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Research Article

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Growth and studies of L-alanine acetate crystals doped with magnesium chloride

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ABSTRACT

Magnesium chloride doped L-alanine acetate (MCLAA) crystals have grown by solution method with by slow evaporation technique. Solubility of the sample is found to be increasing with increase in temperature. Structural analysis was carried out by XRD method and the crystal of MCLAA is observed to be crystallizing in orthorhombic structure. The functional groups of the samples have been identified by FTIR spectral studies. The optical transmission studies were carried out to determine the transmittance and optical band gap. EDAX analysis was done to identify elements present in the magnesium chloride doped L-alanine acetate crystals. The second harmonic generation efficiency was measured by Kurtz-Perry powder technique. Microhardness was measured at different applied load to understand the mechanical stability of the sample. Dielectric constant and dielectric loss of the samples were measured at different frequencies. Thermal studies were carried out to test the thermal stability of MCLAA crystal. Photoluminescence light was measured at different wavelengths for the grown crystal.

Keywords: L-alanine acetate; doping; single crystal; solution growth; spectroscopy; SHG; dielectrics; photoluminescence

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INTRODUCTION

Alanine is an amino acid which is an important source of energy for muscle tissue, the brain and central nervous system . L-alanine is an isomer of alanine with the chemical formula CH_3CHNH_2COOH next to glycine. L-alanine molecule can exist in zwitterionic form and it can form novel nonlinear optical (NLO) compounds [1-3]. Moreover, it is an ideal candidate for a wide range of applications in electron paramagnetic resonance (EPR) dosimetry due to the particular properties of the associated radiation-induced radicals such as the linear signal response over a wide dose range, good dose yield factors, tissue equivalence and stability of the EPR signal [4-6]. Many researchers have shown interest on L-alanine complex crystals and these crystals have been studied for NLO behavior [7-10]. L-alanine acetate crystal is an NLO material which can be formed by mixing L-alanine and acetic acid in 1:1 molar ratio [11,12]. It is reported that dopants influence the properties of the crystals like growth kinetics, surface morphology, optical, electrical and mechanical properties, etc. Doping NLO crystals with various dopants can alter physical and chemical properties and the doped NLO crystals find wide applications in optical communication, optical computing and optoelectronics [13-16]. In this work, the magnesium chloride is introduced into the lattice of L-alanine acetate crystals to alter the various properties. Magnesium chloride is an inorganic material and if it is doped into the lattice of an organic crystal like L-alanine acetate, NLO properties of the host material will be improved. In this work, magnesium chloride doped L-alanine acetate crystals are grown by solution method for the first time and the results of various studies of the grown crystals are reported in this paper.

EXPERIMENTAL SECTION

2.1. Growth of crystals

Single crystals of undoped and magnesium chloride doped L-alanine acetate were grown by solution method with slow evaporation technique. Undoped L-alanine acetate (LAA) crystals were grown by dissolving L-alanine and acetic acid in 1:1 molar ratio in double distilled water. To obtain the magnesium chloride doped LAA crystals, 5 wt% of magnesium chloride was added into the solution of L-alanine acetate. The filtered solutions undoped and magnesium chloride doped LAA samples were kept separately in two growth vessels for crystallization. After a period of 30 days, transparent crystals were harvested. During the growth period, the beakers were covered with perforated polythene papers and they were kept in a vibration free platform. The harvested crystals are shown Fig.1. The morphology of magnesium chloride doped LAA crystal is observed to be altered when magnesium chloride is added as the dopant into the host LAA crystal.

(a) **(b)**

Figure 1: Harvested crystals of (a) magnesium chloride doped and (b) undoped L-alanine acetate crystals

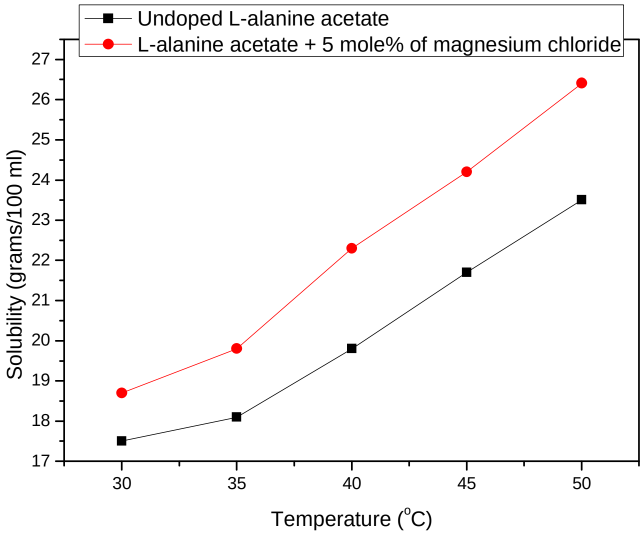

Figure 2: Variation of solubility with temperature for undoped and magnesium chloride doped L-alanine acetate crystals

2.2 Solubility studies

Solubility is defined as the amount of solute present in 100 ml of saturated solution and it is determined by gravimetrical method using a constant temperature bath (CTB). The powder form of the grown crystal was added step by step to double distilled water in an air-tight container kept in the CTB and the stirring was continued till a small precipitate was formed at 30 ^{o}C. Then, 5 ml of the solution was pipetted out and taken in a petri dish and it was warmed up till the solvent was evaporated out. By measuring the amount of salt present in the petri dish, the solubility of the sample in water was determined. The solubility of the sample was determined by similar method at other temperatures. The variations of solubility with temperature for undoped and magnesium chloride added L-alanine acetate samples are shown in Figure 2. From the results, it is noticed that the solubility increases with temperature for both the samples, showing the positive temperature coefficient of solubility. The results show that the solubility of magnesium chloride doped LAA sample is more than that of undoped LAA sample.

2.3 Techniques

X-ray diffraction studies were carried out on the grown undoped and magnesium chloride doped L-alanine acetate crystal by employing an ENRAF Nonius CAD-4/MACH single crystal X-ray diffractometer, with Mo K$_{\alpha}$ radiation (λ=0.71073 Å).

Kurtz and Perry powder method was used to determine second harmonic generation (SHG) efficiency of the samples [17]. Microhardness, stiffness and yield strength of the samples were determined by Vickers hardness test. The dielectric parameters such as dielectric constant and dielectric loss for the grown single crystal were measured using an LCR meter (Agilent 4284A) at various frequencies in the range 10^2 - 10^6 Hz. FTIR studies of the samples were carried out the infrared region 4000-400 cm^{-1} using a spectrophotometer (Model: Perkin Elmer RXI Spectrophotometer) using a KBr pellet technique. The photoluminescence spectra were recorded for magnesium chloride doped LAA crystal in the range of 240–700 nm with the excitation wavelength of 240 nm using a Perkin-Elmer photoluminescence spectrometer (Model: LS45). TG/DTA thermal curves were recorded for the samples using a TG/DTA thermal analyzer in the nitrogen atmosphere.

RESULTS AND DISCUSSION

3.1 FTIR studies

Fourier Transform Infrared (FTIR) spectral studies were carried out for the samples to identify the functional groups. The recorded FTIR spectra of pure and magnesium chloride doped L-alanine acetate crystals are shown in figures 3 and 4. In the spectra, the broad peak around 3100-2800 cm^{-1} is assigned to the stretching vibration of NH_3^+. Multiple combination and overtone bands are observed in the region 2500-1900 cm^{-1}. The peaks in the region 1620-1590 cm^{-1} for the samples are due to COO^- stretching or NH_2 bending vibration. The C-C-N stretching shows around 885-895 cm^{-1}. The CH_3 bending modes are assigned to the peaks in the range 1355-1450 cm^{-1}. NH_3^+ torsion and COO^- deformation bands are noticed in the region 550-470 cm^{-1}. From FTIR spectra, it is confirmed that L-alanine is protonated by getting a proton from acetic acid and thus L-alanine acetate is formed. There are not much change of absorption bands/peaks of FTIR spectra of undoped and magnesium chloride doped L-alanine acetate crystals but the intensity of bands have been altered and there are slight of shifting of bands are noticed. This is due to presence of magnesium chloride in the interstitials of the lattice of the doped sample.

3.2 XRD studies

The grown crystals of undoped and magnesium doped L-alanine acetate were subjected to single crystal X-ray diffraction studies using an ENRAF NONIUS CAD4 diffractometer with MoK$_{\alpha}$ radiation (λ=0.71073 Å) to determine the crystal structure. The obtained values of cell parameters of undoped L-alanine acetate crystal in this work are found to be in close agreement with the data reported in literature [18]. The single crystal XRD data for magnesium chloride doped L-alanine acetate are provided in the table 1. The crystal system is found to be orthorhombic and the number of molecules per unit cell is 4. The space group of magnesium chloride doped LAA crystal is $P2_12_12_1$ and this space is recognized as a non-centrosymmetric. It is the essential requirement for SHG from the sample.

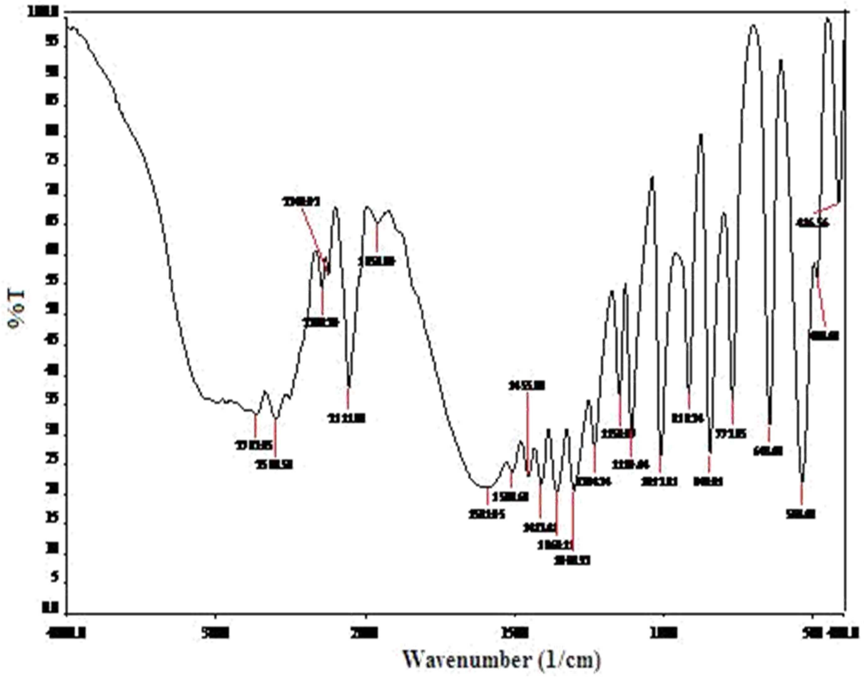

Figure 3: FTIR spectrum of undoped L-alanine acetate crystal

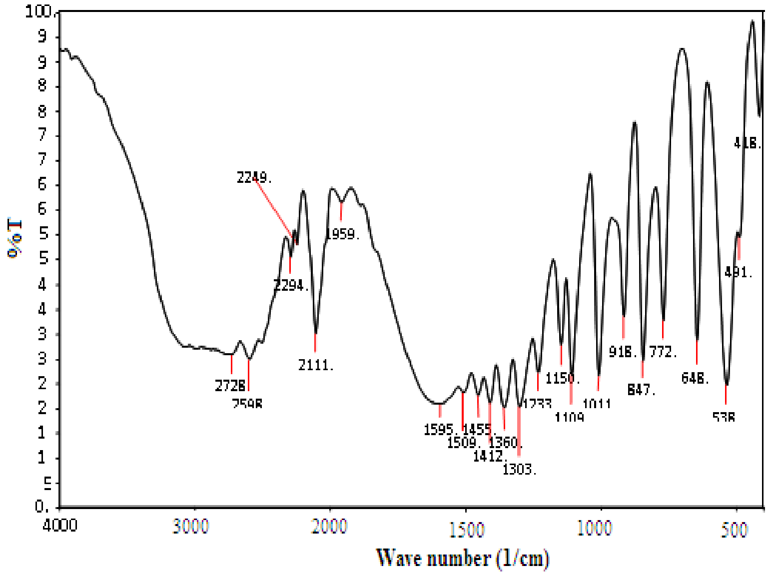

Figure 4: FTIR spectrum of magnesium chloride doped L-alanine acetate crystal

Table 1: XRD data for crystal of magnesium chloride doped LAA

Diffractometer	ENRAF NONIUS CAD-4
Radiation, wavelength	MoK_α, 0.71069 Å
Refinement method	
Symmetry	Full matrix Least square method
Space group	Orthorhombic structure
Lattice constants	$P2_12_12_1$
	a= 5.365(2) Å
	b=6.248(2) Å
	c=13.206(3) Å
	α=90°
	β=90°
Volume	γ=90°
Z	442.67 $Å^3$
	4

3.3 Measurement of SHG efficiency

A high intensity Nd:YAG laser (λ = 1064 nm) with a pulse duration of 6 ns was used for the measurement of second harmonic generation (SHG) efficiency of the undoped and magnesium chloride doped LAA samples. In this experiment, potassium dihydrogen phosphate (KDP) was used as the reference. The SHG behavior was confirmed from the output of the laser beam having the green emission (λ = 532 nm) and the samples are the potential materials for frequency conversion. From the results, it is observed that undoped LAA sample has the relative SHG efficiency of 1.13 times and magnesium chloride doped LAA sample has 1.35 times that of the KDP sample.

3.4 UV-visible-NIR transmittance studies

The UV-visible-NIR spectrum gives information about the structure of the molecule because the absorption of UV and visible light involves the promotion of electron in σ and π orbitals from the ground state to higher energy states. The UV-visible transmittance spectrum of magnesium chloride doped LAA crystal was recorded using a double beam spectrophotometer in the wavelength region 190-1100 nm and the recorded spectrum is shown in the figure 5. It is observed from the spectrum that the cut-off wavelength for the crystal is 252 nm. Using the formula $E_g = 1240/\lambda$, the optical band gap (E_g) was determined to be 4.92 eV for the grown magnesium chloride doped LAA crystal. As the optical spectrum of undoped LAA crystal has been already given in literature, it is not shown here.

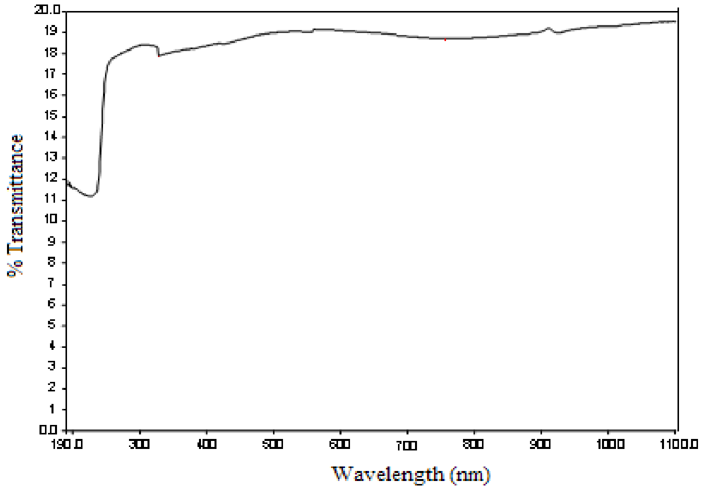

Figure 5: UV-visible-NIR spectrum of magnesium chloride doped L-alanine acetate crystal

3.5 Thermal studies

The thermal studies such as TG/DTA studies were carried out for magnesium chloride doped LAA crystal in the temperature range 40–900 °C. The recorded TG/DTA thermal curves for magnesium chloride doped LAA crystal are shown in the figure 6. From the figure, the sharp endothermic peak indicates the sample have good crystallnity. From the TG curves, it is noticed that there is a large weight loss at the decomposition point at 268 °C. The results show that the sample has no water of crystallization and it has high thermal stability. After decomposition of the sample, the residue of the sample is found to be almost zero. Since the sample has the decomposition point more 250 °C, it can be used as a better candidate for NLO applications.

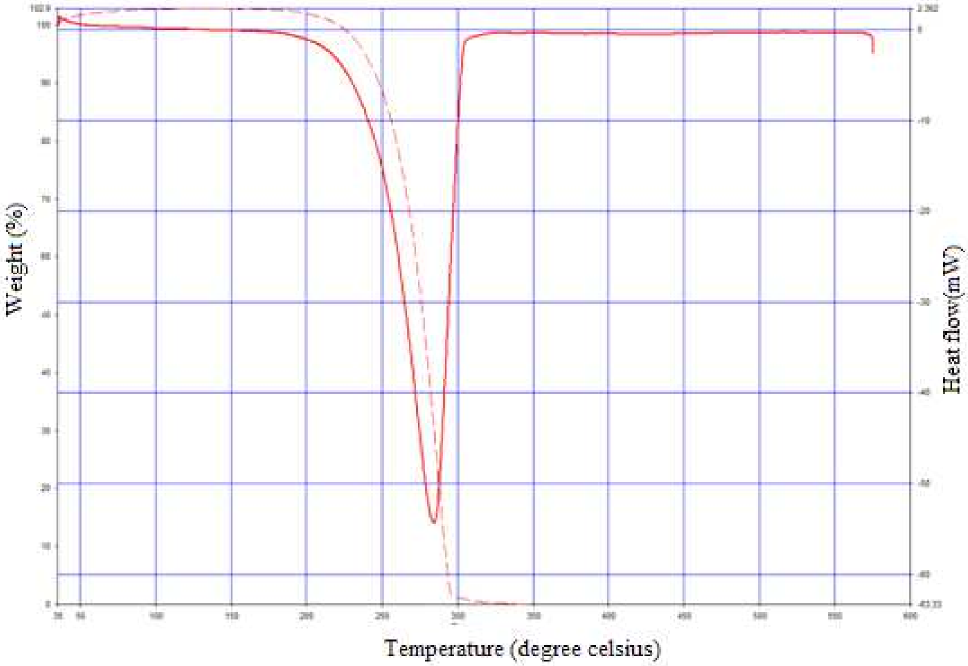

Figure 6: TG/DTA thermal curves for magnesium chloride doped LAA crystal

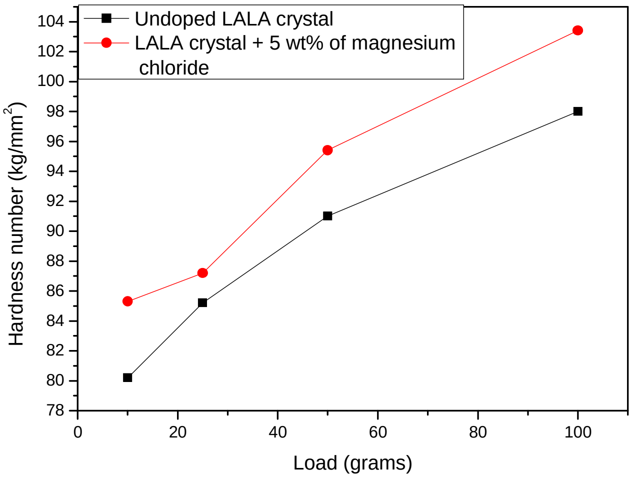

Figure 7: Plots of microhardness with the applied load for the grown crystals of undoped and magnesium chloride doped LAA

3.6 Measurement of microhardness

The microhardness of the undoped and magnesium chloride doped L-alanine acetate crystals was measured using a Vickers hardness tester. Microhardness measurement was made using a Leitz microhardness tester fitted with a diamond pyramidal indenter. The samples were subjected to microhardness studies and the applied loads are 25, 50, 75, 100 g for a constant indentation period of 10 s. The Vickers hardness number H_v was calculated using the relation $H_v = 1.8544\ P/d^2$ kg/mm^2 where ‘P’ is the applied load in kg and‘d’ is the diagonal length of the impression in mm [19]. The variations of H_v with applied load for grown crystals are is shown in the figure 7. It is evident from the plots that the microhardness of the crystals increases with increasing of load. The increase in the microhardness values of the crystals with increasing of load is in agreement with the reverse indentation size effect (RISE). It is observed that the hardness of magnesium chloride doped LAA crystal is more than that of undoped LAA crystal. This is due to strengthening of the doped sample when magnesium chloride has entered into the lattice of LAA crystal.

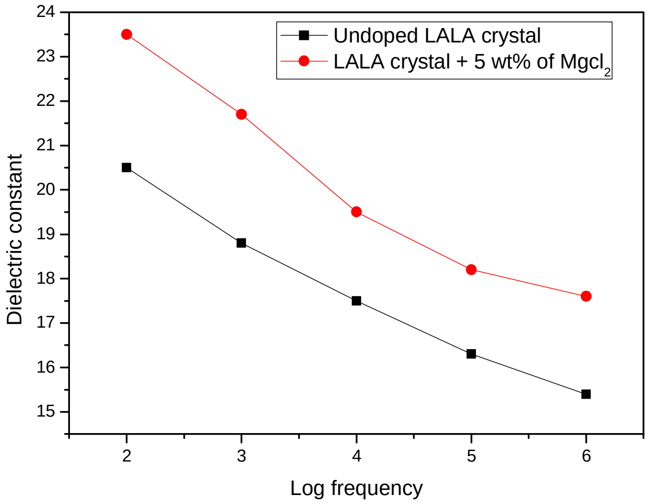

Figure 8: Variation of dielectric constant with frequency for undoped and magnesium chloride doped L-alanine acetate crystals

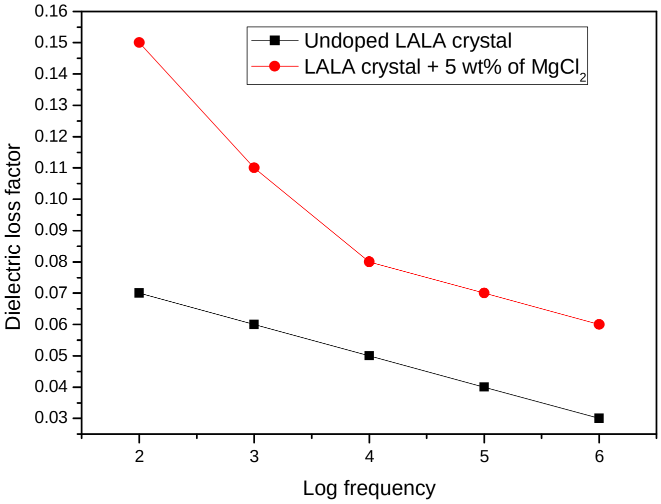

Figure 9: Variation of dielectric loss with frequency for undoped and magnesium chloride doped L-alanine acetate crystals

3.7 Dielectric parameters

Dielectric studies were carried out to investigate the electrical parameters such as dielectric constant (ε_r) and dielectric loss (tan δ). The presence of a dielectric between the plates of a condenser enhances the capacitance. The dielectric parameters depend on the applied frequency and temperature of the samples. The variations of dielectric parameters of the samples with frequencies are presented in the figures 8 and 9. From the graphs, it is observed that dielectric parameters like dielectric constants and loss factors decrease with increase in frequency and the high values of ε_r at low frequencies may be due to presence of space charge polarization and its low value at high frequencies may be due to the loss of significance of the four type of polarizations viz. space charge, orientational, ionic and electronic polarization. It is to be noted here that space charge polarization is dominant whereas electronic and ionic polarizations are not very much active in low frequency range [20]. In accordance with Miller's rule, the low value of dielectric constant at higher frequencies may be due to the fact that the dipoles cannot follow up the fast variation of the applied field and is a suitable parameter for the enhancement of SHG coefficient and extending the samples application towards photonic, electro-optic and NLO devices [21].

3.8 Identification of elements by EDAX method

Energy dispersive X-ray spectroscopy (EDAX) was used to identify the elements present in the samples. The EDAX spectrum was taken using Jeol 6390LV model scanning electron microscope. The EDAX spectrum of the grown magnesium chloride doped L-alanine acetate crystals was recorded and it is shown in the figure 10. From the results, it is confirmed that the elements such as carbon, oxygen, chlorine, magnesium and nitrogen are present in the samples. It is to be mentioned here that hydrogen cannot be identified from samples.

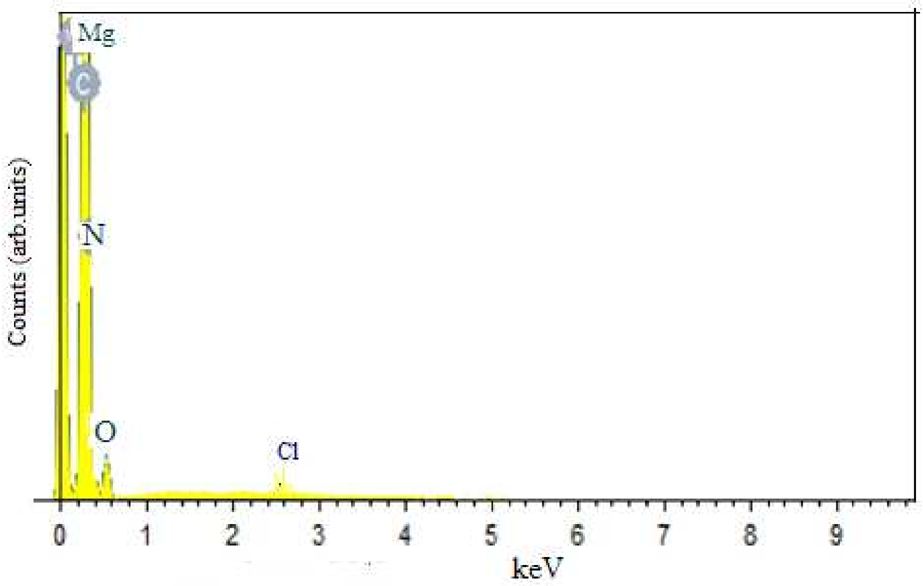

Figure 10: EDAX spectrum of magnesium chloride doped L-alanine acetate crystal

3.9 Measurement of photoluminescence

The photoluminescence light from sample was measured at different wavelengths and the emission spectrum was recorded for magnesium chloride doped LAA crystal in the range of 240–700 nm with the excitation wavelength of 240 nm. The recorded spectrum of the sample is shown in the figure 11. The results show four emission bands: a medium UV emission band at 356 nm, a strong blue band at 445 nm, and a weak blue band at 492 nm and a red band at 684 nm. From the results, it is confirmed that the grown magnesium chloride doped LAA crystal emits UV light, green, blue and red fluorescence light when the they are excited with UV light of wavelength at 240 nm.

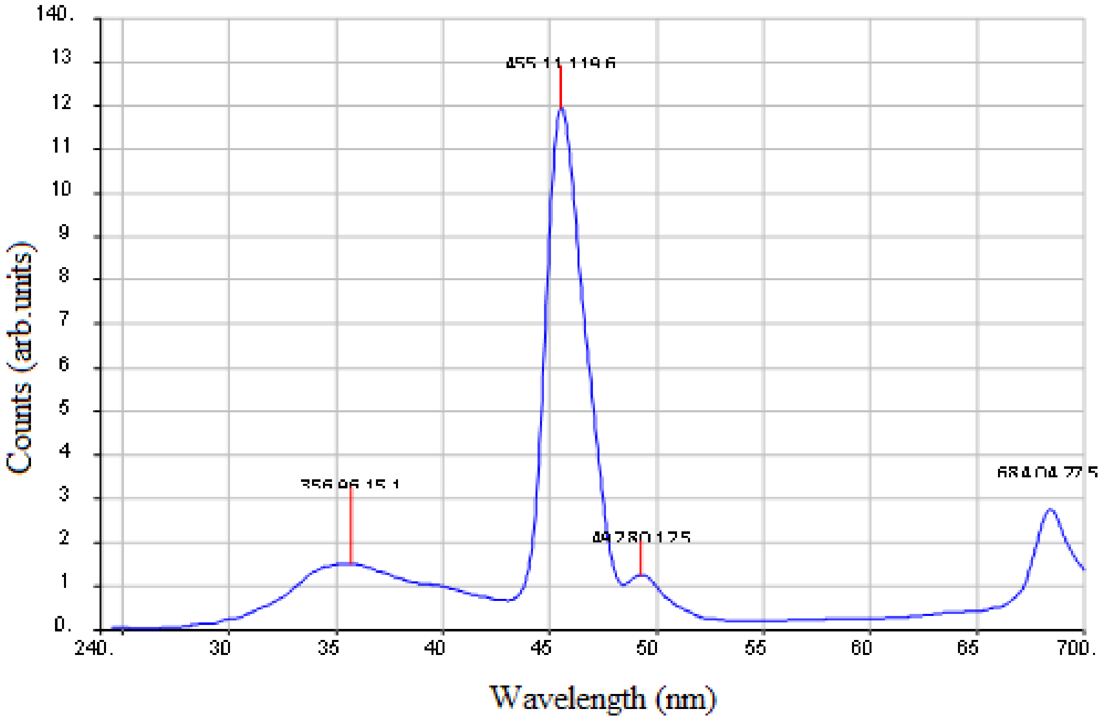

Fig.11: PL emission spectrum of magnesium chloride doped L-alanine acetate crystal

CONCLUSION

Single crystals of undoped and magnesium chloride doped L-alanine acetate were grown by slow evaporation technique. The lattice dimensions were determined from the single crystal XRD technique and found that samples belong to orthorhombic system. Optical spectra of the samples have been recorded and band gap values are determined. SHG efficiency was measured for the samples and it is found to be more than one and hence the samples are the better candidates for NLO applications. EDAX studies were carried out to find the presence of elements in the doped sample. Thermal stability and mechanical strength were identified to be more for the samples and hence the samples are better for NLO device fabrication. The transparency and optical band gap were determined the dielectric behavior of the samples have been analysed. The photoluminescence spectrum of magnesium chloride doped L-alanine acetate crystal show four emission bands when it is excited with 240 nm.

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