Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Physics Research, 2010, 1 (2): 1-7
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0976-0970

Electrical, Mechanical, Thermal and nonlinear optical properties of pure and doped L-Threonine acetate single crystals

T. Sujatha[1], P. Praveen Kumar[2], J. Merline Shyla[1] and J. Madhavan[1]

[1]Department of Physics, Loyola College, Chennai, India
[2]Department of Physics, Presidency College, Chennai, India

Abstract

In the present investigation, influence of metal ($Cu^{2+}$and Mg^{2+}) dopant on the Electrical, Mechanical, Thermal and nonlinear optical properties of pure LTA crystals has been studied systematically. The exact weight percentage of the $Cu^{2+}$and Mg^{2+} present in doped crystals were determined by Atomic Absorption Studies. Single crystal X-ray diffraction studies were carried out for the pure and doped crystals. Dielectric and photoconductivity studies were carried out for the grown crystals. Mechanical and thermal stability of the grown crystals are determined by Vickers microhardness and thermal studies. Nonlinear optical properties were studied by SHG studies.

Keywords: Electrical studies, Mechanical studies, Thermal studies, NLO, LTA.

INTRODUCTION

Nonlinear optical (NLO) organic crystals with high conversion efficiencies are required for optical second harmonic generation (SHG) owing to their practical applications in the domain of optoelectronics and photonics [1, 2]. Aminoacid family crystals are of great interest due to their attracting nonlinear optical properties [3–4]. In recent years, more promising NLO materials with better properties have been discovered and studied. Amino acid L-threonine acetate (LTA) crystal has been reported as a promising NLO material with SHG efficiency higher than that of KDP, and can be used for the fabrication of optoelectronic devices [5]. In the present study, influence of metal ($Cu^{2+}$and Mg^{2+}) dopant on the Electrical, Mechanical, Thermal and nonlinear optical properties of pure LTA crystals has been carried out.

Pure and doped LTA crystals are 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 LTA crystals with the addition of 2 mol % of Cu^{2+} and Mg^{2+} into the respective solution. Single crystal XRD studies were carried out, and it is observed from the XRD that both pure and doped LTA belongs to orthorhombic structure with space group of P212121. In the case of doped LTA crystals slight variations in the lattice parameters and cell volume are observed. The hardness of both pure and doped LTA crystals reveals that these crystals are soft materials. The photoconductivity studies of both the pure and doped LTA crystals show that they possess positive photoconductivity. The dielectric loss with frequency of the pure, Cu^{2+} and Mg^{2+} doped crystals proves that these materials possess enhanced optical quality with lesser defects. Pure, Cu^{2+} and Mg^{2+} doped LTA crystals were subjected to thermo gravimetric analysis (TGA) and the thermal stability were found. The SHG efficiency of pure, Cu^{2+} and Mg^{2+} doped crystals are 1.4, 2.4 and 2.9 times, respectively higher that of KDP. The doped LTA crystals are found to have efficiency higher that of pure LTA.

MATERIALS AND METHODS

Analytical grade L-threonine (AR grade) and acetic acid were dissolved in double deionized water according to the stoichiometric ratio. The resulting aqueous solution was filtered and allowed to evaporate under optimized conditions to grow crystals by slow evaporation method at room temperature. The synthetic reaction is as follows,

$$C_4H_9NO_3 + CH_3COOH \longrightarrow C_4H_{10}NO_3^+CH_3COO^-$$

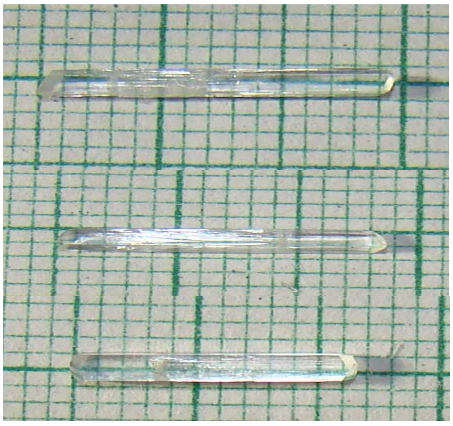


Figure 1: Photographs of LTA, Cu-LTA and Mg-LTA crystals

2 mol % of CuO and MgO is added to the LTA solution in order to grow the metal (Cu^{2+} and Mg^{2+}) doped crystals. The incorporation of dopant into the parent solution has promoted the growth rate. The pure, Cu^{2+} and Mg^{2+} doped LTA crystals were grown by slow evaporation technique at room temperature. Figure 1 shows the photographs of the as grown pure and doped LTA crystals. The grown pure and doped crystals are found to be transparent and free from defects.

RESULTS AND DISCUSSION

Single crystal X-ray diffraction

Single crystal X-ray diffraction studies of pure and $Cu^{2+}$and Mg^{2+} doped LTA crystals were carried out using ENRAF NONIUS CAD4-F single X-ray diffractometer. Both the pure and doped LTA crystals crystallize in to the orthorhombic crystal system with the space group of $P2_12_12_1$. The lattice parameter values of Cu^{2+} and Mg^{2+} doped crystals were also calculated, and they show slight variations. These variations may be due to the incorporation of $Cu^{2+}$and Mg^{2+} in the LTA crystal lattice. The lattice parameters of the pure and doped crystals are shown in Table 1.

Table 1: Lattice parameter values for the pure and doped LTA

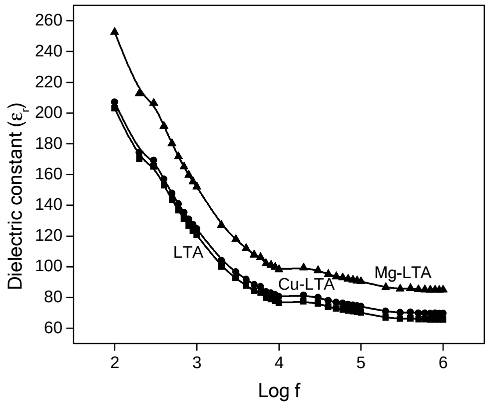
Lattice parameters	Pure LTA	Cu^{2+} - LTA	Mg^{2+}- LTA
a (Å) b (Å) c (Å)	5.164 7.783 13.680	5.242 7.839 13.786	5.312 7.942 13.836
Crystal System	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Volume (Å^3)	549.818	566.495	583.711

Atomic Absorption studies

10 mg of fine powder of the Cu^{2+} and Mg^{2+} doped LTA crystals were dissolved in 100 ml of triple distilled water respectively, and the prepared solutions were subjected to Atomic Absorption Spectroscopy (AAS) Analysis. The exact percentage of the $Cu^{2+}$and Mg^{2+} present in the respective doped crystals is determined. The results shows that only 0.35 % of Cu^{2+} and 1.48 % of Mg^{2+} are present in the respective samples, out of 2 % of the dopant.

Dielectric studies

The dielectric study of pure and doped LTA single crystals were carried out using the instrument, HIOKI 3532-50 LCR HITESTER. The capacitance of the sample was noted for the applied frequency that varies from 100 Hz to 5 MHz at room temperature. The dielectric constant is high at low frequencies and decreases with the applied frequency. The plot of dielectric constant (ε_r) versus log frequency and the variation of dielectric loss with frequency for pure and doped crystals is shown in Figure 2. The low dielectric loss with high frequency of the pure, Cu^{2+} and Mg^{2+} doped crystals proves that these materials possess enhanced optical quality with lesser defects. This characteristic is an important parameter for nonlinear optical materials in their applications. The dielectric loss of both the pure and doped LTA shows similar trend, but there is a shift. This may due to the presence of metal dopant in the doped crystals. Thus, it is concluded the presence of metal dopants have slightly altered the dielectric nature of the crystals.



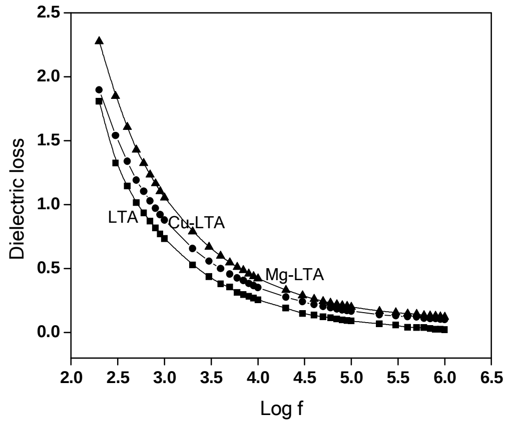


Figure 2: Plot of dielectric constant and dielectric loss of pure and doped single crystals

Photoconductivity studies

Photoconductivity studies were carried out at room temperature for the pure and doped LTA crystals, using keithley 485 picoammeter. The dark current was recorded for the samples by keeping them unexposed to any radiation. The light from the halogen lamp (100 W) containing iodine vapour is focused on the respective samples and the photo currents of the samples were measured. The DC inputs were increased in steps and the photo currents were measured. Figure 3 shows the plot of photocurrent and dark current as a function of the applied field for pure, Cu^{2+} and Mg^{2+} doped LTA. It is observed from the plot that dark current (I_d) and photo current (I_p) of the sample increase linearly with the applied field and the photocurrent is always higher than the dark current, hence it is concluded that LTA shows positive photoconductivity. This phenomenon can be attributed to generation of mobile charge carriers by the absorption of photons [6].

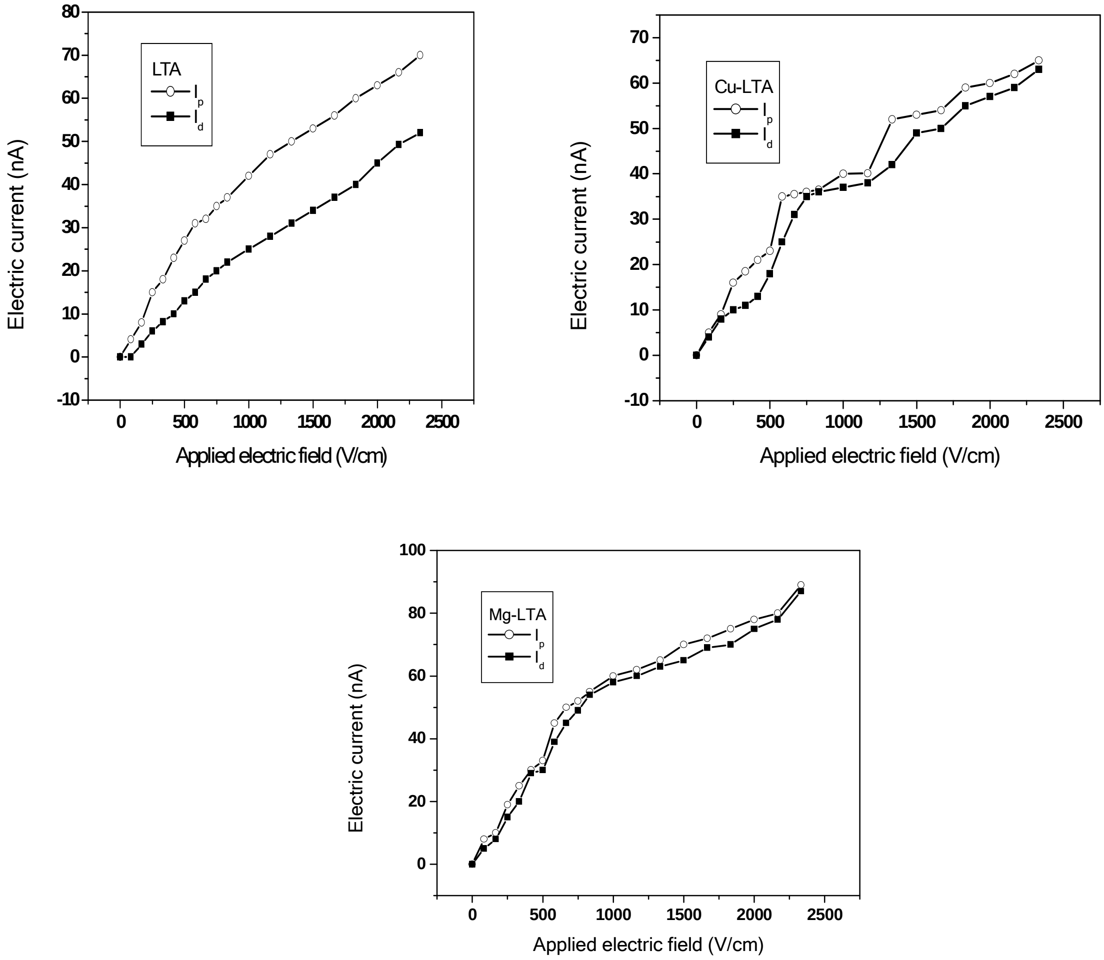


Figure 3: Photoconductivity of pure, Cu^{2+} and Mg^{2+} doped LTA

Microhardness measurements

The fastest and simplest method to evaluate the mechanical properties of the crystals is the hardness measurement. Pure, Cu^{2+} and Mg^{2+} doped LTA crystals which are free from cracks and transparent were selected for microhardness measurements. Micro hardness studies were carried out for the pure and doped crystals using Leitz Wetzlar Vickers micro hardness tester by varying the applied load from 10 g to 50 g. The indentation time was kept as 5s for all the loads. Figure 4 shows the variations of Vickers hardness number with applied load for (010) plane of the pure and doped crystals. The values of work hardening coefficient (n) of the pure and metal doped crystals were found to be 1.75, 1.63, 1.69 and respectively. Since the value of n is greater than 1.6, these crystals are soft materials.

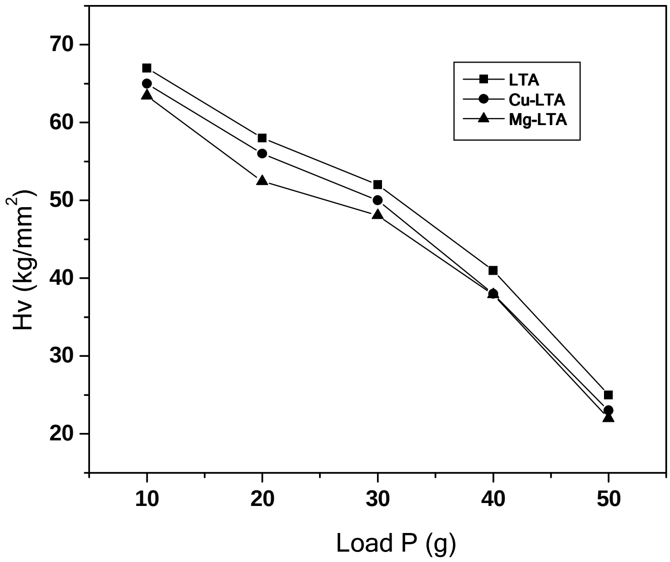
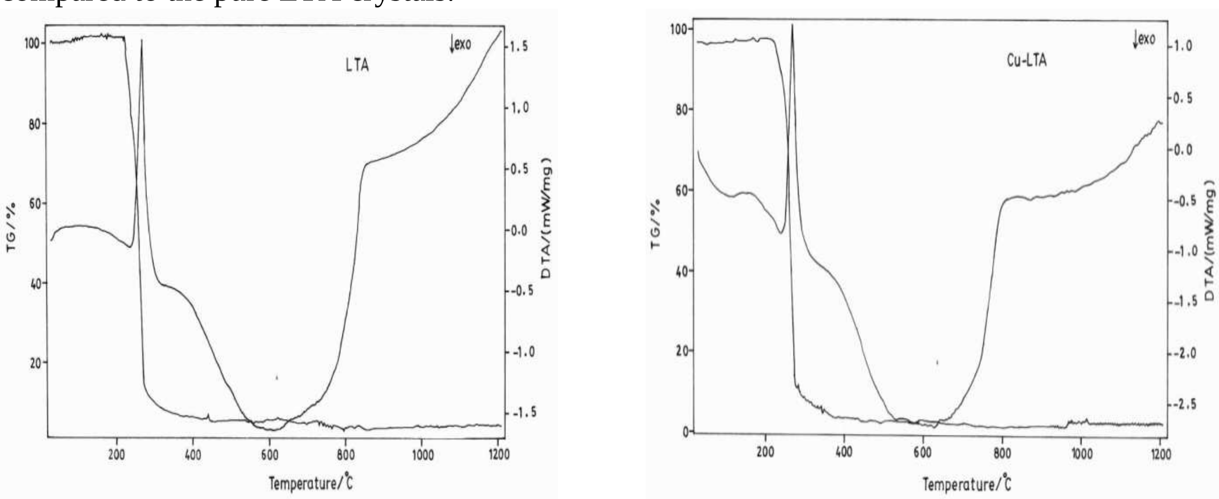


Figure 4: Variation of hardness with applied load for the plane (010)

Thermal studies

Single crystals of pure, Cu^{2+} and Mg^{2+} doped LTA crystals were subjected to thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) simultaneously using STA 409C instrument, in the nitrogen atmosphere at a heating rate of 10 K/min. Figure 5 shows the resulting TGA and DTA traces of the pure and doped crystals. The decomposition of the material starts at 230º C. The material is found to be thermally stable up to 230º C. The DTA trace of LTA shows that, there is a sharp endotherm matching with the decomposition of LTA.TG analysis shows that the softening starts at 230˚ C, 228˚ C and 229˚ C for both the pure and doped LTA. There is a reduction in the decomposition temperature of the doped crystals compared to the pure LTA crystals.



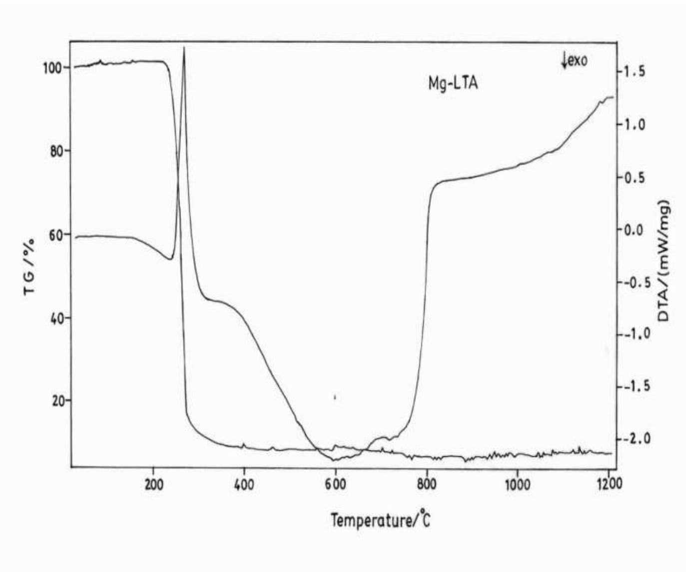


Figure 5: TGA and DTA curves of the pure and doped LTA crystals

NLO studies

Nonlinear optical (NLO) property of pure and doped LTA were found by subjecting them to Kurtz powder SHG test using the Nd:YAG Q-switched laser beam. The pure and doped samples were illuminated using Q-switched, mode locked Nd:YAG laser with input pulse of 6.2mJ. The second harmonic signal generation in the crystals was confirmed by the emission of green radiation from the crystals.

The second harmonic signal of 136.28 mW, 233.62 mW and 282.20 mW, respectively were obtained for pure, $Cu^{2+}$and Mg^{2+} doped LTA with reference to KDP (97.3 mW). Thus, the SHG efficiency of pure, Cu^{2+} and Mg^{2+} doped crystals are 1.4, 2.4 and 2.9 times, respectively higher that of KDP. The doped LTA crystals are found to have efficiency higher than that of pure LTA. The increase in the SHG efficiency of the doped crystals is due to the presence of metal dopant in the crystal lattice [7]. Thus, it is concluded that $Cu^{2+}$and Mg^{2+} metal dopant has improved the NLO property of respective pure LTA crystals.

CONCLUSION

Single crystals of pure, $Cu^{2+}$and Mg^{2+} doped L-threonine Acetate (LTA) were grown successfully by slow evaporation technique. Atomic Absorption studies of both the $Cu^{2+}$and Mg^{2+} 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. Single crystal X-ray diffraction studies were carried out, and the lattice parameters are calculated. The hardness of both pure and doped LTA crystals reveals that these crystals are soft materials. The photoconductivity studies of both the pure and doped LTA crystals show that they possess positive photoconductivity. The dielectric loss with frequency of the pure, Cu^{2+} and Mg^{2+} doped crystals proves that these materials possess enhanced optical quality with lesser defects. The TGA and DTA studies show that the metal dopants have not altered the thermal stability of the molecules. NLO studies proved that the $Cu^{2+}$and Mg^{2+} metals have increased the efficiency of pure LTA. The presence of dopants has improved the Nonlinear optical (NLO) properties of the grown crystals and hence the $Cu^{2+}$and Mg^{2+} doped LTA crystals can be used as a promising material for nonlinear device fabrication.

Acknowledgements
The authors acknowledge University Grants Commission (UGC), India for funding this research project - F.No. 33-11/2007 (SR).

REFERENCES

[1] R.W. Boyd, Nonlinear Optics, Academic press, San Diego, **1992**.
[2] B.E. Saleh, M.C. Teich, Fundamentals of Photonics, Wiley, New York, **1991**.
[3] S. Aravazhi, R. Jayavel, C. Subramanian, *Mater. Res. Bull.*, **1997**, 32, 279.
[4] K.L. Bye, P.W. Whipps, E.T. Keve, *Ferroelectrics*, **1972**, 4, 253.
[5] G. Ramesh Kumar, S. Gokul Raj, R. Mohan, R. Jayavel, *Journal of Crystal Growth*, **2005**, 283, 193.
[6] V.N. Joshi, Photoconductivity, Marcel Dekker, New York, **1990**.
[7] P. Praveen Kumar, V. Manivannan, S. Tamilselvan, S. Senthil, Victor Antony Raj, P. Sagayaraj, *J. Madhavan*, *Optics Communications*, **2008**, 281, 2989-2995.