

Influence of alkali metal sodium doping on the properties of potassium hydrogen phthalate (KHP) crystals

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Abstract The effect of doping sodium on the growth process and properties of potassium hydrogen phthalate (KHP) single crystals by slow evaporation solution growth technique has been investigated. Incorporation of sodium into the crystalline matrix even in the presence of low dopant concentration in aqueous growth medium is well confirmed by energy dispersive X-ray spectroscopy and quantified by atomic absorption spectroscopy and inductively coupled plasma emission spectrometer (ICP) techniques. The FT-IR spectral analysis confirms the slight distortion of the structure of the crystals as a result of doping. The TG-DTA studies reveal the purity of the material and no decomposition is observed up to the melting point. Low Na-doping (10 mol%) slightly increases the second harmonic generation efficiency, whereas heavy doping {[KHP]:[Na] = 1:1} results in significant enhancement. It has also been found that the doping results in morphological changes.

Keywords Potassium hydrogen phthalate (KHP) · Nonlinear optical properties · Sodium · TG · DTA · Energy dispersive X-ray spectroscopy (EDS) · ICP and FT-IR

Introduction

Potassium hydrogen phthalate (KHP) crystal is well known for its application in the production of crystal analyzer for long wave X-ray spectrometer [1, 2]. KHP possesses piezoelectric, pyroelectric, elastic, and nonlinear optical properties [3–5]. It crystallizes in orthorhombic structure with space group $Pca2_1$ [6]. It has platelet morphology with perfect cleavages along (010) plane. Using the periodic bond chain analysis, the morphology of KHP has been determined [7]. Recently, KHP crystals are used as substrates for the growth of highly oriented film of conjugated polymers with nonlinear optical susceptibility [8, 9]. KHP is chosen as a model compound because of its well-developed surface pattern on the (010) face consisting of high and very low growth steps which can be relatively easily observed by means of optical microscopy [10, 11]. It is used as a substrate for the deposition of thin films of NLO materials like urea with high mechanical stability [12]. Fe/Ce impurity effect on KHP has been studied in detail [13]. Influence of various kinds of impurities on spiral growth phenomena on (010) KHP indicates the existence of different mechanisms of interaction [14, 15]. Hottenhuis and Lucasius [16] have made detailed investigations on the surface morphology and the growth kinetics of the KHP (010) face.

The sodium concentration in Na-doped barium borate single crystal has a strong influence on the material properties including surface morphology, thermoluminescence, and optical properties [17]. The effects of the crystal structure, defectiveness on magnetic state of lanthanum manganites by sodium doping have been investigated [18]. The amount of sodium in sodium-doped lanthanum manganites has an influence on the structure, is confirmed by XRD and micro-Raman data [19]. The second harmonic

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generation (SHG) conversion efficiency is enhanced by the presence of alkali and alkali earth metal in KHP crystals [20]. These aspects prompted us to use sodium as a dopant material in the technologically important KHP crystals.

Recently, we have investigated the influence of EDTA doping on the SHG efficiency and crystalline perfection of trithiourea zinc(II) sulfate (ZTS) crystals [21]. Accommodating capability of ADP crystals with dopants like KCl and oxalic acid reveals some interesting features [22]. Influence of Mn(II) on the NLO properties of ZTS reveals a good correlation of SHG efficiency and the crystalline perfection [23]. As a continuation of our studies to ascertain, the influence of doping on the properties of some technologically important crystals in this study was undertaken. Literature reveals that mostly doping studies were carried with dopants having close atomic/ionic radii of host crystal. In this investigation, we have used a light alkali metal of much smaller size for doping and the effects on properties of crystals are systematically analyzed. It has been reported that in the case of calcium tartrate single crystals [24], the doping atom prefers substitutional sites when alkaline earth atoms are used while it occupies interstitial sites when a transition metal is used. Also, the cations with a radius close to that of Ti^{4+} can substitute for Ti^{4+} in titania crystals, whereas the cations with large radius such as Nd^{3+} , Ag^+ , La^{3+} , Ni^{2+} , Y^{3+} , and Rb^+ occupy interstitial sites [25]. In this investigation, the doping of the alkali metal was carried out intentionally to study the effect of doping on the properties of KHP crystals.

Experimental

Synthesis and crystal growth

KHP (E. Merck) was purified by repeated recrystallization. The crystals were grown by a slow evaporation solution growth technique (SEST). A saturated aqueous solution of KHP was prepared (12 g per 100 mL). Na(I) in the form of NaCl was used as such. Different concentrations of Na [10 mol% (low, l), 1:1 (heavy, h)] were introduced into the aqueous growth medium as dopant. The seed crystals are allowed to float on the surface of the saturated solution and left for slow evaporation at room temperature (30 °C). Triply distilled water was used as solvent. The prepared solution was filtered with a micro-filter. The crystallization took place within 15–20 days and the crystals were harvested when they attained an optimal size and shape. It is visually observed that the growth rate of crystals is high with low concentration of dopants. Quite likely, at high concentrations of the dopant, the adsorption film blocks the growth surface and inhibits the growth process [26, 27]. Bulk crystals are grown using optimized growth

parameters. High-quality transparent crystals were harvested from the growth medium at low concentrations of dopants. Photographs of the as-grown doped and undoped crystals are shown in Fig. 1.

Characterization techniques

The FT-IR spectra were recorded using an AVATAR 330 FT-IR instrument by KBr pellet technique. Bruker Axs (Kappa Apex II) X-ray diffractometer was used for single crystal XRD studies. The incorporated sodium in the specimen was analyzed on a Philips Atomic Absorption Spectrometer. Morphologies of the samples and the presence of dopants in the specimens were observed using a JEOL JSM 5610 LV scanning electron microscope with the resolution of 3.0 nm, an accelerating voltage 20 kV, and maximum magnification 300,000 times. The standard used to study energy dispersive X-ray spectroscopy (EDS) was NaCl for sodium doping.

The SHG test on the crystals was performed by the Kurtz powder SHG method. An Nd:YAG laser with modulated radiation of 1064 nm was used as the optical source and directed on the powdered sample through a filter. The grown crystals were ground to a uniform particle size of 125–150 μm and then packed in a micro-capillary of uniform bore and exposed to laser radiation. The output from the sample was

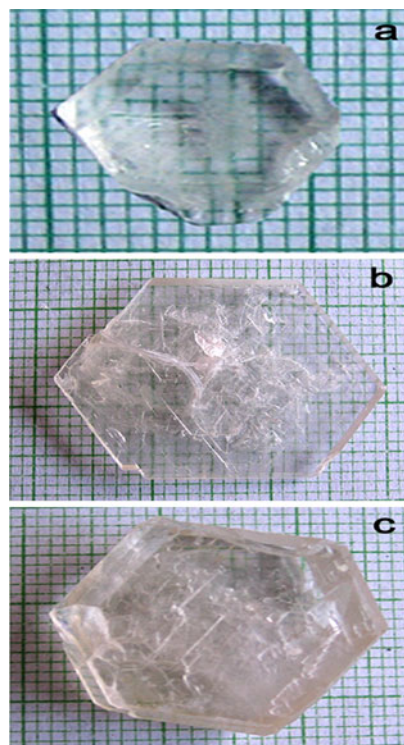


Fig. 1 Photographs of KHP as-grown crystals: **a** pure, **b** low sodium-doped, and **c** heavy sodium-doped

monochromated to collect the intensity of the 532 nm component and to eliminate the fundamental. ICP studies were recorded using a Varian Cary 5E UV–Vis–NIR spectrophotometer. TG–DTA curves were simultaneously obtained in nitrogen atmosphere at a heating rate of 20 °C/min.

Results and discussion

FT-IR analysis

A very slight shift in some of the characteristic vibrational frequencies of pure KHP is observed because of doping with Na. It could be due to the lattice strain developed as a result of doping (Fig. 2). The important stretching frequencies are given in Table 1.

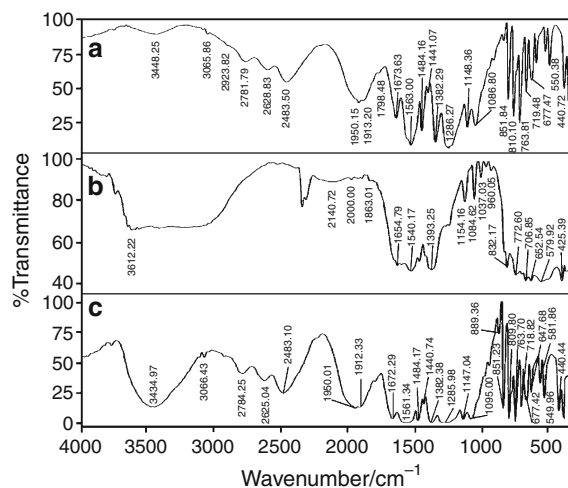


Fig. 2 FT-IR spectra of KHP crystals: **a** pure, **b** low sodium-doped, and **c** heavy sodium-doped

Table 1 Observed FT-IR spectral frequencies of pure and sodium-doped KHP crystals [28]

Pure/cm ⁻¹	10 mol% sodium-doped/cm ⁻¹	1:1 mol sodium-doped/cm ⁻¹	Assignment
1563	1540	1561	C=O symmetrical stretching
1484	1484	1484	O=C ring stretching
440	435	440	C=O symmetrical stretching
1382	1383	1383	C=C stretching
1086	1084	1095	C–C=O stretching
851	832	851	C–H out of plane bending
3448	3612	3434	O–H stretching (hydrogen bonding)
719	709	718	O–H out of plane bending

SEM and EDS

The effect of the influence of dopants on the surface morphology of KHP crystal faces revealed some interesting features. Plate morphology was observed for the undoped KHP and the highest surface roughness by doping could be due to bunched steps or macro-steps. The investigations confirmed that the doping changes the morphology and it results in crystal voids (Fig. 3).

The presence of Na in the doped specimen was confirmed by EDS (Fig. 4) and the higher concentration of the incorporated Na into the crystalline matrix with higher dopant concentration is observed. Analysis of surface at different sites reveals that the incorporation is non-uniform over the surface, connected with absorption mechanisms at the ledges of step strains.

Atomic absorption spectroscopy

This technique was used to quantify the concentration of the dopants employed in KHP crystals using a graphite line as internal standard. The data reveal that the dopant concentrations incorporated into the KHP lattices were 9.82 ppm (10 mol% Na) and 19.62 ppm (1:1 sodium-doped). It is clear that the incorporation of the dopant into KHP crystalline matrix is not in tune with the amount of dopant taken in the crystallization process. The quantity of foreign metal ion entering into the crystalline matrix is much less in comparison with the quantity introduced into the aqueous growth medium. It could be due to the limitations of the accommodating capability of the material. ICP analysis confirms the above observations.

Thermal (TG–DTA) analysis

The TG–DTA curves reveal that there is no physically observed water in the molecular structure of crystals grown

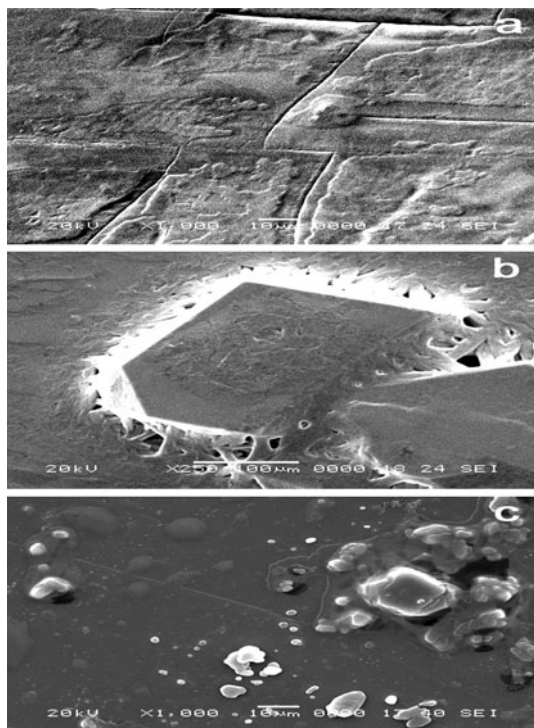


Fig. 3 SEM images of KHP crystals: **a** pure, **b** low sodium-doped, and **c** heavy sodium-doped

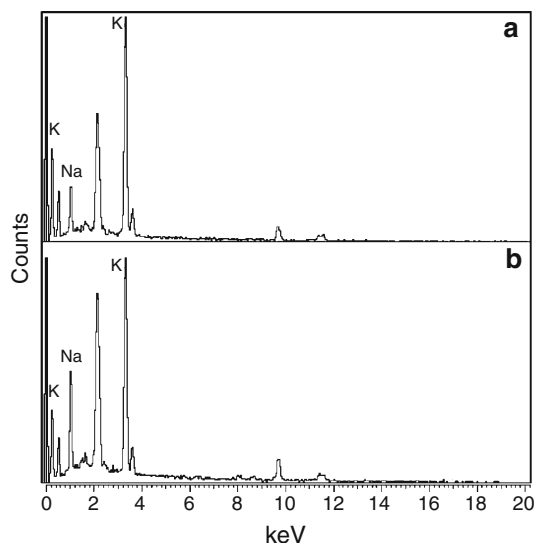


Fig. 4 EDS spectra of KHP crystals: **a** low sodium-doped and **b** heavy sodium-doped

from sodium-added KHP solution. The TG curve also shows a gradual mass loss and residual mass obtained at 600 °C is only 51% (Fig. 5) and endothermic peak is obtained in DTA for heavy doped KHP crystals at a little bit higher temperature (320 °C) compared to the pure KHP crystals (301 °C) [29, 30].

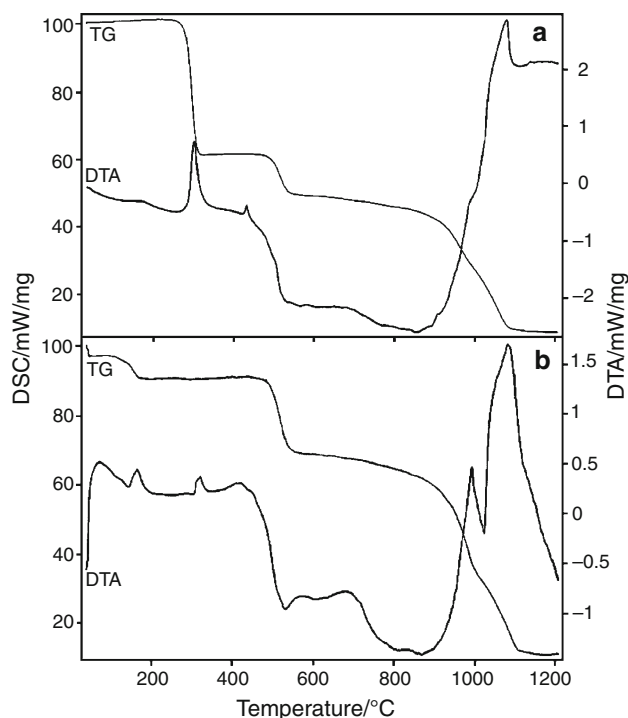


Fig. 5 TG–DTA curves of KHP crystals: **a** pure and **b** sodium-doped SHG efficiency

SHG test was performed on the powder samples with the input radiation of 2.5 mJ/pulse. The output SHG intensities (Table 2) for pure and doped specimens give relative NLO efficiencies of the measured specimens. Significant enhancement of SHG efficiency is reached with a high dopant concentration and it also observed that the SHG efficiency is concentration (of the dopant) dependent.

The depressed SHG efficiency is quite likely due to the disturbance of charge transfer. The efficient SHG demands specific molecular alignment of the crystal to be achieved facilitating nonlinearity in the presence of a dopant. It has been reported that the SHG can be greatly enhanced by attaining the molecular alignment through inclusion complexation [31]. Recently, we have reported that enhancement in crystalline perfection could lead to improvement in SHG efficiency [32].

XRD analysis

The lattice constants for low sodium-doped KHP(l) obtained by cell refinement, with least square fitting of the lines in the range of $20^\circ \leq 2\theta \leq 120^\circ$ are $a = 9.6924 (\pm 0.003) \text{ \AA}$; $b = 13.3042 (\pm 0.004) \text{ \AA}$; $c = 6.4756 (\pm 0.006) \text{ \AA}$; $v = 830.1692 (\pm 1.7) \text{ \AA}$. The corresponding values for 1:1 sodium-doped KHP(h) are $a = 9.6525 (\pm 0.04) \text{ \AA}$; $b = 13.3030 (\pm 0.06) \text{ \AA}$; $c = 6.4706 (\pm 0.08) \text{ \AA}$; $v = 830.11 (\pm 3) \text{ \AA}$. The lattice constant values for pure

Table 2 SHG outputs

System	$I_{2\omega}/mV$
Pure KHP	29
Na-doped KHP (l)	32
Na-doped KHP (h)	56

KHP are $a = 9.6120 \text{ \AA}$; $b = 13.3290 \text{ \AA}$; $c = 6.4820 \text{ \AA}$, and $v = 830.46 \text{ \AA}^3$. Quantitative data show slight changes in the lattice parameter values and hence the unit cell volume. The ionic radius of the dopants Na (115 pm) is very small compared with that of K (151 pm) [33]. Hence, it is reasonable to believe that the dopant can enter into the KHP crystalline matrix without causing much distortion.

Conclusions

We have used XRD, FT-IR, SEM, EDS, TG–DTA, atomic absorption spectroscopy (AAS), ICP, and single crystal XRD lattice parameter values to study the influence of doping with sodium on KHP crystals. A close observation of XRD profiles of doped and undoped samples reveals some minor structural variations. The studies indicate that the crystal undergoes considerable lattice stress as a result of doping. FT-IR studies also clearly confirmed the above observations. SEM images reveal that the external morphology of KHP crystal is changed by doping. EDS confirms the presence of large amount of sodium in the specimen. AAS and ICP studies are used to quantify the amount of Na in the lattice of KHP crystals. The TG–DTA studies reveal the purity of the material and no decomposition is observed up to the melting point. The SHG efficiency of KHP is dramatically increased by heavy doing of alkali metal.

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