Growth, Dielectric studies on pure and $CuSO_4$ added L(+) - tartaric acid single crystals

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Abstract- Single crystals of pure and $CuSO_4$ added L(+) - tartaric acid were grown by slow evaporation technique. The molar concentration of $CuSO_4$ used in the present study were 0.005M, 0.01M and 0.05M. The grown crystals were characterized by energy dispersive spectroscopy, powder x-ray diffraction, Fourier transform infrared spectroscopy and dielectric measurements. The elements presented in the grown crystals were identified by the energy dispersive x-ray analysis. The powder x-ray data were indexed and the lattice constants were determined. Fourier transform infrared spectrum revealed that all the functional groups are presented in the pure and $CuSO_4$ added L(+) - tartaric acid crystals. The variation of dielectric constant were calculated in the range 20Hz to 20KHz and it was found that the dielectric constant was increasing when the $CuSO_4$ concentration was increased.

Index Terms **-** L(+)-tartaric acid crystals, EDAX, PXRD, FTIR, dielectric constant

I. INTRODUCTION

Organic nonlinear optical (NLO) materials have attracted a great deal of attention due to their applications in optical devices, such as optical switches, optical modulators, optical communications, optical data storage etc. [1 – 4]. Due to the increasing need for cheap and easily processable materials for the industrial applications, several studies dealing with organic, inorganic and semiorganic materials for nonlinear optics (NLO) have been reported. Among these, organic nonlinear materials will be the key role industrial technologies. A number of such materials have been reported in literature for their applications as NLO materials [5 – 6].

L(+) - tartaric acid is a good organic nonlinear optical material. L(+) - tartaric acid belongs to the monoclinic system with space group $P2_1$. Growth and optical studies of L(+) - tartaric acid have been reported in the literature [7 – 10]. The effect of dopants on various properties of single crystals are of great interest from both solid state science as well as technological points of view. Additions of dopants have a profound influence on the growth kinetics, morphology, second harmonic efficiency and dielectric properties of grown crystals. In the present work, pure and $CuSO_4$ added L(+) – tartaric acid single crystals were grown by slow evaporation technique. The grown crystals were subjected to various characterizations to study the structure and dielectric properties. The details are presented herein.

II. EXPERIMENTAL

Analytical reagent grade samples L(+) - tartaric acid, $CuSO_4.5H_2O$ and doubly distilled water were used in the present work for the growth of single crystals from aqueous solution by slow evaporation method after recrystallization. The saturated concentration of the L(+) - tartaric acid at room temperature was found to be 3.2 M. The concentrations of $CuSO_4$ used in present study were 0.005, 0.01 and 0.05M. Copper sulphate was mixed with the pure solution directly. The growth solution was kept in a constant temperature bath in the predetermined temperature. Crystals of maximum size were obtained in about 5-7 days. The maximum size of the grown crystals was 50 x 15 x 10 mm^3. Figure 1 shows that the pure and $CuSO_4$ added L(+) - tartaric acid crystals. It is observed that the transparency of the pure L(+) – tartaric acid crystal decreases with increasing $CuSO_4$ concentration.

The entry of $CuSO_4$ into the crystal lattice was confirmed by energy dispersive x-ray analysis (JEOL Model JED - 2300). X-ray diffraction studies were carried out using powder x-ray diffractrometer (PANalytical make, ModelX'per PRO). The vibrational measurements were carried out at room temperature using FT-IR spectrometer (JASCO – 4100LE with ATR facility) in the region 4000-400cm^{-1}. The dielectric properties of all the samples were carried by measuring capacitance of the samples using HIOKI 3532-50 LCR meter in the frequency range of 200 Hz to 200 kHz

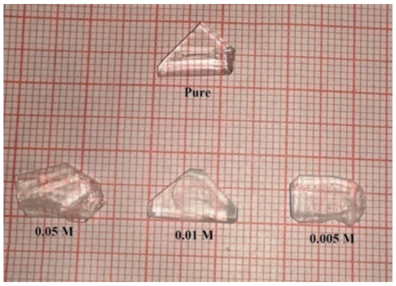


Figure 1: Photograph of the grown pure and $CuSO_4$ added L(+) – tartaric acid crystals

III. RESULT AND DISCUSSION

A. Energy dispersive spectral analysis

The energy dispersive spectrum of the $CuSO_4$ added L(+) - tartaric acid crystals are presented in figure 2. The characteristic peaks at the energies 0.277keV, 0.525keV, 2.307keV and 8.040keV shows the presence of carbon, oxygen, sulphur and copper atoms respectively in the grown crystals. The observed and calculated concentration of copper sulphate in the grown crystal is presented in table 1. The concentration of Cu and S in the grown crystal was found to be nearly equal to that of the actually taken for the crystal growth.

Table 1: Calculated and observed concentration of pure and $CuSO_4$ added L(+) - tartaric acid crystals

Concentration of Copper (in M)		Concentration of Sulphur (in M)	
actually taken	Observed	actually taken	Observed
0.005	0.0043	0.005	0.0039
0.01	0.0095	0.01	0.012
0.05	0.043	0.05	0.046

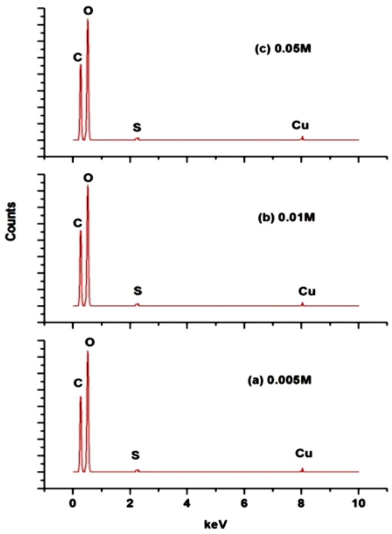
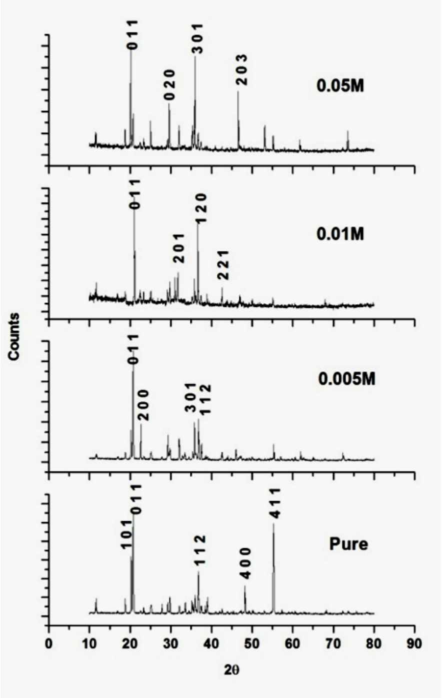


Figure 2: Energy dispersive spectrum of $CuSO_4$ added L(+) - tartaric acid crystals

B. X- Ray diffraction analysis



The x-ray diffraction pattern for the pure and $CuSO_4$ added L(+) - tartaric acid is presented in the figure 3. The data were indexed using power x software [11] and the lattice parameters were determined. The indexed data of pure L(+) - tartaric acid was compared and it is in good agreement with JCPDS data [File No. 33 1883]. The x-ray diffraction pattern of the pure and $CuSO_4$ added L(+) - tartaric acid single crystals differed in their relative intensities and the lattice spacing of the crystals.

Considering high reflection, the lattice parameters of all the grown crystals were calculated using $\alpha = \gamma = 90^o$ and $\beta = 100.16^o$. The lattice parameters obtained for the crystals grown in the present study are presented in table 2.

Table 2 : Variation of lattice constants and lattice volume of the grown crystals

Crystal	Lattice parameter (Å)		
	a	b	c
Pure L(+) – tartaric acid	7.5421	6.0415	6.0650
0.005M $CuSO_4$ added L(+) – tartaric acid	7.8011	6.0319	6.3469
0.01M $CuSO_4$ added L(+) – tartaric acid	8.1146	5.6281	6.5981
0.05M $CuSO_4$ added L(+) – tartaric acid	7.9380	6.0556	6.5056

Figure 3: XRD pattern of pure and $CuSO_4$ added L(+) - tartaric acid crystals

Lattice variation was observed in the doped crystals in comparison with the pure crystals. Lattice volume of the pure and $CuSO_4$ added L(+) – tartaric acid were calculated. The lattice volume of the pure, 0.005M, 0.01M and 0.05M $CuSO_4$ added L(+) – tartaric acid are 273.06 $Å^3$, 281.88 $Å^3$, 296.61 $Å^3$ and 307.82 $Å^3$ respectively. The increase in the lattice volume of the doped crystals compared with the pure crystals confirms entry of the $CuSO_4$ in the grown crystals.

C. FT-infrared analysis

The Fourier transform infrared spectra recorded for the grown crystals are presented in figure 4. The two strong peaks at 1719 and 3396 cm^{-1} are due to C = O and O – H stretching mode respectively. The band at 1190 cm^{-1} is attributed to the C – O – C asymmetric stretch of carbonyl group. The peak at 1441 cm^{-1} is due to C–H bending modes. The peaks of various intensities at 1078 and 940 cm^{-1} are due to out of plane O–H deformation and C–O stretching. The band at 657 cm^{-1} is absorbed due to O = C = O bending mode. The

FTIR spectra and the corresponding band assignment clearly indicate that the functional groups of pure L(+) – tartaric acid are not altered by the addition of the copper sulphate.

D. Dielectric studies

The grown crystals were powered and made into pellets of 2mm thickness and 13mm diameter. The pellets are placed in a two probe arrangement. In order to ensure good electrical contact between the sample and the electrodes, silver paste was applied on both surfaces of the samples. Dielectric measurements were made in the frequency range 200 Hz – 200 KHz at room temperature (305 K). Figure 5 and 6 shows the plot made between dielectric constant and dielectric loss versus frequency for pure and $CuSO_4$ added L(+) – tartaric acid crystals samples respectively.

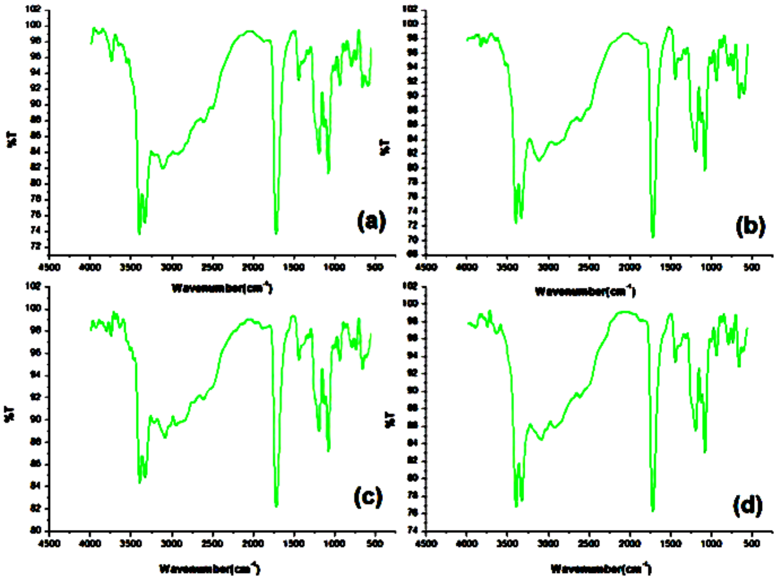


Figure 4: FTIR spectra of (a) pure (b) 0.005 M (c) 0.01 M (d) 0.05M $CuSO_4$ added L(+) – tartaric acid crystals

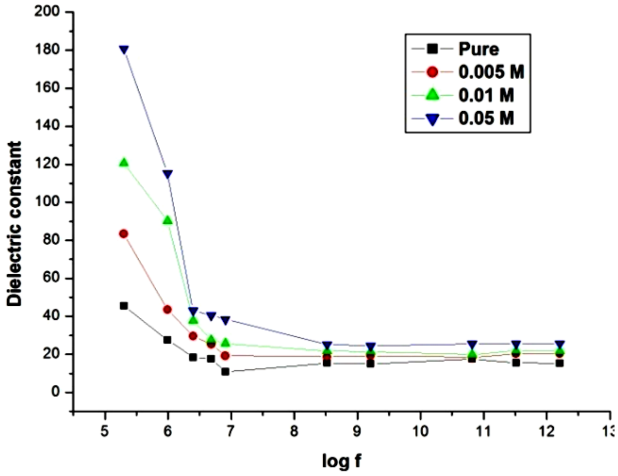


Figure 5: Frequency dependence of dielectric constant at room temperature for pure and $CuSO_4$ added L(+) – tartaric acid crystals

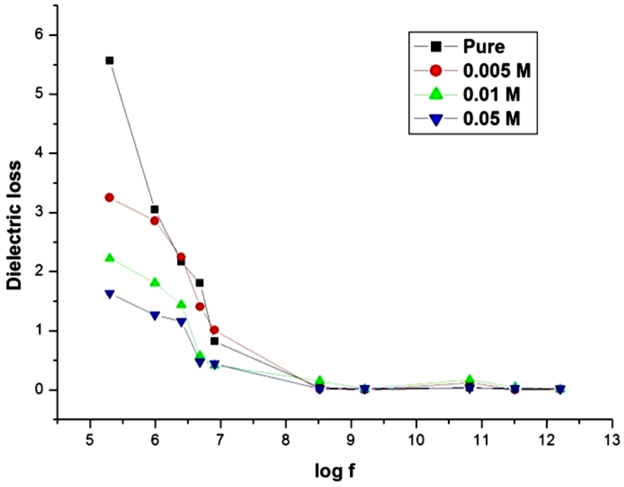


Figure 6: Frequency dependence of dielectric loss at room temperature for pure and $CuSO_4$ added L(+) – tartaric acid crystals

From the plots it can be seen that the dielectric constant decreases exponentially as the frequency of applied field increases. The electronic exchange of the number of ions in the crystals gives local displacement of electrons in the direction of the applied field, which in turn gives rise to polarization. As the frequency increases, a point will be reached where the space charge cannot be sustained and comply with the variation of external field, hence polarization decreases, which gives rise to diminishing values of dielectric constant [12]. The same trend is observed in the case of dielectric loss versus frequency. At relatively lower frequency, the higher the temperature, the larger is the dielectric constant. The characteristics of low dielectric constant and dielectric loss with high frequency for a given sample suggests that the sample possesses enhanced optical quality with less defects and this parameter is of vital importance for various nonlinear optical materials and their applications [13-14].

IV. CONCLUSION

Pure and $CuSO_4$ added L(+) – tartaric acid crystals were grown by slow evaporation method in a predetermined temperature. The molar concentrations used in the present were 0.005M, 0.01M and 0.05M. All the grown crystals were subjected to energy dispersive x-ray analysis, powder x-ray diffraction analysis, Fourier transform infrared analysis and dielectric measurements. The energy dispersive x-ray spectrum confirmed the presence of $CuSO_4$ in the grown crystals. The variation of lattice parameter were observed and it was found that the lattice volume increases in increase of $CuSO_4$ concentrations. Fourier transform infrared spectra revealed that the presence of all the functional groups in the pure L(+) – tartaric acid crystals and these were not altered by the addition of the $CuSO_4$. The variation of dielectric constant and dielectric loss with the frequency at room temperature were measured and it was found to decreases as the frequency of applied field increases.

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