A new Non-Linear Optical Material and Mechanical Studies for pure and Sarcosine Doped L-Tartaric acid of Single Crystal by slow Evaporation Method

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Abstract - **A new non-linear optical material of sarcosine doped L-tartaric acid crystal grown by slow evaporation method by room temperature. The vibrational frequencies of functional groups doped L-tartaric acid in the grown crystal identified by FTIR spectral analysis. The optical transmission study reveals the improved is good transparency of doped crystal in the entire visible region for NLO applications. The crystalline size and cell parameter were characterized by powder X-Ray diffraction and Single X-Ray diffraction analysis. The presence of dopent in the sample grown by L-tartaric acid crystal with addition of sarcosine was determined by the spectral analysis. The Vickers Microhardness studies reveal that the mechanical strength of the grown crystal. The SHG efficiency of pure sarcosine doped L-tartaric acid crystal confirmed by Nd:YAG pulsed laser employing the Kurtz- Perry powder technique.**

KeyWords - **Sarcosine, L-tartaric acid, FTIR, UV, Vickers hardness test, Single crystal XRD, EDAX, SHG**

I. INTRODUCTION

In recent years semi organic nonlinear optical (NLO) crystals have attracted much attention for their large nonlinear coefficient, high laser damage threshold [1, 2]. However, most of organic NLO materials have poor mechanical and thermal properties, resulting in the damage of crystal during processing. To avoid this drawback, a new type of NLO material has been grown from organic-inorganic complexes. The semi organic NLO materials have high optical nonlinearity of a purely organic compound combined with the mechanical and thermal properties of inorganic materials [3]. Amino acids have attracted a wide interest of the researchers, since all the compounds in the class consist of an optically active property. Thus, amino acids have special physical properties which make them an ideal candidate for their NLO applications [4]. In Pure and sarcosine doped L-Tartaric acid crystals have increased attention for photo induced nonlinear optical effects and dispersion of the linear and nonlinear optical susceptibilities. Photo induced nonlinear optical effects of L-tartaric acid single crystals show that the increasing time of illuminations leads to slight changes in the absorption backgrounds without changes in the spectral features [5]. Dispersion of the linear and nonlinear optical susceptibilities of   L –tartaric acid

single crystals was reported [6]. In the present work, a systematic study has been carried out on the growth of pure and Sarcosine doped L-tartaric acid crystals. Single crystal X-ray diffraction study has been carried out to confirm the grown pure and doped grown crystal. FT-IR, UV-VIS-NIR, Microhardness, dielectric analysis and NLO property were studied for grown pure and doped crystals. The second harmonic generation (SHG) studies had been carried out for the grown pure and doped crystals.

II. EXPERIMENTAL
2.1 Solubility measurements

The growth of bulk crystals from solution growth, slow evaporation technique requires selection of solvent in which the molecule is moderately soluble. The size of the grown crystal depends on the amount of material available in the solution which in turn is decided by the solubility of the material in that solvent. Hence the solubility measurements of Pure L-Tartaric acid were carried out in double distilled water for various temperatures $20^\circ C$ to $70^\circ C$. A sealed container charged with water & the solute, maintained at a constant temperature was used to determine the equilibrium concentration. The solution was stirred continuously for 12 hours. The content of the solution was analyzed gravimetrically and the results are presented in Fig. 1. It is seen that the solubility increases with the increases of temperature. The solubility is much higher in water. Hence water was selected as the solvent for crystal growth for these materials. It is seen from the curve that solubility of L-Tartaric mixed Sarcosine sample is reduced as compared to Pure L-Tartaric acid and increased as comparison with Pure and sarcosine doped L-tartaric acid crystal.
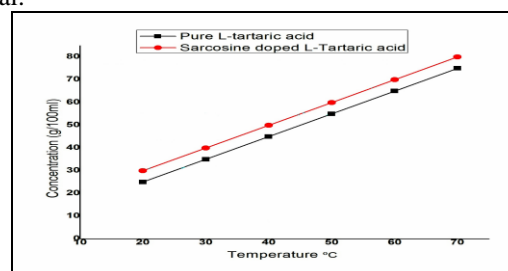

Fig 1. Solubility diagram for pure and sarcosine doped L-Tartaric acid

2.2 Crystal growth

Pure and doped Sarcosine doped L-tartaric acid crystal was grown by slow evaporation technique using water as a solvent. Analytical grade (AR) Sarcosine and L-Tartaric acid was taken in equimolar ratio was Saturated solution was prepared, filtered, and allowed to evaporate at room temperature under optimized conditions. Seed crystals were obtained in a period of 25 days. In Good quality crystals were obtained by successively recrystallization method. Saturated solution of 1 mol% of Sarcosine doped L-Tartaric acid was papered. Slow evaporation of the solution by single crystals of size $8 \times 5 \times 4$ mm³. The incorporation of dopant into the pure solution has improved the growth rate and the quality of the crystals. The grown crystal was further studied by various characterization techniques. The photographs of grown pure and Sarcosine doped L-Tartaric acid crystals are shown in Fig 2.

Fig2. Grown crystal for sarcosine doped L-Tartaric acid crystal

III. RESULTS AND DISCUSSIONS

3.1 Fourier-Transform Infrared Spectroscopy Studies

The FTIR Spectrum of sarcosine doped L-Tartaric acid was recorded in the KBr Pellet in the frequency region 400cm⁻¹ – 4000cm⁻¹ using Perkin Elmer spectrometer is shown in fig 3. The assignments of various functional groups are given table 1. The stretching frequency at 3774cm⁻¹ and 3220 cm⁻¹ shows the presence of O-H stretching and 2924cm⁻¹ C-H₂ symmetric stretching. In multiple fine structures at the lower energy mode indicate the strong hydrogen bonding of NH₃⁺ groups. The strongest band observed at 1603 cm⁻¹ indicates the presence of P-O-H bending in the spectrum. The presence of strong peak ranges from 1404 cm⁻¹ to 1055 cm⁻¹ for the N-H stretching. In the lower wave number region, the bands at 602 cm⁻¹ and 415 cm⁻¹ are due to the ring asymmetric, symmetric stretching and plane deformation.
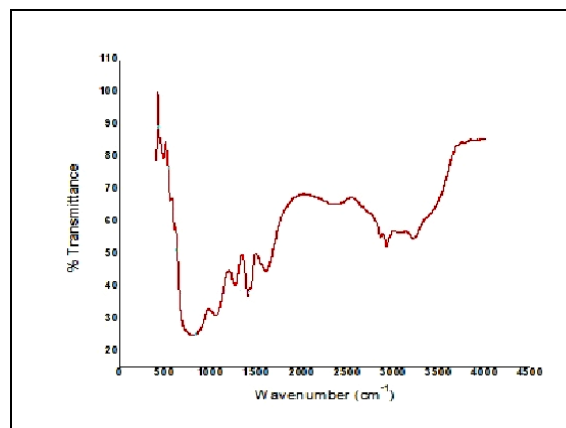

Fig.3. FTIR Spectrum for Sarcosine doped L-tartaric acid

Table 1. FTIR Spectrum for Sarcosine doped L-Tartaric acid

Wave Number (cm⁻¹)	Assignments
3774	O-H Stretching
3220	Asymmetric stretching of NH3⁺
2924	C-H₂ stretching
2856	C-H₃ stretching
2375	C=H stretching
1603	P-O-H bending
1404	N-H bending of dopents
1055	P=O stretching
602	P=O stretching
415	C-O bending

3.2 UV-VIS-NIR Spectral Analysis

The UV-Vis-NIR absorption and transmittance spectral analysis of pure and doped single crystals with 1 mm thickness was carried out using UV-Vis-NIR spectrophotometer in the wavelength range of 200 nm to 1100 nm and the results are shown in Fig. 4(a). The absorbance spectra show that there is an improvement in the absorbance percentage from 58 % to 89 % caused by the addition of the dopant. The UV transparency lower cutoff wavelength of pure and Sarcosine doped L-tartaric acid single crystals occurs around 281 nm. As there is no absorption in the entire visible region, Sarcosine doped L-Tartaric acid can be used as a potential material for second harmonic generation in the visible region. The optical absorption coefficient α can be calculated from the transmittance using the following relation:

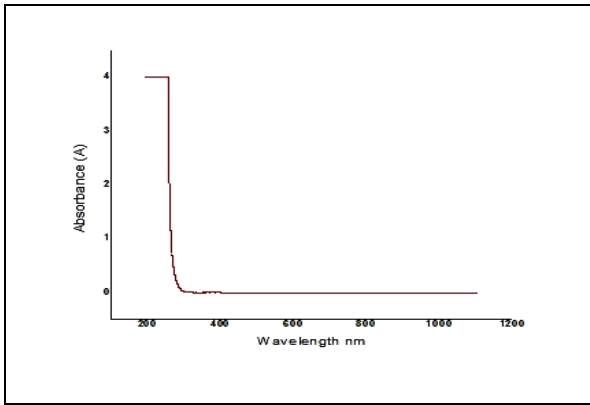$$\alpha = \frac{2.3036 \log[\frac{1}{T}]}{d}$$

Fig.4(a). UV-Visible Spectral studies of sarcosine doped L-Tartaric acid.

Where, T is the transmittance and d is the thickness of the crystal. Several wide band gap materials possess excellent transmittance properties in the visible region. The energy dependence of the absorption coefficient provides information on the type of band gap. Similar to an indirect band gap semiconductor, the crystal under study has an absorption coefficient obeying the following relation for high photon energies hυ:

$$(\alpha h\upsilon)^{1/2} = A(E_g - h\upsilon)$$

Where, E_g is the optical band gap of the crystal, and A is a constant. The variations of $(\alpha h\upsilon)^2$ versus hυ in the fundamental absorption region are plotted in Fig. 4(b). E_g can be calculated by extrapolation is linear part of the plot. The optical band gap is found to be 4.49eV in sarcosine doped L-Tartaric acid by single crystal.
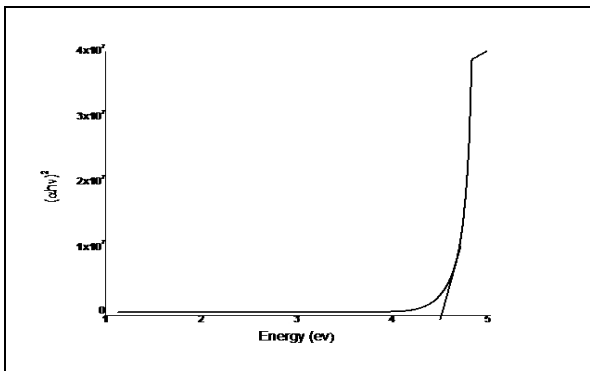

Fig.4(b).A graph plot for $(\alpha h\upsilon)^{1/2}$ band gap energy

3.3 Single Crystal X-ray diffraction Analysis

Single crystal X-ray diffraction analysis was carried out using ENRAF NONIUS Cad4 diffractometer to identify the lattice parameters. The compound of Sarcosine doped L-Tartaric acid crystallized in monoclinic system with space group $P2_1$ and its all atoms placed in general position. The lattice parameters are found to be a=5.057A°, b=6.637A°, C=11.593A°, and α=β=υ=90^0 with volume V=539A°3. The cell parameter of the grown crystal from the pure and sarcosine doped L-Tartaric acid is non-centrosymmetric in nature which fulfils the fundamental criterion for the SHG activity of the material.

3.4 Microhardness Studies

To analysis of mechanical property in the grown crystal is fabrication of optical devices. The resistance offered by a material to the motion of dislocation, deformation or damage under an applied stress is measured by the hardness of the crystal. The microhardness studies have been carried out on a selected well transparent single crystal using microhardness tester is fitted with a Vickers dimond pyramidal indenter. The indentation were made on the sarcosine doped L-Tartaric acid crystal with applied load ranging from 25g to 100g. The time of indentation was kept constant for 5S. The values of Vickers microhardness at different loads were calculated using the relation:

$$Hv = \frac{1.8544\ P}{d2}\ (Kg/mm^2)$$

Where, P is the applied load and d is the mean diagonal length of the indentation From Fig 5(a) shows that the variation of hardness with the applied load. It was observed that the hardness of sarcosine doped L-Tartaric acid increasing load upto 100g, which the indentation size effect. The release of internal stress generated locally by indentation. The work hardening coefficient (n) of the material was calculated using the relation,

$$P = kd^n$$

Where, P is the applied load in gram, k is the material constant, n is the mayer's index which can be determined from the graph is plotted between Log P and Log d as shown in fig 5(b). The mayer's index of the grown crystal was calculated as 2.057 which indicate the grown crystal belong to the soft category of the materials. The value of n is above 1.6; it is belongs to the hard materials. Hence the grown single crystals can be used for the applications in the magnetic field like communication device fabrication.
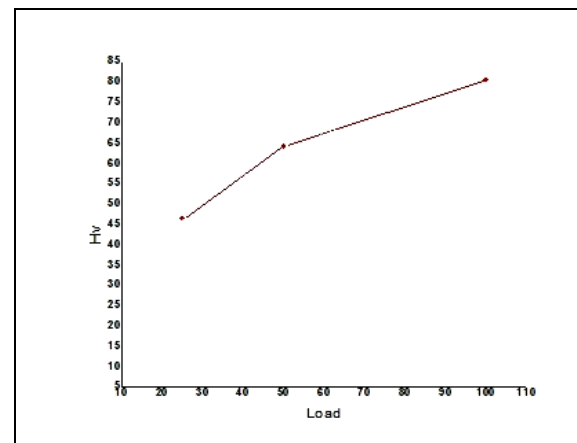

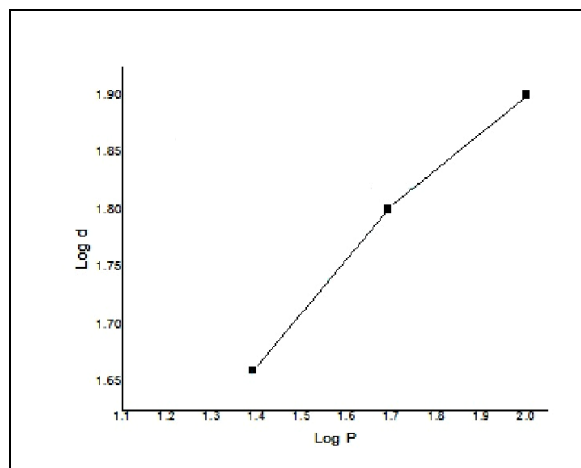Fig.5(a) A graph plot for Load Vs Hv sarcosine doped L-tartraic acid

Fig.5(b) A graph plot for Log P Vs Log d sarcosine doped   L-tartraic acid

3.5 NLO Test – Kurtz Powder SHG Method

The Kurtz powder technique is used to identify the materials with non-centrosymmetric crystal structures and is the most widely used technique for confirming the SHG efficiency of NLO materials. The NLO property of the sample was tested using a Q-switched Nd: YAG laser beam of wavelength 1064nm and 10ns pulse width with an input rate of 10Hz. The output of the grown crystal was measured as 8mV while the KDP gave an SHG signal of 16mV for input beam energy of 6.5mJ/Pulse. The green radiation generated confirms the second harmonic signal generated in the crystalline sample. The standard NLO inorganic KDP was used as the reference material. The emission of green light (λ=532 nm) from the Sarcosine doped L-tartaric acid crystals confirmed their non-centrosymmetric crystal structure. The SHG efficiencies of the doped crystals are 1.6 times greater than the standard ADP crystals were grown. The SHG efficiency is decreased due to lower polarizing ability of the material.

4. CONCLUSION

Pure and sarcosine doped L-tartaric acid single crystal was grown by slow evaporation technique. From the single crystal XRD data obtained, it is proved that the crystals belong to monoclinic structure and non-centrosymmetric space group $P2_1$. The presence of a wide transparency window lying between 200 nm and 1100 nm with λ max =240 nm is represented by the UV spectrum. The bandgap was estimated to be of 4.49eV which is typical of dielectric material. The wide energy band gap confirms that the defect concentration in the grown crystal is very low and large transmittance in the visible region. The crystal was mechanical stability which is confirmed by the Vickers microhardness analysis. By Meyer's law, the value of Meyer's index n estimated to be 2.057 indicates that the crystal belongs to soft material category. The nonlinear optical nature of the crystal was confirmed by Kurtz-Perry powder technique. The transmission near the Nd:YAG laser fundamental wavelength (1064 nm) and second harmonic wavelength (λ=532 nm) is reduced . This reduction contributes to the resistance of the material to laser damage threshold. The SHG efficiencies of the doped crystals are 1.6 times greater than the standard ADP

crystals were grown. The SHG efficiency is decreased due to lower polarizing ability of the material. This transmission range of the crystal makes it valuable for applications that require green light. High frequency shift and good NLO property and other physicochemical properties make this material a good laser converter.

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