Characterization of Alkali Metal-Doped L-Ascorbic Acid Crystals Grown by Conventional Slow Evaporation

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ABSTRACT

Nonlinear optics (NLO) deals with the interactions of applied electromagnetic fields with materials to generate new electromagnetic field altered in phase, frequency, amplitude or other physical properties. Nonlinear optics has been investigated for several decades as a promising field with essential applications in the domain of opto-electronics and photonics. Saccharide materials crystallize in chiral noncentrosymmetric space groups and, apart from being transparent over a wide range of wavelengths in the crystalline state, have excellent physical, chemical and thermal properties. In the present investigation, pure and Mg doped L-Ascorbic acid single crystals were grown *via* conventional slow evaporation method. The structural, vibrational and optical properties of grown crystals were characterized using powder X-ray diffraction (XRD), Fourier transform infra-red spectroscopy (FTIR)and UV-Visible (UV-Vis) spectroscopy. The mechanical strength of the pure and Mg doped L-Ascorbic acid crystals were determined by Vicker's microhardness test. The second harmonic generation efficacy was examined by powder Kurtz method.

***Keywords**: Non-linear optics, L-Ascorbic acid, slow evaporation method, Vicker's microhardness,Second harmonic generation*

I. INTRODUCTION

Non-linear optical (NLO) materials have wide attention in modern years owing to their potential applications in the field of optoelectronics and photonics [1]. Currently, inorganic oxides, semiconductors, conjugated organic polymers, octopolar metal complexes, organic and organo-metallic materials, semi-organic materials have been used as third order non-linear optical (NLO) materials. Among them, organic crystals have been explored as potential candidate owing to its extraordinary nonlinear coefficients, large birefringence, high damage thresholds and large transparency range [2]. Moreover, their applications were limited due to their poor chemical stability, poor phase matching as well as red shift of the cut off wavelength possessed by organic π- conjugated system. These issues can become by developing metal containing organic crystals resulting semi organic complex crystals [3].

L-ascorbic acid (L-ASA), vitamin C, is a well-known widely used drug material in pharmaceutical applications [4]. L-ASA is naturally existing antioxidants and radical scavengers which protect cellular components against oxidative damage caused by oxygen free radicals. Besides, it supports as an electron donor for several enzymatic reactions as well as defense mechanisms [5]. L-ASA crystal possesses less optical transparency and SHG efficiency. In order to overcome this drawback for practical applications variety of dopants such as amino acids, organic and inorganic compounds have been introduced. Incorporation of inorganic additives into an organic material can alter the physical properties. The presence of alkali metal additives in the organic compounds generally enhances the optical and mechanical properties. However, metal doped organic single crystals revealed enhanced NLO response than that of pure organic single crystals. Here we attempt to modify the physical and optical properties of pure L-ASA by doping magnesium (Mg).In present investigation, pure and Mg doped L-ASA single crystals were grown by slow evaporation method and characterized by Powder XRD, FT-IR, UV-Visible, Vickers microhardness test as well as NLO properties.

II. METHOD & MATERIAL

Growth of Pure L-Ascorbic Acid and Magnesium doped Single Crystal

The commercially available L-Ascorbic acid powder (98 % purity;Merck, India) was used for the experiment. Mixture of the water and isopropyl alcohol with 3:1 ratio was used as solvent. 1 M (8.8065 g) of L-ascorbic acid was dissolved in 50 ml of mixed solvent and continuously stirred. After three hours the homogeneous solution was filtered by Whattmann filter paper and pH value of solution was found to be 4.5. The filtered solution was covered with a perforated cover and kept at room temperature for slow evaporation method. The good quality transparent Pure L-ASA single crystals were obtained after 15-20 days [5]. For doped L-ASA single crystals, 1 M (8.8065 g) of L-ascorbic acid with two different concentration of $MgCl_2$ (0.03 M) was added in 50 ml of mixed solvent and continuously stirred then kept at room temperature for controlled evaporation. After 25-30 days, Mg doped L-Ascorbic acid single crystals were obtained and named as L-ASA+ Mg. The photographs of the pure and Mg doped L-Ascorbic acid crystals are presented in Figure1.

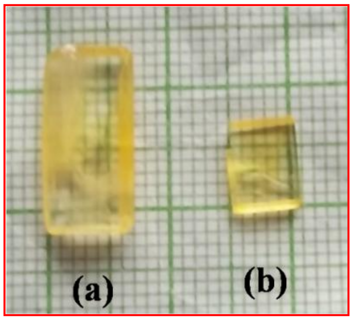

Fig. 1. Photograph of pure (a), 0.03 M Mg doped L-Ascorbic acid crystals

III. RESULTS & DISCUSSION

Powder X-ray diffraction

Powder X-ray diffraction studies of the finely crushed pure and Mgdoped L-Ascorbic acid crystalline powder was carried out by Rigaku mini flex II X-ray diffractometer with CuKα radiation ($\lambda = 1.5418$ Å). The powder diffraction pattern of pure and magnesium doped L-ascorbic acid crystals are shown in Figure 2. The sharp and well defined Bragg's peaks at specific 2θ angles confirm the crystalline nature of the grown crystals. From the figure it is clear that each diffraction pattern contains all the original peaks of pure L-ascorbic acid only, which shows that the phases of L-Ascorbic acid remain unchanged with Mg doping. L- Ascorbic acid is reported to crystallize in monoclinic system with space group $P2_1$ [6]. The Bragg's reflections for the pure and Mg doped L-Ascorbic acid crystals are indexed by using PowderX software and the values of lattice parameters are calculated using the formula

$$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2}\right)$$

Table 1. Lattice parameters of pure and Mg doped L-Ascorbic acid crystals

Lattice parameters	L-ASA	L-ASA+ Mg	L-ASA reference [6]
a (Å)	17.1593	17.4185	17.299
b (Å)	6.3908	6.4221	6.353
c (Å)	6.4164	6.4228	6.411
β	102°88'	103° 38'	102° 32'

The lattice parameters values of pure L-Ascorbic acid crystal exhibited good match with the reported values (Table 1). The Mg doped L-Ascorbic acid crystals showed slightly increased values than the pure crystal which confirms the interstitial substitution of Mg ions into the L-Ascorbic acid crystal.

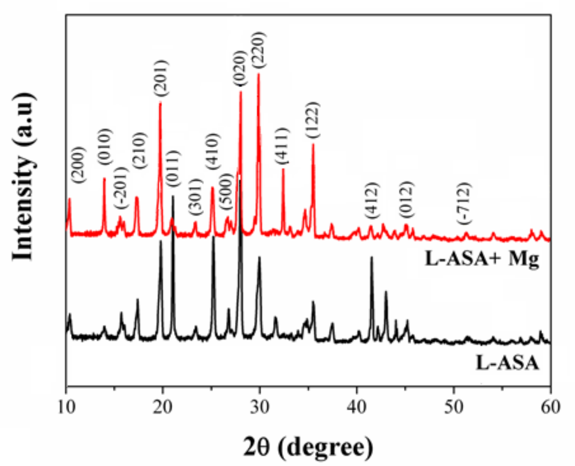

Fig. 2. Powder XRD patterns of pure and Mgdoped L-Ascorbic acid crystals

FT-IR analysis

The FT-IR spectrum of the grown pure and Mgdoped L-ascorbic acid crystals were recorded in the range 400 to 4000 cm^{-1} using Bruker Tensor 27 spectrophotometer is shown in Figure 3. From the FT-IR spectrum, various functional groups present in the compounds were observed and the assignments correspond to various absorption bands in the spectrum are listed in the Table 2. The absorption peaks observed in the high frequency region such as 3533 cm^{-1}, 3414 cm^{-1} and 3032 cm^{-1} are assigned to OH stretching. The absorption peak at 2909 cm^{-1} is assigned to C-H stretching.

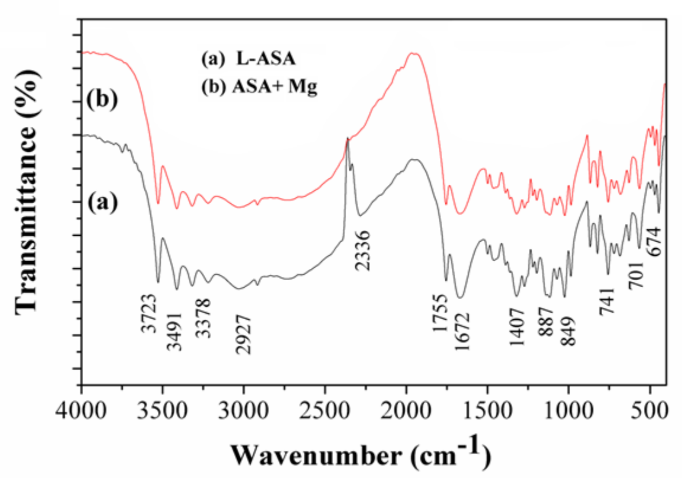

Fig.3. FTIR spectra of pure and Mgdoped L-Ascorbic acid crystals

The absorption peak at 1754 cm^{-1}, 1671 are assigned to C=O and C=C stretching vibration. The in- plane and out-plane bending vibrations of L-ascorbic acid are observed as absorption bands at 1326 cm^{-1} and 861 cm^{-1} respectively. The band observed at 1453 cm^{-1} is O-H in- plane attributed to bending and C-O stretching. The bands at 756 cm^{-1} and 673cm^{-1} are assigned to C-H bending vibration.The FTIR spectrum of Mg doped L-ascorbic acid shows slight decrease in intensity for the entire band. The interaction and entry of the dopant into the lattice sites of L-ascorbic acid is clearly indicated by the some peaks shift in the higher and lower frequencies of the FTIR spectra [5,7].

Table 2. Vibrational band assignments for pure and Mgdoped L-Ascorbic acid crystals

Observed IR frequencies (cm^{-1})		**Assignments**
L-ASA	**L- ASA+ Mg**	

3533	3524	O-H stretching
3414	3404	O-H stretching
3032	3037	O-H stretching
2909	2914	C-H stretching
1754	1756	C=O stretching
1671	1671	C=C stretching
1453	1453	O-H in plane bending and C-O stretching
1326	1323	C-O stretching and O-H in plane bending; C=C stretching
861	861	C-H out of plane bending
756	761	C-H out of plane bending
673	678	C-H bending vibration

UV- Visible spectral analysis

The UV-Visible spectral analysis of pure and Mg doped L-ascorbic acid single crystals were carried out using Perkin Elmer Lambda 35 spectrometer (UV-VIS-NIR) in the range between 190-1100 nm. The UV–vis spectra recorded for pure and Mg doped L-ascorbic acid crystals are shown in Figure 4. It is clear from the figure that the crystal has sufficient transmission in the entire visible and IR region. The optical transparency of the L-ascorbic acid crystal is increased by the doping of Mg. It was noticed that the cut off wavelength slightly decreased for Mg doped L-ascorbic acid crystals, when compared to the pure L-ascorbic acid. The addition of the doped Mg in the optimum conditions to the solution is found to suppress the inclusions and improve the quality of crystal with higher transparency.

The measured transmittance (T) was used to calculate the absorption coefficient (α) using the formula

$$\alpha = \frac{2.3026 \log\left(\frac{1}{T}\right)}{d}$$

Where T is the transmittance, d is the thickness of the crystal. The energy gap of the material was calculated by the following equation [8-9],

$$\alpha h\upsilon = A\,(h\upsilon - E_g)^r$$

where A is a constant, E_g the optical band gap, h is the plank's constant and υ is the frequency of the incident photos and n is an index which assumes the values 1/2, 3/2, 2 and depending on the nature of electronic transitions responsible for absorption [10]. The band gap was obtained by plotting $(\alpha h\upsilon)^2$ versus $h\upsilon$ in the high absorption range followed by extrapolating the linear region near after the absorption edge to the energy axis (Figure 5). It has also been observed that the band gap is almost the same (3.94 eV) for pure and Mg doped L-ascorbic acid crystals. As a consequence of wide band gap, the grown crystals has large transmittance in the visible region which is essential for nonlinear opticalapplications [11].

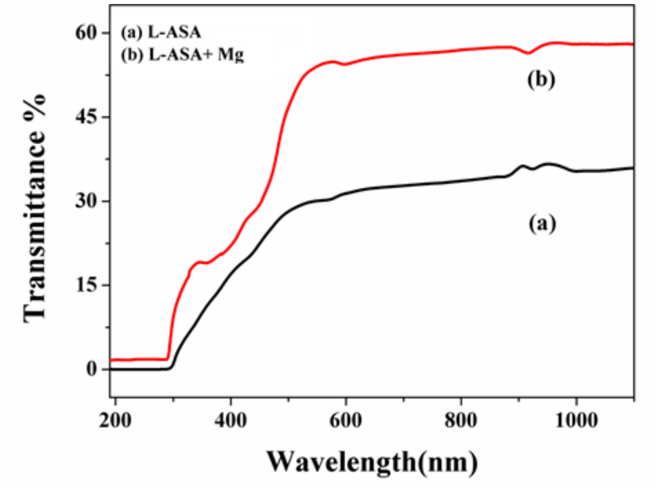

Fig. 4. UV-Vis Transmittance spectra of pure and Mgdoped L-ascorbic acid crystals

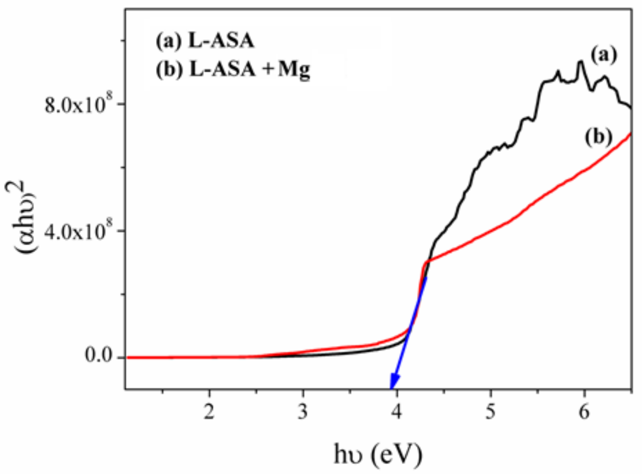

Fig. 5. Band gap energy of pure and Mgdoped L-ascorbic acid crystals

Microhardness studies

Mechanical strength of the grown crystals were studied using Shimadzu HMV- 2T Vickers microhardness tester. The load P was varied between 25 and 100 g and the time of indentation was kept constant as 10 s for all trials. The diagonal lengths of indentation (d) were measured in µm for various applied load (P) in g. The Vickers's hardness number (H_v) was calculated using the relation [12]

$$Hv = 1.8544 \frac{P}{d^2} (kg/mm^2)$$

Where H_v is the Vickers hardness number, P is the applied load and d is the average diagonal length of the indentation mark. The variation of H_v with the applied load P is shown in Figure 6. According to the normal indentation size effect (ISE), microhardness of crystals decreases with increasing load and in reverse indentation size effect (RISE) hardness increases with applied load. It is observed that the microhardness of pure and Mg doped L-ascorbic acid crystals follows a linear behavior with load and exhibit reverse ISE. The hardness value of L-ascorbic acid is found to be higher than Mg doped L- ascorbic acid crystals**.** The hardness increases with increase in load up to 100 g and on further increase multiple cracks develops in the crystal surface due to the release of internal stresses generated locally by indentation. The normal ISE occurs in brittle materials while the reverse ISE occurs in single crystals, which undergo plastic deformation [13].

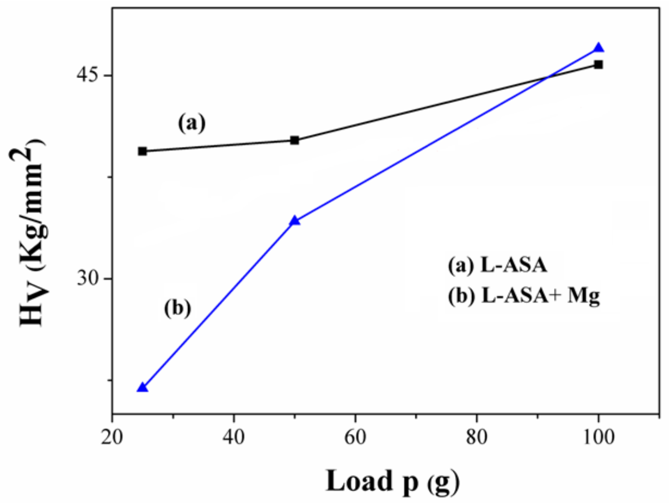

Fig. 6. Load Vs Hardness of pure and Mg doped L-ascorbic acid crystals

Meyer's index number was calculated from Meyer's law, which relates the load and indentation diagonal length as

$$\log p = \log k + n \log d$$

where k is the material constant and 'n' the Meyer's index. In order to find the value of 'n', a graph is plotted for log P against log d shown in Figure 7. According to Onistch, for hard materials n lies between 1 and 1.6 and for soft material it is above 1.6 [14]. The values of n determined using least squares fit method for pure and Mg doped L-ascorbic acid crystals were found to be 2.60 and 1.798 respectively, which indicates that pure and Mg doped L-ascorbic acid crystals are soft material category [15,16]. It sussests that the material having appreciable hardness values shall withstand higher laser damage threshold values which may be useful for the high frequency conversion devices.

Table 3. Load Vs Hardness

Load (g)	Hardness(kg/mm^2)	
	L-ASA	L-ASA+0.01 M Mg
25	39.4	21.9
50	40.2	34.25
100	45.8	47

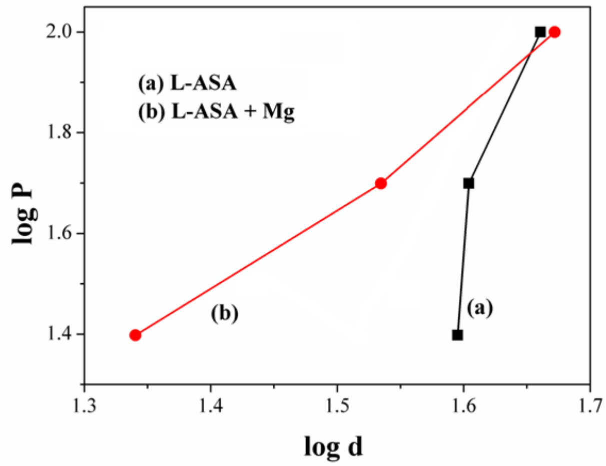

Fig. 7. Plot between log P Vs log d of pure and Mg doped L-ascorbic acid crystals

Second harmonic generation studies (SHG)

SHG test was used to study the NLO properties of pure and Mg doped L-ascorbic acid crystals. Powder second harmonic generation efficiency was carried out by using the modified Kurtz and Perry powder method. The grown crystals were grained into powder and densely packed in between two transparent glass slides. A Q- switched 10 ns Nd: YAG laser operating at the fundamental wavelength 532 nm with 10 Hz repetition rate and delivering 50 mJ/pulse of energy was used as light source in our experiment [17].

Table 4. SHG efficiency of pure and Mg doped L-ascorbic acid

S.No	Compound	SHG efficiency
1.	L-ascorbic acid	1.07 times that of KDP
2.	L-ascorbic acid + Mg	1.93 times that of KDP

The second harmonic generation efficiency of the grown crystals was confirmed by the emission of bright green flash from the pure and Mg doped L-ascorbic acid single crystals Table 4. The SHG relative efficiencies of pure and 0.03 M of Mg doped L-ascorbic acid crystals are 1.07 and 1.93 times higher than that of KDP crystal. This results shows that the SHG efficiency is highly enhanced by Mg doping.

IV. CONCLUSION

Good quality single crystals of pure and Mg doped L-ascorbic acid crystals were grown by slow evaporation solution growth technique. The powder XRD pattern of pure L-ascorbic acid crystal matches well with the reported values. Mg doped L- Ascorbic acid crystals exhibits slight shifts in XRD peak position and lattice parameter values. The functional groups of the pure and Mg doped L- Ascorbic acid crystals were identified using FT-IR spectroscopy. Mg doped L-ascorbic acid crystals has enhanced optical transparency when compared to pure L-ascorbic acid crystal. Vicker's microhardness test showed that the hardness value increased with increasing load and the material belongs to soft material category. The SHG relative efficiencies of pure and 0.03 M Mg doped L-ascorbic acid crystals are 1.07 and 1.93 times higher than that of KDP crystal.The results such as optical, thermal and mechanical studies show that the alkali metal doped L-Ascorbic acid single crystal would be a potential candidate for opto-electronic applications.

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