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Effect of L-Valine on the growth and characterization of Sodium Acid Phthalate (SAP) single crystals

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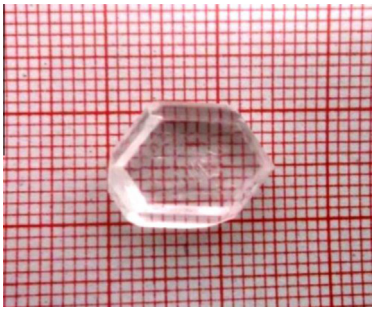
HIGHLIGHTS

- Pure and L-Valine doped SAP single crystal have been grown by slow evaporation method.
- Vibrational bands were analyzed by FTIR spectra.
- Thermal stability and melting point increased in L-Valine doped SAP crystal.
- Mechanical stability and SHG efficiency increased due to doping.
- The doping enhances the optical applications of L-Valine doped SAP crystal.

GRAPHICAL ABSTRACT



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ABSTRACT

Undoped and amino acid doped good quality single crystals of Sodium Acid Phthalate crystals (SAP) were grown by slow evaporation solution growth technique which are semiorganic in nature. The effect of amino acid (L-Valine) dopant on the growth and the properties of SAP single crystal was investigated. The single crystal X-ray diffraction studies and FT-IR studies were carried out to identify the crystal structure and the presence of functional groups in undoped and L-Valine doped SAP crystals. The transparent nature of the grown crystal was observed using UV–Visible spectrum. The thermal decomposition of the doped SAP crystals was investigated by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA). The enhancement in the NLO property of the undoped and L-Valine doped SAP crystals using KDP crystal as a reference was studied using SHG measurements. Vickers micro hardness measurements are used for the study of mechanical strength of the grown crystals.

Introduction

The search for new nonlinear optical materials is the subject of intense research because the NLO crystals with high conversion efficiencies for SHG which are transparent in the visible and UV regions are required for numerous device applications [1–5]. In order to satisfy the day-to-day technological requirements, many organic and inorganic materials are in practice. Even though the organic NLO materials have large nonlinear optical susceptibilities, they have poor mechanical, thermal properties and low laser damage threshold [6]. In the case of inorganic NLO materials, they have excellent mechanical and thermal properties, but relatively modest optical linearities due to the lack of extended π-electron delocalization [7–11]. Hence, much recent work focused on new type called semi-organic NLO materials. The addition of small quantity of impurities in a crystallizing system can modify the properties, growth and morphology of the crystal [12–15]. Most of the amino acid based semi organic single crystals crystallize in non-centro symmetric space group and they have the advantages of both organic and inorganic materials [16]. Crystals of derivatives of phthalic acid are potential compounds for NLO and electro-optic processes. The semiorganic hydrogen phthalate crystals are widely used in the applications of long-wave X-ray spectrometers. Acid

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Phthalate crystals are used as substrates for deposition of thin films of organic nonlinear materials [17]. Sodium Acid Phthalate single crystal is an excellent compound for SHG applications in the phthalic acid family. There are only a few reports available on the effect of amino acid on the NLO efficiency of SAP crystals. Synthesis, growth and characterization of Sodium Acid Phthalate (SAP) single crystal was reported by Bairava Ganesh et al. [18], and Krishnan et al. [19]. The effect of metallic dopants on KAP single crystals was reported by Chithambaram et al. [20] and Kejalakshmy and Srinivasan [21]. In continuation of the above works, an attempt is made to reveal the effect of L-Valine on the growth and characterization of Sodium Acid Phthalate single crystals. The results of the characterization studies conclude that the amino acid (L-Valine) dopant play a significant role in the view point of device applications.

Experimental procedure

Synthesis and crystal growth

Pure Sodium Acid Phthalate salt was synthesized using a slow evaporation technique by dissolving stoichiometrical amounts of sodium bicarbonate and phthalic acid in equimolar ratio in double distilled water. The saturated solution of the above synthesized salt was prepared and the undoped SAP crystals were grown by slow evaporation solution growth technique at room temperature. Good quality optically transparent and non-hygroscopic crystals were collected from the mother solution in a time span of 20 days which is shown in Fig. 1.

The mother solution was prepared as before using SAP salt in double distilled water and the amino acid L-Valine was taken as a dopant with 0.5% concentration by weight in the mother solution. The saturated solution was filtered with the microfilter and it was kept in the dust free atmosphere for evaporation. Optically transparent crystal of L-Valine doped SAP crystal was obtained within 30 days which is shown in Fig. 2.

Results and discussion

Single crystal X-ray diffraction studies

The grown doped crystal was subjected to single crystal X-ray diffraction studies using an ENRAFNONIUS CAD 4 diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) to determine the unit cell parameters. The observed lattice parameter values of L-Valine doped SAP crystal are found to be $a = 6.75$ Å, $b = 9.28$ Å, $c = 26.72$ Å and $V = 1682$ Å^3 and the crystal belongs to the space group of B2ab which is in good agreement with the reported values [18,19] of undoped SAP crystal as in Table 1. The slight variations in the cell parameters indicated the incorporation of L-Valine into the crystal lattice of undoped SAP crystals.

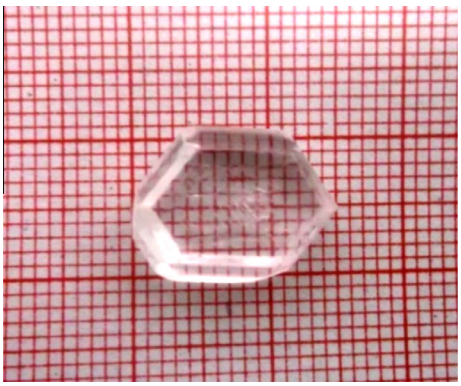

Fig. 1. Photograph of as grown SAP crystal.

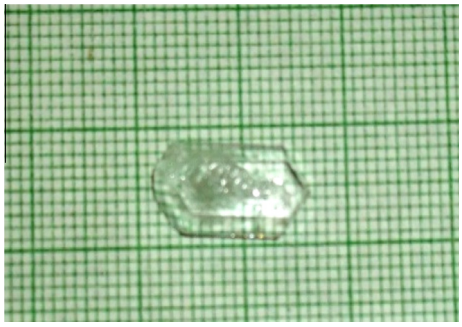

Fig. 2. Photograph of as grown L-Valine doped SAP crystal.

FT-IR spectral studies

The powdered samples of undoped and L-Valine doped SAP crystals were subjected to FT-IR analysis by Perkin Elmer RXI FT-IR Spectrometer using KBr pellet technique in the wavelength range between 400 and 4000 cm^{-1}. The recorded FT-IR spectrum of undoped and L-Valine doped SAP crystals were recorded as shown in Fig. 3 and the observed bonds along with their vibrational assignments were tabulated in Table 2. The observed spectra of these crystals were similar except for a small shift in the peak positions and hence the crystals are expected to preserve nearly the same interactions among the groups and ions. The Carboxyl group C═O vibrations appeared near 1710 cm^{-1}. The peak at 1613 cm^{-1} was due to the C—C skeletal aromatic ring vibration. The absorption band in the region 500–900 cm^{-1} was due to C—H out-of-plane deformations of the aromatic ring which were in good agreement with the reported values [18].

Optical transmission studies

Transmission spectra are very important for any NLO material because an NLO material is used for practical purposes only if it has a wide transparent window. To determine the suitability and the transmission range of the grown crystal for optical applications, the UV–Visible spectrum was recorded in the range 200–1200 nm by using LAMBDA-35 UV–Visible spectrometer. The grown L-Valine doped crystal was well polished and a specimen of 3 mm thick was subjected to transmission measurements in the specified spectral region. The recorded spectrum of L-Valine doped SAP single crystal was shown in the Fig. 4. This agreed well with the spectrum of undoped SAP crystal [18,19]. The lower cutoff wavelength around 330 nm is due the n–π^* transition of the carbonyl group of the carboxyl function. This transition causes its

Table 1
Unit cell parameters of doped and undoped SAP crystals.

Crystal data	SAP [18]	L-Valine doped SAP
a	6.75 Å	6.75 Å
b	9.31 Å	9.28 Å
c	26.60 Å	26.72 Å
Volume	1662 Å^3	1682 Å^3
System	Orthorhombic	Orthorhombic
Space group	B2ab	B2ab