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Influence of formic acid on electrical, linear and nonlinear optical properties of potassium dihydrogen phosphate (KDP) crystals

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ABSTRACT

In present investigation 0.5 and 1 mol% formic acid (FA) added potassium dihydrogen phosphate (KDP) crystals have been grown by a slow evaporation technique. The cell parameters of the grown crystals were determined using single crystal X-ray diffraction analysis. The presence of different functional groups has been qualitatively analyzed by the FT-IR spectral analysis. The optical transparency and optical constants were assessed employing UV–visible studies in the range of 200–900 nm. The wide optical band gap of 1 mol% FA added KDP has been found to be 5 eV. The frequency dependent dielectric measurements were studied for pure and KDP added FA crystals. The enhanced second harmonic generation (SHG) efficiency of grown crystals was determined by a classical Kurtz–Perry powder technique. The encouraging third order nonlinear properties were examined employing a Z-scan technique using He–Ne laser, at 632.8 nm. The effective negative index of refraction and high figure of merit (FOM) essential for laser stabilization were determined for grown crystals.

1. Introduction

Nonlinear optical materials capable of efficient laser frequency conversion have been actively sought over the last three decades due to enlarged commercial significance and scope of these materials in the field of optical communication, signal processing, optical switching and optical data storage. Potassium dihydrogen phosphate (KDP) is a model system for potential nonlinear optical device applications with high range of thermal stability [1–4]. The improvement in the optical quality, nonlinearity and different properties of KDP crystals can be realized with suitable noncentrosymmetric and polar dopant. The influence of thiourea, glycine, L-arginine and histidine on the growth, structural, thermal, optical properties and SHG efficiency of KDP crystal has been reported in the literature [3–5]. Formic acid belongs to the family of carboxylic acid, restrains its research impact with distinct amino acids viz. L-arginine, glycine, L-alanine, L-threonine exhibiting better nonlinearity and physico-chemical properties [6–9]. Rajesh et al. recently reported effect of DL-malic acid and oxalic acid on structural, optical, thermal, mechanical and dielectric properties of ADP crystal [10–11]. The effect of different amino acids, metal ions on KDP has been reported by many researchers, however studies on FA added KDP crystal are yet to be explored. Therefore, present communication reports the effect of FA on electrical, linear and nonlinear optical properties of KDP crystals for its effective NLO applications.

2. Synthesis and growth

The AR grade KDP (KH_2PO_4) salt was dissolved in deionized water and supersaturation is achieved. The doping was achieved by adding 0.5 and 1 mol% FA to supersaturated solution of KDP in separate beakers. The solutions were allowed to stir well at a constant speed for six hours to achieve the homogeneity throughout the aqueous volume. The purity of the synthesized salts was achieved by successive recrystallization process. The filtered solutions were kept for evaporation in a constant temperature bath of accuracy ± 0.01 at 36 °C. Highly transparent and well phased crystals of FA added KDP were harvested in 20 days. 0.5 and 1 mol% FA added KDP crystals are shown in Figs. 1 and 2.

3. Results and discussion

3.1. Single crystal X-ray diffraction

The cell parameters of the grown crystals were determined using the single crystal NONIUS CAD4 X-ray diffractrometer.

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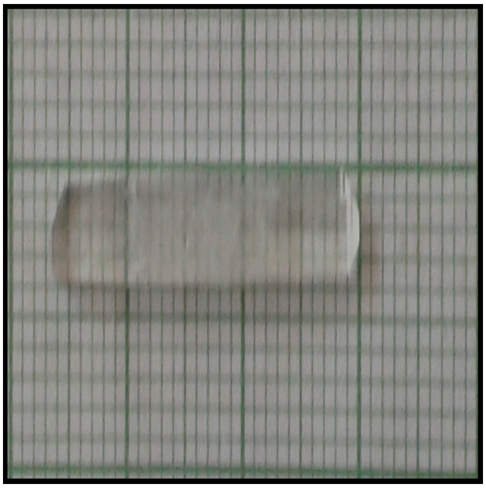

Fig. 1. Crystal of KDP+FA 0.5 mol.

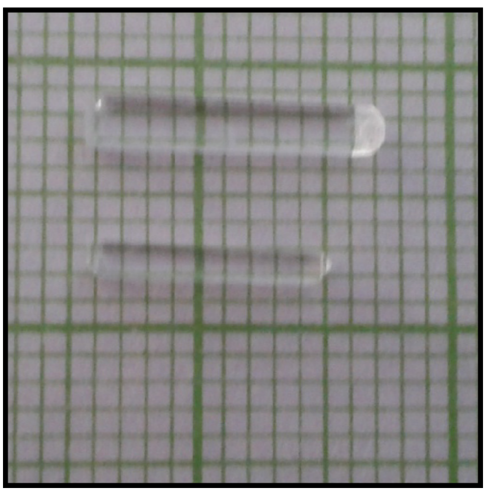

Fig. 2. Crystal of KDP+FA 1 mol.

Table 1
Cell parameters.

Samples	$a=b$, c (Å)	V (Å)^3
KDP	7.44, 6.94	384
KDP+FA 0.5 mol	7.46, 6.97	388
KDP+FA 1.0 mol	7.49, 6.99	392

The grown FA added KDP crystals were revealed to be crystallized with tetragonal symmetry. The cell volume of the FA added KDP crystals was observed to have slight increase with increase in concentration of FA. The volumetric parameters of grown crystals are discussed in Table 1.

3.2. SHG efficiency test

Kurtz's powder technique was employed to investigate the enhancement in SHG efficiency of KDP crystal due to addition of different mole% of FA [12]. The studies were carried using Nd–YAG laser operating at 1064 nm with repetition rate of 10 Hz and pulse width of 8 ns. The error bar in measurement with the current setup was determined to be ± 1 mV. The second harmonic signals generated by the crystalline sample were confirmed from emission of green radiations. The relative SHG signals generated for pure KDP, 0.5 and 1 mol% FA added KDP were 75 mV, 82 mV and 85 mV.

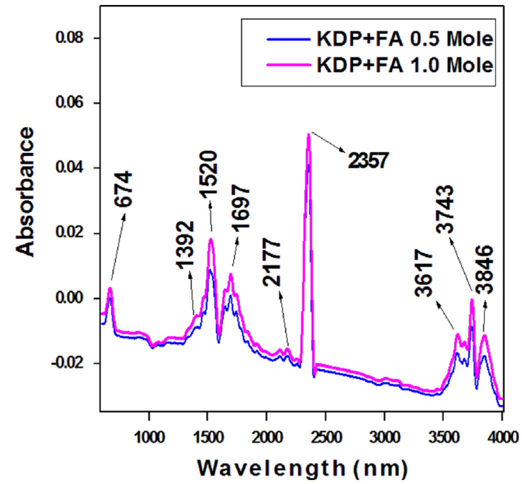

Fig. 3. FT-IR spectrum.

The highest enhancement in SHG efficiency is procured by 1 mol% FA added KDP crystal. It is found to be 1.13 times that of standard KDP material. Thus FA added KDP crystal can be subjected to effective laser frequency conversion and NLO applications such as optical modulation [13]. The enhancement in SHG efficiency of KDP is notable with increasing FA mole%.

3.3. FT-IR spectral analysis

The influence of formic acid in KDP has been analyzed by recording the vibration spectrum of grown crystals using a Bruker α-ATR instrument in the range of 600–4000 cm^{-1}. The absorption FT-IR spectral vibrations for different characteristic bonds are depicted in Fig. 3.The absorption peak observed at 624 cm^{-1} is due to O–H bending vibrations. The C–H bond deformation peak of formic acid is assigned at 1392 cm^{-1}. The prominent peak at 1520 cm^{-1} is evident of C–H bond bending while the peculiar O=P=OH symmetric stretching mode of KDP is assigned at wavenumber 1697 cm^{-1}. The occurrence of C–H stretching vibration is evident at 2177 cm^{-1}. The sharp absorption peak cited at 2357 cm^{-1} is assigned to P–O–H bending vibrations. The mild peak observed at 3617 cm^{-1} corresponds to O–H bond stretching. The peaks at 3743 cm^{-1} and 3846 cm^{-1} are attributed to CH_2 stretching vibrations. The incorporation and presence of FA in KDP has been confirmed from vibrational spectrum.

3.4. UV–visible studies

The UV–visible transmission spectra of FA added KDP crystals were recorded using a Shimadzu UV-2450 spectrophotometer in the range 200–900 nm. The materials suitability for optoelectronics applications can be well understood exploring the transmittance in visible region, shown in Fig. 4. 1 mol% FA added KDP crystal exhibited highest transparency in entire visible region and lowest cut off wavelength (291 nm) substantive for effective laser frequency conversion [14]. The optical band gap of the material is of vital importance to illustrate the electron transitions in different electronic band structures. The absorption coefficient was also calculated by using the transmittance spectrum, $\alpha=2.303[\log(1/T)]/d$, were T is the transmittance, α is the absorption coefficient, and d is the thickness of the crystal. The optical band gap (E_g) can be calculated using relation, $(\alpha h\nu)^2=A\ (h\nu-E_g)$. The values of band gap of the grown crystals were determined from Tauc's extrapolation plot depicted in Fig. 5. The band gap of 1 mol% FA added KDP crystal is found to be 5 eV indicating its suitability for fabrication of optoelectronic devices [15]. The change in