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Influence of tartaric acid on linear-nonlinear optical and electrical properties of KH_2PO_4 crystal

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A B S T R A C T

KH_2PO_4 (KDOP) is widely demanded technological crystal for applications in laser driven photonic devices. Therefore, present article is focused to investigate the effect of tartaric acid (TA) on laser induced nonlinear optical properties of KDOP crystal. The optically transparent TA doped KDOP crystal of size $15 \times 10 \times 04$ mm^3 has been grown by slow solvent evaporation technique at 35 °C. The structural analysis of pure and TA doped KDOP crystal has been achieved by means of single crystal X-ray diffraction technique. The functional groups of TA doped KDOP crystal has been identified by means of Fourier transform infrared spectral analysis. The UV–visible studies have been performed to determine the optical transparency and evaluate the linear optical constants of pure and TA doped KDOP crystal. The Kurtz-Perry test has been employed to confirm the frequency doubling phenomenon of crystal and the SHG efficiency of TA doped KDOP crystal is found to be 5.68 times higher than that of standard KDP material. The Z-scan technique has been employed to explore the third order nonlinear optical (TONLO) refraction (n_2), absorption (β) and susceptibility (χ^3) of pure and TA doped KDOP crystal at 632.8 nm. The TA facilitated optical switching in TONLO response of KDOP crystal is found to be an interesting effect to examine. The laser damage threshold of TA doped KDOP crystal has been determined at 1064 nm using the Nd:YAG laser. The comparative electrical analysis on pure and TA doped KDOP crystal has been accomplished by means of dielectric and photoconductivity characterization studies.

1. Introduction

The recent path breaking developments in nonlinear optical (NLO) photonic crystals offering excellent features has opened new vendors for designing and modeling high-end telecommunication, optical modulation, optoelectronics and optical switching devices [1–3]. The known NLO crystals currently grown on large scale for solid-state laser applications are β-BaB_2O_4 (BBO), LiB_3O_5 (LBO), KH_2PO_4 (KDP), $KTiOPO_4$ (KTP), $LiNbO_3$ (LNO) and NH_3PO_4 (ADP) [4]. It is fascinating at the same time worth mentioning fact that amongst all the crystals KDOP is the leading crystal which displays promising ferroelectric, piezoelectric, electro-optic and nonlinear optical response [5] also it is frequently utilized for manufacturing frequency convertors and optical switches for high power laser systems [6]. The advantageous factors that pronounce the superiority of KDOP crystal are easy bulk growth, high optical homogeneity, wide optical operating window, high nonlinear response and huge threshold to laser damage [7,8]. To discuss the optical device utility of crystal at high laser intensity the analysis of NLO phenomenon reinforced in KDOP crystal due to laser treatment are of huge importance. As a consequence of which, in current scenario the study of photoinduced NLO effects in KDOP crystal is rapidly flourished topic engaging large research fraternity throughout the globe to perform theoretical as well experimental investigations. The influence of crystal orientation on laser damage threshold (LDT) of KDP crystal has been explored [9]. The effect of TiO_2 nanoparticles on third order nonlinear optical and LDT properties of KDP crystal is found to be interesting and significant [10,11]. Very recently, our research group firstly introduced the idea of doping carboxylic acid in KDP crystal. The enhancing impact of several carboxylic acids namely formic acid [12], oxalic acid, maleic acid [13,14], citric acid [15] and salicylic acid [16,17] on UV–visible, second harmonic generation, third order nonlinear optical and dielectric properties of KDP crystal has been scrupulously analyzed. The carboxylic acids were found to be the potential dopants in order to raise the merit of optical performance of KDP crystal. The

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high impetus of carboxylic acid for tuning the very essential properties of KDP crystal motivated us to dope tartaric acid (TA) in potassium dihydrogen orthophosphate (KDOP) crystal. On the other hand the TA is potential π-bond dominant carboxylic acid which might offer enhanced charge transfer that triggers the nonlinear optical response in the material. Therefore, in present investigation the undoped and TA doped KDOP crystal has been comparatively analyzed by structural, UV–visible, Kurtz-Perry test, Z-scan, laser damage threshold, dielectric and photoconductivity characterization techniques to explore the possible usability of TA doped KDOP crystal for NLO facilitated device applications.

2. Experimental procedure

The readily available potassium dihydrogen orthophosphate (KDOP) was gradually dissolved in 100 ml of double distilled water till the saturated solution of KDOP was obtained at room temperature. The 0.5 mol of TA was precisely measured and slowly added to the saturated solution of KDOP so as to facilitate the homogeneous mixing of dopant throughout the saturated solution. The TA mixed KDOP solution was allowed to agitate on medium speed for 4 h and later filtered in a clean beaker using the membrane filter paper of 4 μm pore size. The filtered solution was kept in an isolated vibration free constant temperature bath to allow the slow solvent evaporation at 35 °C. The TA doped KDOP crystals were harvested and the recrystallization process was adopted till the good quality crystals were obtained. Optically transparent TA doped KDOP (TA-KDOP) single crystal of dimension 15 × 10 × 04 mm^3 (Fig. 1) was harvested after third recrystallization in 10 days.

3. Results and discussion

The single crystal X-ray diffraction (XRD) technique has been employed to determine the structural parameters of grown crystals using the Enraf Nonious CAD4 single crystal X-ray diffractometer. The determined crystallographic data is given in Table 1. The analysis of XRD data reveals that the dopant has significant impact on lattice dimensions of KDOP crystal however the crystal system and space group remains unaltered. The structure of grown crystals is found to be tetragonal. The slight variations in unit cell dimensions and the volume confirms the successful influence of dopant TA in KDOP crystal.

The Fourier transform infrared (FTIR) analysis of TA-KDOP single crystal has been performed in the range of 600–4000 cm^{-1} using the Bruker Alpha ATR spectrophotometer to confirm the functional groups present. The recorded transmittance FTIR spectrum is shown in Fig. 1b. The absorption observed at 660 cm^{-1} is contributed by the C–O–H bending vibration. The P–O–H bond stretching vibration is evident at 1024 cm^{-1}. The O=P–OH stretching vibration associated with KDOP crystal is attributed at 1532 cm^{-1}. The characteristic peak of C=O stretching vibration is evident at 1704 cm^{-1}. The P–H bond vibration is attributed at wavenumber 2323 cm^{-1}. The O–H bond vibration associated with grown crystal is evident at 2825 cm^{-1}, 2925 cm^{-1}, 3604 cm^{-1}, 3730 cm^{-1} and 3860 cm^{-1}. The analysis of FTIR spectrum confirms the coordination and inhabitation of TA in KDOP.

Table 1
Crystallographic data.

Crystal	a (Å)	b (Å)	c (Å)	V $(Å)^3$	Structure	Space group
KDOP	7.472	7.472	6.951	388.07	Tetragonal	I42d
TA-KDOP	7.476	7.476	6.967	389.38	Tetragonal	I42d

The crystal with wide operative range in visible spectrum serves huge advantage and extends its liability for distinct optical device applications. This necessitates the in-depth analysis of linear optical constants of the given material in visible region for which the pure and TA-KDOP crystals of 2 mm thickness have been scanned in the range of 200–900 nm using the Shimadzu UV-2450 spectrophotometer. The spectrophotometer was configured to medium scan speed with slit width of 1 nm and scan interval of 0.5 nm. In a crystal medium the transmission of optical signal is controlled by several intrinsic and extrinsic factors namely (a) the orientation of crystal (optical anisotropy along the planes), (b) optically active functional units (bonding scheme) and (c) structural/crystalline defects (voids, inclusions, impurities, pits, striations) [18–20]. The transmittance spectrum of pure and TA-KDOP crystal is shown in Fig. 2a. It is observed that the transmittance attributed by KDOP crystal is 75% while the transmittance offered by TA-KDOP crystal is 83%. The observed enhancement in transmittance of TA-KDOP crystal indicates that presence of TA facilitates elimination of defect centers which minimizes the internal absorption/scattering of light in crystal medium and offers more optical homogeneity to crystal. The crystals such as TA-KDOP that exhibit high optical transparency are vital candidates for applications in UV-tunable lasers and transmission of SHG signal [21,22]. Further identification of crystal liability for photonic device applications can be claimed by evaluating the optical constants of the crystal. The transmittance data is the source for the formulae available in literature [23], which allows us to evaluate the refractive index and reflectance of the crystals. The variation in refractive index and reflectance with respect to wavelength are shown in Fig. 2b and c. It reveals that the refractive index and reflectance of KDOP crystal significantly decreases later to doping of TA. As low reflectance

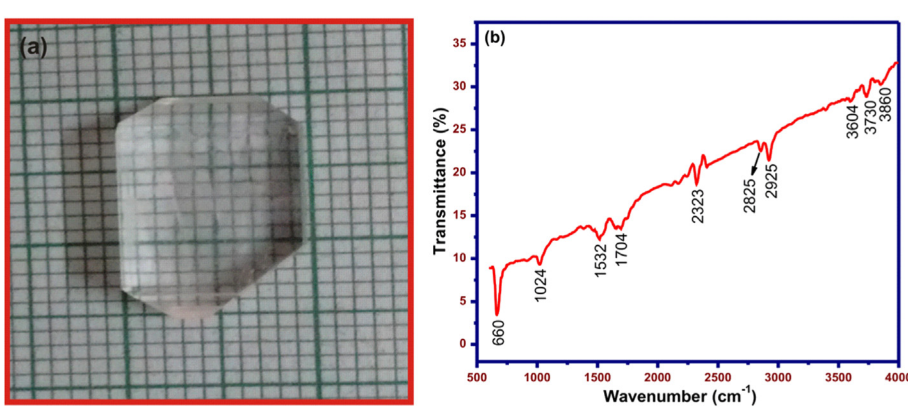

Fig. 1. (a) Single crystal of TA-KDOP (b) FTIR spectrum of TA-KDOP.