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Influence of Cd(II) doping on the properties of potassium hydrogen phthalate(KHP) crystals

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Abstract: The influence of transition metal (Cd) doping on the properties potassium hydrogen phthalate (KHP) crystals has been studied. The concentration of dopant in the mother solution was 1, 5 and 10 mol%. In composition of dopant into the crystalline matrix even at a low concentration was well confirmed by energy dispersive spectroscopy (EDS). A close observation of FT-IR and XRD profiles of doped and undoped samples reveals some minor structural variations. It appears that the crystal undergoes considerable lattice stress as a result of doping of the bivalent cadmium. TG-DTA studies reveal the purity of the sample and no decomposition is observed below the melting point. The pure and doped KHP single crystal shows good transparency in the entire visible region, which is suitable for optical device applications. Scanning electron microscope (SEM) photographs exhibit the effectiveness of the impurity in changing the surface morphology of KHP crystals. The non-linear optical property of the grown crystal has been confirmed by Kurtz powder second harmonic generation (SHG) test. The dopant of 5 and 10 mol% shows higher second harmonic generation result than pure potassium hydrogen phthalate crystals.

Keywords: Non-linear; Optical materials, Cadmium doping; X-ray diffraction; FT-IR; TG-DTA; XRD

Introduction

The search for new materials with non-linear optical (NLO) properties has been subject of intense research due to their application in a wide range of technologies such as optical computing and optical[1-3]. Potassium hydrogen phthalate (KHP) crystal, with the chemical formula $K[C_6H_4COOH–COO]$, is well known for its application in the production of crystal analyzers for long-wave X-ray spectrometers[4-5]. Also, potassium hydrogen phthalate have piezoelectric, pyroelectric, elastic and non-linear properties[6-8]. KHP has a well-developed surface pattern on the (010) plane consisting of high and very low growth steps which can be easily observed by means of optical microscopy[9,10]. A semi-organic compound of potassium hydrogen phthalate crystallizes in an orthorhombic system with the space group of $Pca2_1$ and its lattice parameters are *a* = 9.605 Å, *b* = 13.331 Å, *c* = 6.473 Å and $\alpha = \beta = \gamma = 90°$[11,12]. The KHP single crystals are promising materials for the qualitative and quantitative X-ray analysis of light elements like Fe, Al, Mg, F, Si etc., in long and mid range spectral area and also serve as good monochromators[13,14]. The presence of small amount of impurities such as Ni^{2+}, Mg^{2+}, Co^{2+} and Li^{2+} plays an important role in the growth rate, habit modification of crystal and its properties[15]. The growth kinetics, optical and mechanical properties of KHP crystals by the effect of deuteration have also been analysed[16].

Cadmium being a transition metal has been employed as a dopant for many materials for many years. Cadmium doped cobalt/carbon nanoparticles can be utilized as a non-precious catalyst in methanol electro-oxidation[17]. Doping of cadmium in lead chalcogenide (PbSe) thin films leads to effective harnessing the solar energy in solar cells[18]. Cadmium as an additive modifies the thermal properties of amorphous Se[19]. The growth of KBr crystals in the presence of cadmium showed two new optical absorptions at 250 and 285 nm[20]. The saturation magnetization and remnant magnetization have been increased with increasing Cd in $Mg_{(1-x)}Cd_xFe_2O_4$[21]. Cd doping enhances the thermal stability of the calcium hydrogen phosphate[22] and also significantly inhibits the growth of anatase crystal size and hence stabilizes the mesoporous TiO_2[23]. The thermal stability of lithium ferrites has been enhanced due to the formation of δ-phase upon doping of Cd[24]. Recently we have investigated the influence of cadmium on the thermal and optical properties of ADP crystals[25]. As a continuation of our previous studies to ascertain the influence by doping on the KHP properties, this work has been undertaken. In the present investigation, we have used Cd(II), a transition metal for doping at different concentrations and the effects on properties of KHP crystals are systematically studied.

Experimental

Crystal growth

Potassium hydrogen phthalate (KHP) crystals were grown by the slow evaporation solution growth technique. According to the reported solubility data (12.5 g/100 mL at 30°C), the saturated solution of potassium hydrogen phthalate was prepared using high purity salt (E. Merck)[26]. Different concentrations of Cd (1, 5 and 10 mol%) 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 a 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. Photographs of the as grown doped crystals are shown in Fig. 1.

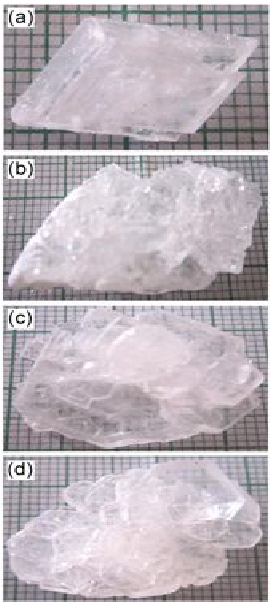

Fig. 1. Photographs of KHP crystals: (a) pure, (b) 1 mol% Cd doped, (c) 5 mol% Cd doped and (d) 10 mol% Cd doped.

Characterization techniques

The grown crystals have been analyzed by different characterization techniques. The functional groups were identified using Perkin Elmer Spectrum 1 in the range of 400-4000 cm^{-1} by KBr pellet techniques. The crystal phases of the grown single crystals of pure and Cd doped KHP were confirmed by single crystal X-ray diffraction using ENRAF NONIUS CAD-4 single crystal X-ray diffractometer with MoK$_\alpha$ radiation. The optical properties of the crystals were examined between 200 and 600 nm using LAMBDA-35 UV-Vis spectrophotometer. TG-DTA curves were recorded on a SDT Q600 (TA instruments) thermal analyzer with a heating rate of 10°C min^{-1} at room temperature to 700°C. The surface morphology was observed using a JEOL JSM 5610 LV SEM. EDS is a chemical microanalysis technique performed in conjunction with SEM. The second harmonic generation tests on the crystals were performed by the Kurtz powder SHG method[27].

Results and discussion

FT-IR spectral analysis

The FT-IR spectra were recorded for both the doped and undoped specimens using Perkin Elmer spectrum 1 in the range of 400-4000 cm^{-1} by KBr pellet technique. This gives sufficient information on the structure of a compound and is shown in Figs. 2a-2d. The observed frequencies of vibrations and their percentage of transmittance were also recorded. The observed frequencies were found to be in good agreement with the reported values[28-30]. The characteristic OH$^-$ stretching appears at 3448 cm^{-1} in the pure KHP is compared with the doped compounds, there was a shift in frequency range ≈3438-3457 cm^{-1}. This shift towards higher energy was due to the replacement K$^+$ ions by Cd^{2+} ions. An absorption band in the region of 500-900 cm^{-1} is due to C-H out of plane deformations of aromatic ring. The spectral band between 950-1225 cm^{-1} is due to in-plane deformation of C-H band in aromatic ring. The peaks at 1484 and 1674 cm^{-1} are due to the C-C skeletal aromatic ring vibrations.

The C-C-O stretching frequency appeared at 1086 cm^{-1}. The carboxylate ion (COO$^-$) asymmetric and symmetric stretching appeared at 1563 and 1382 cm^{-1}. The pH of the solution depends on the concentration of H$^+$ ions present in the solution. Here the dopant Cd^{2+} ion may replace the K$^+$ ion or it may get into the interstitial sites without disturbing the H$^+$ ions in the solution. Therefore it is possible that the doped metal Cd^{2+} ion may replace K$^+$ ions in the KHP crystal without changing the carboxylate hydrogen ion. From the FT-IR spectrum, the presence of the functional groups in the compound has been confirmed in Table 1.

Table 1. Observed FT-IR spectral frequencies of Pure and Cd doped KHP crystals

Pure (cm^{-1})	Cadmium doped (cm^{-1})			Assignment
	1 mol%	5 mol%	10 mol%	
3448	3457	3441	3438	O–H stretching (hydrogen bond)
1563	1566	1565	1565	C-C skeletal aromatic ring
1484	1484	1485	1485	C=O ring stretching
1382	1382	1383	1383	COO- symmetrical stretching
1086	1079	1090	1094	C–C-O stretching
851	852	853	852	C–H out-of-plane bending
719	720	720	720	O-H out-of-plane bending

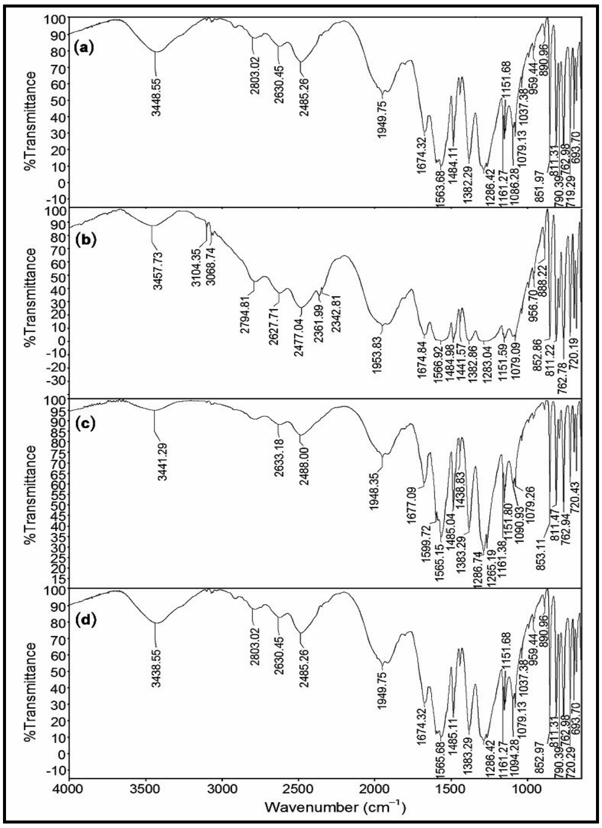

Fig. 2. FT-IR spectra of KHP crystals:(a) Pure (b) 1 mol% Cd doped, (c) 5 mol% Cd doped and (d) 10 mol% Cd doped

Powder and single crystal XRD analysis

The powder XRD patterns of Cd doped KHP crystals are compared with that of pure materials. The XRD profiles show that all the samples were of single phase without detectable impurity. A general observation is that the relative intensities have been reduced and a slight shift in the peak position is observed as a result of doping X-ray powder pattern have been taken at room temperature for 1, 5 and 10 mol% Cd doped KHP single crystals are shown in Figs. 3a-3c.

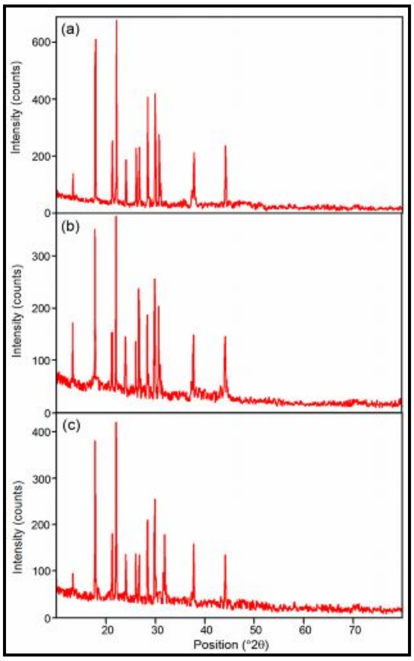

Fig. 3. XRD patterns of KHP crystals: (a) 1 mol% Cd doped, (b) 5 mol% Cd doped and (c) 10 mol% Cd doped

The interplanar distance (*d*) has been calculated for all the prominent peaks using Bragg's equation. Using the values of '*d*' and 2θ the h, k, l for all the reflection have been assigned and the lattice parameters values of pure and doped KHP crystals were calculated and the data is given in Table 2. There is a slight change in the lattice parameter of the doped crystals. This may be due to the lattice distortion by doping in the parent compound. From the powdered X-ray analysis, it was confirmed that all the doped materials crystallized in the orthorhombic structure.

Table 2. Lattice parameter values for pure KHP and Cd doped crystals

Crystal	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)	System
Pure KHP	6.473	9.605	13.331	838	Orthorhombic
KHP + 1 mol% Cd	6.510	9.640	13.390	840	Orthorhombic
KHP + 5 mol% Cd	6.490	9.630	13.350	834	Orthorhombic
KHP + 10 mol% Cd	6.470	9.620	13.310	829	Orthorhombic

UV-Vis spectral analysis

Since the absorption, if any in the NLO materials near the fundamental or second harmonic will lead to loss of conversion efficiency, it is necessary to have good optical transparency is an NLO crystal in the UV region. Optical absorption spectra have been recorded at room temperature (28°C) in the range between 200 and 600 nm using pure KHP and 1, 5 and 10 mol% Cd doped KHP crystals. The recorded absorption spectra are shown in Figs. 4a-4d. From the spectra, it is evident that the grown crystals are having good transparency from 200 to 300 nm, which is sufficient for SHG laser radiation of 1064 nm or other applications in the blue region. Hence, these crystals are useful for optoelectronic applications and the second harmonic generation from the Nd:YAG laser. The optical band gap (E_g) has been evaluated from the absorption spectra and the optical coefficient (α) near the absorption edge is given by

$$h\nu\alpha = A\ (h\nu - E_g)^{1/2}$$

Where A is a constant, E_g the optical band gap, h the Planck's constant and ν the frequency of the incident photons. The band gap of pure and different concentrations of Cd ion doped KHP crystals were estimated by plotting $(\alpha h\nu)^2$ *Vs* $h\nu$ as shown in Figs. 5a-5d which the linear portion of the plot was extrapolated near the onset of absorption edge to the energy axis. In this manner, the band gap for all the crystals of pure and Cd doped KHP were obtained and presented in Table 3.

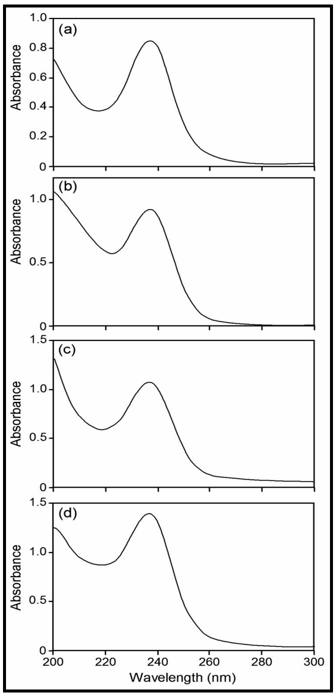

Fig. 4. UV-Vis spectra of KHP crystals: (a) pure, (b) 1 mol% Cd doped, (c) 5 mol% Cd doped and (d) 10 mol% Cd doped

Table 3. Optical band gap energy (E_g) for KHP and Cd doped KHP crystals sample

System	E_g (eV)
Pure KHP	3.92
KHP + 1 mol% Cd	4.30
KHP + 5 mol% Cd	4.45
KHP + 10 mol% Cd	4.70

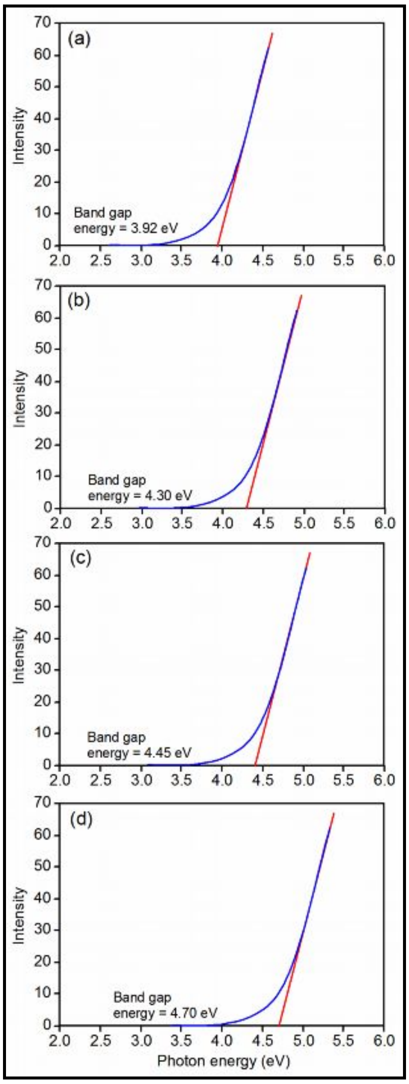

Fig. 5. Band gap energy of KHP crystals: (a) Pure, (b) 1 mol% Cd doped, (c) 5 mol% Cd doped and (d) 10 mol% Cd doped

Thermal analysis

TG and DTA analysis are of immense importance as far as fabrication technology is concerned, as they provide thermal stability of the material for fabrication, where a considerable amount of heat is generated during the cutting process. Thermal analysis was performed on the grown crystals to study the thermal stability and melting point. TG and DTA curves for 1, 5 and 10 mol% doped crystals are shown in Figs. 6a-6c. The curves have been obtained for the temperature range of 20-600°C. The percentage of weight loss due to temperature for each sample has been observed to be increased for these crystals compared to pure KHP. In TG, there is no weight loss up to 240°C. This indicates that there is no inclusion of water in the crystal lattice, which was used as the solvent for crystallization. It is seen that the major weight loss starts at 240°C and it continuous up to 315°C with mass loss of almost 45% suggesting the sublimation of the compounds. The nature of weight loss indicates the decomposition point of the material. In DTA, the strong endothermic peaks located ~240°C depict the crystallization of some of the phases of the decomposed material. No decomposition below the melting point ensure the suitability of the material for application in lasers where the crystals are required to withstand high temperatures.

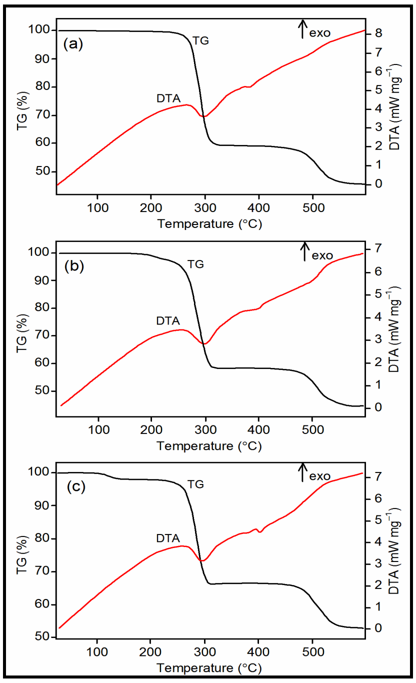

Fig. 6. TG-DTA curves of KHP crystals: (a) 1 mol% Cd doped, (b) 5 mol% Cd doped and (c) 10 mol% Cd doped

SEM and EDS analysis

The investigation of the influence of various concentration of Cd doped on the surface morphology of KHP crystal faces reveal structure defect centres as seen in the SEM pictures (Figs. 7a-7c). The SEM photos exhibit the effectiveness of the impurity in changing the surface morphology of doped crystal. The energy dispersive spectra (EDS) is an important tool for characterizing the elements present in the crystal and to determine the chemical composition of these elements. Incorporation of dopant into the crystalline matrix was observed by EDS and is shown in Figs. 8a-8c. From the experimental data, the presence of dopants in the doped crystals can be easily identified.

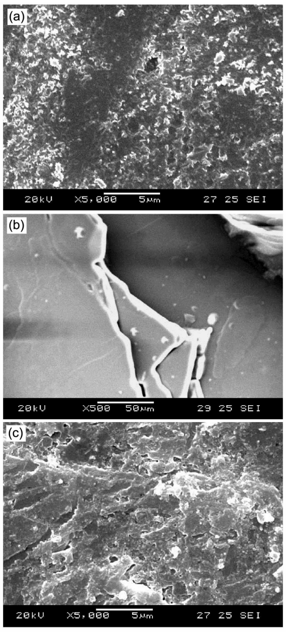

Fig. 7. SEM images of KHP crystals: (a) 1 mol% Cd doped, (b) 5 mol% Cd doped and (c) 10 mol% Cd doped

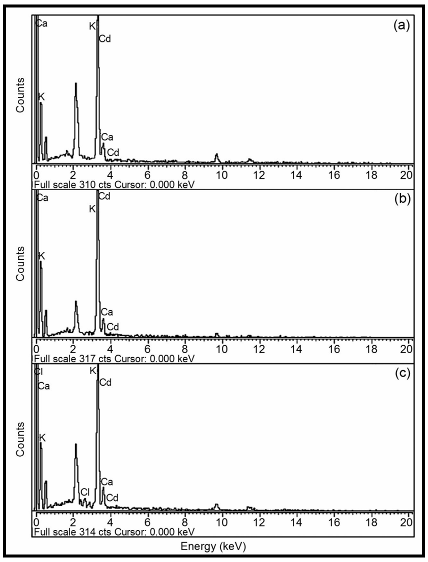

Fig. 8. EDS of KHP crystals: (a) 1 mol% Cd doped, (b) 5 mol% Cd doped and (c) 10 mol% Cd doped

Powder SHG measurement

The SHG conversion efficiency of pure and different concentration of Cd doped KHP crystals were estimated using modified setup of Kurtz and Perry at the Indian Institute of Science (IISC), Bangalore[27]. A Q-switched Nd:YAG laser beam of wavelength 1064 nm was used with an input power of 2.15 mJ and pulses width 10 ns with a repetition rate of 10 Hz. The output from each sample was monochromated to collect the intensity of 532 nm component. The green radiation of 532 nm was observed from the pure and doped KHP crystals confirming the second harmonic generation (SHG). The SHG efficiency of pure and doped crystals was estimated with reported to standard KDP and is given in Table 4. From Table 4, it can be seen that the SHG efficiency is increases with increasing the concentration of dopant when compared to pure KHP crystals.

Table 4. SHG efficiency of the pure and doped KHP crystals

Crystals	$I_{2\omega}$ (mV)
Pure KHP	6.8
KHP + 1 mol% Cd	6.9
KHP + 5 mol% Cd	7.8
KHP + 10 mol% Cd	9.7

Conclusion

The influence of doping the transition metal, Cd(II) at different concentration on KHP crystals has been studied. A close observation of FT-IR and XRD profiles of doped and undoped samples reveals some minor structural variation. These results indicate that the crystal undergoes considerable lattice stress as a result of doping. The SEM photograph exhibit the effectiveness of the impurity in changing the surface morphology of pure KHP crystals. The incorporation of dopants into the crystalline matrix was observed by EDS. The UV-Vis spectral studies reveal that there is no change in transmission window for doped KHP crystals as compared to that of pure KHP crystal. The good transmission property of the doped crystal in the entire visible region ensures its suitability for SHG applications. Thermal analysis confirms no decomposition of the crystal up to the melting point. SHG efficiency was observed that when doping concentration increased from 1, 5 and 10 mol%, the non-linear optical properties also increased.

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