Physica B 449 (2014) 61–66

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

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

Mohd Anis [a], M.D. Shirsat [b], Gajanan Muley [c], S.S. Hussaini [a,*]

[a] Crystal Growth Laboratory, Department of Physics, Milliya Arts, Science & Management Science College, Beed 431122, Maharashtra, India

[b] Intelligent Material Research Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431005, Maharashtra, India

[c] Department of Physics, Sant Gadge Baba Amravati University, Amravati 444602, Maharashtra, India

ARTICLE INFO

Article history:
Received 12 March 2014
Received in revised form
29 April 2014
Accepted 1 May 2014
Available online

Keywords:
Crystal growth
Growth from solution
Nonlinear optical materials
Optical studies
Electrical studies

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.

* Corresponding author. Tel.: +91 9325710500.
E-mail address: Shuakionline@yahoo.co.in (S.S. Hussaini).

http://dx.doi.org/10.1016/j.physb.2014.05.007
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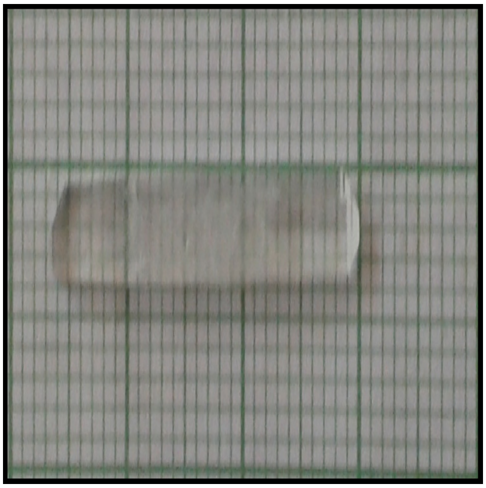

Fig. 1. Crystal of KDP+FA 0.5 mol.

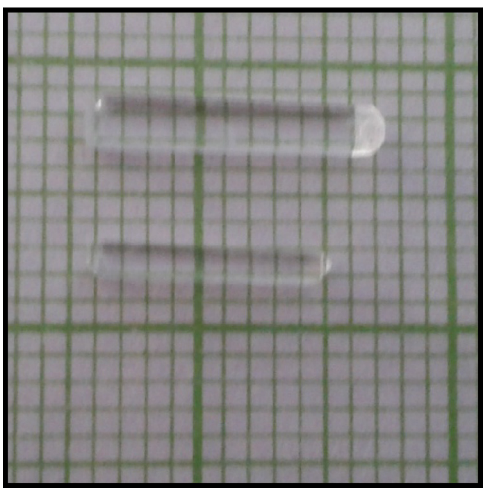

Fig. 2. Crystal of KDP+FA 1 mol.

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.

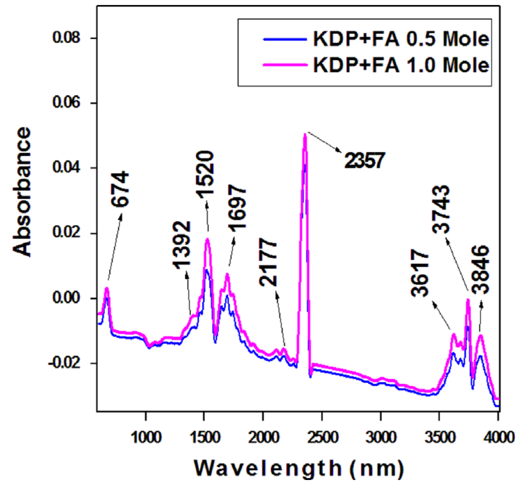

Fig. 3. FT-IR spectrum.

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

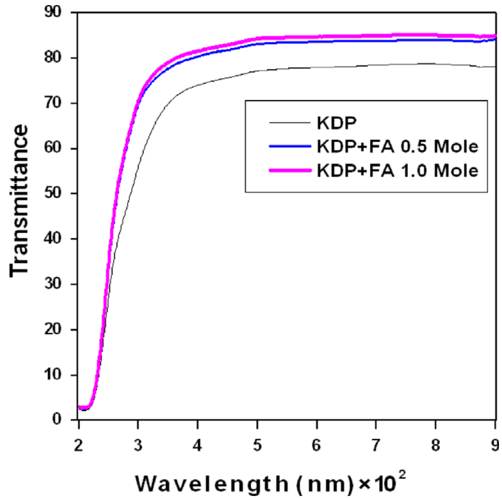

Fig. 4. Transmittance spectrum.

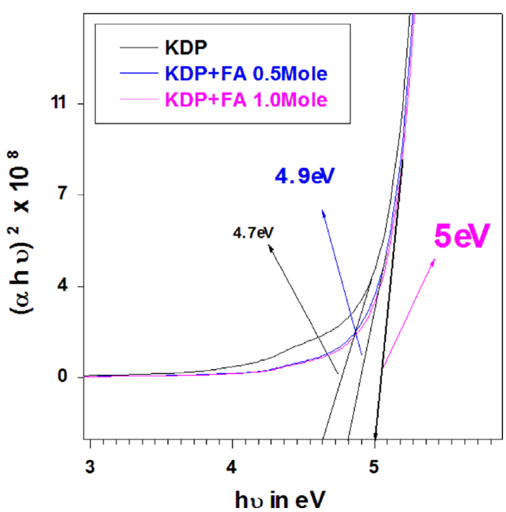

Fig. 5. Tauc's plot.

velocity of electromagnetic wave in the material medium can be assessed with the innate behavior of refractive index in UV–visible region. The variation of refractive index and reflectance with wavelength is shown in Figs. 6 and 7. The high transmittance with lower refractive index and reflectance of 1 mol% FA added KDP crystal in the entire visible region realizes its prominence for antireflection coating in solar thermal devices [14]. The optical conductivity, electrical conductivity and susceptibility are shown in Figs. 8, 9 and 10. The high magnitude of optical conductivity indicates the potential candidature of the grown crystals for information processing and computing [14]. The lower electrical conductivity and susceptibility of FA added crystals are promising properties for semi-conducting devices [14]. The lower values of extinction coefficient and optical dielectric constant exhibited by FA added crystals are prerequisite properties for high conversion efficiency shown in Figs. 11 and 12 respectively. The systematic analysis of data shown in Table 2 revealed that the rising FA concentration triggers improved optical properties to KDP crystals vital for NLO applications.

The measure of loss of electromagnetic energy in visible region due to scattering and absorption phenomenon can be realised with lower extinction coefficient of material [16]. The extinction coefficient indicates the propagation of electromagnetic wave through material evaluated using the relation $k=\alpha\lambda/4\pi$. The electrical susceptibility can be examined in visible region with $\chi=n^2-1$, were n is the refractive index of the material.

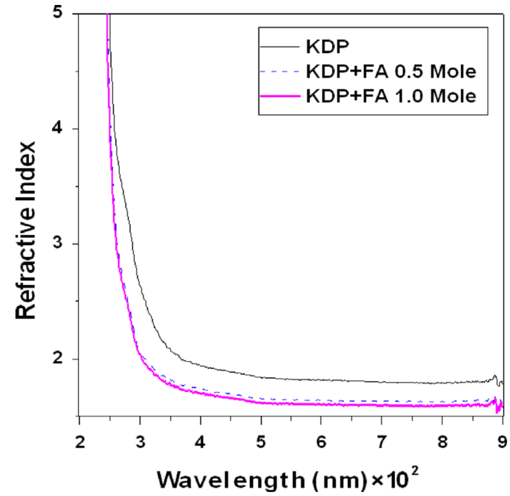

Fig. 6. Refractive index vs. wavelength.

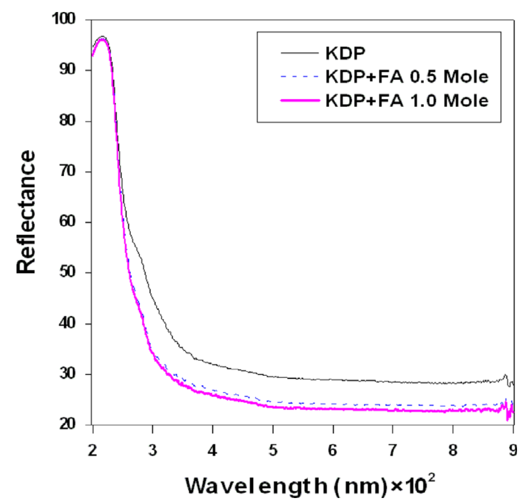

Fig. 7. Reflectance vs. wavelength.

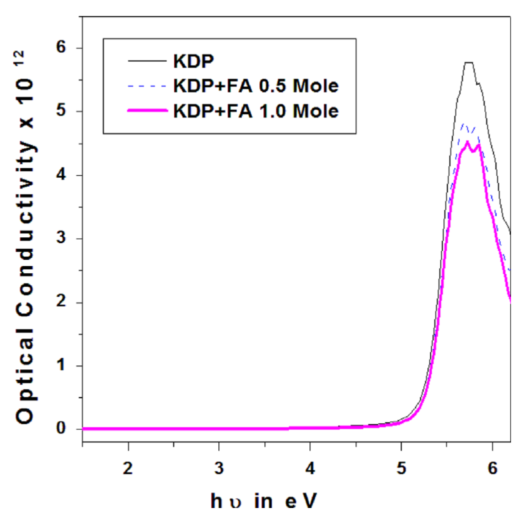

Fig. 8. Optical conductivity vs. photon energy.

3.5. Dielectric studies

The dielectric responses of the grown crystals were studied using the Gwinstek-819 LCR meter at room temperature. The variation of dielectric constant for pure and FA added KDP crystals

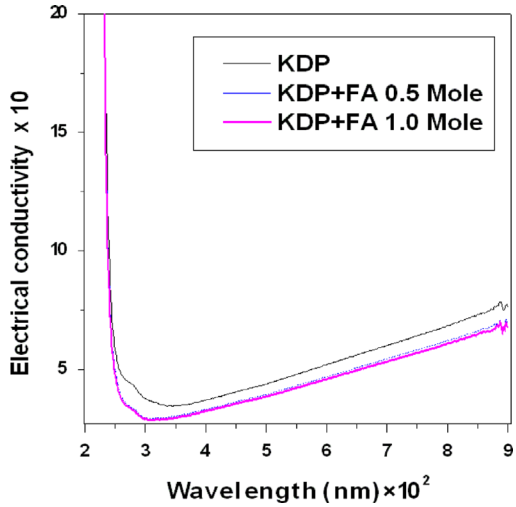

Fig. 9. Electrical conductivity vs. wavelength.

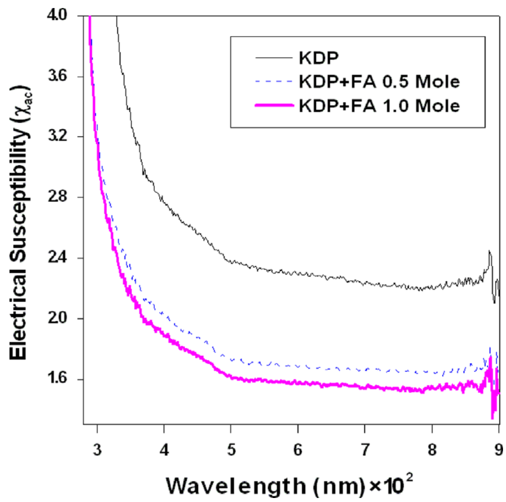

Fig. 10. Electrical susceptibility vs. wavelength.

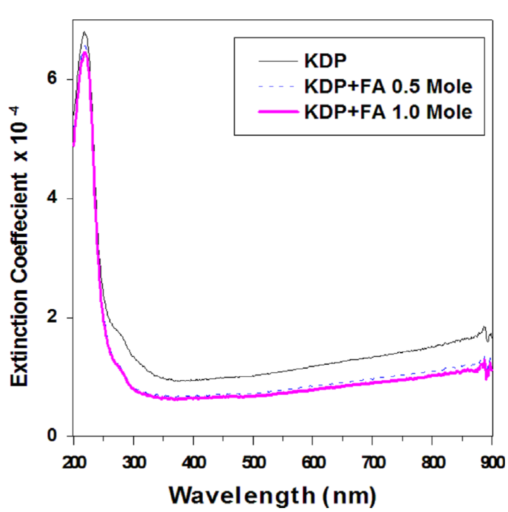

Fig. 11. Extinction coefficient vs. wavelength.

is shown in Fig. 13. The dielectric constant is higher at lower frequencies ascribed to electronic, ionic, dipolar and space charge polarization mechanism of molecular dipoles and saturates with further increasing frequency [17]. The 1 mol% FA added KDP crystal

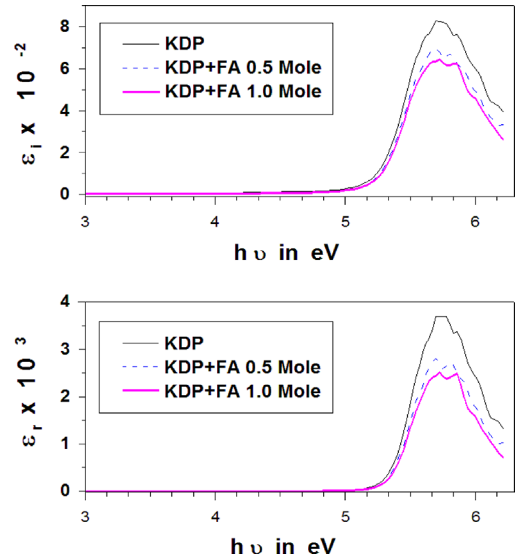

Fig. 12. Real and imaginary parts of dielectric vs. $h\nu$ (eV).

Table 2
Optical parameters.

Parameters	KDP	KDP+FA 0.5 mol	KDP+FA 1 mol
Cutoff wavelength	337 nm	295 nm	291 nm
Band gap	4.7 eV	4.9 eV	5 eV
Reflectance	36.6	29.9	28.8
Extinction coefficient	1×10^{-4}	7×10^{-5}	6.5×10^{-5}

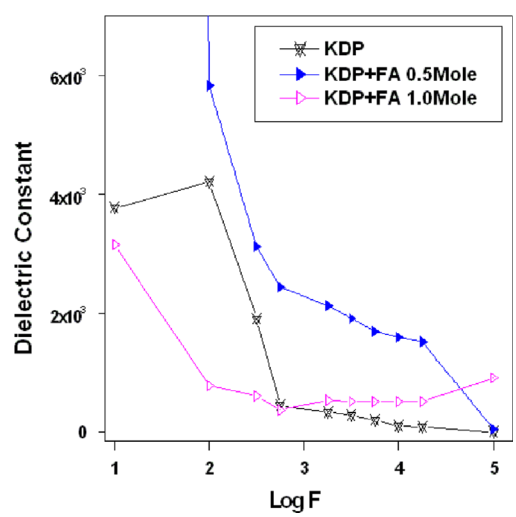

Fig. 13. Dielectric constant vs. Log *F*.

traces decreasing dielectric constant with increasing frequency indicating crystal lattice perfection and suppressed space charge polarizations, which benefits material for increasing SHG coefficient [18]. The decreasing dielectric loss with increasing frequency is depicted in Fig. 14. Thus FA added KDP crystals possess enhanced optical quality and low level defects making it potential candidate for nonlinear optical device fabrication [17–18].

3.6. Z-scan measurements

The optically transparent FA added KDP crystals were employed to collect the prefocal and post-focal open and closed aperture Z-scan data using Q-switched He–Ne laser operating at

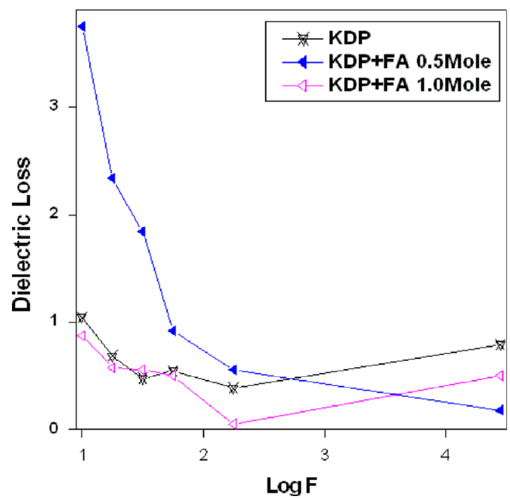

Fig. 14. Dielectric loss vs. Log *F*.

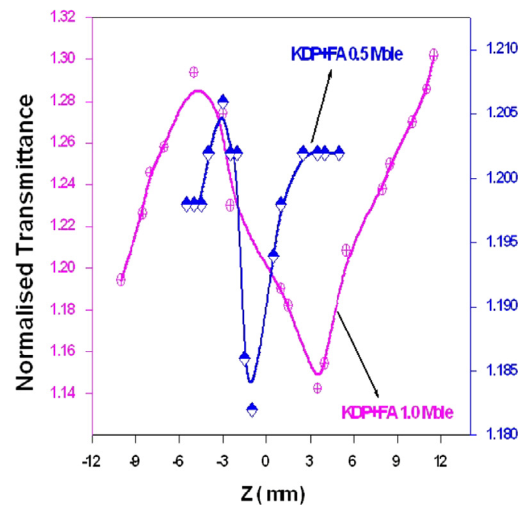

Fig. 15. Closed aperture curve.

Table 3
Spectral resolution of Z-scan setup.

Laser beam wavelength (λ)	632.8 nm
Lens focal length (f)	12 cm
Optical path distance (Z)	115 cm
Spot-size diameter in front of the aperture (ω_a)	1 cm
Aperture radius (r_a)	4 mm
Incident intensity at the focus (Z=0)	3.13 MW/cm^2

632.8 nm. The spectral resolution of the Z-scan setup used in present study is discussed in Table 3. The studied crystals were translated with the laser beam intended to focus on a crystal through a convex lens which causes the spatial distribution of temperature at the crystal surface due to localized absorption of incident energy. As the sample is translated along the *Z* direction the alternation in intensity evidences the change in refractive index pre and post the focal point (Z=0). The difference between the maximum value of peak and valley transmission (ΔT_{p-v}) is evaluated as follows:

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}|\Delta\phi| \quad (1)$$

where $S=[1-\exp(-2r_a^2/\omega_a^2)]$ is the aperture linear transmittance, r_a is the aperture radius and ω_a is the beam radius at the aperture. The nonlinear refractive index was calculated as follows:

$$n_2 = \frac{\Delta\phi}{KI_0L_{eff}} \quad (2)$$

where $K=2\pi/\lambda$ (λ is the laser wavelength), I_0 is the intensity of the laser beam at the focus, $L_{eff}=[1-\exp(-\alpha L)]/\alpha$, is the effective thickness of the sample depending on linear absorption coefficient (α) and L is thickness of the sample. The nonlinear absorption coefficient (β) of FA added KDP crystals is evaluated as shown below

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0L_{eff}} \quad (3)$$

where ΔT is the one valley value at the open aperture Z-scan curve. The real and imaginary parts of nonlinear susceptibility are calculated using the relations depicted as follows:

$$\text{Re}\chi^{(3)}(\text{esu}) = 10^{-4}(\varepsilon_0C^2{n_0}^2n_2)/\pi(\text{cm}^2/\text{W}) \quad (4)$$

$$\text{Im}\chi^{(3)}(\text{esu}) = 10^{-2}(\varepsilon_0C^2{n_0}^2\lambda\beta)/4\pi^2(\text{cm/W}) \quad (5)$$

$$\chi^3 = \sqrt{(\text{Re}\chi^3)^2+(\text{Im}\chi^3)^2} \quad (6)$$

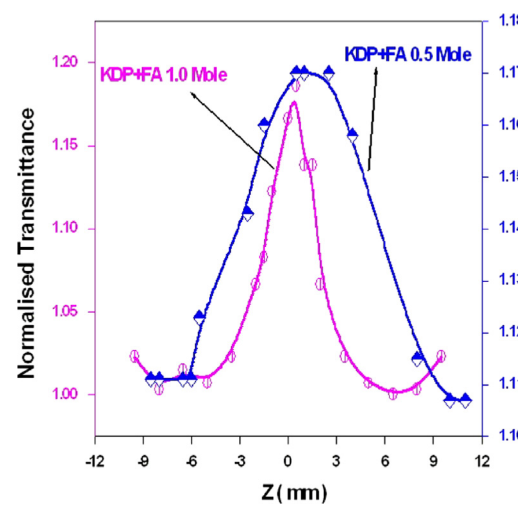

Fig. 16. Open aperture curve.

where ε_0 is the vacuum permittivity, n_0 is the linear refractive index of the sample and c is the velocity of light in vacuum. The variation in index of refraction can be evaluated from the closed aperture transmittance curve. The peak-to-valley transmission configuration cited in Fig. 15 interprets the self-defocusing nature of 0.5 and 1 mol% FA added KDP crystals. The negative index of refraction is ascertained with addition of FA indicating the prominence for optical limiting devices and laser stabilization [19]. The saturation absorption (SA) or the reverse saturation absorption (RSA) phenomenon identifies the potential absorptive nonlinearity of the material subjected to open aperture transmission data. The open aperture transmission data shown in Fig. 16 assists the FA added crystals with effective nonlinear absorption coefficient (β). The β values of 0.5 and 1 mol% FA added KDP crystals are found to be 1.15×10^{-7} cm/W and 1.16×10^{-7} cm/W. Thus nonlinear absorption coefficient marginally decreases with increasing concentration of FA. The large quantitative nonlinear susceptibility is of vital importance as it induces higher polarizing innate characteristic to material [20]. The third order nonlinear susceptibility (χ^3) of FA added crystals was found to be of the order 10^{-7} esu which is appreciably larger than pure KDP and KBBF crystal [20–21]. The nonlinear optical properties are influenced by intrinsic defects i.e. oxide of phosphorous and π-electron cloud of FA leading to enhanced values of third order nonlinear susceptibility [22–23]. The high nonlinearity and diverse optical device

Table 4
Nonlinear optical parameters.

FA concentration in KDP	$n_2 \times 10^{-18}$ cm^2/W	$\beta \times 10^{-7}$ cm/W	$\chi^3 \times 10^{-7}$ esu	FOM
KDP+FA 0.5 mol%	−2.23	1.15	3.96	327
KDP+FA 1 mol%	−1.41	1.16	3.81	522

suitability of the grown crystals can be explored via figure of merit (FOM=$\beta\lambda/n_2$) [24]. The higher FOM achieved with increasing FA concentration extends the scope of grown crystals for optical switching and photonics applications [23–24]. The improved nonlinear optical parameters achieved with increasing concentration of FA are discussed in Table 4.

4. Conclusion

The grown formic acid (FA) added KDP crystals showed improved electro-optic properties and effective nonlinear behavior with increasing FA concentration. The XRD study confirms the tetragonal structure with slight change in cell parameters of FA added crystals. The presence of different functional groups was confirmed by FT-IR spectral analysis. The increased FA concentration favored high optical transparency in the entire range of visible spectrum. The optical band gap of 1 mol% FA added KDP is found to be 5 eV. The lower dielectric constant and dielectric loss are achieved with high FA concentration in KDP. The SHG efficiency of KDP was found to be enhanced with addition of FA and is 1.13 times greater than KDP for 1 mol% of FA. Third order nonlinear behavior of grown crystals was ascertained by the Z-scan technique at 632.8 nm. The influential self-defocusing nature and large FOM values empowers the FA added KDP crystals with enticing qualities for applications in laser stabilization and photonics device fabrication. All studies indicate that FA added KDP crystals are promising NLO materials for lasers and integrated optical applications.

Acknowledgments

The authors are thankful to the Department of Science and Technology (DST/SR/S2/LOP-22/2010), and University Grants Commission (UGC/41–591/2012/SR), New Delhi, for financial assistance. One of the authors (Mohd Anis) is thankful to Prof. Sastikumar, Department of Physics, NIT, Tiruchерapalli for extending the Z-scan measurement facility.

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