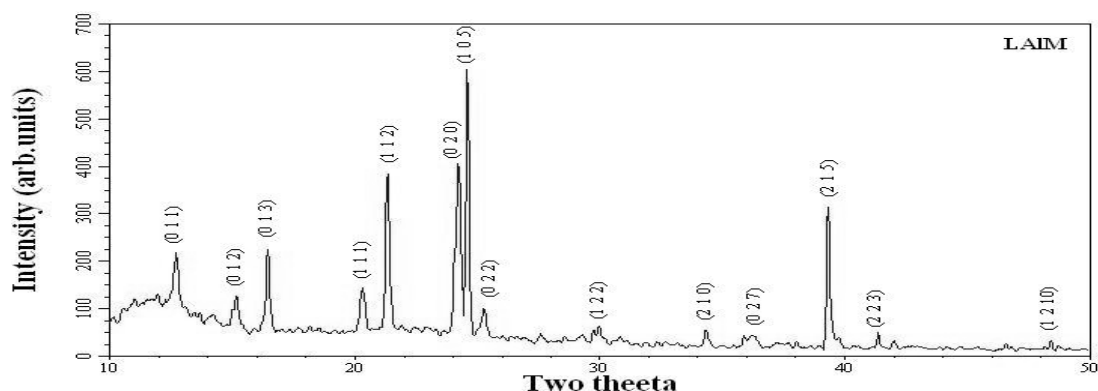


Figure 3(a) XRD pattern of LAIM

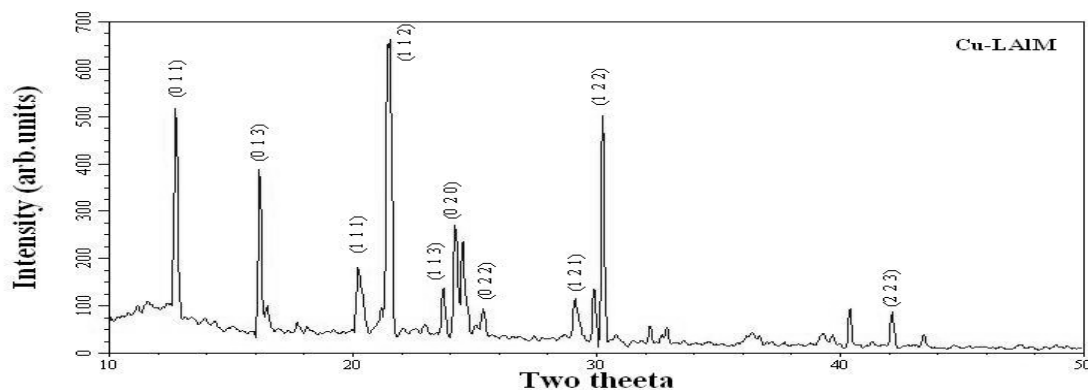


Figure 3(b) XRD pattern of Cu-LAIM

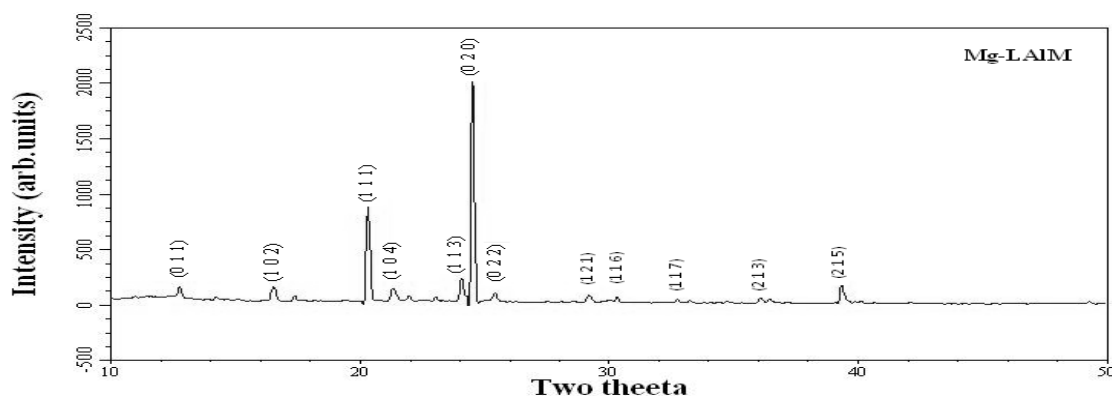


Figure 3(c) XRD pattern of Mg-LAIM

Table 1 Lattice parameter values for the pure and doped LAIM

Lattice parameters	Pure LAIM	Cu ²⁺ - LAIM	Mg ²⁺ - LAIM
a (Å)	5.584	5.590	5.586
b (Å)	7.378	7.381	7.380
c (Å)	23.710	23.692	23.691
Crystal System	Orthorhombic	orthorhombic	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁
Volume (Å ³)	976.82	977.526	976.65

3.2 Atomic Absorption studies

The exact weight percentage of the Cu²⁺ and Mg²⁺ present in doped crystals is determined. 10mg of fine powder of the doped LAIM crystals were dissolved in 100ml of triple distilled water respectively, and the prepared solutions were subjected to Atomic Absorption Spectroscopy (AAS) Analysis. The results shows that only 0.85 % of Cu²⁺ and 1.22 % of Mg²⁺ are present in the respective samples, out of 2 % of the dopant. It is seen that the amount of dopant incorporated in to the doped crystal is less than the concentration of the dopant in the corresponding solution. It is also seen that more Mg ions have gone into the LAIM lattice

compared to Cu ions. This may be due to the radius of Mg (0.65 \AA) compared to Cu ions (0.72 \AA).

3.3 UV-Vis-NIR spectra

Optical absorption data were taken on the pure and doped LAIM polished crystal samples of about 4 to 6 mm thickness using a Varian carry 5E model dual beam spectrophotometer between 200 – 1200 nm. The spectra (Figure 4) indicate that the pure and doped LAIM crystals have minimum absorption in the entire region between 250–1200 nm. From the spectra, it is seen that the doped LAIM crystals have better lower cut-off wavelengths than that of the pure LAIM crystals. Interestingly, both the Cu^{2+} and Mg^{2+} doped crystals have reduced absorption. The required properties for NLO activity are minimum absorption and low cut-off wavelength. These properties are improved in the doped crystals.

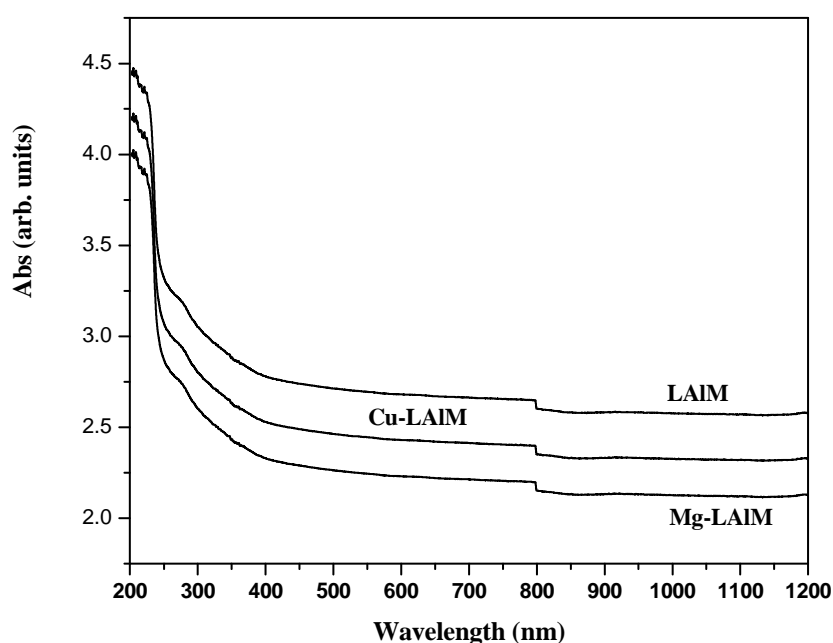


Figure 4 UV spectrum of LAIM, Cu- LAIM, Mg- LAIM

3.4 FT- IR spectra

In order to qualitatively analyze the presence of functional groups in LAIM, FT-IR spectra of the pure and metal doped LAIM crystals were recorded in the range 400 cm^{-1} to 4000 cm^{-1} , using KBr pellet on BRUKKER IFS FT-IR Spectrometer. The FT-IR Spectra of both the pure and doped LAIM crystals are shown in Figure 5. A broad, strong absorption in the $3300\text{--}2300 \text{ cm}^{-1}$ range, including the absorptions at 3206 and 2930 cm^{-1} correspond to the stretching bands of the NH_3^+ ion of the aminoacid. This region results from superimposed O–H and NH_3^+ stretching bands. Absorption in this region is also characterized by multiple fine structures on the lower wavenumber side of the band and the weak absorptions due to COO^- ions. A strong band arising from C– COO^- stretching is observed at 1219 cm^{-1} . Further strong carbonyl absorption at 1720 cm^{-1} confirms the COOH and COO^- groups of the compound. Other characteristic vibrations establishing the identity of the functional groups present in the compound are represented in Table. 2. The FT-IR Spectra of both the pure and doped LAIM confirm the structural aspects of

pure compounds. The spectra do not show any significance change due to the addition of metal dopant into the crystal lattice.

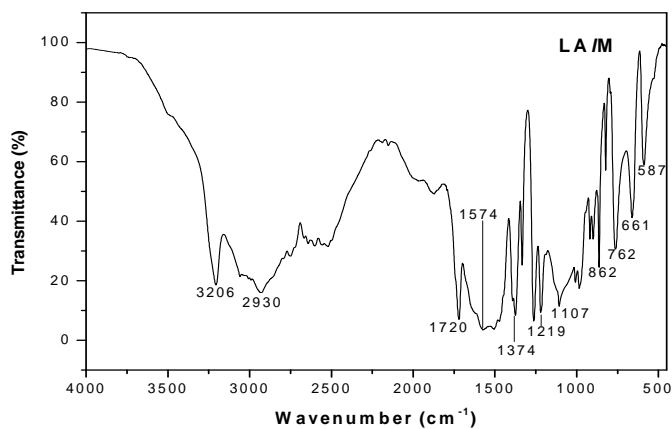


Figure 5 (a) FTIR spectrum of LAIM

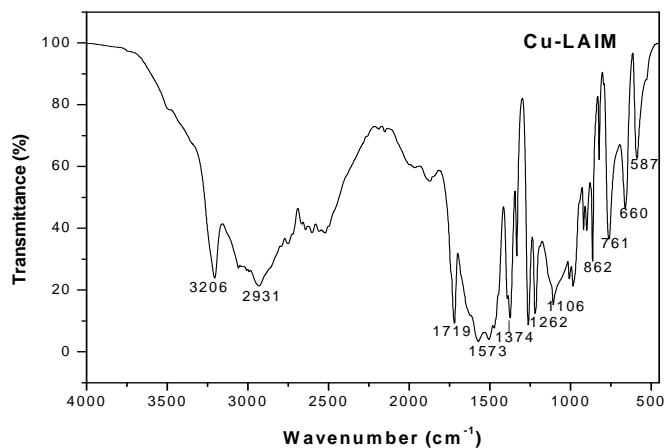


Figure 5 (b) FTIR spectrum of Cu-LAIM,

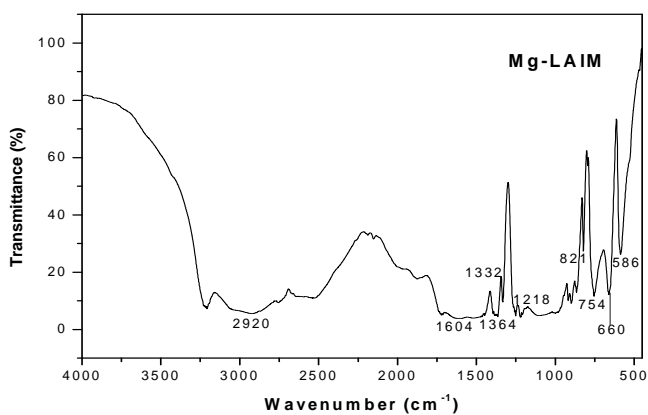


Figure 5 (c) FTIR spectrum of Mg- LAIM

Table 2 FT-IR spectral assignments of pure and doped LAIM

Wave number (cm ⁻¹)			Assignments
Pure LAIM	Cu ²⁺ - LAIM	Mg ²⁺ - LAIM	
3206	3206	3206	NH ₃ asymmetric stretching
2930	2920	2931	C-H stretching
1720	1719	1719	COO ⁻ asymmetric stretching
1374	1364	1374	COO ⁻ symmetric stretching
1219	1218	1218	COO ⁻ vibration
1107	1106	1106	C-O stretching
862	862	862	C-C stretching
762	754	761	CH ₂ rocking
661	660	661	COO ⁻ plane deformation
587	586	587	COO ⁻ wagging

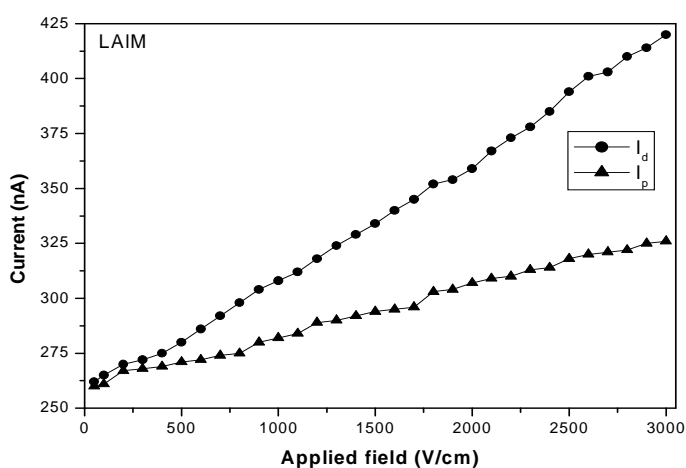


Figure 10 (a) Field dependent conductivity of LAIM crystal

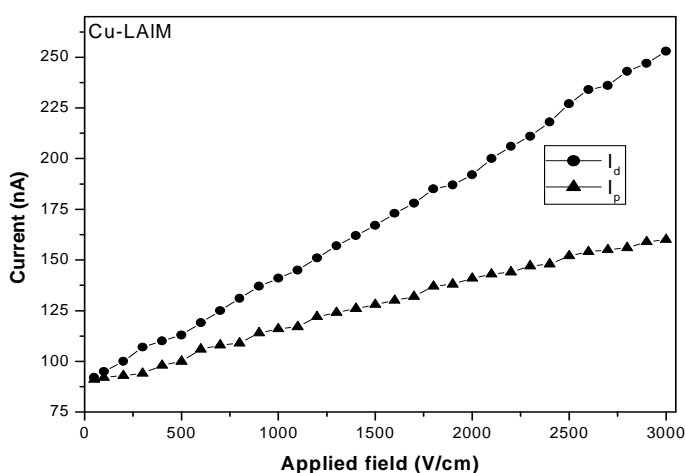


Figure .10 (b) Field dependent conductivity of Cu- LAIM crystal

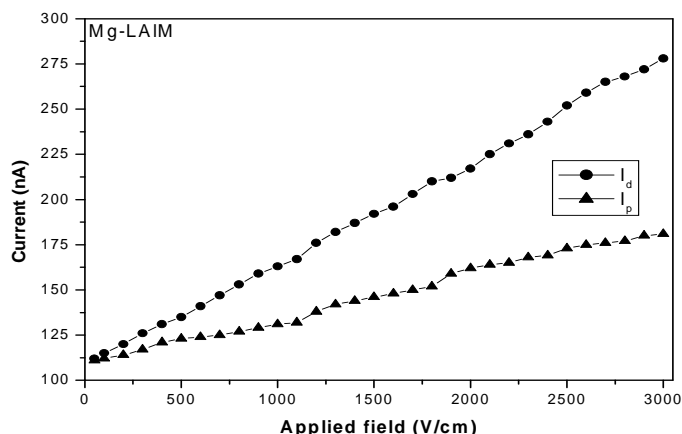


Figure 10 (c) Field dependent conductivity of Mg-LAlM crystals

3.5 NLO studies

The grown crystals of pure and doped LAlM were subjected to Kurtz 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, 325 mW and 375 mW, respectively were obtained for pure, Cu^{2+} and Mg^{2+} doped LAlM with reference to KDP (275 mW). Thus, the SHG efficiency of pure, Cu^{2+} and Mg^{2+} doped crystals is nearly 1.1, 1.2 and 1.4 times greater than KDP.

3.6 Photoconductivity Studies

Field dependence of dark and photocurrent of pure and doped LAlM are shown in Figure 10. The photocurrent is found to be less than the dark current at every applied electric field. This phenomenon is known as negative photoconductivity. It is interesting to note that both pure and doped LAlM crystals exhibit negative photoconductivity.

CONCLUSION

Single crystals of pure and doped LAlM are conveniently grown by employing slow evaporation technique. The grown crystals were confirmed by powder crystal XRD. The various functional groups present in the crystals were identified and confirmed. It is further observed from the FT-IR spectra of doped LAlM that the intensities of different peaks are marginally shifted from that of the parent compound. The cut-off wavelength of pure sample was found to be 250 nm. However the doped samples are more transparent than the parent crystal. The above study reveals that the doped crystals possess improved optical properties. NLO test confirms the enhancement of the NLO property for the doped samples. The photoconductivity studies confirm the negative photo conducting nature of the samples.

REFERENCES

- [1] Prasad, P. N.; Williams, D. J. Introduction to Nonlinear Optical Effects in Molecules and Polymers; Wiley: New York, **1991**.
- [2] Marder, S. R.; Sohn, J. E.; Stucky, G. D., Ed.; Materials for Non-Linear Optics; American Chemical Society: Washington, DC, **1991**.
- [3] Saleh, B. E. A.; Teich, M. C. Fundamentals of Photonics; Wiley: New York, **1991**.

- [4] Madhavan J., Aruna S., Ambujam K., Joseph Arul Prakasam A., Ravikumar S.M., Gulam Mohamed M. and Sagayaraj P., *Cryst. Res. Technology*, 41, 1211-1216 (2006).
- [5] M. Alagar, R. V. Krishnakumar, M. Subha Nandhini and S. Natarajan (2001) *Acta Cryst.* (2001). E57, o855-o857
- [6] Vasantha K. and Dhanuskodi S., (2004), *J. Crystal Growth*, Vol. 269, pp.333–341.
- [7] Natarajan S., Umamaheswaran M., Kalyana sundar J., Suresh J., Martin Britto Dhas S.A., *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2010).