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# OPTICAL AND STRUCTURAL CHARACTERIZATION OF PURE AND DOPED L-ARGININE MALEATE CRYSTALS

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**Abstract**
*Pure and Doped L- Arginine Maleate (LArM) a nonlinear optical material has been successfully grown from slow evaporation method. FTIR analysis was used to confirm the presence of various functional groups in the grown crystals. Kurtz powder SHG measurements confirm the NLO property of the grown crystal.*

**Keywords:** X- Ray powder diffraction studies have been carried out in order to calculate the lattice parameter values

## Introduction

Nonlinear optical (NLO) materials find extensive opto electronic applications such as optical frequency conversion, optical data storage, optical switches etc. Of this second order NLO materials capable of high efficiency in frequency conversion of infrared or visible laser radiation to visible or ultraviolet wavelengths. Therefore presently there is a need to produce high efficiency NLO materials [1-4]. KDP group of materials are widely used in frequency conversion due to their modest nonlinearities [5]. Inorganic materials are also used in these applications due to their high melting point, high mechanical strength and high degree of chemical inertness. But their optical nonlinearity is poor. Organic materials are optically more nonlinear than inorganic materials [6]. The search for effective NLO materials reveals that L Arginine based crystals are effective with excellent optical, thermal and mechanical properties [7]. L Arginine forms a number of salts with organic and inorganic acids with NLO properties [8, 9]. L Arginine Maleate is a promising organic NLO crystal with second harmonic generation efficiency greater that of KDP [10]. In the present study, we report the growth and characterization of promising non-linear organic crystals of both pure and doped LArM crystals. These crystals were grown by slow evaporation solution growth technique. Good quality, transparent and defect free tiny crystals were formed due to spontaneous nucleation. The same procedure was adopted to grow doped LArM crystals with the addition of 2 mol % of $La^{3+}$ and $Nd^{3+}$ into the respective solution. The cell parameters were estimated by powder XRD, it is observed from the XRD that both pure and doped LArM belongs to triclinic structure. In the case of doped LArM crystals slight variations in the lattice parameters and cell volume were observed. The FT-IR spectra were recorded for both pure and doped LArM crystals and the functional groups were identified. The SHG efficiency of pure

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and doped LArM crystals was found to be higher than that of KDP. The hardness of both pure and doped LArM crystals was assessed. The dielectric studies of both pure and doped LArM crystals were also studied.

**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 (Fig. 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 Fig. 2.

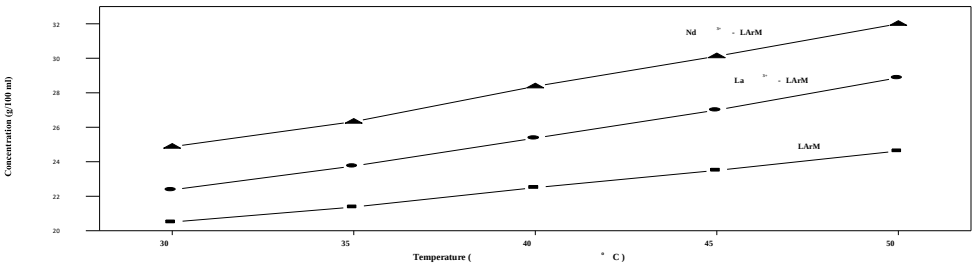


**Fig. 1 Solubility curves of pure and doped LArM crystals**

**Fig 2. Photograph of LArm Pure and doped single crystals**

## I. 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, $La^{3+}$and $Nd^{3+}$ doped LArM crystals were carried out, using Siemens D500 X-ray diffractometer with Cu $K_\alpha$ ($\lambda$ = 1.5406 Å) radiation. The samples were scanned for 2θ values from 10˚ to 50˚ at a rate of 2˚ /min. Fig. 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

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reported literature. It is seen that both the pure and doped crystals crystallizes in triclinic $P_1$ 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 $La^{3+}$and $Nd^{3+}$ in the LArM crystal lattice.

### 3.2 Inductively Coupled Plasma Analysis

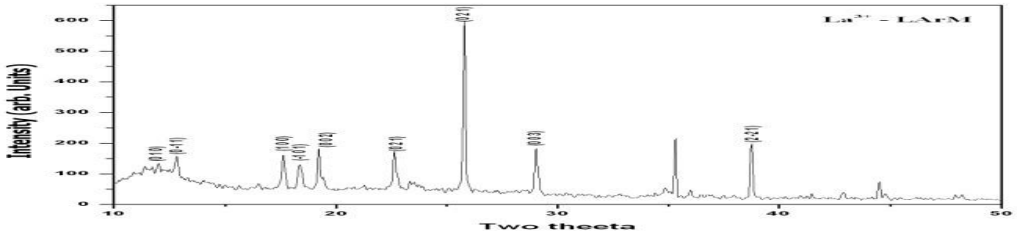
The exact weight percentage of the $La^{3+}$and $Nd^{3+}$ present in doped crystals is determined. 10mg of fine powder of the doped LArM crystals were dissolved in 100ml of triple distilled water respectively, and the prepared solutions were subjected to inductively coupled plasma Analysis. The results shows that only 0.91 % of $La^{3+}$and 1.31 % of $Nd3^{+}$ 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 Nd ions have gone into the LArM lattice compared to La ions.

### 3.3 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, 292.12mW, 382.48mW and 494.39mW were obtained for KDP, pure LArM, $La^{3+}$ and $Nd^{3+}$ doped LArM respectively. Thus, the SHG efficiencies of pure, $La^{3+}$ and $Nd^{3+}$ doped crystals are 3.2, 4.2 and 5.4 times respectively higher that of KDP. Thus, the $La^{3+}$and $Nd^{3+}$ metals have increased the efficiency of pure LArM.

| Lattice parameters | Pure LArM | $La^{3+}$ - LArM | $Nd^{3+}$- LArM |
|---|---|---|---|
| a (Å) | 5.268 | 5.272 | 5.276 |
| b (Å) | 8.041 | 8.049 | 8.051 |
| c (Å) | 9.788 | 9.791 | 9.781 |
| α° | 106.20 | 106.6 | 106.8 |
| β° | 97.26 | 97.22 | 97.29 |
| γ° | 101.68 | 101.67 | 101.72 |
| Crystal System | Triclinic | Triclinic | Triclinic |
| Space group | $P_1$ | $P_1$ | $P_1$ |

**Table 1. Lattice parameters of Pure and Doped LArM**



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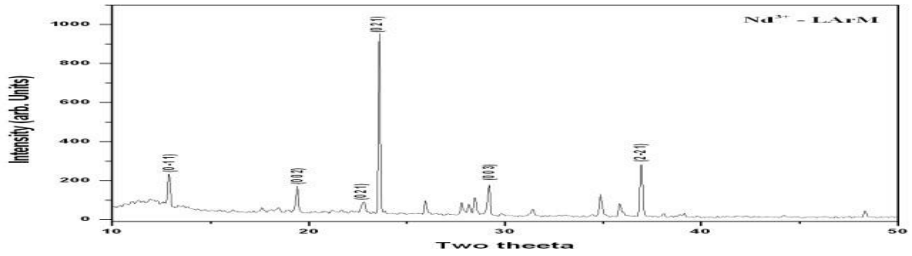


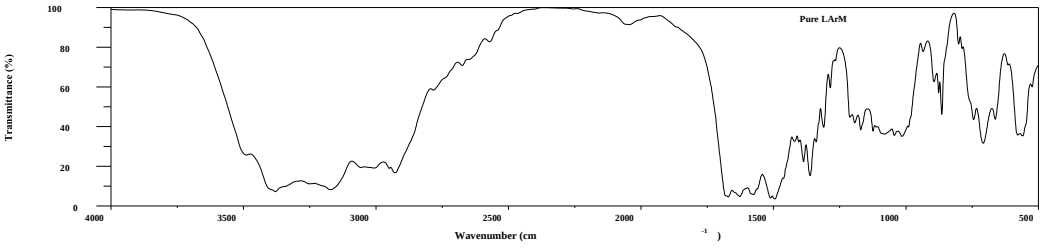

**Fig 3. XRD pattern of Pure and Doped LArM single crystals**

### 3.3 FT-IR Studies

The FT-IR spectra of LArM, $La^{3+}$-LArM, and $Nd^{3+}$-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 Fig 4. 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 characteristic bands of FT-IR spectrum also confirmed the ionization of L-arginine and maleic acid in the crystal lattice of LArM.

**Table 2. FTIR Assignments of LArM Pure and Doped single crystals**

| Wave number ($cm^{-1}$) | | | Assignments |
|---|---|---|---|
| Pure LArM | $La^{3+}$- LArM | $Nd^{3+}$-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 |



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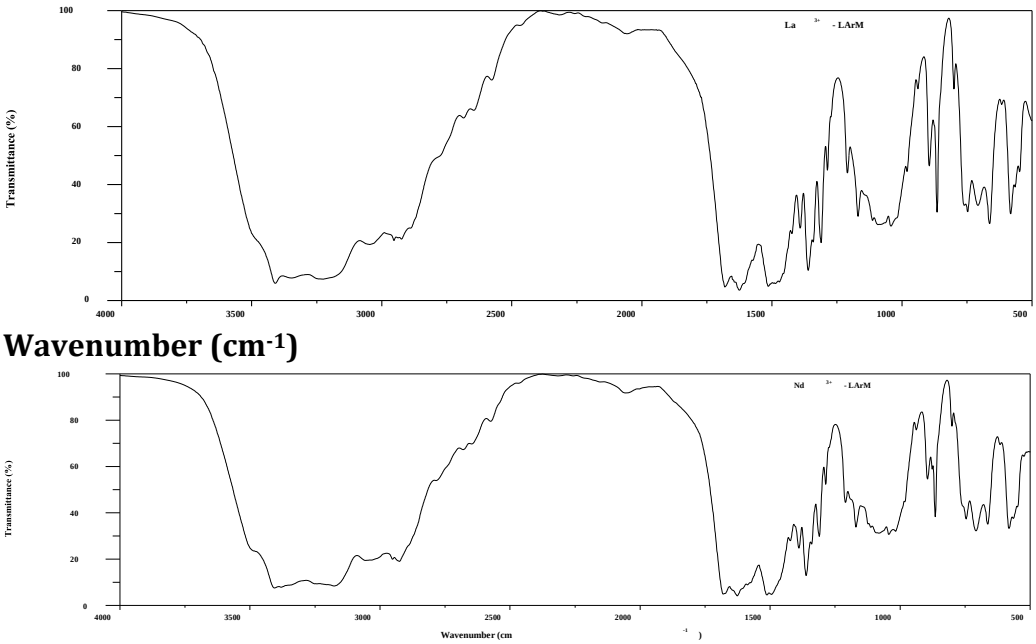


**Fig 4. FTIR spectrum of Pure and LArM single crystals**

### 3.4 Microhardness Studies

Microhardness behaviour of pure and doped LArM single crystal was tested by employing Vickers microhardness tester. Measurements were taken by varying the applied load from 5 to 25 gm. As micro cracks were developed at higher loads, the maximum applied load was restricted to 25 gm only. The plot of variations of Vickers hardness number with applied load for (100) plane of pure and doped LArM are shown in Fig 5. From the plot, it can be noted that the hardness of the crystal decreases with increasing load both for pure and doped samples. The work hardending coefficient 'n' for the (100) plane was found to be less than 2 for both pure LArM, $La^{3+}$ doped LArM and $Nd^{3+}$ doped LArM ('n' values are 1.51,1.49 and 1.64 respectively), which in turn supports the concept of Onitsch.

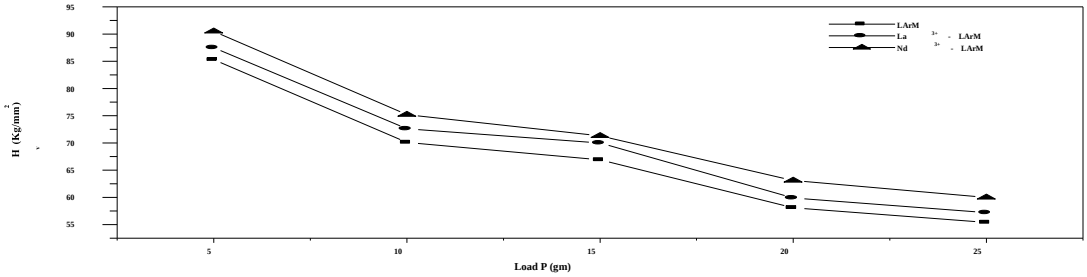


**Fig 5. Variation of hardness with applied load**

### 3.5 Dielectric studies

The dielectric studies on the pure and doped LArM single crystal was carried out using the instrument, HIOKI 3532-50 LCR HITESTER. Pure and doped samples of dimensions about 4x2x1.2 $mm^3$ having silver coating on the opposite faces were placed between the two copper electrodes and thus a parallel plate

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capacitor was formed. The variations of dielectric constant and dielectric loss as a function of log frequency are illustrated in Fig 6 and 7. For both pure and doped crystals the dielectric constant decreases with increase in frequency. The decrease is rapid in the low frequency range and then it starts decreasing very slowly. In high frequency region both dielectric constant and dielectric loss are fairly remaining constant. The high dielectric constant at low frequency is due to better orientation of dipoles in the molecules. With increase in frequency the dipoles oscillate in resonance to oscillating field. Broadly speaking, the graphs exemplify the fact that the dielectric constant and the dielectric loss are both sensitive to frequency. The low value of dielectric loss indicates that the pure and doped crystals have lesser defects, which is a desirable property for NLO applications.

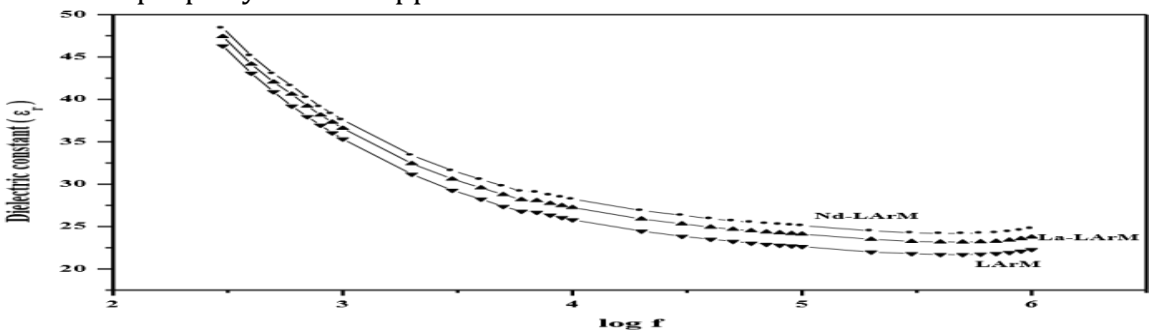


**Fig 6. Variation of dielectric constant of pure and doped LArM**

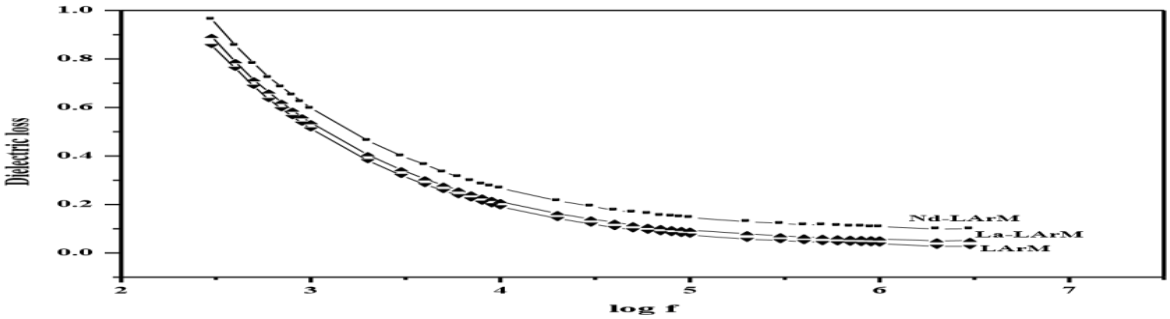


**Fig 7. Variation of dielectric loss of pure and doped LArM**

**Conclusion**

Single crystals of pure, $La^{3+}$and $Nd^{3+}$ doped L-Arginine Maleate (LArM) were grown successfully slow evaporation technique. Atomic Absorption studies of the doped crystals shows that the amount of dopant incorporated in to the doped crystal is less than the concentration of the dopant in the corresponding solution. Powder X-ray diffraction studies were carried out, and the lattice parameters are calculated. The presence of functional groups in pure and doped LArM were analysed by FT-IR studies. Hardness studies reveal that pure and doped LArM crystals are hard materials. Dielectric studies for the pure and doped grown crystals are studied. NLO studies showed that the metal doped crystals have efficiency greater than the pure LArM. Thus, it is concluded that the metal doped crystals can be effectively used as promising NLO material for device fabrication for the desired applications.

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