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CHARACTERIZATION OF STRONTIUM CHLORIDE DOPED L-TARTARIC ACID (SCLTA) CRYSTALS GROWN BY AQUEOUS SOLUTION METHOD

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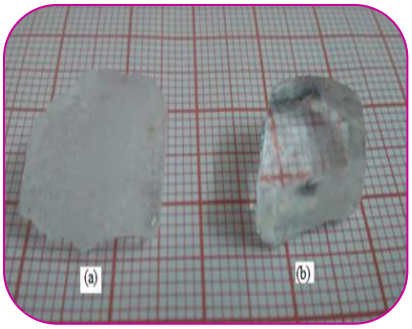
ABSTRACT



Single crystals of undoped L-tartaric acid (LTA) and strontium chloride doped L-tartaric acid (SCLTA) were grown by slow evaporation solution growth technique. Solubility of the samples was measured by gravimetric method using water as the solvent at different temperatures. The lattice parameters and crystal structure of LTA and SCLTA crystals were found by XRD technique. The relative SHG efficiency was measured for the samples by Kurtz-Perry powder method. Functional groups of the samples have been identified by FTIR analysis. Thermal stability of the SCLTA crystal was found by TG/DTA studies and linear optical studies were carried out to find the transmittance, band gap and linear absorption coefficient. Photo current and dark current for the samples have been measured and the results are analyzed.

KEY WORDS: *Single Crystal, Solution Method, Doping, XRD, Solubility, SHG, NLO, TG/DTA, FTIR, Optical Transmittance.*

1. INTRODUCTION

Nonlinear optical crystals have a lot of important applications in laser frequency conversion, optical computing, optical information processing, optical storage, laser remote sensing, and optical communication. Thus these crystals are the technologically important materials. Nonlinear optical (NLO) crystals are used to generate UV laser and visible laser light for the applications in optical communication, photonics and optical computing. NLO crystals can mainly be classified into organic, inorganic and semiorganic NLO crystals. Organic NLO crystals have been of particular interest because of the large second order nonlinear optical coefficients and high laser damage threshold. Large second optical linearity originates from organic conjugated molecules having an electron acceptor group at one end and a donor group at the opposite end. Some of the merits of organic NLO crystals are optically more nonlinear, high optical damage threshold, intrinsic tolerability, low cost, broad spectral range and birefringence used for phase matching [1]. L-tartaric acid (LTA) crystal is an organic NLO crystal and it crystallizes in monoclinic system [2]. Growth and various studies of L-tartaric acid crystals are reported by many authors [3-6]. To improve the various properties of LTA crystals, an inorganic salt viz., strontium chloride was added into the host LTA crystal (SCLTA). The literature shows that the dopants like organic and metal dopants have been added into many NLO crystals to alter their properties [7-11]. Here the aim the paper is to grow and study the LTA and SCLTA crystals and the results are presented.

2. CRYSTAL GROWTH

The crystals of this work were grown by solution method with slow evaporation technique and the solvent used here was the double distilled water. Aqueous saturated solution of L-tartaric acid (LTA) was prepared and stirred well and this solution was filtered using Whatmann filter paper. This solution was taken in a growth vessel for the crystal growth. 2 mole% of strontium chloride was added into the aqueous solution of LTA and saturated solution was prepared in a separate growth vessel. Both the growth vessels were covered with perforated papers for slow evaporation process. After a growth period of about 45 days, the single crystals of LTA and SCLTA were harvested for the characterization studies. The harvested crystals of undoped and strontium chloride doped L-tartaric acid crystals are shown in the Figure-1. It is noticed that there are morphological changes when L-tartaric acid crystal is doped with strontium chloride.

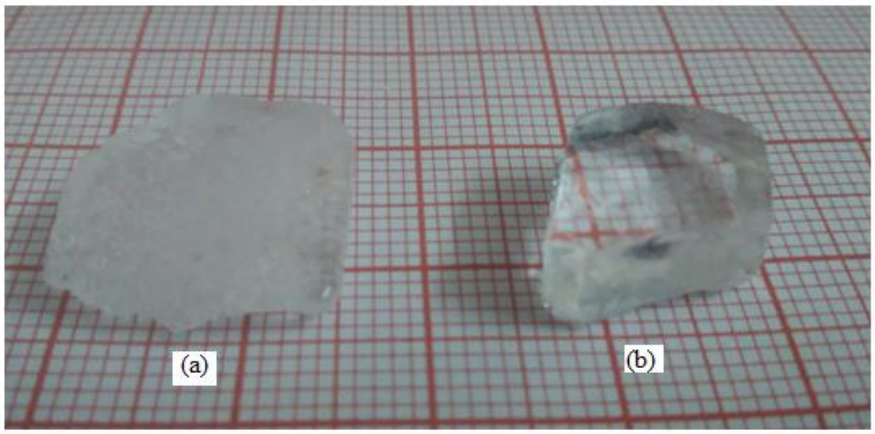


Fig.1.Grown crystals of (a) undoped and (b) strontium chloride doped L-tartaric acid crystals

3. RESULTS AND DISCUSSION

3.1 Solubility studies

Solubility study was carried out for the samples by gravimetric method and the values of solubility of the samples were measured at different temperatures in the range 30-50°C. The obtained values are given in the Figure-2. It is observed from the results that the solubility increases with increase of temperature for the samples and it is found to be more for strontium chloride doped L-tartaric acid (SCLTA) crystal. It is clear that for the SCLTA sample, the solvent is able to accommodate an increased amount of solute for the saturation at the same temperature. Since solubility increases with temperature, the samples have positive temperature coefficient of solubility.

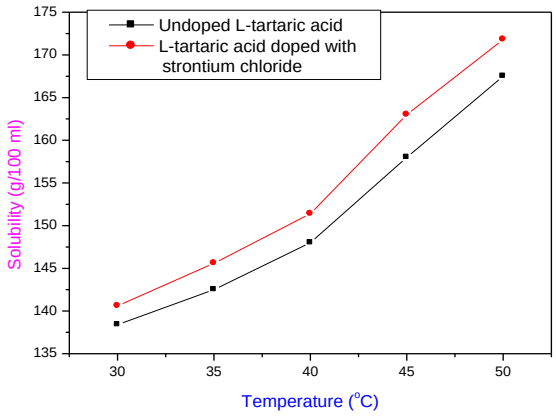


Fig. 2: Solubility curves for undoped and strontium chloride doped L-tartaric acid crystals

3.2 XRD studies

X-ray diffraction (XRD) is a method to determine the lattice parameters of crystalline materials. The grown crystals were subjected to single crystal XRD studies using a single X-ray diffractometer (Bruker-Nonius MACH3/CAD4) and the structural data were obtained. The obtained lattice parameters of the samples are provided in the Table-1. Single crystal XRD analysis indicates that the grown crystals crystallize in monoclinic structure. The space group of the both the samples are observed to be $P2_1$. This space group is a non-centrosymmetric space group of the monoclinic crystal system and hence second harmonic generation is possible from undoped and strontium chloride doped L-tartaric acid crystals.

Table 1: Crystallographic data for LTA and SCLTA crystals

Unit cell constants	Undoped L-tartaric acid [2]	SCLTA crystal (Present work)
a (Å)	6.203(5)	6.212(4)
b (Å)	6.018 (3)	6.025(5)
c (Å)	7.720(6)	7.719 (2)
α, β and γ	90°, 100.10°, 90°	90°, 100.16°, 90°
Crystal System Space group Volume of unit cell	Monoclinic, $P2_1$ 283.72 Å^3	Monoclinic, $P2_1$ 284.37 Å^3

3.3 SHG studies

In order confirm nonlinear optical property, microcrystalline form of grown crystals was subjected to Kurtz-Perry powder test [12]. The single crystals were powdered and were irradiated by an incident radiation (1064 nm) of pulse width 8 ns from Q-switched quanta RAY GCR Nd: YAG laser. KDP was used for calibrating the SHG intensity. The output power of the crystal was measured using a power meter and the NLO property of the crystals was confirmed from the emission of green radiation from the samples. The obtained values of the relative SHG efficiency of LTA and SCLTA crystals are 0.98 and 1.25 respectively in comparison with that of KDP. Since the SHG efficiency of SCLTA crystal is more than that of undoped L-tartaric acid, the SCLTA crystal is the most suitable material for NLO applications.

3.4 Identification of functional groups

Using the infrared spectrum of a sample, the functional groups present in the sample can be identified. The infrared absorption spectrum originates from vibrations of bonds which cause a change in the dipole moment of the molecule. The vibrational frequencies, their relative intensities and shapes of the infrared bands recorded in a double beam spectrometer and it is used for the qualitative characterization of the sample. Fourier transform infrared (FTIR) technique is based on the blending of a Michaelson Interferometer with a sensitive infrared detector and a digital minicomputer. FTIR spectrometer has the higher resolution, total wavelength coverage; higher accuracy in frequency and intensity measurements and the instrument also possesses greater ease and speed of operation. FTIR is perhaps the most powerful tool for identifying types of chemical functional groups. The FTIR spectrum of the grown strontium chloride doped L-tartaric acid (SCLTA) crystal was recorded in the region 400-4000 cm^{-1} with Perkin Elmer Fourier transform infrared spectrometer (Model: Spectrum RXI) using KBr pellet technique and it is shown in the Figure-3. The strong broad band in the range 3550-3300 cm^{-1} is corresponding to O-H stretching in the

carboxyl group. The presence of C=O group is confirmed by the peak at 1713 cm^{-1}. The stretching vibration of COO^- group is observed at 1627 cm^{-1}. The deformation vibration of the CH_2 is noticed at 1212 cm^{-1}. The CH deformation is observed at 989 cm^{-1} and the peak at 663 cm^{-1} is corresponding to CH out of plane bending vibration. The assignments for the FTIR absorption peaks are given in the Table-2. The FITIR spectrum of undoped L-tartaric acid crystal is reported elsewhere [13].

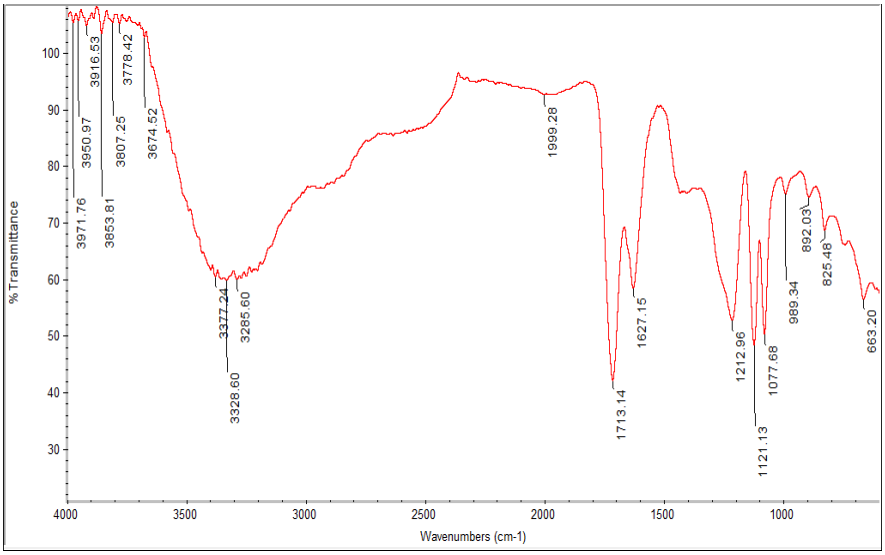


Fig. 3: FTIR spectrum of SCLTA crystal

Table 2: FTIR absorption peaks/bands and their assignments for SCLTA crystal

FTIR peaks/bands (cm^{-1})	FTIR assignments
3550-3300	OH stretching of carboxyl group
1999	CH stretching
1713	C=O stretching
1627	COO^- stretching
1212	CH_2 deformation
1121	COO^- deformation
989	CH deformation
892	CH_2 rocking
825	COO^- wagging
663	CH out of plane bending

3.5 TG/DTA studies

The thermal characterization of the samples was carried out by recording the TG/DTA thermal curves in the temperature range 35-800^oC. This study helps to find out the weight change, energy change and various endothermic and exothermic transitions in the samples with the change of temperature. The thermal stability and decomposition point of SCLTA crystal was identified by thermal analyses. The recorded

TG/DTA thermal curves of SCLTA crystal are shown in the Figure-4. There is a slight weight loss up to 50°C and this is due to removal of moisture of the sample. The endothermic peak at 167°C is due to the decomposition point of the sample. There is a huge weight loss in the temperature range 200-600°C and this is further decomposition of the sample. The broad exothermic peak in the temperature range 450-600°C is corresponding to the emission of gaseous particles after the decomposition. Finally, about 15% weight percentage of the sample is left out after 700°C. It is reported that the melting point/decomposition of the undoped L-tartaric acid (SCLTA) is about 172°C [14]. But the decomposition point of strontium chloride doped L-tartaric acid crystal is noticed to be 167°C and hence thermal stability of SCLTA crystal is slightly less compared to the undoped L-tartaric acid crystal. The reduction in decomposition point may be due to the reduction of bond strength when L-tartaric acid is doped with strontium chloride.

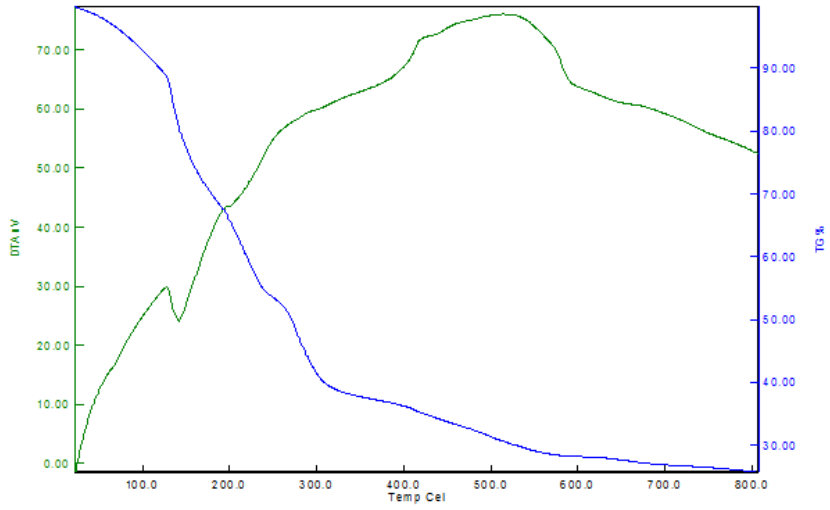


Fig. 4: TG/DTA thermal curves for SCLTA crystal

3.6 Linear optical studies

When ordinary UV-visible light is used to record the transmittance spectra of crystals, linear optical phenomena will take place and hence linear optical parameters can be studied. Using a spectrophotometer, the UV-visible spectra of undoped and strontium chloride doped LTA crystals are recorded in wavelength range 190-1100 nm and the same are presented in the Figure-5. The results indicate that the transmittance of strontium chloride doped LTA crystal is more than that of undoped L-tartaric acid crystal. The UV lower cut-off wavelength for both the samples is observed to be 248 nm and both samples have high transmittance in the visible region of the electromagnetic spectrum. The linear absorption coefficient (α) was determined using the relation $\alpha = (2.303/t)\ \log_{10}(1/T)$ where T is the transmittance and t is thickness of the crystal. The calculated values of linear absorption coefficient are given in the form of plots as shown in the Figure-6. The values of linear absorption coefficient for undoped and strontium chloride doped L-tartaric acid crystals are found to be low in the visible region. From Figure-5 also, the lower cut-off wavelength for both samples is noticed to be 248 nm. Using the Tauc's equation, the values of optical band gap of the samples are determined and Tauc's equation is given by $\alpha h\nu = A(h\nu - E_g)^{1/2}$ where E_g is the optical energy gap, A is a constant and α is the linear absorption coefficient, n is the frequency of light and h is the Planck's constant. Using this relation, Tauc's plots for undoped LTA and SCLTA crystals are drawn and the same are shown in the figure 7. The values of optical band gap for the samples are obtained from the Figure 7 and the extrapolation to the X-axis by the arrow marks gives the band gap energy values. The values optical band gap for both the sample crystals are the same and it is found to be 5.002 eV.

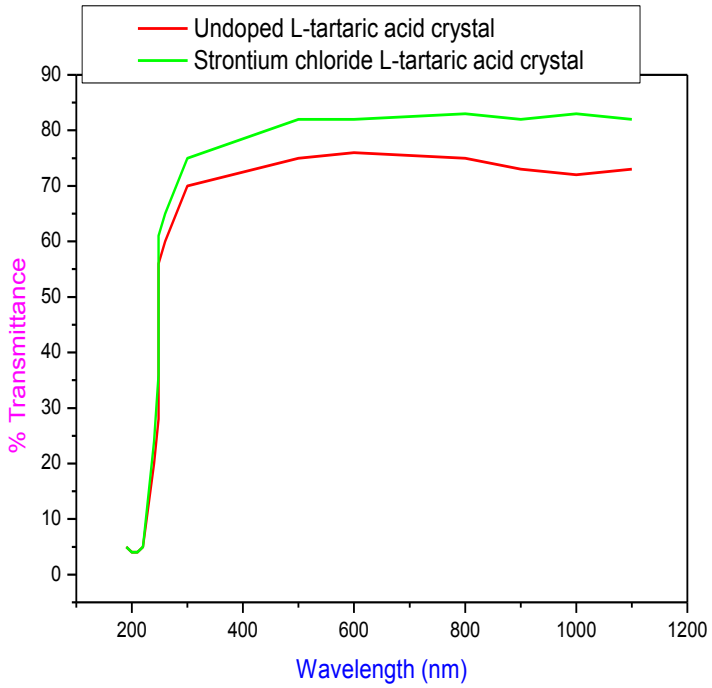


Fig.5: UV-visible-NIR transmittance spectra of undoped and strontium chloride doped L-tartaric acid crystals

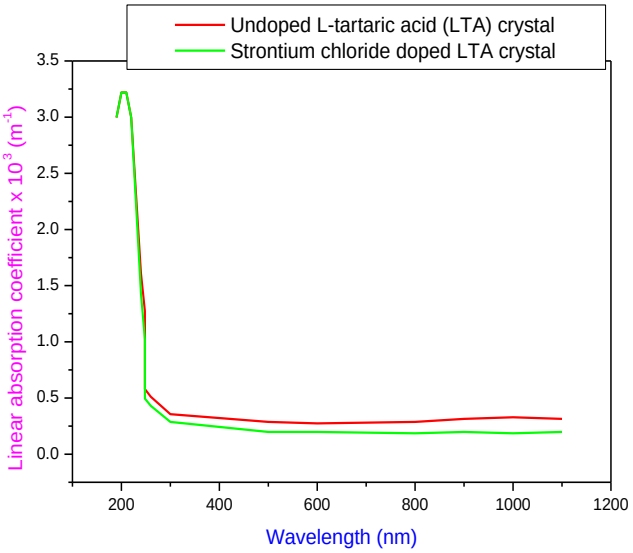


Fig. 6: Plots of linear absorption coefficient versus wavelength for undoped and strontium chloride doped L-tartaric acid crystals

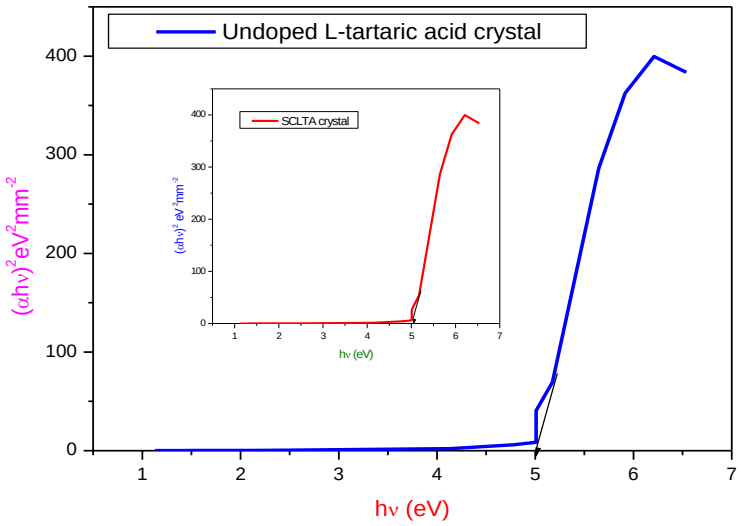


Fig.7. Tauc's plot for undoped L-tartaric acid (SCLTA) crystal; Inset: Tauc's plot for SCLTA crystal

3.7 Measurement of photo and dark currents

Dark and photo currents of the samples were measured using a photoconductivity set-up with a Keithley 485 picoammeter. Dark current was measured for samples without exposure of light and photo current was measured when the samples are exposed with light. For measuring the photo current, the samples were illuminated with a halogen lamp by focusing the light with the help of a convex lens. For different values of DC voltages, the dark and photocurrents were measured. The variations of dark and photo currents for undoped and strontium chloride doped L-tartaric acid crystals are presented in the figure 8. It is observed that the values of dark current and photo current increase with increase of applied electric field and it is found that the photo current is more than the dark current and hence the samples have positive photoconductivity. When L-tartaric acid crystal is doped with strontium chloride, it is noticed that the photo and dark currents are increased and this is due to the presence of inorganic dopant ions in the doped SCLTA crystal.

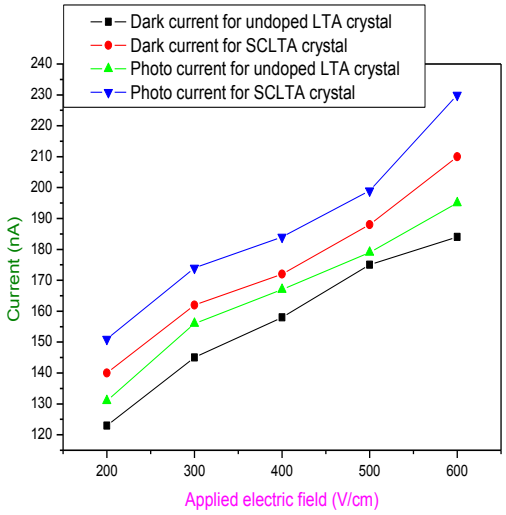


Fig.8. Plots of dark or photo currents with applied electric field for undoped LTA and SCLTA crystals

4. CONCLUSIONS

Solution method was adopted to grow undoped and strontium chloride doped L-tartaric acid crystals using water as the solvent. The morphology of the doped crystals is observed to be different from that of undoped crystal. The grown crystals are found to be crystallizing in monoclinic crystal system and the doping seems not to be changing the crystal structure. The samples have positive temperature coefficient of solubility. SHG efficiency is observed to be more when L-tartaric acid crystals are doped with strontium chloride. The transmittance in the visible region and photoconductivity of the SCLTA crystal are found to be increasing when compared to those of undoped LTA crystal. Using the Tauc's plots, the values of optical band gap of the undoped and strontium chloride doped LTA crystals are found be 5.002 eV. The decomposition point of SCLTA crystal is observed to be at 167 ^{o}C.

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