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Growth, structural, spectral and nonlinear optical studies on potassium hydrogen phthalate single crystals with glycine as additive

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Glycine added potassium hydrogen phthalate single crystals were grown at different glycine concentrations by aqueous slow evaporation technique. Powder diffraction studies indicate that the crystal belongs to orthorhombic system with space group $Pca2_1$. The grown crystals were found to be transparent in the entire visible region with a low cut off wavelength of 300 nm. The presence of second harmonic generation (SHG) effect in the pure and doped KHP crystal confirms the nonlinear optical property.

Keywords: Nonlinear optical material, crystal growth, FT-IR, optical properties, refractive index.

Introduction

The search for NLO materials with good transparency has led to the development of photonic and optoelectronic technologies[1]. Semi-organic compounds of Potassium Hydrogen Phthalate (KHP) have been explored by many researchers for their piezoelectric, pyroelectric, elastic and nonlinear optical properties[2]. KHP crystallizes in the orthorhombic system with lattice parameters a = 9.605 Å, b = 13.331 Å, c = 6.473 Å and space group $Pca2_1$[3]. KHP used as an analyzer material in X-ray spectroscopy[7]. Hence, several attempts were made to grow this material in the recent years.

Experimental

Synthesis and crystal growth:

An equimolar ratio of phthalic acid (Merck 99.5%) and potassium hydroxide (Merck 99%) were dissolved in deionized water of resistivity 18.2 MΩ cm for the synthesis of potassium hydrogen phthalate. Glycine at 1 mol% was introduced into the saturated aqueous solution of KHP and stirred well for about 10 h to get homogeneous solution. The transparent, good quality crystals were collected after 20–25 days. The photograph of the pure and glycine doped KHP crystals are shown in Fig. 1(a-d).

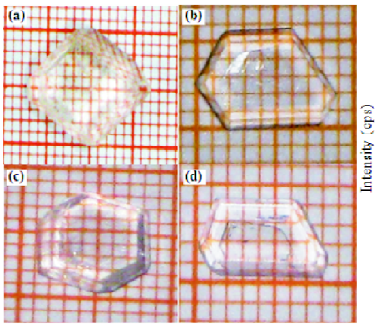

Fig. 1. Photograph of (a) pure KHP, (b), (c) and (d) glycine (1, 5 and 10 mol%) doped KHP.

Results and discussion

Powder XRD analysis:

The X-ray powder diffraction studies were carried out using Bruker D8 ADVANCE diffractometer (λ = 1.54187 Å). The XRD patterns were observed over the range of 5–50° with a Cu target and Ni filter at 40 KV and 30 mA with the scanning rate of 0.02°/s. The powder XRD patterns are shown in Fig. 2(a-d). It was found that the XRD pattern of pure KHP matched well with the JCPDS Card No. 311855.

FT-IR spectral analysis:

FT-IR spectra of pure and glycine doped KHP samples

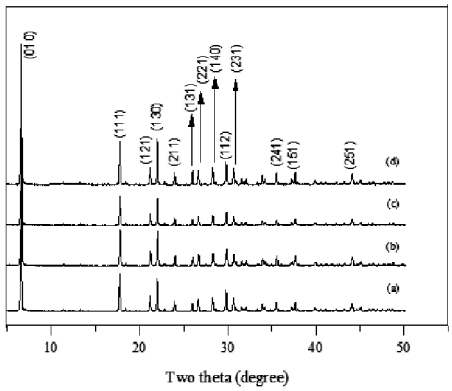

Fig. 2. XRD spectra of (a) pure KHP, (b), (c) and (d) glycine (1, 5 and 10 mol%) doped KHP.

were recorded on Nicolet Avator 330A spectrophotometer in the range 4000–400 cm^{-1}. Fig. 3(a-d) shows the FT-IR spectra of pure and glycine doped KHP crystals. The observed frequencies of vibrations their assignments are given in Table 1. The NH_3^+ rocking is observed in the range 490–510 cm^{-1} for all the glycine doped KHP confirms the presence of amine group in the crystalline material[4].

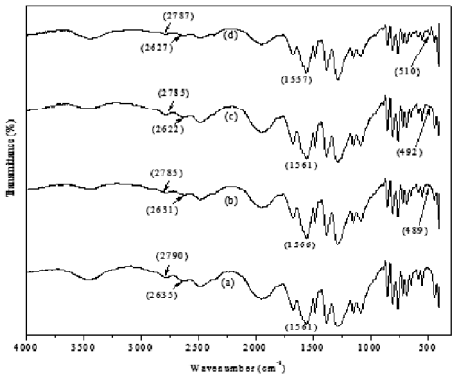

Fig. 3. FT-IR spectra of (a) pure KHP, (b), (c) and (d) glycine (1, 5 and 10 mol%) doped KHP.

SHG test:

The non-linear optical behavior of the pure and glycine doped KHP powder samples were tested with Nd:YAG laser (1064 nm). The bright emission of green (532 nm) signal confirms the NLO property of the crystal[5]. A constant input energy of 5.8 mJ/pulse is used. The output intensities for pure and glycine doped specimens are found to be 23.5, 21.7, 18.0 and 15.7 mV respectively.

Table 1. Vibrational frequencies for pure and glycine doped KHP crystals

Assignments	Wavenumber (cm^{-1})			
	KHP	1GKHP	5GKHP	10GKHP
O-H stretching hydrogen bond	3470	3445	3443	3440
O-H stretching	2790	2785	2785	2787
	2635	2631	2622	2627
	2488	2488	2492	2488
C-C asymmetric stretching	1950	1950	1951	1951
C-C stretching	1670	1672	1675	1672
C-C stretching	1561	1566	1561	1557
C-H bending	1486	1482	1482	1486
C-O stretching	1385	1381	1385	1385
C-OH bending	1285	1285	1286	1286
C-C stretching	1148	1148	1148	1148
C-C stretching	1088	1088	1088	1088
C-H out-of-plane bending	851	851	851	851
CO_2 bending	809	806	806	806
KO symmetric stretching	761	763	761	761
C-H out-of-plane bending	718	716	719	719
CO_2 bending	683	683	683	683
KO symmetric stretching	582	579	581	581
C=C-C symmetric ring bending	548	548	548	548
NH_3^+ rocking	–	489	492	510
Symmetric ring torsion	440	444	440	444
KC stretching	405	405	408	405

Conclusions

Good quality pure and glycine doped KHP crystals have been grown by solution growth technique. Crystal structure, functional groups and second order nonlinearity of the samples were confirmed and analyzed through powder XRD, FTIR and SHG studies.

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