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Growth and characterization of pure and doped NLO L-arginine acetate single crystals

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Abstract. **Single crystals of pure, Cu^{2+} and Mg^{2+} doped L-arginine acetate (LAA) were grown successfully by slow evaporation technique. In order to improve the device characteristics of LAA crystals, metal dopants of Cu^{2+} and Mg^{2+} were incorporated into the parent crystals. The grown pure and doped crystals were confirmed by X-ray powder diffraction studies. The pure and doped crystals were characterized by Fourier transform Raman (FT–Raman) and thermal studies. Absorptions of these grown crystals were analysed using UV–Vis–NIR studies, and it was found that these crystals possess minimum absorption in the entire visible region. Nonlinear optical studies of pure and doped crystals were carried out and it reveals that the dopants have increased the efficiency of LAA crystals.**

Keywords. **NLO; SHG; solution growth; LAA.**

1. Introduction

L-arginine phosphate monohydrate (LAP) was first reported by Xu *et al* (1983) as a promising nonlinear optical (NLO) material. LAP is nearly three times more nonlinear than KDP. Monaco *et al* (1987) reported the formation of LAP and its chemical analogs from the strongly basic amino acid and various other acids. Nonlinear optical (NLO) organic materials play an important role for optical second harmonic generation (SHG) due to their applications in the domain of optoelectronics and photonics (Saleh and Teich 1991; Boyd 1992). Amino acids are strong candidates for optical second harmonic generation (SHG) because they contain chiral carbon atom and crystallizes in non-centrosymmetric space groups. Amino acid crystal, L-arginine acetate (LAA), has been reported as a promising NLO material by Pal *et al* (2003). L-arginine acetate (LAA) has powder SHG efficiency nearly three times that of KDP (Muralidharan *et al* 2003). In the present work, attempts have been made to improve the physicochemical properties by incorporating metal dopants. A systematic study has been carried out on the growth of pure and metal (Cu^{2+} and Mg^{2+}) doped LAA crystals. Powder X-ray diffraction studies were carried out and the lattice parameters of the grown pure and doped crystals are evaluated. The content of Cu and Mg has been determined by atomic absorption studies. FT–Raman, UV–Vis–NIR, and thermal studies were carried out for the grown pure and doped crystals. The SHG efficiency of the pure and doped LHA crystals were also studied using Nd : YAG Q-switched laser.

2. Experimental

2.1 *Synthesis, purification and crystal growth*

Aqueous solution of pure, Cu^{2+} and Mg^{2+} doped LAA were prepared by dissolving stoichiometric L-arginine (AR grade) and acetic acid in double deionized water. The pure and doped LAA crystals were grown by slow evaporation technique at room temperature (30°C). The reaction that takes place between L-arginine and acetic acid in water medium is as follows:

$$(NH_2)NHCNH(CH_2)_3CH(NH_2)COOH + CH_3COOH \rightarrow$$
$$(NH_2)_2^+CNH(CH_2)_3CH(NH_3)^+COO^-CH_3COO^-.$$

Figure 1 shows the photograph of the as grown pure and doped crystals in a period of 50 days. The crystals are found to be transparent and free from defects. The growth of metal substituted crystal is achieved by using the same procedure by adding dopants of 2 mole% concentration (each) of Cu^{2+} and Mg^{2+} to the LAA solution.

3. Characterization

3.1 *Atomic absorption studies*

10 mg of fine powder of the doped LAA crystals was dissolved in 100 ml of triple distilled water, respectively

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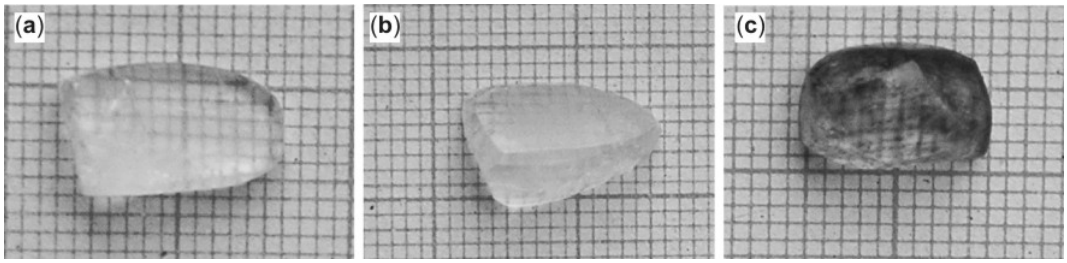

Figure 1. Photographs of as grown (**a**) pure LAA, (**b**) Cu^{2+} doped LAA and (**c**) Mg^{2+} doped LAA crystals.

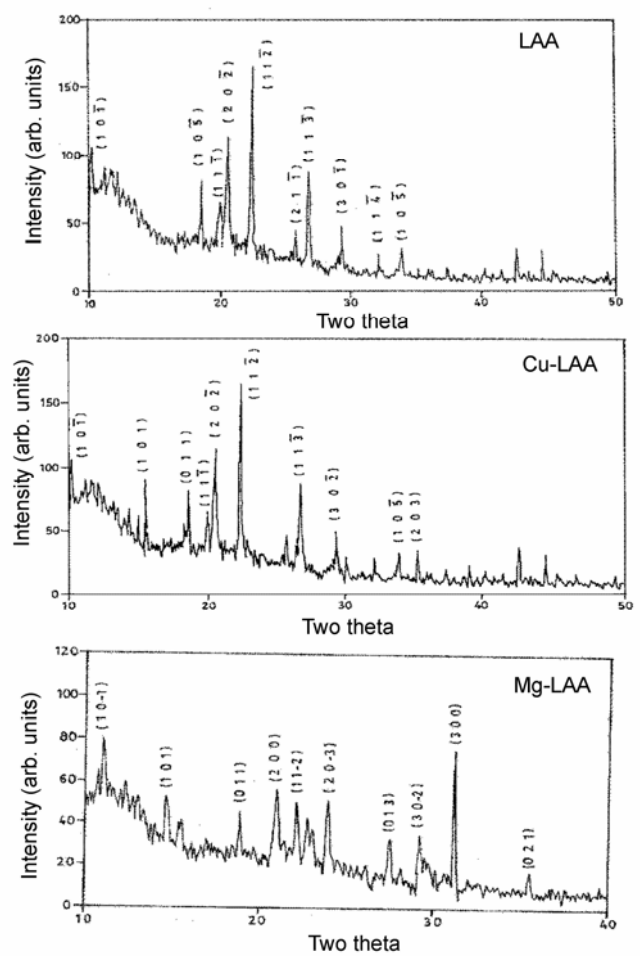

Figure 2. Powder X-ray diffraction pattern of LAA, Cu–LAA and Mg–LAA.

and the prepared solutions were subjected to atomic absorption spectroscopy (AAS) analysis. The results showed that 0·24 μg/ml and 1·03 μg/ml are present in the respective samples. The weight percentage of the metal present will be equal to (concentration × volume)/weight of the sample. The calculation shows that only 0·24% of Cu^{2+} and 1·03% of Mg^{2+} are present in the respective samples, out of 2% of the dopant. It is seen that the amount of dopant incorporated into 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 LAA lattice compared to Cu ions. This may be due to the radius of Mg (0·65 Å) compared to Cu ions (0·72 Å) (Haja Hameed *et al* 1999).

3.2 *XRD studies*

Powder X-ray diffraction studies of pure and Cu^{2+} and Mg^{2+} doped LAA crystals were carried out using Siemens D500 X-ray diffractometer with CuK_α (λ = 1·5418 Å) radiation. The samples were scanned for 2θ values from 10°–70° at a rate of 2°/min. Figure 2 shows the powder XRD pattern of the pure and doped LAA crystals. The powder patterns were indexed and the lattice parameter values for the pure and doped LAA crystals were calculated by fitting the XRD data with 'least square method' using 'XRDA' program. It is observed that both the pure and doped crystals crystallize in monoclinic $P2_1$ space group. The lattice parameters of the samples are presented in table 1 along with the reported values (Muralidharan *et al* 2003). 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 LAA crystal lattice.

3.3 *FT-Raman spectra*

In order to qualitatively analyse the presence of functional groups in LAA, the polarized Fourier transform Raman (FT–Raman) spectra were recorded for the pure and doped LAA in the range 50–3500 cm^{-1}. The recorded spectra are shown in figure 3. The NH_3^+ stretching frequencies are found between 3100 and 2600 cm^{-1} in the form of a broad strong band with multiple peaks. The characteristic band at 1579 cm^{-1} is due to the asymmetric NH_3 deformation. The weak absorption band observed at 3065 cm^{-1} shows the N–H stretching of amino group. It is inferred from the peaks at 1283 cm^{-1}, 1415 cm^{-1} and 1626 cm^{-1} that they are due to the C=O stretching of carboxylic group. The absence of peak at 1626 cm^{-1} for C=O stretching in the Cu–LAA may be due to the metal linkage with the carboxylic group. The Mg–LAA spectra shows that absence of peak at 2125 cm^{-1} which may be responsible for metal linkage with N of amino group.

Table 1. Lattice parameter values for the pure and doped LAA.

Lattice parameters	Pure LAA	Cu^{2+}–LAA	Mg^{2+}–LAA	Reported values
a (Å)	9·29	9·21	9·11	9·226
b (Å)	5·09	5·21	5·10	5·243
c (Å)	13·1	12·8	12·78	13·049
$\alpha°$	90	90	90	90
$\beta°$	109·61	107·66	107·85	108·92
$\gamma°$	90	90	90	90
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$
Volume (Å^3)	586·20	581·38	570·73	597·14

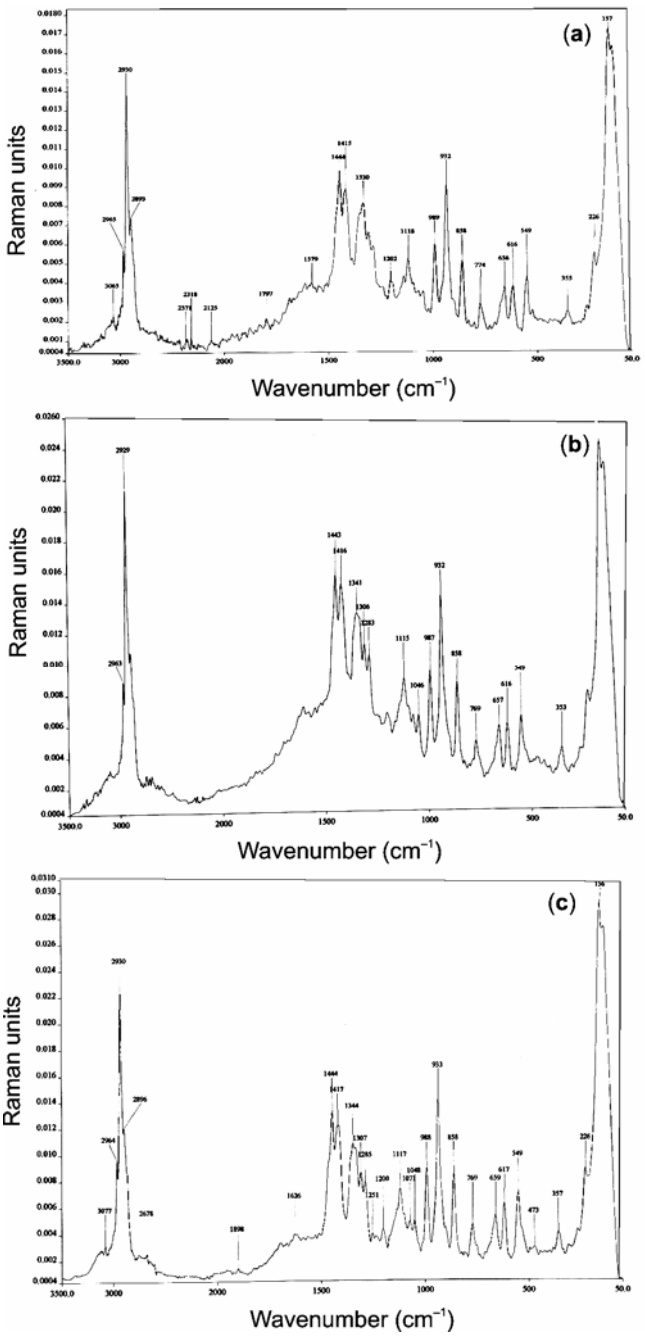

Figure 3. FT-Raman spectra of (**a**) pure LAA, (**b**) Cu^{2+} doped LAA and (**c**) Mg^{2+} doped LAA.

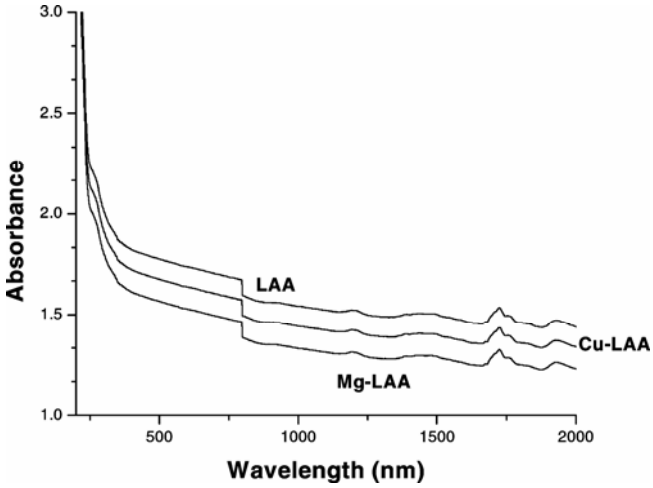

Figure 4. Optical absorption spectra of pure, Cu^{2+} and Mg^{2+} doped LAA.

3.4 *UV–Vis–NIR spectra*

Optical absorption data were taken on these polished crystal samples of about 4–6 mm thickness using a Varian carry 5E model dual beam spectrophotometer between 200 and 2000 nm. The spectra (figure 4) indicate that the pure and doped LAA crystals have minimum absorption in the entire visible region. From the spectra, it is also seen that the pure and doped LAA crystals have better lower cut-off wavelengths. Interestingly, both the Cu^{2+} and Mg^{2+} doped crystals have decreased absorption. The required properties for NLO activity are minimum absorption and low cut-off wavelength. These properties are improved in the doped crystals.

3.5 *NLO studies*

The grown crystals of pure and doped LAA were subjected to Kurtz second harmonic generation (SHG) test using the Nd : YAG Q-switched laser beam for the nonlinear optical (NLO) property (Kurtz and Perry 1968). The sample of same size was illuminated using Q-switched, mode locked Nd : YAG laser with input pulse of 6·2 mJ. The second harmonic signal of 820 mV,

Table 2. Summarized TGA and DTA results of LAA.

Stage	Decomposition temperature range (°C)	Decomposition steps	Weight loss observed (%)	Calculated
1	200–350	$C_6H_{14}N_4O_2C_2H_4O_2$ ↓	58·85	56·35
2	350–510	$C_2H_{10}N_2C_2H_4$ ↓	17·16	14·51
3	510–680	$C_2H_4C_2H_4$	24·93	23·05

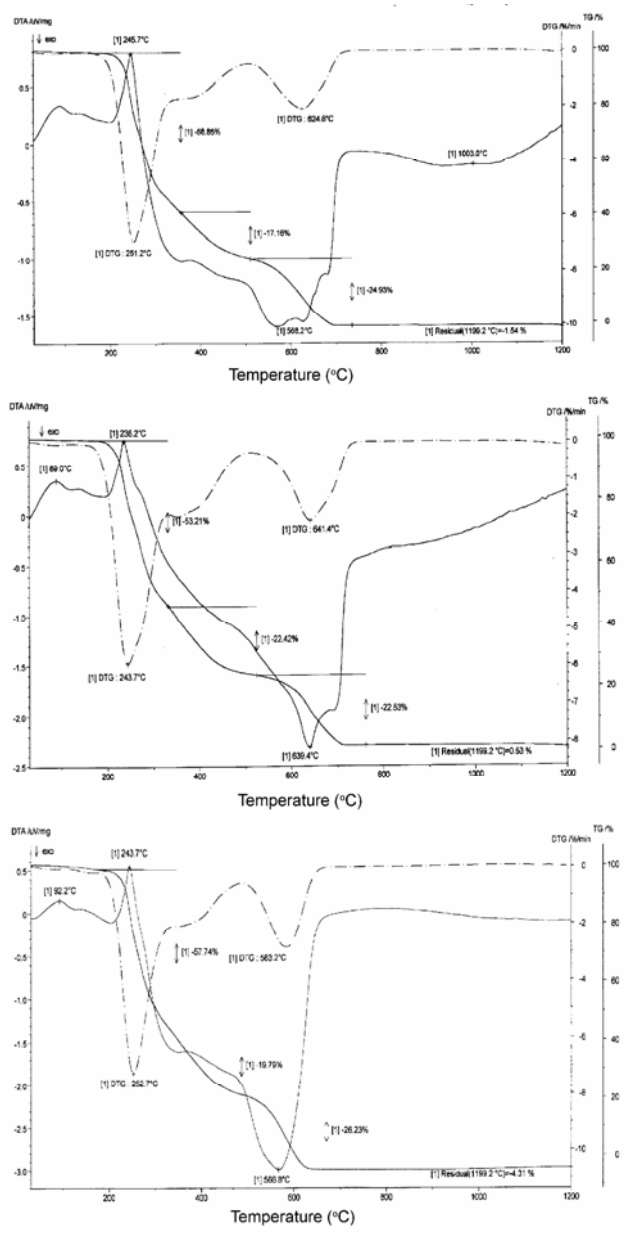

Figure 5. TGA, DTA and DTG curves of pure, Cu^{2+} and Mg^{2+} doped LAA single crystals.

885 mV and 920 mV, respectively were obtained for pure, Cu^{2+} and Mg^{2+} doped LAA with reference to KDP (275 mV). Thus, the SHG efficiency of pure, Cu^{2+} and Mg^{2+} doped crystals is nearly 3, 3·2 and 3·35 times greater than KDP. It is seen that the Cu^{2+} and Mg^{2+} metal dopants have increased the efficiency of pure LAA.

3.6 *Thermal studies*

The thermogravimetric analyses of pure and doped LAA crystals were carried out between 23 and 1200°C using STA 409C instrument, in the nitrogen atmosphere at a heating rate of 10 K/min. Figure 5 shows the resulting TGA and DTG traces of the pure and doped crystals. The sharp weight loss of the material starts around 200°C. The crystal is completely free of any water of crystallization or any physically adsorbed water on the surface. The absence of significant band in the region 3500–3400 cm^{-1} confirms the absence of water molecule (Kanagadurai *et al* 2006). The DTA trace of LAA shows that, there is a sharp endotherm matching with the decomposition of LAA. Heating the material above 200°C results in the formation of volatile substances, probably carbon dioxide and ammonia. The Cu^{2+} doped LAA crystals show same features as that of pure LAA, but there is a distinct shift in the decomposition temperatures. As a result of Cu^{2+} doping, the peak maximum in DTG corresponding to first stage of decomposition is shifted to lower value (7°C). The Mg^{2+} doped LAA crystals show similar features as that of pure LAA, but with a shift in the peak maximum of the first stage of decomposition. Summarized TGA and DTA results are shown in table 2.

4. Conclusions

Good quality single crystals of pure, Cu^{2+} and Mg^{2+} doped L-arginine acetate (LAA) were grown successfully by slow evaporation technique. X-ray diffraction studies were carried out, and the lattice parameters calculated. Atomic absorption studies of the doped crystals show that the amount of dopant incorporated into the doped crystal is less than the concentration of the dopant in the corresponding solution. The pure and doped LAA crystals are transparent in the entire visible region, and have minimum absorption between 240 and 1380 nm. The TGA and DTG studies show that the metal dopants have not altered the thermal stability of the molecules. NLO stu-

dies proved that the Cu^{2+} and Mg^{2+} metals have increased the efficiency of pure LAA. The presence of dopants has improved the nonlinear optical (NLO) properties of the grown crystals and these crystals can be promising materials for nonlinear device fabrication.

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