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Optical, spectral and dielectric studies of l-histidine added potassium hydrogen phthalate crystals

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ABSTRACT

Optically transparent pure and amino acid added potassium hydrogen phthalate (KHP) single crystals were grown by slow evaporation technique at 32 °C. The entry of amino acid in the parent compound was confirmed by powder X-ray diffraction by the change in lattice parameters and also from the presence of amino group in the FT-IR and FT-Raman spectra in the case of amino acid added KHP crystals. The thermal and mechanical stability of the crystal was increased by the addition of amino acid. The optical studies revealed that the crystals have high transmittance in the entire visible region. The PL yield was also high for the crystals at 523 nm when excited with 480 nm. The SHG measurement confirms the emission of green light and the addition of amino acid has increased the SHG efficiency of the crystal. The crystals were also subjected to the dielectric study by varying the temperature and frequency.

1. Introduction

Most of the researchers have shown much interest in searching of new materials for frequency conversion [1]. The organic materials have high NLO efficiency but having poor thermal and mechanical stability and inadequacy to grow large size good quality crystals. The inorganic materials have their properties in contrary to the organic materials. The good qualities of both organic and inorganic crystals give birth to the semi-organic crystals. It plays a major role due to its high nonlinear optical property [2]. In these crystals, polarizable organic molecules are bound within the inorganic material. [3–6].

Crystals of alkali metal hydrogen phthalates have covalent, ionic, van der Waals and intermolecular hydrogen bonds [7]. The theoretical study shows that the hydrogen bonds enhance the nonlinear optical property of the crystals [8]. KHP is a semi-organic material crystallize in the orthorhombic system with lattice parameters $a = 9.609$ Å, $b = 13.852$ Å and $c = 6.466$ Å with $\alpha = \beta = \gamma = 90°$. The crystal structure of KHP consists of potassium ions and alkali phthalate ions with the space group $Pca2_1$ and point group $mm2$ [9,10]. There are four chemical units of the formula $K(C_6H_4{\cdot}COOH{\cdot}COO)$ in a unit cell.

The present work deals with the effect of amino acid (l-histidine) as a dopant on the growth and properties of potassium hydrogen phthalate crystals. The doping of amino acid is quite interesting since they have high nonlinear optical efficiency due to its zwitter ionic property. The crystals were grown by slow evaporation technique at constant temperature and it was characterized by structural, spectral, thermal, mechanical, electrical, linear and nonlinear optical studies.

2. Crystal growth

The raw materials used to grow the crystals were AR grade of potassium hydrogen phthalate (Merck), l-histidine (HiMedia) and Millipore water with resistivity 18.2 MΩ cm as the solvent. The saturated solutions of KHP were prepared and 0.05 M l-histidine was added in that solution and stirred well. After achieving the homogeneous solution, the solutions were filtered and covered with perforated sheets. The pH of the two solutions was 4.42 and 4.58 for pure KHP (KHP) and l-histidine added KHP (LHKHP) respectively. The pH depends on the concentration of H^+ ions present in the solution. The two solutions were kept in a constant temperature bath at 32 °C with the accuracy of 0.01 °C using cryostat facility. The crystals were grown by slow evaporation technique. Single crystals with good transparency were harvested with a span of 25 days. The photograph of the grown crystals is shown in Fig. 1. The dimensions of the grown crystals are $24 \times 18 \times 7\ mm^3$ for KHP and $17 \times 14 \times 4\ mm^3$ for LHKHP.

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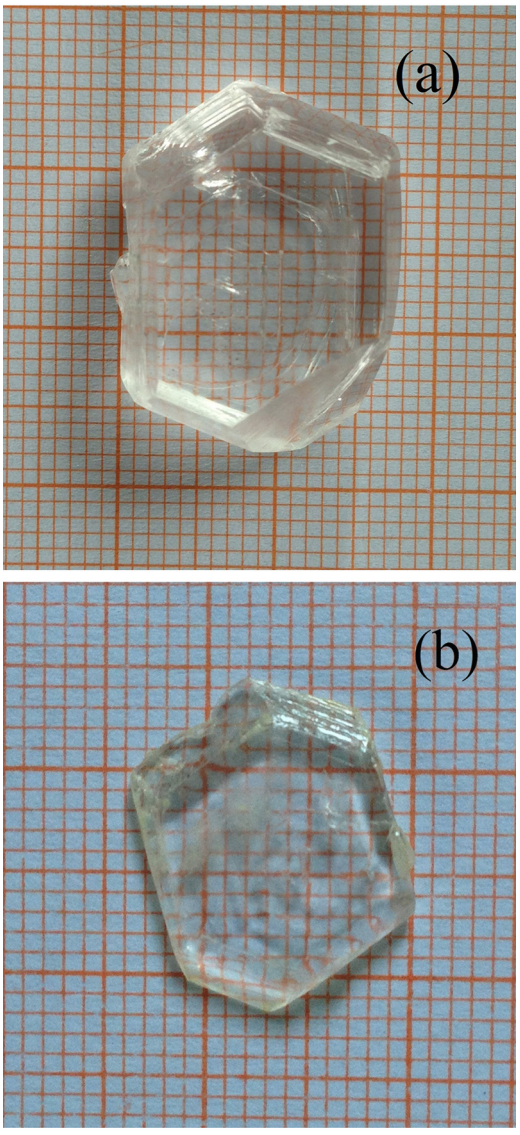

Fig. 1. Photograph of (a) KHP crystal (b) LHKHP crystal.

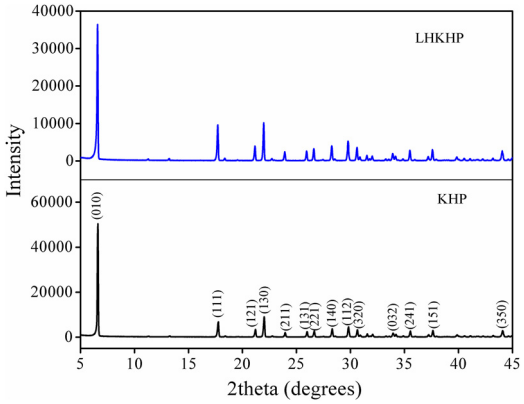

Fig. 2. Powder XRD pattern for (a) KHP (b) LHKHP.

Table 1
Lattice parameters for the grown crystals.

Lattice parameters	KHP	LHKHP
a (Å)	9.6097(7)	9.6155(7)
b (Å)	13.3125(9)	13.3182(8)
c (Å)	6.4743(5)	6.4777(4)
Volume (Å^3)	828.2516(9)	829.5417(8)
$\alpha = \beta = \gamma$	90°	90°

3. Characterization studies

The grown crystals were subjected to powder X-ray diffraction (XRD) analysis using PANalytical X'Pert PRO diffractometer with Bragg–Brentano geometry and CuKα_1 radiation of wavelength 1.5406 Å. An X'Celerator detector was employed to collect XRD data over the 2θ angular range from 5° to 45° with a step size of 0.017° and a counting time of 60 s/step. The Fourier transform infrared spectra were recorded in the range of 550–4000 cm^{-1} using JASCO FT/IR-4100 spectrophotometer by attenuated total reflectance (ATR) method. The FT-Raman spectrum was measured using a Lab Ram HR800 spectrometer with 514 nm line of Ar^+ laser as an excitation source and recorded in the region 300–3300 cm^{-1}. The crystal was directly placed in the source and the spectra were recorded with the resolution of 4 cm^{-1} for the spectral studies. The nitrogen content present in the crystals was determined using Elementar Vario EL III model CHN analyzer. To identify the thermal stability, thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG/DTA) were carried out in the temperature range from 30 °C to 950 °C at the heating rate of 10 °C/min under nitrogen atmosphere using TG-DTA Perkin Elmer, mod Pyris Diamond equipment. Optical transmittance spectra were recorded using SHIMADZU UV–2600 UV–vis–NIR spectrophotometer in the wavelength region 200–1100 nm. The source was allowed to pass through (0 1 0) face of the grown crystals with a thickness of 2 mm. The Photoluminescence spectra were measured using JOBIN YVON Flurolog-3 spectrofluorimeter excited with xenon lamp of wavelength 480 nm and recorded in the region 500–750 nm. The SHG efficiency of the grown crystals was determined using Kurtz and Perry powder method. The Q-switched Nd:YAG laser of wavelength 1064 nm was used as the source with the pulse energy of 4.6 mJ/Pulse, pulse width of 8 ns and repetition rate of 10 Hz. PMT monochromator was used as a detector. The dielectric measurement for the grown crystal was carried out using a Hewlett-Packard 4192A impedance analyzer. Single crystals of KHP and LHKHP were cut in the rectangular specimen with area of cross section 35 mm^2 and thickness 3.3 mm and 2.5 mm, respectively. Silver paste was coated on both surfaces of the sample to make contact between the crystal and the electrode of cell. Measurements were recorded during a heating and cooling cycle, in the frequency range from 10^2 to 10^6 Hz with an applied voltage of 1 V, over the temperature range from 330 to 470 K. The relative dielectric permittivity (ε'_r) and dielectric loss tangent ($\tan\delta$) were measured using parallel capacitor technique. The mechanical stability was determined for the grown crystals using Vickers microhardness tester Shimadzu HMV-2T fitted with diamond indenter for three different loads.

4. Results and discussion

4.1. Powder X-ray diffraction analysis

The powder XRD pattern for the grown crystals is shown in Fig. 2. The observed pattern was compared with the JCPDS data (Card nos. 311855 and 241870). The sharp peaks observed in the XRD pattern reveals that the grown crystals have high crystalline nature. Both the crystals belong to the orthorhombic system with the space group $Pca2_1$ and the lattice parameters are listed in Table 1. The l-histidine affects the KHP crystal structure by the small shifting of peaks and also decreases the intensity of the peaks. It is notified that the inclusion of l-histidine increases the cell volume, since the