Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Physics Research, 2011, 2 (1): 183-189
(http://scholarsresearchlibrary.com/archive.html)

Scholars Research Library
ISSN 0976-0970
CODEN (USA): APRRC7

Investigations on the linear and nonlinear optical properties of pure and doped L-Arginine Maleate (LArM) Crystals

M. Victor Antony Raj and J. Madhavan*

Department of Physics, Loyola College, Chennai - 600034, India

---

ABSTRACT

Single crystals of pure and doped L-Arginine maleate (LArM) were grown successfully by slow evaporation technique. In the present study, to improve the device characteristics of LArM crystals, metal dopant was incorporated into the pure crystals. The grown pure and doped LArM crystals were confirmed by X-ray powder diffraction studies. The pure and doped crystals were characterized by Fourier Transform Infrared (FT-IR). Absorptions of the grown crystals were analyzed using UV-Vis-NIR studies. Nonlinear optical studies of pure and doped crystals were carried out and it revealed that the dopant has increased the efficiency of the pure crystal.

INTRODUCTION

Nonlinear optical (NLO) materials capable of generating second harmonic frequency play an important role in the domain of optoelectronics and photonics. Nonlinear optical (NLO) crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible and ultraviolet ranges are required for numerous device applications [1, 2, 3]. Within the last few years, much progress has been made in the development of nonlinear optical (NLO) organic materials for second harmonic generation (SHG). L-Arginine is one of the essential amino acids widely distributed in biological substances. The functions and role of L-arginine molecules in living matter are characterized by strong basicity of the guanidyl group. As a result L-arginine forms a number of salts with organic and inorganic acids showing non-linear optical properties [4]. L-Arginine maleate ($C_6H_{14}N_4O_2$ $C_4H_4O_4$,$2H_2O$) is one of these L-arginine salts which is a complex of strongly basic amino acid, carboxylic acid and provides useful information in relation to molecular interaction in present day biological systems and to prebiotic self-organism [5]. It is also a nonlinear optical material with second harmonic generation efficiency 1.68 times that of KDP. In the present work, we report the growth of a promising nonlinear organic crystal of both pure and doped LArM crystals which are grown by slow evaporation solution growth technique. The grown crystals were characterized by powder crystal X-ray diffraction, UV-Vis-NIR and FT-IR. The grown crystals are also subjected to dielectric, photoconductivity, mechanical and thermal studies.

MATERIALS AND METHODS

Experimental Procedure

L-arginine maleate ($C_6H_{14}N_4O_2C_4H_4O_4.2H_2O$) LArM was synthesized by the reaction between a weak organic maleic acid ($C_4H_4O_4$) and the strongly basic amino acid, L-arginine (Merck) taken in equimolar proportions. Purification of the synthesized salt was done by repeated crystallization until optically clear crystals were obtained. The solubility (Figure 1) of LArM in water was determined by saturating the aqueous solution at high temperature and then slowly reducing the temperature in the presence of precipitated solid to maintain equilibrium and then sampling and analyzing the solution at defined temperatures. Initially single crystals of LArM were grown by solvent evaporation of the saturated aqueous solution of LArM at constant temperature (35°C). Saturated aqueous solution of LArM was taken in a crystallizing vessel with perforated covers and placed in a constant temperature bath. The as grown crystals are shown in Figure 2.

3 Characterization

3.1 Powder XRD studies

The structural properties of single crystals of pure and doped LArM have been studied by X-ray powder diffraction technique. Powder X-ray diffraction studies of pure, $Cu^{2+}$and Mg^{2+} doped LArM crystals were carried out, using Siemens D500 X-ray diffractometer with Cu K_α (λ = 1.5406 Å) radiation. The samples were scanned for 2θ values from 10˚ to 70˚ at a rate of 2˚ /min. Figure 3 shows the Powder XRD pattern of the pure and doped LArM crystals. The diffraction patterns of the pure and doped LArM crystals have been indexed by least square fit method. The lattice parameter values of the pure LArM 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 triclinic P1 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 LArM crystal lattice.

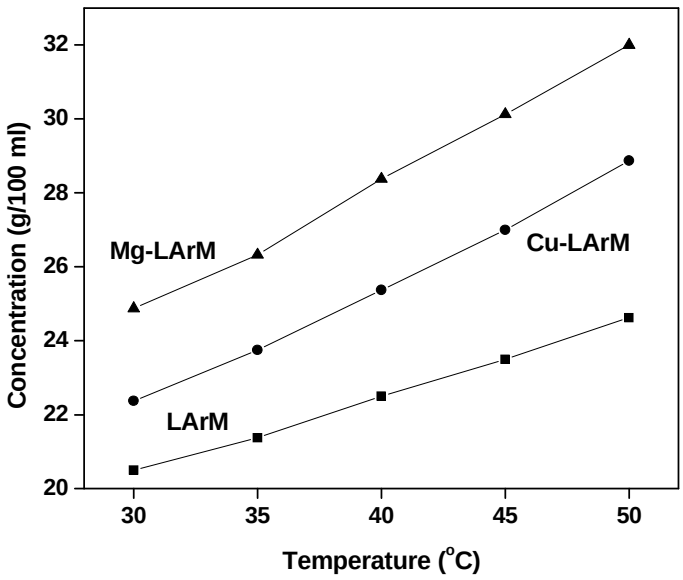

Figure 1 Solubility curves of pure and doped LArM crystals

2 Photographs Figure of the as grown (a) pure LArM, (b) Cu-LArM and (c) Mg-LArM crystals

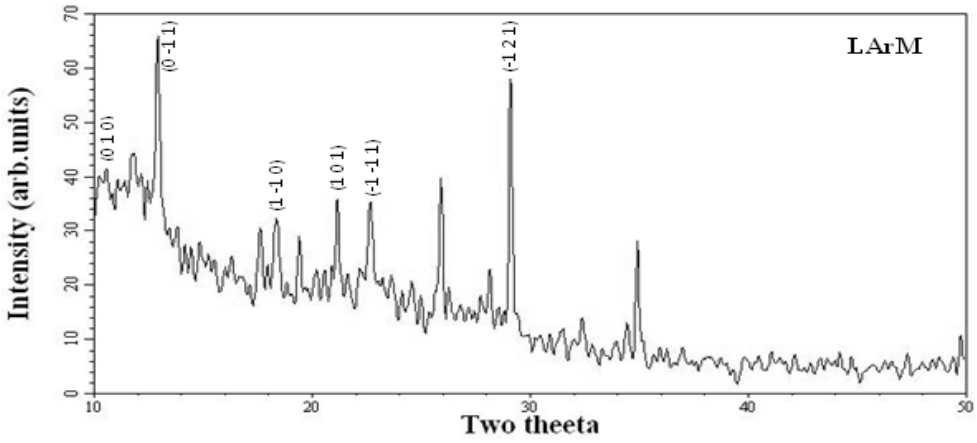

Figure 3 (a) XRD pattern of LArM

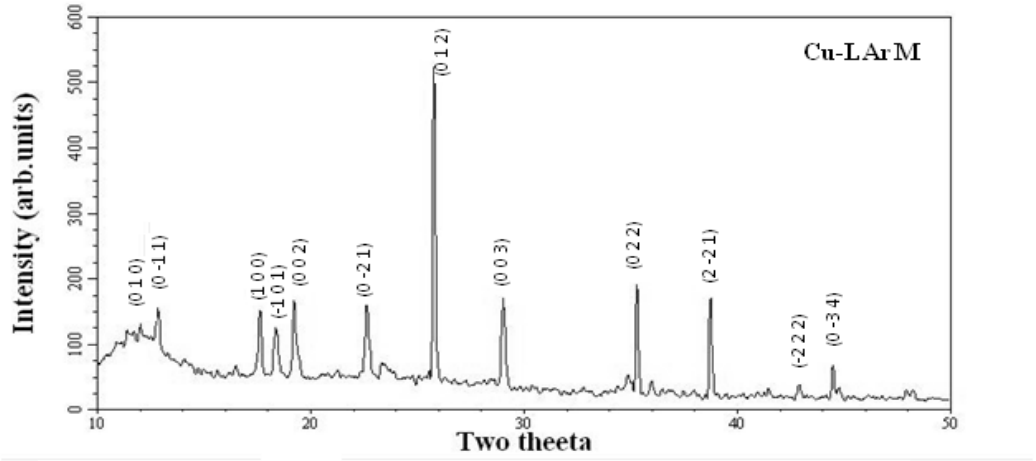

Figure 3 (b) XRD pattern of Cu-LArM

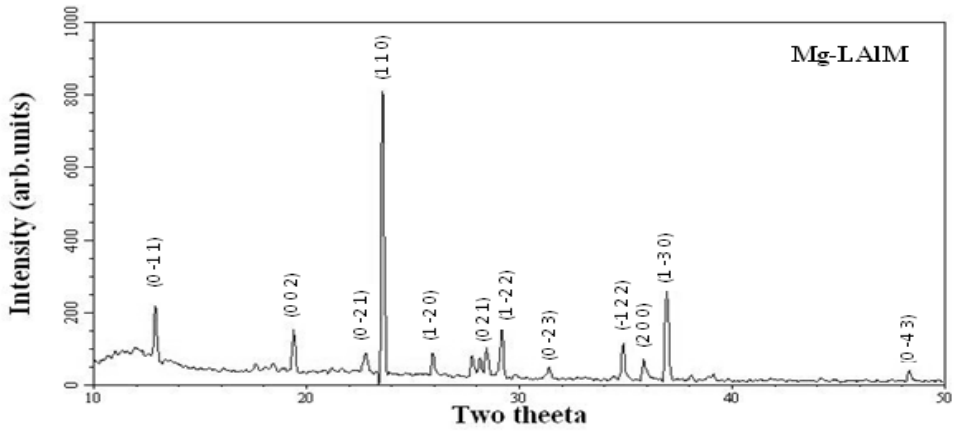

Figure 3 (c) XRD pattern of Mg-LArM

Table 5.1 Lattice parameter values for the pure and doped LArM

Lattice parameters	Pure LArM	Cu^{2+} - LArM	Mg^{2+}- LArM
a (Å) b (Å) c (Å) α° β° γ°	5.268 8.041 9.788 106.20 97.26 101.68	5.271 8.048 9.790 106.4 97.22 101.66	5.275 8.050 9.791 106.8 97.28 101.70
Crystal System	Triclinic	triclinic	triclinic
Space group	P1	P1	P1

3.2 Atomic Absorption studies

The exact weight percentage of the $Cu^{2+}$and Mg^{2+} present in doped crystals is determined. 10mg of fine powder of the doped LArM 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 0.91 % of $Cu^{2+}$and 1.31 % of Mg^{2+} 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 LArM lattice compared to Cu ions. This may be due to the radius of Mg (0.65 Å) compared to Cu ions (0.72 Å).

3.3 UV-Vis-NIR Studies

The optical transmission spectrum of LArM single crystal was recorded in the wavelength region of 200-2000 nm using VARIAN CARY 5E spectrometer. The spectra of pure and doped LArM crystals are shown in Figure4. It is evident that the pure crystal possesses a wide optical transparency window from 390 -980 nm. It is also clearly indicates that the UV cut-off wavelength lies at 290 nm. The presence of low cut-off wavelength and the wide optical

transmission window are the suitable parameters for frequency doubling of laser radiation. From the spectra it is seen that the doped LArM crystals are more transparent than the parent crystal in entire transmission range of 300 - 1100 nm without any absorption peak. The above studies reveal that the doped crystals possess improved optical properties.

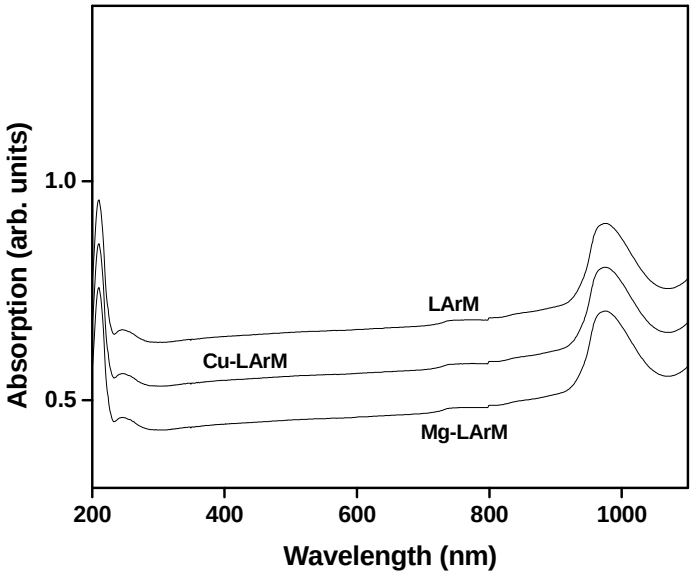

Figure 4 Optical absorption spectra of pure LArM, Cu-LArM and Mg-LArM crystals

3.4 NLO studies

Kurtz SHG tests were carried out on the pure and doped LArM samples using the Nd:YAG Q-switched laser beam as a source. For a laser input of 6.2mJ, the second harmonic signal (532nm) of 91.66mW, 272.12mW, 352.48mW and 434.39mW were obtained for KDP, pure LArM, Cu^{2+} and Mg^{2+} doped LArM respectively. Thus, the SHG efficiencies of pure, Cu^{2+} and Mg^{2+} doped crystals are 3, 3.8 and 4.7 times respectively higher that of KDP. Thus, the $Cu^{2+}$and Mg^{2+} metals have increased the efficiency of pure LArM.

3.5 FT-IR Studies

The FT-IR spectra of LArM, Cu^{2+}-LArM, and Mg^{2+}-LArM were recorded on BRUKER IFS 66V FT-IR SPECTROMETER using KBr pellet in the range 4000 cm^{-1} to 400 cm^{-1} and are shown in the Figures 5.5 .Investigating the absorption bands of LArM below 1000 cm^{-1} three characteristic bands were identified, one at 662 cm^{-1} (COO^- in plane deformation), one at 578 cm^{-1} (COO^- wagging mode) and the third one at 864 cm^{-1} (C-C stretching). The band corresponding to NH_3^+ asymmetric deformation vibration occurs at 1681 cm^{-1}, COO^- asymmetric stretching at 1513 cm^{-1}. High wave number region (3750 - 2300 cm^{-1}) contains the NH and CH, stretching vibration and combination of them. Band at 3409 cm^{-1} is due to the presence of water molecules which is again confirmed from X-ray diffraction study. The characteristics bands of FT-IR spectrum also confirmed the ionization of L-arginine and maleic acid in the crystal lattice of LArM.

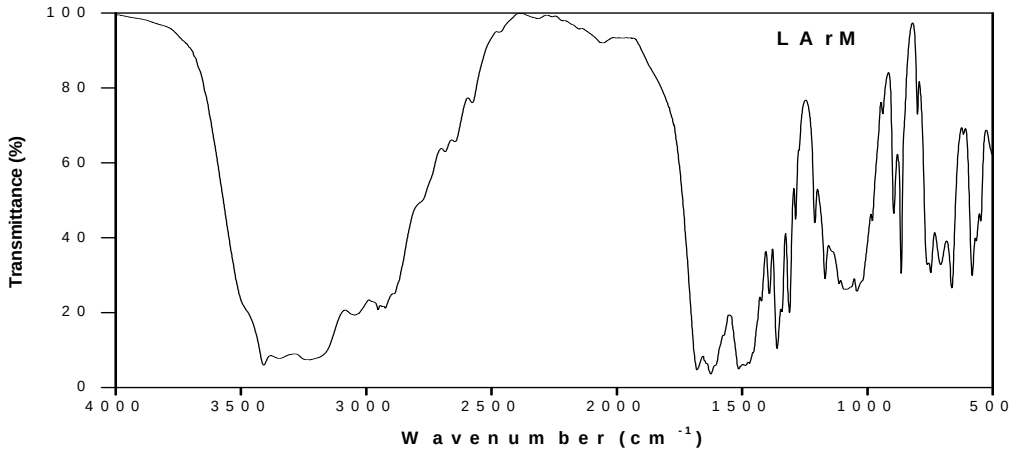

Figure 5 (a) FTIR spectrum of LArM

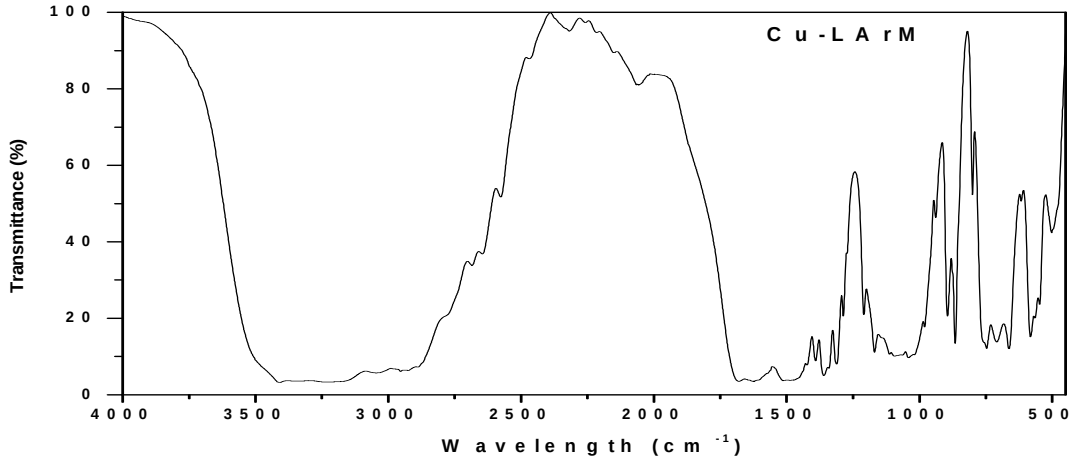

Figure 5 (b) FTIR spectrum of Cu-LArM

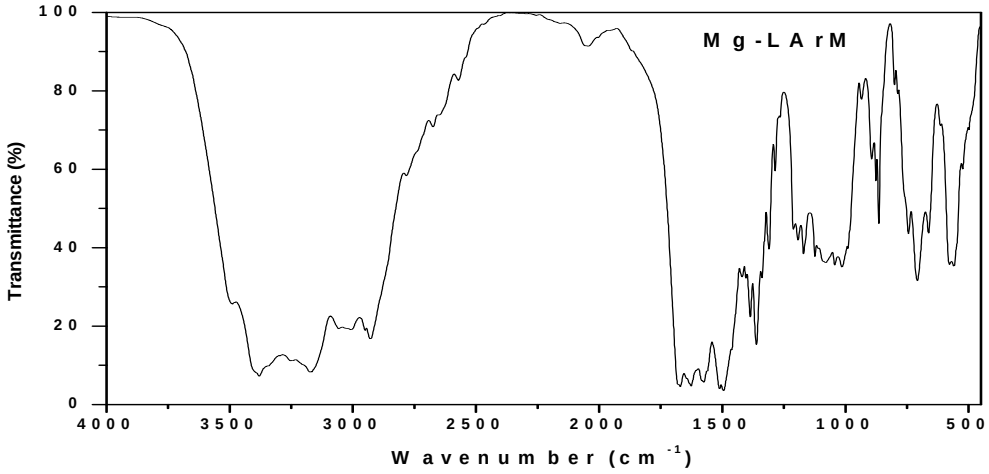

Figure 5 (c) FTIR spectrum of Mg-LArM

Table 5.2 FT-IR spectral assignments of pure and doped LArM

Wave number (cm^{-1})			Assignments
Pure LArM	**Cu^{2+}- LArM**	**Mg^{2+}-LArM**	
3750 - 2300	3750 - 2300	3750 - 2300	NH and CH stretching vibration
1681	1682	1670	NH_3^+ asymmetric deformation
1513	1513	1513	COO^- asymmetric stretching
1360,1400	1360,1400	1361,1400	COO^- symmetric stretching
1170	1170	1170	NH_3^+ rocking
1042	1041	1041	C-N stretching
864	865	864	C-C stretching
662	662	662	COO^- plane deformation
578	582	560	COO^- wagging mode

CONCLUSION

Single crystals of pure and doped LArM are conveniently grown by employing slow evaporation technique. Powder XRD studies confirm the structure of grown crystals. The presence of dopants has marginally altered the lattice parameters without affecting the basic structure of crystals. The optical transmission spectra of pure LArM confirm that the crystals possess higher percentage of transmission over a wide range from 250-900 nm. The presence of dopants has improved the transparency window. SHG in the pure and doped crystals were confirmed by NLO test.

REFERENCES

[1] 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**).
[2] Madhavan J., Aruna S., Anuradha A., Prem Anand D., Vetha Potheher I., Thamizharasan K. and Sagayaraj P., *Optical Materials*, 29, 1211-1216 (**2007**).
[3] Tanusri Pal, Tanusree Kar, *Materials Chemistry and Physics*, 91, 343-347 (**2005**).
[4] Tanusri Pal, Tanusree Kar, Gabriele Bocelli and Lara Rigi. (**2003**), *Crystal Growth and Design*, 3, 13 -16 (**2003**).
[5] Sun Z.H, Yu W.T, Yu J.D, Wang X.Q *Acta Cryst.* (**2007**). E63, o2805-o2807