GROWTH AND CHARACTERIZATION OF L-ARGININE ACETATE CRYSTALAS DOPED WITH METHYL ORANGE AND MAGNESIUM CHLORIDE

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Abstract

Single crystals of magnesium chloride and methyl orange doped L-arginine acetate were grown by solution method with slow evaporation technique. Solubility of the samples was measured at different temperatures. The grown crystals were subjected by X-ray diffraction techniques to identify the crystal structure and by Fourier Transform Infrared (FTIR) spectra to identify the functional groups. Second harmonic generation (SHG) efficiency was measured by Kurtz-Perry technique. Thermal stability was analysed by thermogravimetric studies. Photoluminescence light output was measured for the samples as a function of wavelength. Microhardness was evaluated at different applied loads. Dielectric constant and dielectric loss of the samples were measured at different frequencies. The obtained results from various studies were discussed.

Key words: Organic NLO; doping; Single crystal; growth from solution; characterization; XRD; spectroscopy.

1. Introduction

Optoelectronic technologies need nonlinear optical materials with high Second Harmonic Generation (SHG) efficiency and high laser damage threshold [1]. Organic nonlinear optical crystals are more resourceful materials for NLO applications compared to inorganic materials due to their large electro-optic coefficient with low frequency dispersion and high nonlinearity [2]. Due to chiral symmetric properties, complex of amino acids are the promising materials for NLO applications [3]. Many researchers have put a lot of interest on amino acid complex crystals and reported that these crystals are the better candidates for NLO and opto-electronic applications [4-8]. L-arginine acetate is an amino acid complex material and like L-arginine phosphate and KDP, L-arginine acetate has high SHG efficiency, high LDT value and it crystallizes in the monoclinic structure with non-centrosymmetric space group [9,10]. 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 [11-14]. In the present study, L-arginine acetate crystals have been added with two kinds of dopants viz. magnesium chloride and methyl orange to alter the physical and chemical properties of the host material. The aim the paper is to present the results of the growth, structural, optical, mechanical, thermal and electrical properties of undoped, magnesium chloride and methyl orange doped L-arginine acetate crystals.

2. Experimental details

2.1. Crystal Growth

Single crystals of pure (undoped), magnesium chloride and methyl orange doped L-arginine acetate were grown from aqueous solutions by slow evaporation technique. L-arginine and acetic acid were dissolved in de-ionized water in the ratio 1:1 to get a saturated solution. Magnetic stirring for an hour was performed to obtain a homogenous solution. The solution was filtered and covered with a porous cover and kept in a dust free environment. Good quality single crystals of L-arginine acetate were harvested after four weeks. 10 wt% of magnesium chloride and methyl orange were added separately into the solutions of L-arginine acetate in two beakers and the solutions were stirred well for about 2 hours. Then the solutions were kept separately for the growth of crystals by slow evaporation. After about four weeks, doped crystals of L-arginine acetate were harvested and the grown crystals were observed to be stable and transparent. The photograph of the grown crystals are shown in Fig.1.

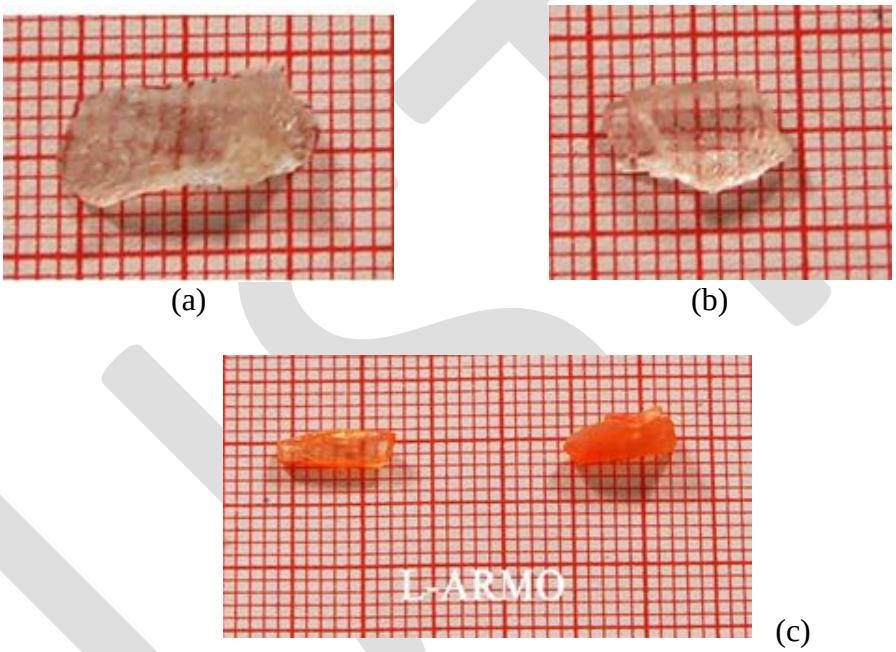


Figure 1: Harvested crystals of (a) pure, (b) magnesium chloride doped and (c) methyl orange doped L-arginine acetate.

2.2. Characterization techniques

Microhardness measurement was carried out using a LEITZ microhardness tester, fitted with a Vickers diamond pyramidal indenter. The well polished crystal was placed on the platform of Vickers microhardness tester and the loads of different magnitudes were applied in a fixed interval of time of 10 seconds. For each load, several indentations were made and the average diagonal length (d) is used to calculate the microhardness number 'H_v' using the relation $H_v = 1.8544\ P/d^2$ kg mm^{-2} where P is the load applied in kg and d is the diagonal length of the indented impressions in mm. Single crystal X-ray diffraction (SCXRD) studies were carried out for the grown crystals using ENRAF NONIUS CAD-4 X-ray diffractometer with MoK_α (λ=0.71069 Å) radiation to evaluate the structural properties. The Fourier transform infrared spectrum (FTIR) of the sample was recorded in the region 400-4000 cm^{-1} with Perkin Elmer Fourier transform infrared spectrometer (Model : Spectrum RXI) using KBr pellet. Thermal analysis of the grown samples were obtained using the instrument NETSZCH SDT Q 600 V8.3 Build 101. Values of dielectric constant and

dielectric loss of the crystals were measured using LCR meter (Agilent 4284A) in the frequency region 10^2 – 10^6 Hz at different frequencies. The Second Harmonic Generation (SHG) conversion efficiency was tested using a set-up of Kurtz and Perry [15] and it was carried out using Q-switched mode locked Nd:YAG laser with first harmonic output at 1064 nm. The grown crystals of this work were powdered with uniform particle size of about 300 □m using a ball mill and the powdered sample was packed densely between two transparent glass slides. In the present study, a multi-shot mode of 8 ns laser pulse with a spot radius of 1 mm was used. The fundamental laser beam of 1064 nm wavelength, 8 ns pulse with 10 Hz pulse rate was made to fall normally on the sample. The power of the incident beam was measured using a power meter. The suitable filter removes the residual 1064 nm and the green light was detected by a photomultiplier tube (PMT) and displayed on a Cathode Ray Oscilloscope (CRO). KDP crystal was powdered into identical size as that of the sample of this work and it was used as reference material in the SHG measurement. The photoluminescence (PL) spectra were recorded for undoepd and rhodamine-B doped LALA crystals in the range of 260–700 nm with the excitation wavelength of 240 nm using a Perkin-Elmer photoluminescence spectrometer (Model: LS45).

3. Results and Discussion

3.1 Solubility studies

Solubility studies of the grown samples were carried out by gravimetrical method [16] at different temperatures in the range 30-50 ^{o}C. The solubility curves for undoped, magnesium chloride and methyl orange doped L-arginine acetate samples are presented in the figure 3. Results show that all the three samples of this work have positive temperature coefficient of solubility indicating as the temperature increases the solubility increases. It is observed that the solubility of L-arginine acetate gets increased when magnesium chloride and methyl orange are added as the dopants into the host L-arginine acetate solutions. The solubility data will be useful in preparing the saturated and supersaturated solutions at a particular temperature for the growth of crystals.

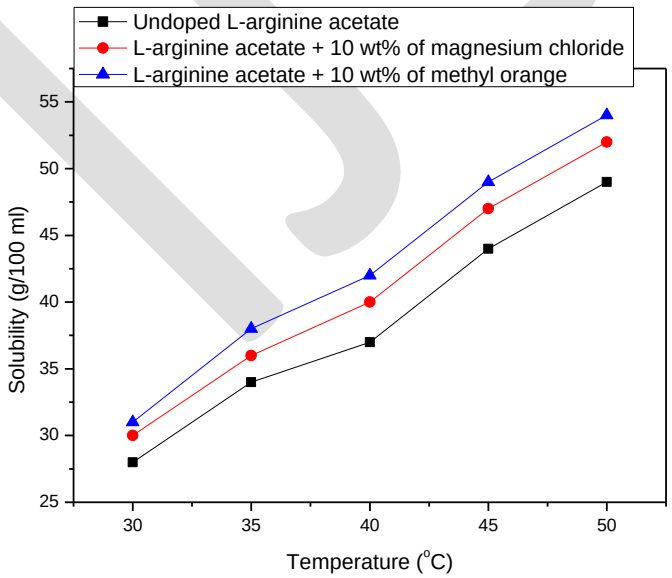


Figure 2: Variation of solubility with temperature for undoped, magnesium chloride and methyl orange doped L-arginine acetate samples

3.2 Identification of crystal structure

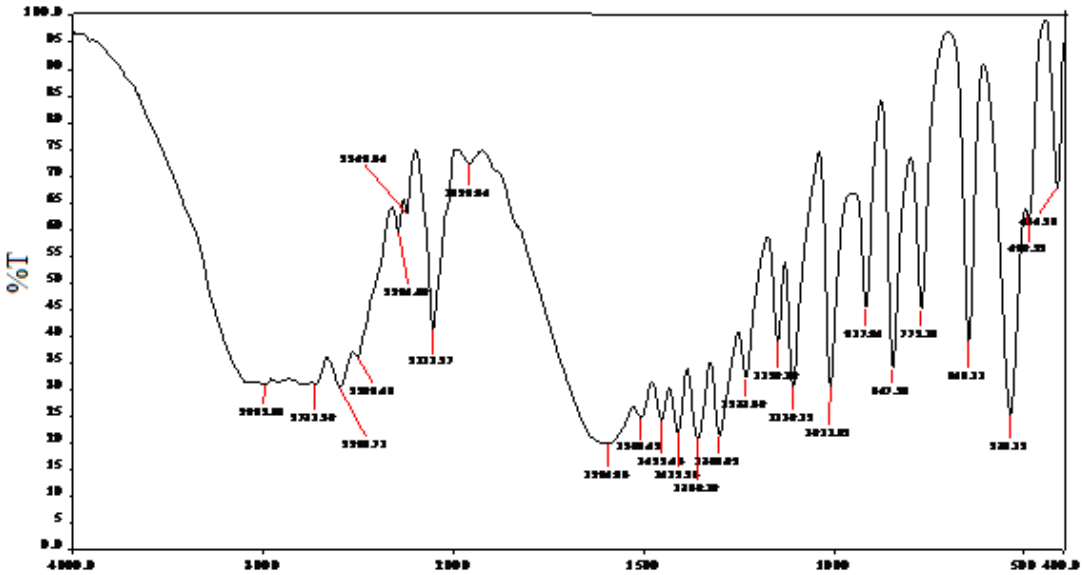
Single crystal XRD studies of the grown crystals were carried out using an ENRAF NONIUS CAD4 diffractometer with Mo Kα radiation (λ = 0.71073 Å) to identify the crystal structure of the sample crystals. The obtained data are provided in the table 1. From the results, it is observed that the grown crystals crystallize in monoclinic structure. The obtained lattice constants of undoped L-alanine acetate (LALA) crystal are observed to be in good agreement with reported data [10]. The data indicates that there are slight alteration in the values of lattice constants and unit cell volume when L-arginine acetate crystals are doped with magnesium chloride and methyl orange.

Table 1: Lattice parameters for undoped, magnesium chloride and methyl orange doped L-arginine acetate crystals

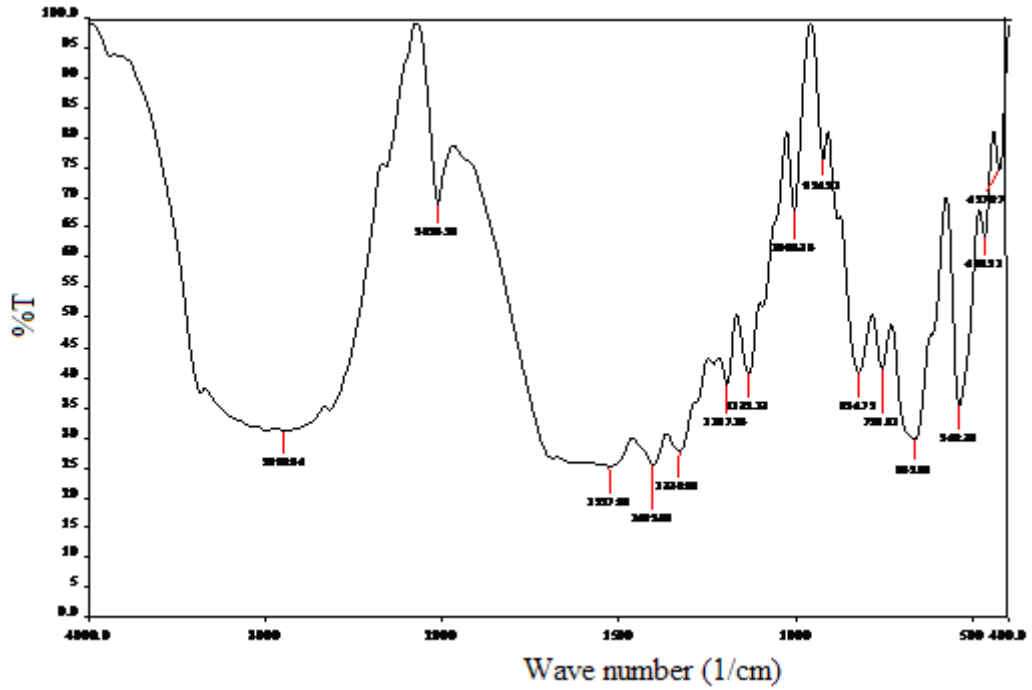
Sample	Cell parameters	Volume $(Å)^3$
Undoped L-arginine acetate crystal	a =9.231 (2) Å b= 5.174 (3) Å c= 13.269 (3) Å □ = 90 °, □= 113.8°, □ □ □ □= 90°	579.85(3)
L-arginine acetate crystal doped with 10 wt% of magnesium chloride	a =9.240 (3) Å b= 5.178 (4) Å c= 13.302 (3) Å □ = 90 °, □= 112.1°, □ □ □ □= 90°	580.96 (2)
L-arginine acetate crystal doped with 10 wt% of methyl orange	a =9.232 (4) Å b= 5.175 (3) Å c= 13.272 (3) Å □ = 90 °, □= 114.4°, □ □ □ □= 90°	577.45(4)

3.3. FTIR spectral analysis

To analyse qualitatively the presence of the functional groups in the grown crystals, the FTIR spectra of the grown crystals were recorded using an FTIR spectrometer in the wave number range 4000 cm^{-1} - 400 cm^{-1}. Figs. 3(a), 3(b) and 3(c) represent the FTIR spectra for pure L-arginine acetate, 10 wt% of magnesium chloride and 10 wt% of methyl orange doped L-arginine acetate crystals. The results show that L-arginine exists in zwitterionic phase in which the amino group exists as ammonium ion (NH_3^+) and the carboxyl group exists as carboxylate ion (COO^-). Amino acids in the form of zwitterions do not show N – H stretching at 3200 cm^{-1} but show a broad band with multiple peaks between 3600 cm^{-1} and 2600 cm^{-1} assigned to asymmetric stretching of NH_3^+ group. In the grown crystals, the same mode can be seen from 3230 cm^{-1} to 2900 cm^{-1}. For the doped crystals, significant difference could not be observed except for broadening and shifting of absorption peaks/bands in the FTIR spectra. This may be due to the inclusion of dopants in small quantity into the interstitials of the host samples.



(a)



(b)

Figure 3: FTIR spectra of (a) magnesium chloride doped and (b) methyl orange doped L-arginine acetate crystals

3.4 Measurement of SHG efficiency

The grown crystals were crushed into powder and they were subjected to Kurtz-Perry powder technique [15]. The second harmonic generation (SHG) behaviour of the samples was confirmed from the output of the laser beam having the green emission (λ=532 nm) and thus the samples are the potential materials for frequency conversion. The second harmonic

generation energy values are 9.24 mJ, 10.29 mJ and 8.27 mJ for undoped, magnesium chloride doped and methyl orange doped L-arginine acetate samples. All the samples including KDP were subjected to an input energy of 0.68 J. The standard KDP sample gave an SHG signal of 8.8 mJ for the same input energy. Thus, it is observed that the SHG efficiency values of the undoped (pure), magnesium chloride doped and methyl orange doped L-arginine acetate crystals are 1.05, 1.17 and 0.94 respectively times that of the standard KDP sample.

3.5. Vickers microhardness studies

Vickers microhardness measurements were carried out on the grown crystals using a Vickers microhardness tester fitted with a diamond indenter. The indentations were made using a Vickers pyramidal indenter for various loads from 25 to 100 g. Vickers microhardness number (H_v) for the sample crystals is calculated using the following 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 indentation impression in millimeter and 1.8544 is a constant of a geometrical factor for the diamond pyramid. Plots between the hardness number and the applied load are presented in the figure 4. From the results, it is observed that hardness number increases with increase of load showing reverse indentation size effect. The hardness number gets increased when L-arginine acetate is doped with magnesium chloride and that gets deceased when L-arginine acetate is doped with methyl orange.

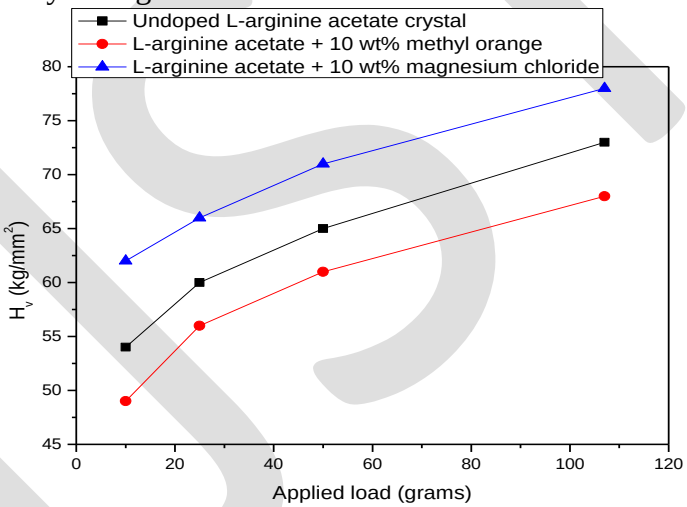


Figure 4: Plots of microhardness number (H_v) versus applied load for undoped, magnesium chloride and methyl orange doped L-arginine acetate crystals

3.6 TG studies To ascertain the thermal stability of the grown sample, Thermogravimetric (TG) studies were carried out in the temperature range 50-600 ^oC and the thermograms are displayed in Figs. 5 and 6. From Thermogravimetric curves, it is noticed that there is no weight loss upto to 210 ^oC and there is a maximum weight loss in the temperature range 220°C – 310 ^oC and hence the samples are observed to be thermally stable and suitable for device applicaitons. The decomposition point values for magnesium chloride and methyl orange doped L-arginine acetate samples are 285 ^oC and 280 ^oC respectively.

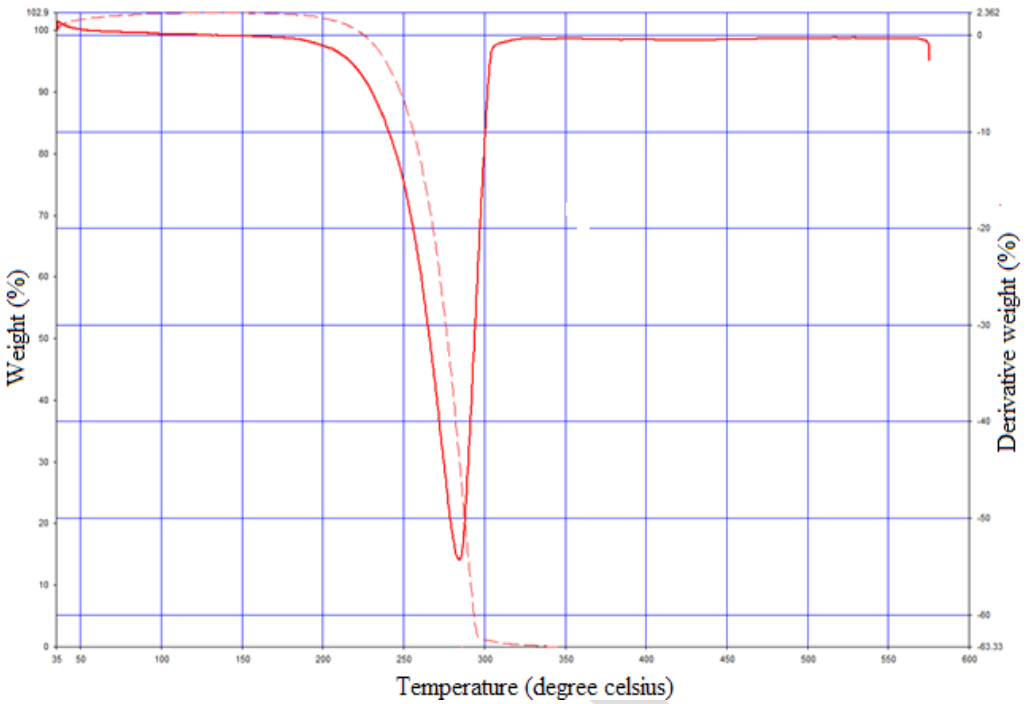


Figure 5: TG thermal curves for magnesium chloride doped L-arginine acetate crystal

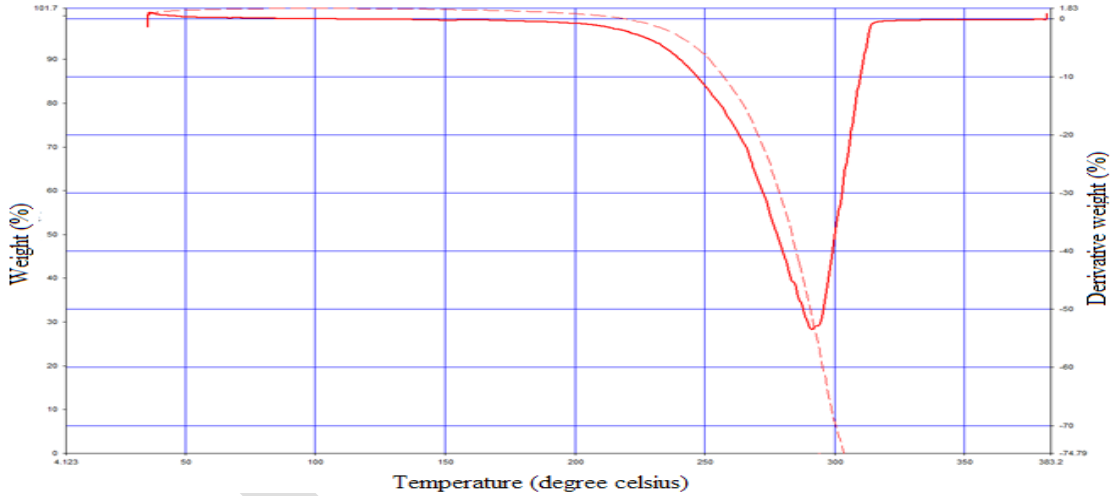


Fig.6: TG thermal curves for methyl orange doped L-arginine acetate crystal

3.7 Dielectric studies

The values of dielectric constant and the dielectric loss (tan □) of the samples were measured for various frequencies at room temperature (30 ^{o}C) . The frequency dependence of the dielectric constant at room temperature is shown in Fig. 7. It is observed that the dielectric constant has higher values at lower frequencies and further it decreases with increase in frequency. The dielectric constant of the materials is due to the contribution of electronic, ionic, dipolar or orientation and a space charge polarization which is high relay upon on the frequencies. The space charge polarization is generally active at lower frequencies [17]. The variations of dielectric loss with the frequency are shown in Fig.8. It is observed that the dielectric loss decreases with the increasing of frequency. The low value of dielectric loss

with high frequency for the samplessuggests that the samples have less number of defects. The results show that the dielectric constant and loss factor of the magnesium chloride doped and methyl orange doped L-arginine acetate crystals are more than that of undoped L-arginine acetate crystal.

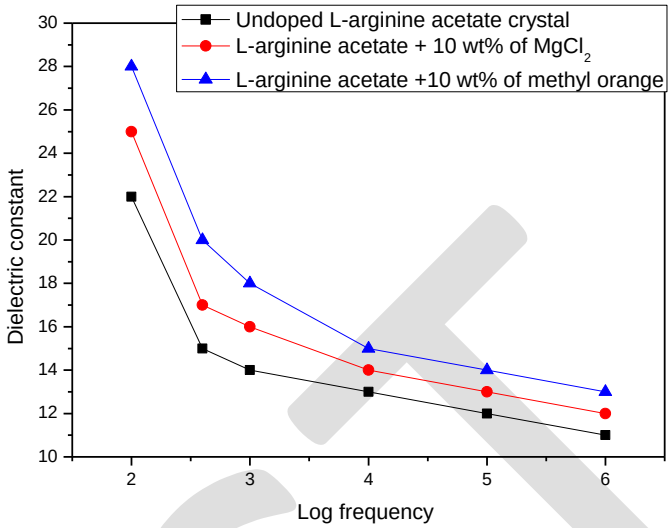


Figure 7: Plots of dielectric constant versus frequency for undoped, magnesium chloride and methyl orange doped L-arginine acetate crystals

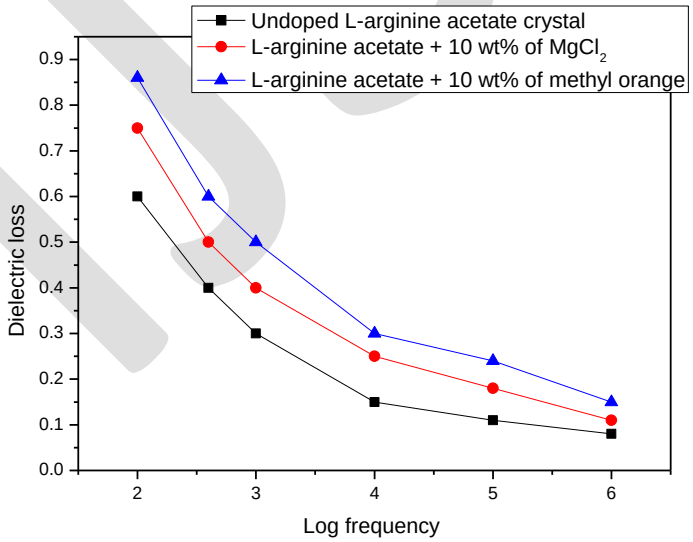


Figure 8: Plots of dielectric constant versus frequency for undoped, magnesium chloride and methyl orange doped L-arginine acetate crystals

3.8 Photoluminescence studies

Photoluminescence (PL) emission spectra were recorded for magnesium chloride doped and methyl orange doped L-arginine acetate crystals in the wavelength range of 250–700 nm with the excitation wavelength of 240 nm and the spectra are shown in the figures 9 and 10. The PL spectrum for magnesium chloride doped L-arginine acetate crystal has emission bands at 344 nm, a strong blue band at 452 nm, and a weak blue band at 480 nm and a red band at 665 nm. The PL spectrum of methyl orange doped L-arginine acetate crystal consists of only two emission bands at 411 nm and a strong red band at 625 nm. It is confirmed that the grown crystals emit UV light, green, blue and red fluorescence light when they doped with magnesium chloride and methyl orange.

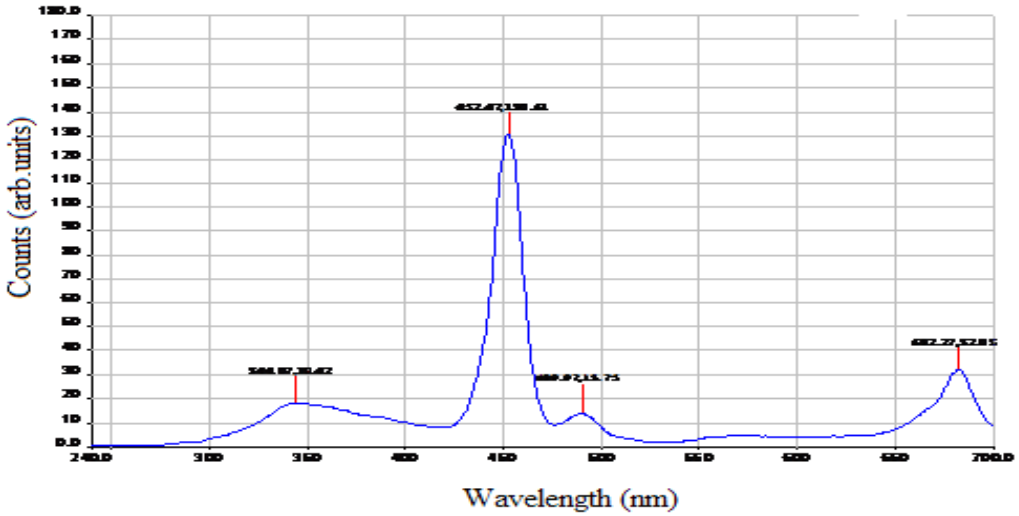


Figure 9: Photoluminescence spectrum of magnesium chloride doped L-arginine acetate crystal

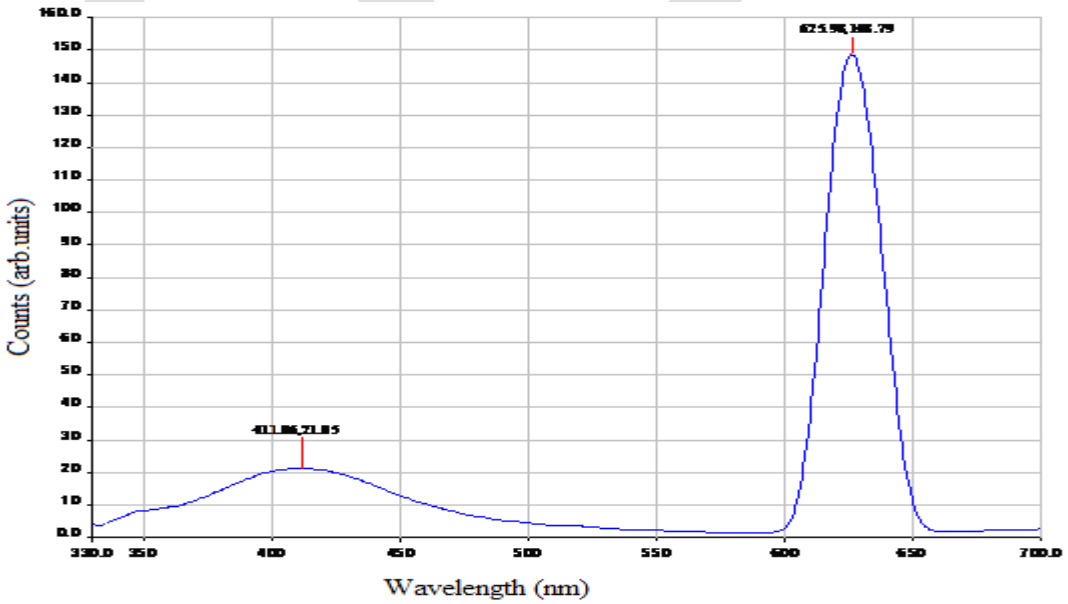


Figure 10: Photoluminescence spectrum of methyl orange doped L-arginine acetate crystal

4. Conclusion

Good quality single crystals of pure, magnesium chloride and methyl orange doped L-arginine acetate were grown by slow evaporation technique. The XRD studies confirm the crystallinity and reveal the crystal structure of the grown crystals. Hardness and thermal stability of the host L-arginine acetate crystals have altered when dopants such as magnesium chloride and methyl orange have added. Dielectric constant and loss factor of the L-arginine acetate crystals are increased when they are doped with magnesium chloride and methyl orange. The grown in the present study can be considered as the promising NLO crystals as they have high SHG efficiency. Results show that the grown crystals are the photoluminescent materials.

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