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Growth, structural, UV–visible, SHG, mechanical and dielectric studies of bis-thiourea zinc chloride doped KDP crystal for NLO device applications

Y. B. Rasal[1], M. Anis[1,2], M. D. Shirsat[3] and S. S. Hussaini*[1]

Optically transparent $11\times10\times4$ mm^3 bis-thiourea zinc chloride (BTZC) doped potassium dihydrogen phosphate (KDP) crystal has been grown by slow evaporation solution technique. The cell parameters of the grown crystal have been determined by single crystal X-ray diffraction analysis. The incorporation of BTZC in KDP crystal has been qualitatively analysed by FT-IR spectral analysis. The optical transparency and vital optical constants of BTZC doped KDP single crystals have been evaluated in the range of 200–900nm. The mechanical behaviour of pure and doped KDP crystals has been investigated under the Vickers microhardness studies. The dielectric parameters of grown crystal have been investigated within the frequency range of 10–100KHz. In Kurtz–Perry powder test, the second harmonic generation (SHG) efficiency of BTZC doped KDP crystal is found to be 1.65 times that of KDP material.

Keywords: Crystal growth, Optical studies, SHG efficiency, Mechanical studies, Dielectric studies

Introduction

In the emerging technological era, the non-linear optical (NLO) phenomena plays a crucial role, which necessitated the rapid pace in development of efficient NLO crystals as they have extended scope in photonics, optoelectronics, laser frequency conversion and integrated optic device applications.[1] The potassium dihydrogen phosphate (KDP) crystal holds a strong technological impetus owing to its high NLO response and excellent optical homogeneity. The attempts have been made in past to uplift the properties of KDP crystal either by doping various impurities or by growing crystal using specific crystal growth technique.[2,3] Several researchers have reported major enhancement in UV-visible and SHG efficiency of KDP crystal owing to addition of variety of metallic impurities namely Li, Ca, Ce and V.[4] It is explored that the mechanical properties of KDP crystal have been successively promoted owing to incorporation of dyes such as; rhodamine, amaranth, methyl orange and violet crystal dye.[5,6] An extensive research has been performed to improve the overall performance of KDP crystal by adding selective quantity of amino acid dopants.[7–9] The literature evidences doping of purely organic and inorganic impurities in KDP crystal. However, not a single trace report is available in literature on doping of semi-organic particularly the organo-metallic materials in KDP crystal. The organo-metallic complex bis-thiourea zinc chloride (BTZC) offers high photo-chemical stability, highly non-centrosymmetric network, wide optical transparency, high NLO response, high mechanical strength and good thermal stability.[10] In this study, successful attempt has been made to enhance the qualities of KDP crystal by doping a selected quantity of BTZC to achieve a desired crystal, which can be exploited for device fabrication. The BTZC doped KDP single crystal has been grown and characterised by single crystal XRD, UV-visible, SHG, microhardness and dielectric studies.

Experimental procedure

The BTZC salt was synthesised by stirring the mixture of 2 : 1 molar ratio of zinc chloride and thiourea in deionised water for four hours[10]. The purity of BTZC salt was achieved by successive recrystallisation method. The high purity KDP salt was dissolved in double distilled deionised water until the supersaturation was achieved. The measured quantity of 0.1 and 0.2mol.-% BTZC was separately added to the supersaturated solution of KDP taken in two beakers. The solutions were allowed to agitate for 6 hours on magnetic stirrer to acquire the homogeneous doping. These doped solutions were filtered and kept for slow evaporation in a constant temperature bath of accuracy ±0.01°C. As the SHG efficiency of 0.2mol.-% BTZC doped KDP crystal was found to be higher, the single crystal of same material was grown at 38°C (±0.01°C) within the period of 12days. The photograph of optical quality BTZC doped KDP (BTZC–KDP) crystal of dimension $11\times10\times4$ mm^3 is shown in Fig. 1.

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[1] Crystal Growth Laboratory, Department of Physics, Milliya Arts, Science and Management Science College, 431122, Beed, Maharashtra, India
[2] Department of Physics, Sant Gadge Baba Amravati University, 444602, Amravati, Maharashtra, India
[3] Intelligent Materials Research Laboratory, Department of Physics, Dr Babasaheb Ambedkar Marathwada University, 431005, Aurangabad, Maharashtra, India

*Corresponding author, email shuakionline@yahoo.co.in

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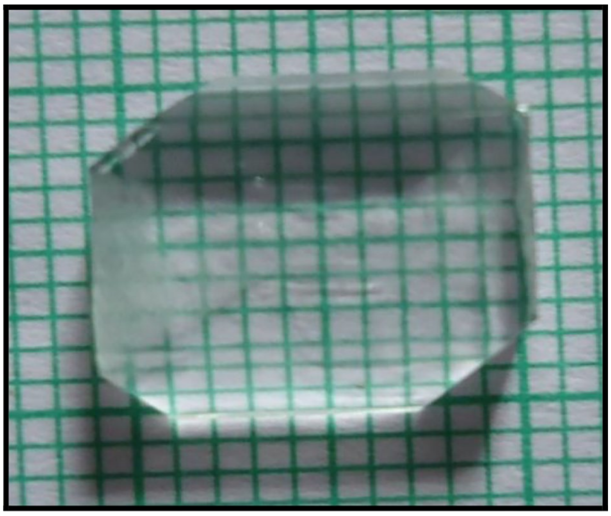
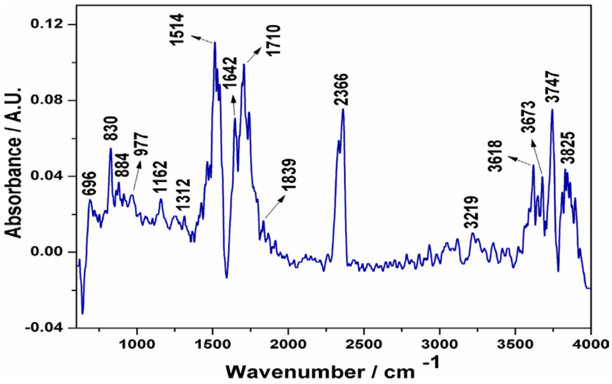
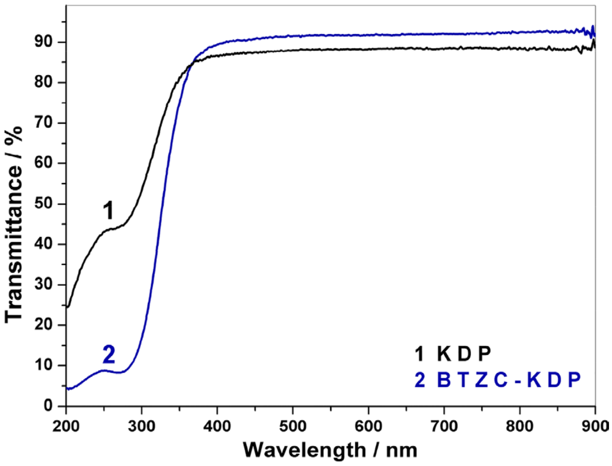


1 Photograph of bis-thiourea zinc chloride (BTZC)–potassium dihydrogen phosphate (KDP) crystal



2 FT-IR spectrum of bis-thiourea zinc chloride (BTZC)–potassium dihydrogen phosphate (KDP) crystal



3 Transmittance spectrum

Results and discussion

Single crystal X-ray diffraction analysis

The pure and BZTC doped KDP crystals were subjected to single crystal X-ray diffraction (XRD) studies at room temperature using the Enraf Nonius CAD4-MV31 crystal X-ray diffractometer. From the single crystal XRD analysis, it is confirmed that the crystals belong to the tetragonal crystal system and the determined lattice parameter values are discussed in Table 1. The slight change in unit cell parameters confirm the lattice strain on KDP crystal reinforced owing to incorporation of dopant BTZC.

FT-IR spectral analysis

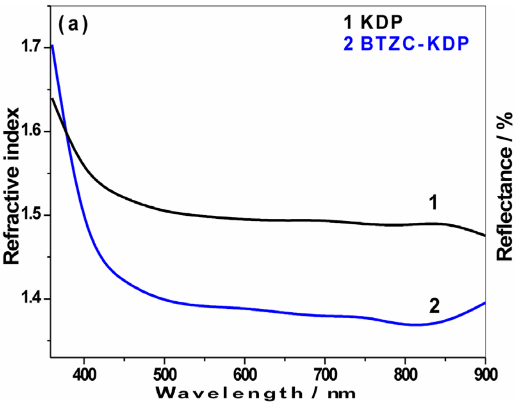
The incorporation of BTZC in KDP was qualitatively analysed by recording the FT-IR spectrum (Fig. 2) using Bruker α-ATR spectrophotometer. The absorption peak observed at 696cm^{-1} corresponds to the C=S stretching vibration of BTZC compound. The P–O–C symmetric bond stretching vibration is attributed at 830cm^{-1}. The P–H wagging is evidenced at wave number 977cm^{-1}. The N–C–N bond stretching vibration associated with BTZC is observed at 1162cm^{-1}. The C–N stretching vibration is observed at 1312cm^{-1}. The sharp absorption peak at 1514cm^{-1} corresponds to N–H bending vibration. The N=O bond stretching vibration is attributed at 1642cm^{-1}. The C=N–OH bond stretching vibration is observed at 1710cm^{-1}. The P–H stretching vibration is attributed at 2366cm^{-1}. The absorption peak at 3216 confirms the N–H stretching vibration. The peaks between 3600 and 4000cm^{-1} appears owing to O–H and N–H bond stretching vibrations.[11]

UV-visible studies

The pure and BTZC doped KDP single crystals of 2mm thickness were subjected to UV-visible study using the Shimadzu UV-2450 spectrophotometer (Slit width=2nm, Scan speed=medium, Data interval=0.5nm, Wavelength range=200–900nm) to assess the optical transparency. The recorded transmittance spectrum (Fig. 3) reveals that KDP crystal is optically transparent upto 88% while the increased transmittance of BTZC–KDP crystal is upto 92% in entire visible region. It is observed that the transmittance (T) of BTZC–KDP crystal sharply falls near 300nm, which is expressed owing to strong *n* to π* transition associated with nitro chromophore of BTZC.[12] The absence of defects and solvent inclusions reduces the density of scattering centres, which is the key factor resulting in enhancement of optical transparency and homogeneity of BTZC–KDP crystal.[13,14]The high optical transparency of BTZC–KDP crystal is most essential parameter for designing NLO and second harmonic generation devices.[13] The detail information of optical parameters of crystal helps to tune the resolution of various technological devices. The decisive optical constants, refractive index ($n=1/T+(1/T-1)^{1/2}$, Fig. 4*a*) and reflectance ($R=((1-n)/(1+n))^2$, Fig. 4*b*) of crystals have been scrutinised in visible region, which helps to identify distinguished technological device applications. It is observed that the refractive index

Table 1 Single crystal XRD data

Crystal	Cell parameters (Å)	Volume (Å)^3	Crystal system	Space group
Potassium dihydrogen phosphate (KDP)	*a*=*b*=7.44, *c*=6.94	384	Tetragonal	I-42d
Bis-thiourea zinc chloride (BTZC)–KDP	*a*=*b*=7.47, *c*=6.98	389	Tetragonal	I-42d



4 *a* Refractive index and *b* reflectance as a function of wavelength

Table 2 Second harmonic generation (SHG) analysis data

Dopants in potassium dihydrogen phosphate (KDP)	Output voltage (mV)	SHG efficiency
Pure KDP	114	1
0.1mol.-% BTZC	150	1.31
0.2mol.-% BTZC	188	1.65
1mol.-% Formic acid[3]		1.13
2mol.-% L-Arginine[7]		1.25
2mol.-% L-Alanine[7]		1.31
0.05mol.-% L-Histidine[8]		1.06

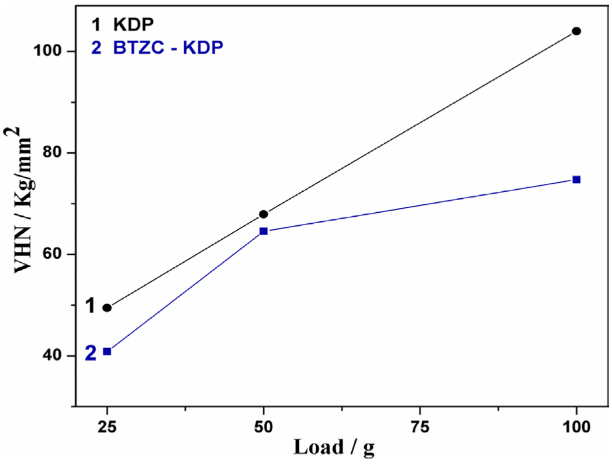
Table 3 Microhardness parameters along <001> plane

Crystal	H_v (Kg mm^{-2})	C_{11} (GPa)
Potassium dihydrogen phosphate (KDP)	73.85	33.89×10^5
Bis-thiourea zinc chloride (BTZC)-KDP	60.05	23.06×10^5

and reflectance of BTZC–KDP crystal are lower in entire visible region. The lower refractive index and reflectance of BTZC–KDP crystal pronounce its potential candidature for calibrating filters, resonators and reflectors, which are vital components of photonic devices.[15] The overall superior optical performance of BTZC-KDP crystal suggests its prominence for electro-optic modulation devices.[16]

SHG efficiency test

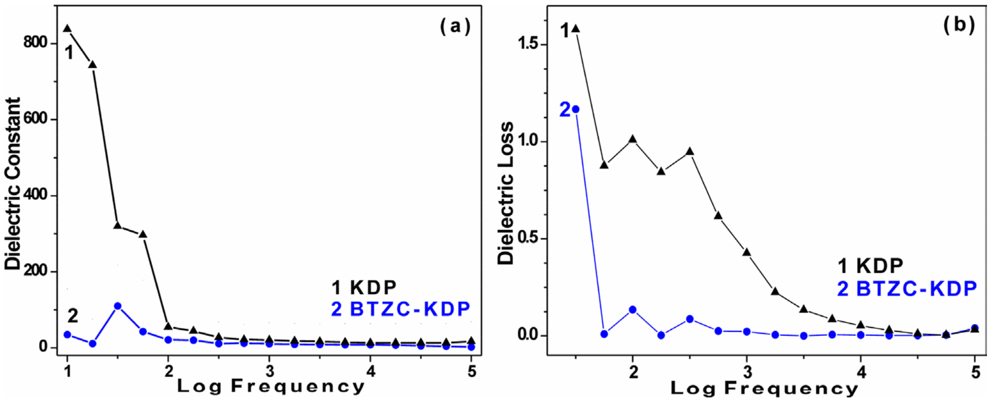
In order to confirm the effective frequency conversion efficiency of BTZC–KDP crystal, the standard Kurtz–Perry powder technique[17] has been employed using the Q-switched Nd:YAG laser delivering the input energy of 4.7mJ/pulse with the repetition rate of 10Hz and pulse duration 8ns. The single crystals of pure and BTZC doped KDP material were powdered to micro-granules and sieved in the microcapillary tube of uniform bore. The polarised beam of 1064nm was multishot on the prepared samples and the emergence of bright green light at the output window confirmed the successful SHG of 532nm. The recorded output voltages and SHG efficiency of grown crystals are shown in Table 2. It is observed that the SHG efficiency of 0.2mol.-% BTZC–KDP crystal is 1.65 times that of KDP crystal, which confirms its superiority over several crystals. In present study, the enhanced SHG efficiency of BTZC–KDP crystal originates owing to enhanced charge transfer through extended non-centrosymmetric crystalline chromophore and modified molecular alignment favoured by organo-metallic BTZC complex.[18]



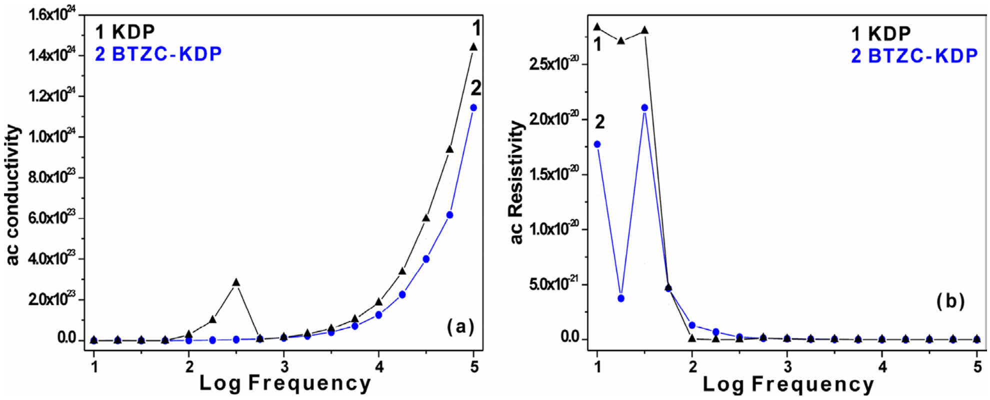
5 Load-dependent hardness.

Mechanical studies

The Vicker's hardness studies have been performed along <001> plane of pure and bis-thiourea zinc chloride (BTZC) doped potassium dihydrogen phosphate (KDP) crystal using the Shimadzu HMV-2T microhardness analyser. The hardness strength of pure KDP and BTZC doped KDP crystals was evaluated by applying load of 25, 50 and 100 g for a constant indentation duration of 5 s for all loads. The Vickers microhardness number (VHN) was calculated using formula,



6 Frequency dependent *a* dielectric constant and *b* dielectric loss



7 Frequency dependent *a* ac conductivity and *b* ac resistivity

H_v=1.8544 (P/d^2) Kg mm^{-2} (Table 3). Where, *P* is the applied load and *d* is the average diagonal length of the indentation mark.[19] The dependence of VHN on indented load is shown in Fig. 5 and it reveals that the VHN of both the crystals increases with increase in load satisfying the reverse indentation size effect theory. The low VHN values of BTZC–KDP crystal for each load justifie that the threshold stress required for nucleation of lattice dislocation is substantially lower than KDP, which indicates the softening impact of BTZC along <001> plane of KDP. The elastic stiffness coefficient ($C_{11}=H_v^{7/4}$) helps to scrutinise the interatomic bond strength between the consecutive atoms of the crystalline lattice.[20] The hardness parameters are most decisive pre-requisities for avoiding breakage/wastage of material during polishing and processing the crystals to exploit it to device fabrication.[13,21]

Dielectric studies

The dielectric studies of pure and BTZC–KDP crystal (2mm thickness) have been carried out within 10–100KHz frequency range using the Gwinstek-819 LCR cubemeter. The nature of dielectric constant ($\epsilon=Cd/\epsilon_o A$, where *C* is the capacitance, *d* is the thickness and *A* is the area of crystal sample) of crystals is depicted in Fig. 6*a*. The higher magnitude of dielectric constant in low frequency domain is contributed by electronic, ionic, dipolar and space charge polarisation mechanism while the lower saturated values of dielectric constant in high frequency domain indicates diminished polarisation activity, which favours fast alignment of molecular dipoles along the applied field.[22] As low dielectric constant material is demanded for device fabrication, the lower dielectric constant of BTZC–KDP crystal strongly suggests its utility for NLO, photonics, microelectronics, electro-optic and THz wave generation devices.[23] The Millers theory indicates that the material with lower dielectric constant exhibits enhanced SHG efficiency,[24] which is also positive in case of BTZC–KDP crystal. The extent of energy dissipation in the material medium can be determined by evaluating the nature of dielectric loss (Fig. 6*b*) of the crystal. The dielectric loss is primarily influenced by the defect density of the crystal system. The lower dielectric loss indicates that the BTZC–KDP crystal is of superior quality.[25] The nature of ac conductivity and ac resistivity of crystals is shown in Fig. 7*a* and *b*, respectively. The lower dielectrics of BTZC–KDP crystal is promising asset to be used in NLO devices.

Conclusions

Optically transparent 11 × 10 × 4mm^3 BTZC–KDP single crystal has been grown by slow evaporation solution technique. XRD studies confirmed that the dopant BTZC has slightly perturbed the unit cell parameters of KDP crystal retaining the tetragonal symmetry. The BTZC–KDP crystal exhibits optical transparency of 92% in entire visible region, which is 4% higher than KDP crystal. The lower refractive index and reflectance in visible region vitalise BTZC–KDP crystal, a potential material for various photonic devices. The SHG efficiency of BTZC–KDP crystal is 1.65 times that of KDP crystal material. Microhardness study revealed that the BTZC–KDP crystal obeys the reverse indentation size effect and its C_{11} is of magnitude 23.06×10^5 GPa. The lower dielectric constant and dielectric loss substantiate the good quality of BTZC–KDP crystal. The improved optical quality, high SHG efficiency, moderate mechanical stability and lower dielectric constant explore the extended scope of BTZC–KDP crystal for NLO, microelectronics, electro-optic and photonic device applications.

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