Optical Materials xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Optical Materials

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

# Exploring the influence of carboxylic acids on nonlinear optical (NLO) and dielectric properties of KDP crystal for applications of NLO facilitated photonic devices

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ARTICLE INFO

*Article history:*
Received 24 January 2015
Received in revised form 27 April 2015
Accepted 28 April 2015
Available online xxxx

*Keywords:*
Dielectric studies
Nonlinear optical materials
SHG efficiency
Z-scan technique

ABSTRACT

The aim of present investigation is to assess the impact of oxalic acid (OA) and maleic acid (MA) on nonlinearity (second and third order) and dielectric behavior of potassium dihydrogen phosphate (KDP) crystal by means of SHG efficiency test, Z-scan analysis and dielectric studies respectively. The enhancement in SHG efficiency of OA and MA doped KDP crystal has been confirmed by means of Kurtz–Perry powder test technique. The close and open aperture Z-scan technique has been employed to study the nature and origin of improved third order NLO behavior of doped KDP crystals at 632.8 nm. The magnitude of third order nonlinear susceptibility ($\chi^3$), nonlinear refraction ($n_2$), nonlinear absorption coefficient ($\beta$) and figure of merit (FOM) of doped KDP crystals has been calculated using the Z-scan transmittance data to explore the suitability of crystals for distinct laser assisted applications. The dielectric constant and dielectric loss of pure, OA and MA doped KDP crystals were measured at different temperatures by means of dielectric studies.



## 1. Introduction

Potassium dihydrogen phosphate (KDP) is an excellent nonlinear optical (NLO) crystal with high growth rate and optical homogeneity owing to which it has wide demand for applications in UV-tunable laser systems, frequency conversion and optical data storage devices, laser based imaging and remote sensing techniques, industrial photonics and optoelectronics devices [1]. To find the exclusive utility of material for NLO assisted photonics and high frequency sensitive laser pulse applications the information of molecular arrangement and nonlinear processes involving SHG coefficient, laser induced self-focusing/defocusing tendency, nonlinear absorption coefficient, magnitude of nonlinear susceptibility (second and third) and figure of merit of single crystal is of vital importance. KDP is a well known technological crystal in which the predominant second order nonlinear optical (NLO) response of KDP crystal is majorly attributed to the phosphate ($PO_4$) group and the magnitude of SHG efficiency coefficient ($d_{36}$) of KDP crystal is reported to be 0.39 pm/V [2]. KDP exhibits interesting third order NLO behavior foreshowing the positive refraction nonlinearity (self focusing tendency) and the magnitude of nonlinear cubic susceptibility ($\chi^3$) of KDP crystal is $3.72 \times 10^{-14}$ esu and $2.04 \times 10^{-14}$ esu at 1064 nm and 532 nm, respectively [3]. In recent studies the successful attempt has been made to promote the nonlinear optical and dielectric behavior of KDP crystal by use of carboxylic acid (formic acid (FA)) as an additive. It has been explored that the doping of 0.5 and 1 mol% FA has significantly enhanced the SHG efficiency and cubic nonlinear susceptibility ($\chi^3$) of KDP crystal [4]. At the same time, the role of other carboxylic acids in upgrading the NLO behavior (second and third order) of KDP crystal has not been studied by any researcher. The organic substituent offer better photochemical stability and more accentric molecular alignment to host material. Oxalic acid (OA) and maleic acid (MA) belong to the family of carboxylic acids that might offer wide bonding network for itinerancy of π-electrons which is the foremost requirement for improving the NLO properties and the electronic response time of single crystal [5].

This manuscript is focused to investigate the effect of additives OA and MA on NLO and dielectric performance of KDP crystal. The investigation has been accomplished by means of SHG efficiency

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http://dx.doi.org/10.1016/j.optmat.2015.04.064
0925-3467/

test, Z-scan analysis and dielectric studies to define the effective utility of doped KDP crystals for distinct NLO assisted integrated optic and photonic device applications.

## 2. Experimental procedure

The high purity readily available KDP salt was gradually dissolved in deionized water at room temperature until the supersaturated solution of KDP was obtained. The calculated amount of 1 mol% of OA and MA was added to the supersaturated solution of KDP and allowed to stir with constant speed for four hours. The homogeneously doped KDP solutions were filtered in the separate beakers using the standard Whatman No. 1 filter paper and kept for slow solution evaporate in a constant temperature bath at 38 °C (±0.01 °C). The optical quality OA and MA doped KDP single crystals grown in a period of 8–10 days are shown in Fig. 1. The purity of the grown crystals has been achieved by repetitive recrystallization process.

## 3. Results and discussion

### 3.1. Second order nonlinear optical studies

The frequency doubling phenomenon of pure and doped KDP crystal materials has been determined at 1064 nm using the standard Kurtz–Perry powder technique [6]. The NLO effects in crystal system are highly expressive owing to accentric structural orientation and high delocalization tendency of charges that make the molecule more polarized when exploited to high intensity optical field [5]. For SHG analysis, the good quality pure and doped KDP single crystals were powdered to micro granules of even size and sieved in a microcapillary tube of uniform bore. The prepared samples in microcapillary tube were photoexcited by the Gaussian beam of Q-switched Nd:YAG laser (1064 nm, 8 ns, 10 Hz, 1.8 mJ pulse$^{-1}$). The emission of intense green light at the output window confirmed the NLO behavior of grown crystal compounds. The corresponding output signals of the samples were collected through the photomultiplier tube and the recorded voltages were displayed on the digital oscilloscope. The SHG output voltage of reference material KDP is found to be 75 mV while the output voltage of OA and MA doped KDP crystal sample is 106 mV and 137 mV respectively. The high SHG efficiency response in doped KDP crystal materials might have been observed due to the predominant photoinduced effect of oxide of phosphorous in KDP [4] and the key role of dopants in enhancing the SHG efficiency is governed by the directional nature of extensive H-bonding network which offers modified noncentrosymmetric molecular alignment and increased intermolecular charge transfer [7]. The materials of doped KDP crystals with high nonlinear response are excellent for SHG device applications. The SHG efficiencies of grown crystals are discussed in Table 1.

**Table 1**
SHG efficiencies of KDP crystals doped with organic acids.

| Crystal | SHG efficiency |
|---|---|
| KDP [Present study] | 1 |
| KDP + MA 1 mol% [Present study] | 1.82 |
| KDP + OA 1 mol% [Present study] | 1.41 |
| KDP + FA 1 mol% [4] | 1.13 |
| KDP + FA 0.5 mol% [4] | 1.09 |

### 3.2. Third order nonlinear optical studies

The study of laser assisted third order NLO properties is of vital importance to find the suitability of crystals for designing biomedical, photonics and optical parametric oscillator devices operative in femtosecond regime [8]. The impression of organic acids on third order nonlinearity of KDP crystals has been extensively studied by means of open and closed aperture Z-scan technique developed by Sheik-Bahae et al. [9]. In present investigation the Z-scan studies of the crystals has been performed using the He–Ne laser operating at 632.8 nm and the influential parameters of the Z-scan setup are detailed in Table 2.

To analyze the closed aperture Z-scan transmittance profile of doped KDP crystals, the individual crystal sample was focused by the intense Gaussian beam of He–Ne laser aligned via convex lens. The crystal was gradually translated pre and post the focus ($Z = 0$) point and the path dependent transmitted intensity offered by the crystal was recorded through the closed aperture of optical detector placed at far field. The closed aperture Z-scan transmittance curve of OA and MA doped KDP crystal is shown in Fig. 2a and b respectively. It reveals that OA and MA doped KDP single crystals show a promising nonlinear refraction (NLR) with a transmittance phase shift of valley to peak profile about the focus, indicating the origin of positive NLR ($n_2$) which is the characteristic property of material inheriting self focusing tendency [10]. The spatial distribution and the localized absorption of highly repetitive incident optical field along the crystal surface are the principle effects

**Table 2**
Optical resolution of Z-scan setup.

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

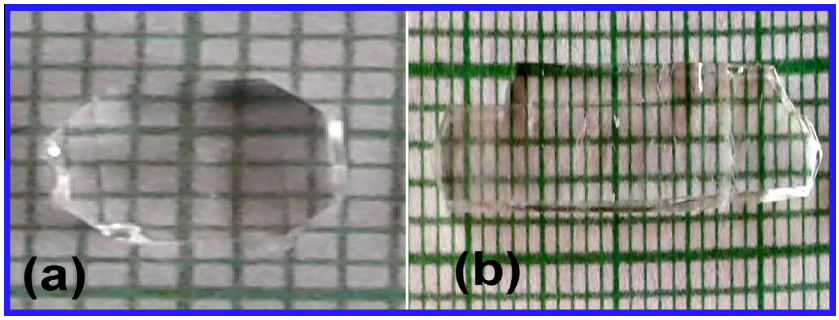


**Fig. 1.** KDP single crystal doped with (a) OA and (b) MA.

Please cite this article in press as: M. Anis et al., Opt. Mater. (2015), http://dx.doi.org/10.1016/j.optmat.2015.04.064

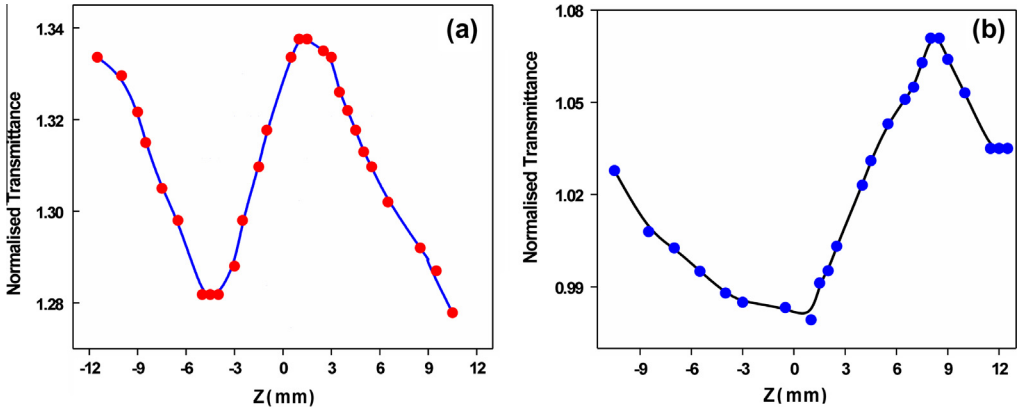


**Fig. 2.** Closed aperture Z-scan transmittance curve of KDP crystal doped with (a) OA and (b) MA.

responsive for refraction nonlinearity [11]. The peak to valley transmittance in terms of phase shift is given as [9],

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

where $S = [1 - \exp(-2r_a^2/\omega_a^2)]$ is the aperture linear transmittance, $r_a$ is the aperture radius and $\omega_a$ is the beam radius at the aperture. The magnitude of third order nonlinear index of refraction of studied crystals was determined using the relation [9],

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

where $K = 2\pi/\lambda$, $I_0$ is the beam intensity at the focus $Z = 0$, the effective thickness of the sample $L_{\text{eff}} = [1 - \exp(-\alpha L)]/\alpha$, depending on linear absorption coefficient ($\alpha$) and $L$ thickness of the sample. The decisive third order NLO parameters of the studied crystals are summarized in Table 3. It is noteworthy that the magnitude of $n_2$ of doped KDP crystal is superior to KDP crystal [4]. The high magnitude of positive NLR evidences the higher Kerr lens modelocking (KLM) ability of doped KDP crystal which is desirable parameter for designing the components for laser alignment and shorter pulse generation systems [12]. The increased Kerr lensing effect in doped KDP crystals is enforced due to trafficking of π-conjugated electron cloud in large molecular orbitals, formed by the linear superposition of carbon $P_z$ atomic orbitals in presence of optical field [13,14], this might have been observed due to inclusion of dopants OA and MA in KDP. The doped KDP crystals with impressive positive nonlinear refraction are exclusively suitable for optical limiting and optical switching devices [15,16].

**Table 3**
Nonlinear optical parameters.

| Dopants in KDP | $n_2$ (esu) | $\chi^3$ (esu) | $\beta$ (cm/W) | FOM |
|---|---|---|---|---|
| Pure KDP [3] | $2.34 \times 10^{-13}$ | $3.72 \times 10^{-14}$ | | |
| FA [4] | $-1.14 \times 10^{-5}$ | $3.81 \times 10^{-7}$ | $1.16 \times 10^{-7}$ | 522 |
| OA [Present] | $2.25 \times 10^{-5}$ | $1.90 \times 10^{-7}$ | $1.14 \times 10^{-7}$ | 322 |
| MA [Present] | $7.92 \times 10^{-5}$ | $2.13 \times 10^{-7}$ | $8.99 \times 10^{-8}$ | 718 |

The open aperture Z-scan transmittance curve of OA and MA doped KDP crystal is shown in Fig. 3a and b respectively. The increase in transmittance at the focus evidences the presence of saturable absorption (SA) in both the studied crystals. The prominent SA profile evidences the dominance of linear absorption coefficient in doped KDP crystals [17]. The nonlinear absorption coefficient ($\beta = 2(2)^{1/2}\Delta T/I_0L_{\text{eff}}$, where $\Delta T$ is the one valley value at the open aperture Z-scan curve) of doped KDP crystals are tabulated in Table 3. The third order nonlinear susceptibility of doped KDP crystals can be determined using the following equations [9],

$$\text{Re}\chi^{(3)}\ (\text{esu}) = 10^{-4}(\varepsilon_0 C^2 n_0^2 n_2)/\pi\ (\text{cm}^2/\text{W}) \quad (3)$$

$$\text{Im}\chi^{(3)}\ (\text{esu}) = 10^{-2}(\varepsilon_0 C^2 n_0^2 \lambda\beta)/4\pi^2\ (\text{cm/W}) \quad (4)$$

$$\chi^3 = \sqrt{(\text{Re}\chi^3)^2 + (\text{Im}\chi^3)^2} \quad (5)$$

where $\varepsilon_0$ is the vacuum permittivity, $n_0$ is the linear refractive index of the sample and $c$ is the velocity of light in vacuum. The calculated values of cubic susceptibility ($\chi^3$) of doped KDP crystals are higher than KDP crystal (see Table 3). It signifies that the doped KDP crystals show higher polarizing nature when interacted with intense

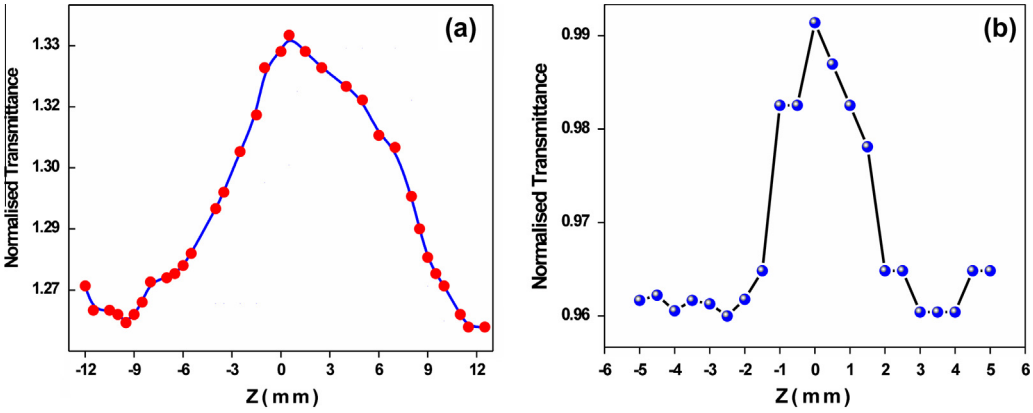


**Fig. 3.** Open aperture Z-scan transmittance curve of KDP crystal doped with (a) OA and (b) MA.

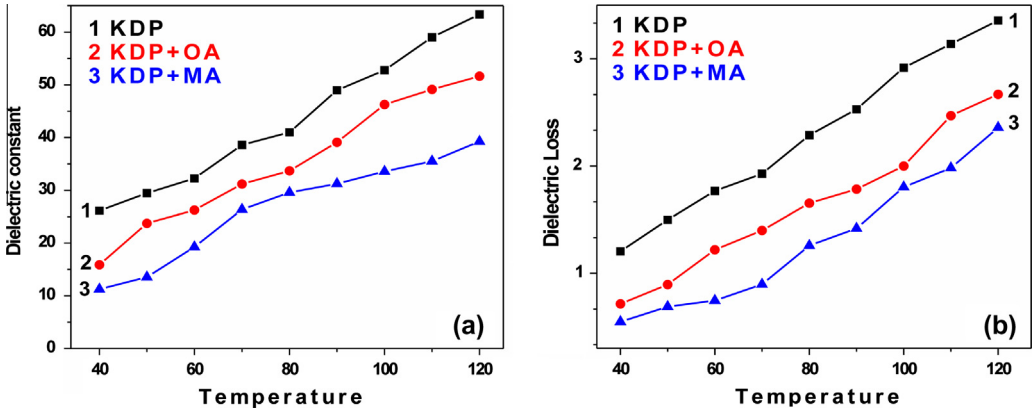


**Fig. 4.** Temperature dependent (a) dielectric constant and (b) dielectric loss.

laser radiation which inculcates high rate to the mobility of π-electron cloud [18]. The figure of merit (FOM = $\beta\lambda/n_2$) of doped KDP crystals has been determined in order to confirm the influence of $n_2$ or $\beta$ in crystal system. The larger values of FOM of doped KDP crystals indicate the dominance of $n_2$ over $\beta$ which suggests the effective usability of crystals for optical power limiting devices [19].

### 3.3. Dielectric studies

The dielectric studies of pure and doped KDP crystals (1.5 mm thickness) were investigated at 100 kHz frequency using the HIOKI 3532-50 LCR meter at different temperatures. To measure the dielectric constant and dielectric loss, good quality crystals were selected and to achieve high precision the parallel faces of the crystal samples were smoothly pasted by silver paste before the connections were made with the electrodes. The dielectric constant offered by pure and doped KDP crystals at different temperatures is shown in Fig. 4a. It confirms that the dielectric constant of all the studied crystals increases with increase in temperature due to active polarizing ability of the material at higher temperatures. The intrinsic defects and polarization effects (ionic, electronic, dipolar and space charge) largely contribute to the dielectric constant of the materials at the same juncture electronic frequency and temperature variation also play an important role [20]. It is notable that there is significant fall in magnitude of dielectric constant of KDP crystal with addition of dopants OA and MA respectively. In accordance to Miller's rule the lower dielectric constant of material is vital parameter for enhancing the SHG efficiency coefficient of the crystal material [20], which is in tune with the high SHG results obtained for doped KDP crystals as shown in Table 1. The knowledge of loss of electromagnetic energy within the material medium is of prime importance for optical communication devices for which the variation of dielectric loss with respect to temperatures is shown in Fig. 4b. It is observed that the dielectric loss of doped KDP crystals is significantly lower than KDP. The lower dielectric loss of doped KDP crystals implies that the material has lower electrically active defect centers leading to high optical quality of crystal [21]. The lower dielectrics of doped KDP crystals is an excellent parameter for fabrication of devices essential for terahertz (THz) wave generators, broadband electro-optic modulators (EOM), field detectors, NLO, high-speed integrated photonics and microelectronics applications [5,22,23].

## 4. Conclusion

The OA and MA doped KDP crystals have been grown by slow solution evaporation technique. The Kurtz–Perry powder test confirmed the enhancement in second order NLO response of KDP crystal with dopants OA and MA. The SHG efficiency of OA and MA doped KDP crystal is found to be 1.41 and 1.82 times that of KDP crystal, respectively. The superior third order NLO behavior of doped KDP crystals has been verified by Z-scan analysis performed at 632.8 nm and the physical origin of observed NLO processes has been exclusively discussed. In closed aperture Z-scan analysis, owing to localized absorption of repetitive optical field the valley to peak phase transition profile infers the origin of positive NLR (self focusing tendency) in doped KDP crystals. The high magnitude of NLR of doped KDP crystals triggers the Kerr lens modelocking (KLM) effect, which holds strong significance while fabricating devices for laser alignment and shorter pulse generation systems. The dominance of linear absorption coefficient in crystal material leads to the SA in both the doped KDP crystals as evidenced in open aperture Z-scan analysis. The higher order of $\chi^3$ ($10^{-7}$ esu) implies the highly polarized nature of doped KDP crystals. The positive NLR, Kerr-lensing ability, larger $\chi^3$ and FOM of doped KDP crystals are attractive parameters for optical switching, optical limiting and optical sensing devices. The photoinduced intermolecular charge transfer through the hydrogen bonding network of dopant carboxylic acids is the elementary factor causing the enhancement in NLO behavior of doped KDP crystals. The dielectric constant and dielectric loss of doped KDP crystals is lower than KDP crystal which implies the high optical quality of crystal with fewer defects. The lower dielectrics are thus desirable for designing EOM and microelectronics devices. Amongst the doped crystals MA doped KDP crystal exhibited superior NLO and dielectric properties. All above studies infers that organic acids (OA and MA) play decisive role in advancing the NLO and dielectric properties of KDP crystal and these parameters are practically advantageous for NLO facilitated ultrafast photonic devices.

## Acknowledgements

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. Author Mohd Anis is thankful to Prof. Sastikumar, Department of Physics, NIT, Tiruchirappalli for extending the Z-scan measurement facility. Authors are thankfull to Dr. P.K. Das, IISc Bangalore for SHG test.

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