

Growth and characterization of L-tartaric acid doped and mixed Di-sodium hydrogen phosphate (DSHP) single crystal for laser applications

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The influence of tartaric acid, an amino acid on NLO properties of DSHP crystal has been studied in the present investigation. Single crystals of tartaric acid doped Di-sodium hydrogen phosphate (DSHP) and tartaric acid mixed DSHP were grown by low temperature solution growth method. The enhancement in SHG efficiency after addition of 5mole% doped tartaric acid and 50% doped (mixed) tartaric acid were observed by Kurtz Powder SHG test. It was found that the SHG efficiencies of DSHP after addition of 5mole% tartaric acid is **2.87** and in tartaric acid mixed it is **10** times more than pure DSHP. The solubility of the materials for different temperatures has been studied. The crystal structure and cell parameters were determined by X- ray diffraction analysis. The functional groups were identified by FT-IR spectral analysis. UV-visible spectral spectra show maximum transmission in the visible range of grown tartaric acid crystals. The grown crystals were subjected to thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) to study thermal decomposition and weight loss.

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1. Introduction

The modern world is witnessing revolutionary advancements in the various aspects of science and technology. Every new day is suppressing its predecessor by some new achievements that require novel ideas leading towards the exploration of new materials for emerging fields, which were hitherto unknown. The generation coherent blue light through Second Harmonic Generation (SHG) from near infrared (NIR) Laser sources is an important technological problem that has attraction in the last few years. Potential applications lie in the fields of high-density optical data storage high resolution printing and Laser spectroscopy [1-4]. Organic nonlinear materials are attracting a great deal of attention as they have large optical susceptibilities inherent ultra fast response times and high optical thresholds for Laser power as compared with inorganic materials [5]. A number of such materials have been reported in Literature for their potential application [6, 7]. The Di-Sodium Hydrogen Phosphate (DSHP) is an interesting inorganic NLO material. In our earlier publication we have studied the NLO property of the organic additive; Thiourea doped DSHP crystal [8].

Among organic class of NLO materials, amino acids exhibit some specific features such as molecular chirality, weak Vander Waals hydrogen bonds, absence of strongly conjugated bonds, wide transparency range in the visible and ultraviolet regions, amenability for synthesis multifunctional substitution, higher resistance to optical damage and maneuverability for device applications etc [9-12]. Among amino acids molecules are usually linked through the hydrogen bond [13]. L-Tartaric acid – Nicotinamide (LTN, C₂₀ H₂₆ N₄ O₁₅) was found to be a new NLO material recently [14]. The transmission range and intense SHG signals from the crystal is better than KDP. A number of L-tartaric acid complexes are known to possess NLO property [15-17]. In the present investigation growth of 5 mole % L-Tartaric acid doped DSHP and 50% L-Tartaric acid mixed DSHP are grown by using slow evaporation technique. The grown crystals were characterized by different techniques such as NLO test, X-ray Ft-IR analysis, UV-Visible spectroscopy and the thermal analysis. The NLO efficiency of studied material is compared with reported NLO Material and it was found that SHG efficiency of 5 mole % doped and 50 mole % mixed L-Tartaric acid are **1.534**, **5.614** times greater than that of pure DSHP for doped and mixed DSHP crystals

hence the grown crystals are more useful for potential NLO application in comparison of pure DSHP crystal.

2. 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 L-Tartaric acid were carried out in double distilled water for various temperatures 30°C to 55°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 24 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 DSHP sample is reduced as compared to Pure L-Tartaric acid and increased as comparison with Pure DSHP.

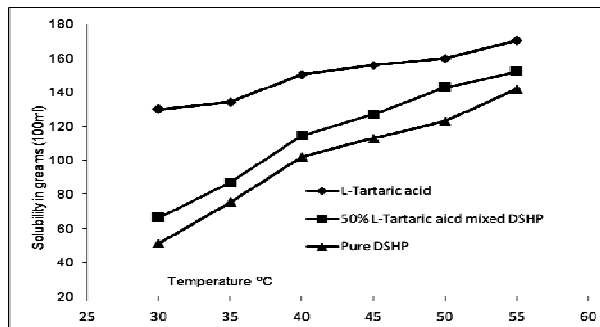


Fig. 1. Solubility curve of pure L-tartaric acid, pure DSHP and 50% L-Tartaric acid mixed DSHP.

2.2 Synthesis and crystal growth

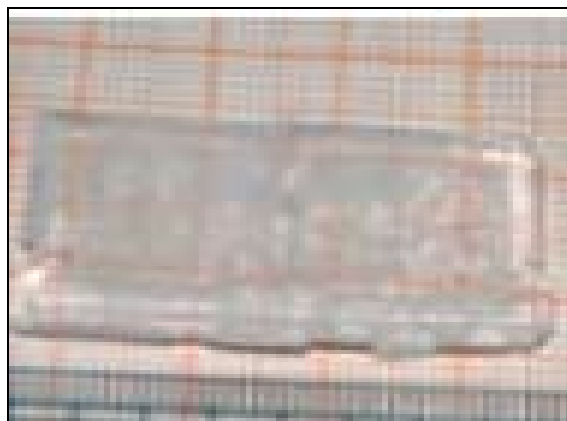
The Di -sodium hydrogen phosphate (DSHP) salt was dissolved in Millipore water. The purity of salt was obtained by repeated recrystallization. The solution of DSHP salt was prepared in a slightly under saturation condition. The solution was stirred well for six hours constantly using magnetic stirrer, then solution was filtered using Whatmann filter paper and it is kept in two different beakers. The amino acid, tartaric acid was added in 5 mole% and secondly 50 % tartaric acid was mixed in the saturated solutions of DSHP and both solutions were stirred well for long period of time. The both solutions were poured in different Petri dishes. We have harvested seeds of these crystals within four to five days. The salts of

5 mole % doped tartaric acid and 50% that is we called hereafter mixed doped DSHP were subjected to SHG test and we observed enhancements in SHG efficiency for both cases and it is **2.87** and **10** times more than pure DSHP respectively.

Therefore the single crystal of 5 mole % tartaric acids doped DSHP and tartaric acid mixed crystals were grown by employing the slow evaporation technique in constant temperature bath of controlled accuracy $\pm 0.01^\circ\text{C}$ at temperature 35°C where the super saturation was achieved. The pH of solution was to be 2.5. After the period of 25 days the large size crystals of 5 mole % tartaric acid doped DSHP and tartaric mixed crystal were harvested. The photograph of grown crystal is shown in Fig. 2 (a, b).



(a)



(b)

Fig. 2. (a): 5 mole% tartaric acid DSHP crystal; (b): tartaric acid mixed DSHP crystal.

2.2 Characterization

The grown L-Tartaric acid mixed and doped DSHP crystals were subjected to various characterizations viz. NLO test, XRD, FTIR, UV-visible spectra study, TGA, DSC analysis and the results were compared with that of pure DSHP.

3. Results and discussion

3.1 SHG efficiency

The NLO conversion efficiency was tested using a modified setup of Kurtz Perry powder technique. A Q-switched Nd: YAG Laser beams of wavelength 1064nm with an input power of 2mJ and pulse width of 10 ns the repetition rate being 10 Hz. The crystals of L-Tartaric doped and mixed Di-Sodium Hydrogen Phosphate (DSHP) were ground with a uniform particle size and then packed in a micro capillary of uniform bore and exposed to Laser radiation. Potassium Dihydrogen Phosphate (KDP) is used as a reference material. The second harmonic signal generated in the crystalline sample was confirmed from emission of green radiation. The intensity was measured using a photomultiplier tube. We have observed out put voltage of 4 mV, 11.5 mV and 41 mV for pure DSHP, 5 mole % tartaric acid doped DSHP and tartaric acid mixed DSHP salts respectively. This indicates that the SHG efficiency of 5 mole % tartaric acid doped DSHP is **2.87**

times more than pure DSHP and in tartaric acid mixed the SHG efficiency is found to be **10** times more than pure DSHP. This increase in SHG of DSHP with addition of L-tartaric acid is due to delocalization of electrons of bonded oxygen along P=O which is expected to largely destroy the double bond character. This behavior may enhance three-dimensional bonding interaction of phosphate with the neighboring units in the crystal in the crystal. The less electro-negativity of sodium is also important in strengthening such interactions [18].

3.2 X-ray diffraction

The X-ray powder diffraction analysis of tartaric acid doped and mixed DSHP crystal was carried out radiation $\lambda = 1.5406\text{\AA}$ from an X-ray generator setting 45kV, 40mA. The cell parameters of both grown crystals were compared with pure DSHP and it was found that there is great variation in the cell parameters of tartaric acid doped and mixed crystals.

Table 1. Lattice Parameter values of 5% L-Tartaric acid doped and Tartaric acid mixed DSHP crystals.

Sample	a (Å)	b (Å)	c (Å)	V (Å ³)
Pure DSHP	9.243	10.955	10.421	1051.8
5%L-Tartaric acid doped DSHP	16.89232	10.32672	6.58923	1149.44
50%L-Tartaric acid mixed DSHP	16.82691	10.30325	6.59488	1143.36

The X-ray pattern of the grown crystals is as shown in Fig. 3. The cell parameters of pure DSHP, 5mole %

tartaric acid doped and tartaric acid mixed crystals are shown in the Table 1.

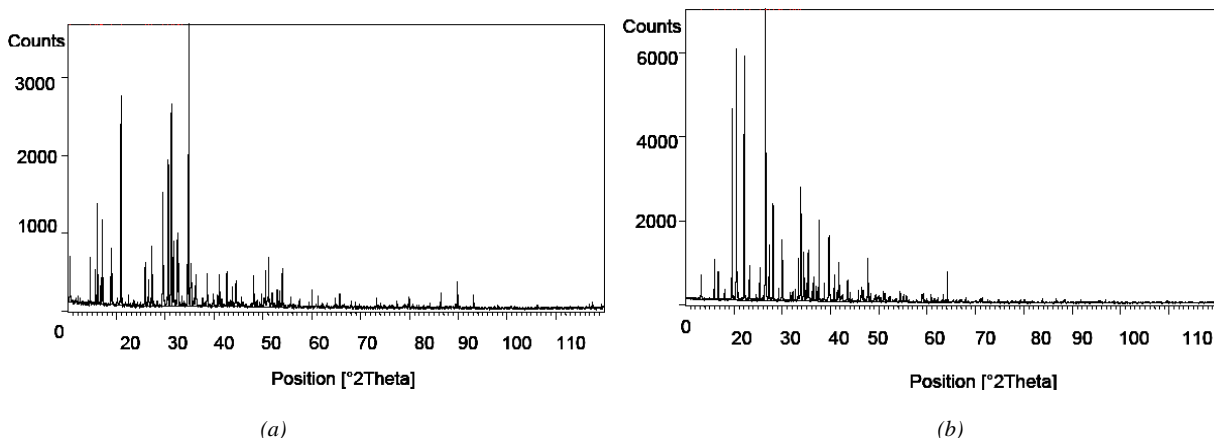
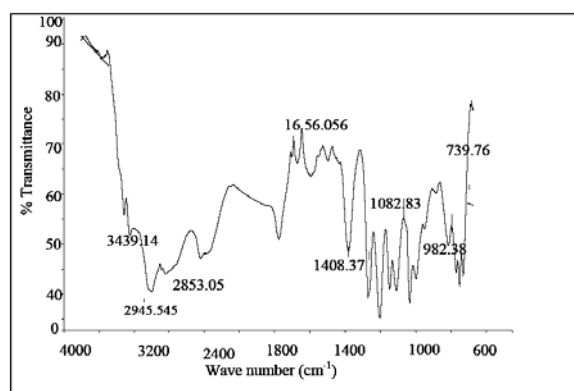


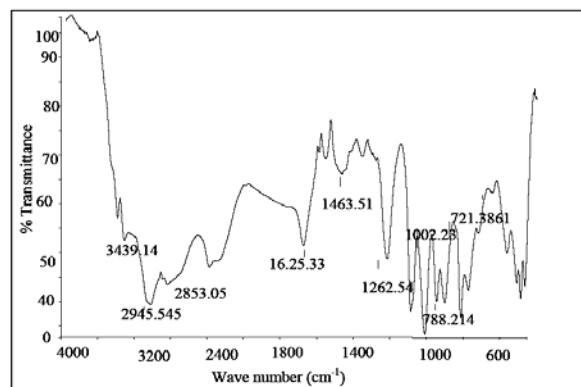
Fig. 3 (a): XRD Pattern of L-tartaric acid doped DSHP; (b): XRD pattern of L-tartaric acid mixed DSHP.

3.2 Fourier transform infrared spectroscopy (FTIR) analysis

The IR spectrum of grown crystals has been recorded in the solid state as KBr dispersion using Perkin-Elmer spectrum-one FT-IR spectrometer. The FTIR spectrum of tartaric acid doped and tartaric acid mixed crystals are shown in the Fig. 4 (a, b).



(a)



(b)

Fig. 4. (a). FTIR spectrum of 5 mole % tartaric acid doped DSHP crystal; (b) FTIR spectrum of tartaric acid mixed DSHP crystal.

The C-H stretching peaks for L-Tartaric acid mixed DSHP are observed at 2925.54cm^{-1} , 2853.05cm^{-1} frequency and C-H stretching peaks are absent for L-Tartaric doped DSHP in the spectra. The C=O stretching is observed at 1671.25cm^{-1} and 1625.15cm^{-1} due to symmetric and asymmetric stretching vibrations. In case of tartaric acid doped DSHP, C=O stretching is observed at 1656.05cm^{-1} and 1649.62cm^{-1} respectively due to symmetric and asymmetric stretching modes. The reduction of C=O stretching frequencies for tartaric acid mixed and doped DSHP clearly indicates the formation of

metal- oxygen bonding ($\text{M}-\text{O}^+=\text{C}<$) during the formation of complex. The appearance of peak at 1448.95cm^{-1} for pure tartaric acid, peak at 1463.51cm^{-1} and 1452.39cm^{-1} for L-Tartaric acid mixed DSHP and peak at 1408cm^{-1} are due to combination of C-O stretching and O-H bending bands. The sharp, intense peak at 1157.08cm^{-1} and 1082.83cm^{-1} for tartaric mixed DSHP and doped DSHP are due to C-O stretching vibration respectively. The sharp bands at 1002.23cm^{-1} for tartaric acid mixed DSHP and 982.38cm^{-1} for doped DSHP are due to O-H out of plane bending vibrations [8]. The shifting of peak positions for functional groups and atoms after tartaric acid doping and mixing with DSHP clearly confirm the existence of L-Tartaric acid in crystal lattice of DSHP.

3.3 UV-visible spectra analysis

The UV-visible spectral studies of grown tartaric acid crystals were carried out using Perkin Elmer spectrophotometer. The spectrum was recorded in the wave length region from 200 to 800 nm. The transmission spectrum of both 5 mole % tartaric acid doped and tartaric acid mixed crystals are shown in the figure 5. It was found that the grown crystal has convenient transparency range from 291 to 750 nm, with maximum transmission in the visible region. It indicates that the crystal is suitable for electro-optic modulation. The spectrum revealed that in the grown crystals the absorption is absent in the visible region, hence tartaric acid crystals are more transparent and may be used as potential candidates for NLO applications.

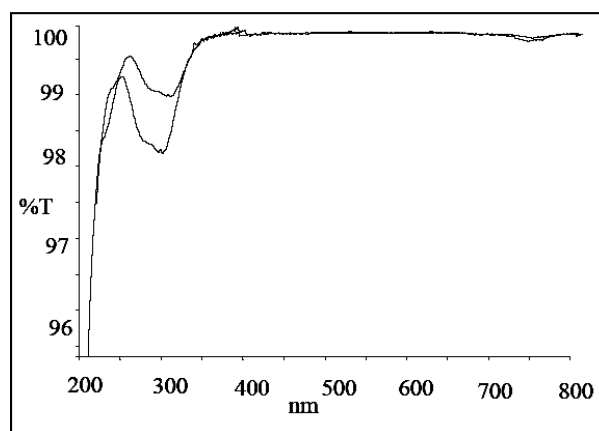
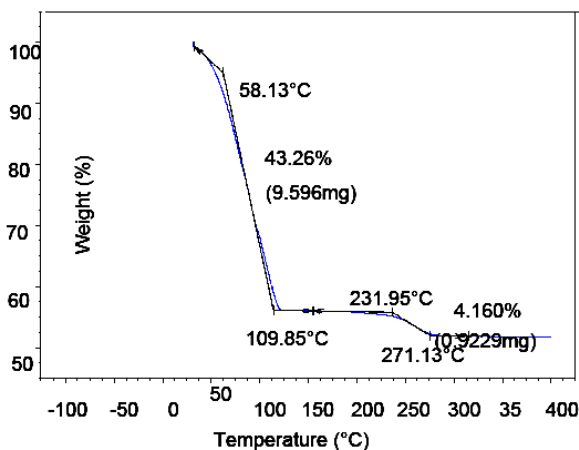


Fig. 5. Transmittance spectrum tartaric acid doped and mixed crystals.

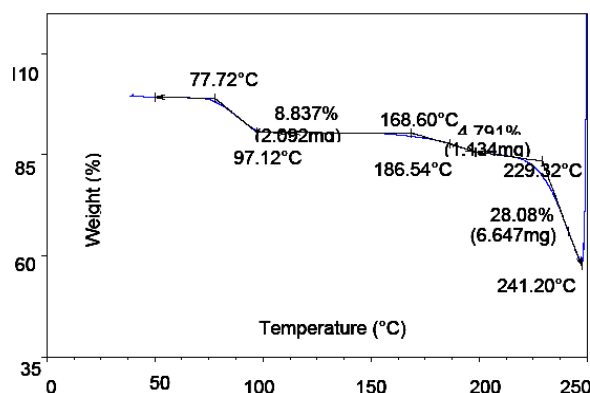
3.4 Thermal analysis

Thermal study of the grown crystals has been carried out by TGA and DSC using TGA-Q500 V6.6 and DSC-Q

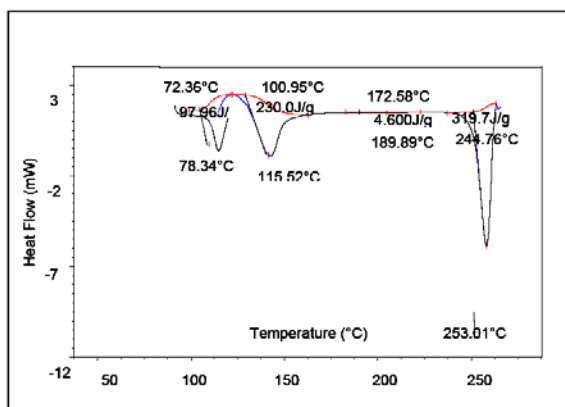
100 V9.7 thermal analyzer system in the temperature range 25°C to 400°C and 25°C to 300°C in nitrogen atmosphere. Same heating rate 10°C/min was applied to all the samples.



(a)



(b)



(c)

Fig. 6. (a) TGA Thermogram of 5mole% L-tartaric acid doped DSHP; (b) TGA thermogram of 50 mole% L-tartaric acid mixed in DSHP; (c) DSC thermogram of L-tartaric acid mixed DSHP.

TGA curve of 5 mole% tartaric acid doped DSHP Fig. 6 (a), recorded clearly indicated that initially there is 43.26% weight loss of the crystal below temperature 109.85°C. A crystal remains thermally stable at 109.85°C to 231.95°C temperature and no weight loss take place. It is also observed that a crystal is completely dehydrated before 231.95°C temperature and decomposed at 271.13°C temperature. A deep study of TGA spectrum of tartaric mixed in DSHP crystal Fig. 6 (b) shows that initially there are 8.837% weight losses below 97.12°C temperature. A sample remains thermally stable at 97.12°C to 168.60°C temperature, no weight loss takes place and after there are various stages where observed in temperature range 168.60°C to 241.20°C due to liberation of volatile substances probably carbon dioxide, hydrate groups and ammonia [19].

As increase of tartaric acid, decreases the decomposition temperature the Differential Scanning Calorimetry was also carried out for sample of tartaric acid mixed crystal. A detailed inspection of DSC spectrum (figure6(c)) shows that there are three major changes takes place while heating the sample, first endothermic peak at 78.34°C, second at 115.52°C and third at 253.01°C temperature respectively. The first and second endothermic peaks correspond to release of water at two stages. After releasing of water, a crystal becomes dry and remains stable up to melting stage. The decomposition of amino molecules associated with sample takes place at 253.01°C.

5. Conclusions

Crystals of amino acid- tartaric acid doped and mixed Di-sodium hydrogen phosphate (DSHP) have been grown from the aqueous solution employing the solvent evaporation method. The NLO property L-Tartaric acid doped and mixed di-sodium hydrogen phosphate crystal has been tested by Kurtz powder method using the Nd: YAG Laser. The SHG efficiency of 5% doped and 50% mixed L-Tartaric acid with DSHP crystal were found be **2.87** and **10** times more than pure DSHP respectively. This indicates that as the concentration of dopant increases the SHG nonlinearity increases. The X-ray diffraction confirms crystal structure and the cell parameters of grown crystals. FT-IR study confirmed the presence of all functional groups and the addition of dopant. In the UV-visible measurement the lower cut off wavelength was observed at 260 nm. The large transmittance window in the visible region enables very good optical transmission of second harmonic frequencies of Nd: YAG Lasers. The thermal study by thermogravimetric analysis and Differential Scanning Calorimetry of grown crystals indicate thermal decomposition of grown crystals and the weight losses at different temperature.

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