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Effect of Sm$^+$ Rare Earth Ion on the Structural, Thermal, Mechanical and Optical Properties of Potassium Hydrogen Phthalate Single Crystals

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Rare earth Sm$^+$ ion doped potassium hydrogen phthalate (KHP) single crystal was grown by slow evaporation technique. Single crystal and powder X-ray diffraction analyses confirm the crystalline perfection of Sm$^+$ ion doped KHP crystal. The functional groups of pure and Sm$^+$ ion doped KHP crystals were identified by Fourier transform infrared spectroscopy (FTIR) spectral studies. Thermogravimetric and differential thermal analyses were carried out to study the thermal behavior of the grown crystals. UV–Vis studies explored the optical transmittance of the grown crystals in the entire visible region. The mechanical strength and etching studies were performed to assess the perfection of the pure and Sm$^+$ ion doped KHP crystals. The refractive index and birefringence properties of the grown crystal were analyzed. The second harmonic generation efficiency of Sm$^+$ ion doped KHP crystals was observed by Kurtz–Perry powder test.

KEY WORDS: Crystal growth; Potassium hydrogen phthalate (KHP) single crystal; Differential thermal analysis; FTIR; Hardness

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1. Introduction

Second order nonlinear optical (NLO) materials have recently attracted much attention because of their potential applications in emerging optoelectronic technologies[1]. Materials with large second-order optical nonlinearities, short optical transparency cut-off wavelengths, and stable physico-thermal performance are needed to realize many of these applications. Semi-organic materials have the potential for combining high optical nonlinearity and chemical flexibility of organics with the physical ruggedness of inorganics. Potassium hydrogen phthalate (KHP) crystal is well known for its application in the production of crystal analyzer for long wave X-ray spectrometer[2,3]. KHP is a semi-organic material that attracted a considerable attention over few decades. KHP crystals can be easily grown and exhibit interesting dielectric, piezoelectric, pyroelectric, elastic, as well as linear and nonlinear optical properties[4–7]. The platelet morphology of KHP crystals has excellent physical properties with good record for long term devices[8,9]. Its cleavage faces find applications as substrates in epitaxial technique and KHP crystals are used as substrates for the growth of highly oriented film of conjugated polymers with high nonlinear optical susceptibility[10]. KHP has a well-developed surface pattern on the (010) plane consisting of high and very low growth steps as can be easily observed by means of optical microscopy[11–13]. KHP with the chemical formula $K(C_6H_4COOH{-}COO)$ belongs to the alkali acid phthalate series, has an orthorhombic symmetry with the space group $Pca2_1$ and its lattice parameters are $a = 0.9605$ nm, $b = 1.3331$ nm, $c = 0.6473$ nm and $\alpha = \beta = \gamma = 90°$[14,15]. In recent years, researchers have reported a few important investigations on the effect of rare earth ions like Ce^{4+}, Th^{4+}, Eu^{2+}, La^{3+}, Tm^{3+}, Er^{3+}, Dy^{3+}, Tb^{3+}, Gd^{3+}, Pr^{3+} doped in organic and semi-organic solution grown NLO materials, which enhanced the crystalline perfection and second harmonic generation efficiency[16–21]. The ionic radius of Sm^+ (0.109 nm) is smaller than that of K^+ ion (0.151 nm); hence, Sm^+ can either replace K^+ or get into the interstitial space, which in both case may create some strain in the lattice. It is well known that doping influences the mechanical, electrical, electronic, optical properties and morphology depending upon the host material and the dopants. In the present work, the KHP was successfully synthesized and the structural and optical properties of the pure and Sm^+ ion doped KHP crystals, which are mandatory in view of NLO applications, have been investigated. To have a full understanding about the structure and its

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nonlinear optical properties of pure and Sm^+ doped KHP crystals, single crystal and powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), TG−DTA (thermogravimetry−differential thermal analysis), UV−Visible, refractive index, Vicker's hardness, etching, birefringence and second harmonic generation measurements were carried out.

2. Experimental

2.1. Synthesis and crystal growth

Pure and Sm^+ ion doped potassium hydrogen phthalate crystals were grown by slow evaporation method. The potassium hydrogen phthalate (Merck-India) compound was used for both pure and Sm^+ ion doped single crystal growth. The KHP salts were further purified by successive recrystallization process. The saturated solutions of pure and 0.1 mol% of Sm^+ ion in the form of samarium chloride doped KHP were prepared, according to the measured solubility data. The seed crystals were prepared by spontaneous nucleation from a supersaturated solution and good quality seed crystals were used for the bulk crystal growth. The growth solutions of pure and Sm^+ ion doped KHP were saturated at 40 °C. Then, it was heated up 5 °C above the saturation and left it for 1 h under stirring to ensure homogeneity. The saturated solutions were allowed for slow evaporation at 40 °C using a constant temperature bath. The pH values of the pure KHP and Sm^+ ion doped KHP supersaturated solutions during the growth period were 3.8 and 3.7, respectively. The transparent pure and Sm^+ ion doped KHP crystals were harvested from the supersaturated growth medium in the period of 3−4 weeks, as shown in Fig. 1(a) and (b), respectively.

2.2. Characterization

The grown pure and Sm^+ ion doped KHP single crystals were subjected to various characterization techniques. Single crystal and powder XRD analyses were performed to estimate the lattice parameters and crystalline quality of the grown crystals using Bruker Nonius CAD-4/MACH 3 single crystal X-ray diffractometer and Bruker AXSCAD4 diffractometer, respectively. FTIR spectroscopy was effectively used to identify the functional groups of the grown crystals and FTIR spectrum of the sample was recorded by JASCO FTIR 410 spectrometer. TG−DTA analyses were carried out with SII TG/DTA 6300 EXSTAR instrument with a heating rate of 10 °C/min under N_2 atmosphere. The optical transmittance spectra of pure and Sm^+ ion doped KHP crystals were recorded with Perkin Elmer Lambda 35 spectrophotometer in the range of 190−1100 nm. The refractive indices along *b*-axis for pure and doped KHP single crystals were analyzed by prism coupling technique. Microhardness measurement was carried out on the grown crystals using Leitz−Weitzler hardness tester fitted with a diamond indenter. The optical birefringence was recorded using modified channel spectrum method (MCS). The relative second harmonic generation (SHG) efficiencies of grown crystals were evaluated by Kurtz powder technique.

3. Results and Discussion

3.1. XRD analyses

The cell parameters of pure and Sm^+ ion doped KHP crystals were collected at room temperature using single crystal XRD analysis. The pure and doped KHP compounds crystallize in orthorhombic crystal system with noncentrosymmetric space group, $Pca2_1$. It is observed that the cell parameters of pure KHP crystal presented in Table 1 are in close agreement with the reported values[15]. The powder XRD patterns of pure and Sm^+ ion doped KHP crystals recorded in the 2θ range of 10°−50° are shown in Fig. 2. The miller indices (*hkl*) of the corresponding planes were indexed. It is observed that pure and Sm^+ ion doped KHP powder XRD crystal data follow the JCPDS standard data (JCPDS PDF No. 311855).

3.2. FTIR spectral studies

FTIR spectra of pure and Sm^+ ion doped KHP crystals recorded in the range of 4000−400 cm^{-1} by KBr pellet technique are shown in Fig. 3. In the spectra, the characteristic OH stretching peaks occur at 3428 and 3450 cm^{-1} for the synthesized pure and Sm^+ ion doped KHP compound, respectively. The C−C aromatic vibrational peaks are observed at 1485 and 1486 cm^{-1} for pure and Sm^+ ion doped KHP compound, respectively. The characteristic vibrational absorptions of Sm^+ ion doped crystal are shifted smaller from pure KHP absorptions. This change could be due to the doping effect of rare earth ion such that Sm^+ ion enters into the lattice by replacing K^+ ion. From the FTIR spectra, the presence of the functional groups in the pure and Sm^+ ion doped KHP compounds has been confirmed. The vibrational frequencies of functional groups

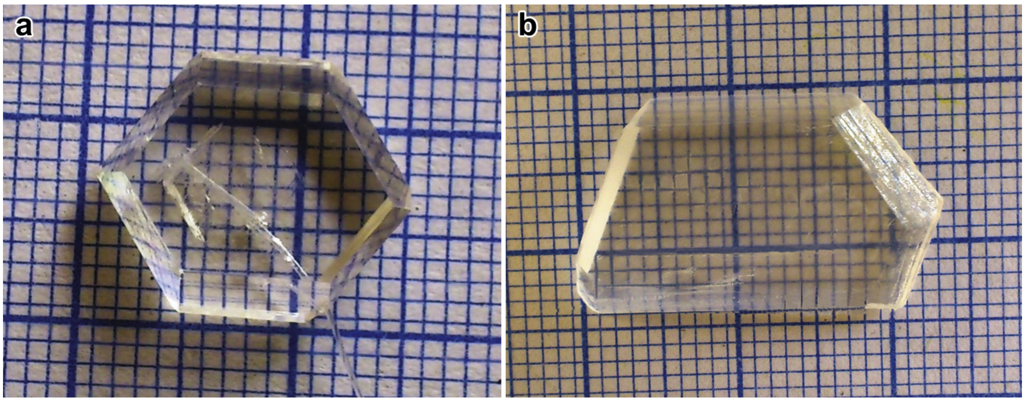

Fig. 1 Photographs of pure KHP (a) and Sm^+ ion doped KHP crystals (b).