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The investigation of potassium tetra thiourea chloride on linear-nonlinear optical, electrical and mechanical properties of KDP crystal for NLO applications

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ABSTRACT
We aimed to investigate the influence potassium tetra thiourea chloride (PTTC) on optical, dielectric and thermal properties of potassium dihydrogen phosphate (KDP) crystals. It was found that by addition of PTTC SHG efficiency has been enhanced. In addition, third order nonlinear properties have been studied by open and close aperture Z-scan technique. The enhanced LDT of grown crystal is found to be 2.08 GW/cm^2. The dielectric response of grown crystal results lowers magnitudes. Thermal stability of grown crystal has been studied by TGA, DTA and DSC. The mechanical strength of doped crystals has been investigated by the Vickers microhardness studies and results are discussed.

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Optical studies; Z-scan; NLO; laser damage threshold; microhardness studies and dielectric studies

1. Introduction

The emerging trends in nonlinear materials (NLO) play very important role in the fields of optical communications, signal processing and optical storage devices. In the upcoming technological field, scope of NLO materials is widely extended in photonics, optoelectronic, laser frequency conversion and integrated optic device instrumentation. The NLO material plays very important role in the field of frequency conversion devices [1–3]. The Potassium dihydrogen phosphate is well known inorganic NLO material having good optical, dielectric and thermal behavior and plays vital role in the field of second harmonic generations and optoelectronics [4–5]. The high transparency in a region of the UV-visible spectrum and possibility of growing big single crystal with high growth rate are good experimental properties of KDP [6–8]. Thiourea is well known organic material having large dipole moment, when combines with metals forms noncentrosymmetric complex [9–13].

In literature, there is least work on thiourea metal complex doped KDP crystals; P. Kumaresan et al [14] have reported the effect of copper thiourea complex on KDP and our group has reported the optical, dielectric and mechanical behavior of bis thiourea zinc

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chloride and bis thiourea nickel nitrate doped KDP crystal [15–16]. The present investigation deals with structural, spectral, optical, thermal, mechanical and dielectric properties PTTC doped KDP crystal for frequency conversion and electro-optic device applications. Also in optical studies we are reporting Z-scan analysis and laser damage threshold study of thiourea metal complex doped KDP crystal.

2. Synthesis

The AR grade thiourea and potassium chloride were dissolved in the deionized water in the molar 4:1 ratio and the solution was well stirred for eight hours. Then the prepared solution was filtered and kept undisturbed for slow evaporation. The purity of Potassium tetra thiourea chloride (PTTC) salt was achieved by successive recrystallization. The 0.1 and 0.2 mol% PTTC was added in the saturated solution of KDP (AR grade). The added solution was allowed to stir for six hours to achieve homogeneous mixture of KDP crystal complex. The PTTC doped KDP solution was filtered in two different rinsed and cleaned beakers by whatmann filter paper. The prepared solutions were allowed to evaporate at room temperature to procure the respective salts. The purity of the salt was gained by successive recrystaliation using deionized water. The SHG efficiency of doped KDP was observed to be enhanced. The 0.2 M% PTTC doped KDP was harvested within two weeks of crystal size $11 \times 15 \times 5\ mm^3$ is as shown in Figure 1.

3. Results and discussion

3.1. Single crystal X-ray diffraction analysis

The pure and PTTC doped KDP crystals were subjected to single crystal X-ray diffraction (XRD) studies using Enraf Nonius CAD4-MV31 crystal X-ray diffractometer. From the

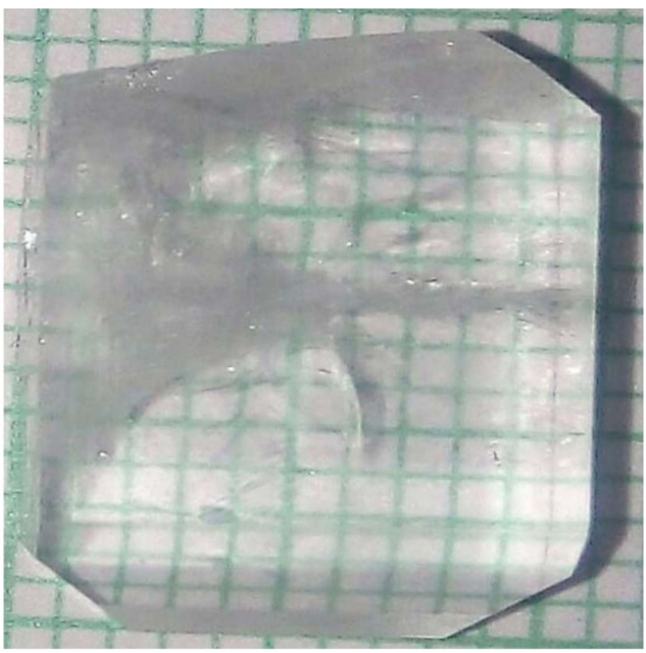

Figure 1. Photograph of 0.2 mol% PTTC doped KDP.

Table 1. Single crystal XRD data.

Crystal	Cell parameters (Å)	Volume (Å)^3	Crystal system
KDP	a = b = 7.44, c = 6.94	384	Tetragonal (I)
PTTC doped KDP	a = b = 7.48, c = 7.00	391	Tetragonal (I)

single crystal XRD analysis, it is confirmed that the crystal belong to the tetragonal crystal system and the determined lattice parameters values are discussed in Table 1. The slight change in unit cell parameters confirm the lattice strain on KDP crystal reinforced due to incorporation of dopant potassium tetra thiourea chloride [17].

3.2. FT-IR analysis

The Fourier transform infra red (FT-IR) spectrum of potassium tetra thiourea chloride doped KDP was recorded by using Bruker α-ATP spectrophotometer as shown in Figure 2. The Table 2 shows comparisons of FT-IR studies on pure and PTTC doped KDP crystals. The P-Cl stretching vibration at 693 cm^{-1} in pure KDP is shifted to at 670 cm^{-1}. The absorption peak observed at 785 cm^{-1} belongs to P-O-C stretching. The C-Cl bond stretching vibration associated with PTTC is observed at peak 841 cm^{-1}. The C=C stretching and NH_2 bending is attributed at 1526 and 1696 cm^{-1} respectively. The absorption peak at 2364 and 3678 cm^{-1} corresponds to Phosphorus acid, ester O-H stretching and O-H asymmetric stretching respectively in pure KDP are shifted to 2367 and 3674 cm^{-1}. The absorption observed at 3740 and 3848 cm^{-1}corresponds to O-H stretching [16, 18–19].

3.3. Optical studies

3.3.1. UV–visible studies

The Optical transparency of pure and PTTC doped KDP single crystal of thickness 2 mm is obtained by using Shimadzu UV-2450 spectrophotometer in the range 200 to 900 nm.

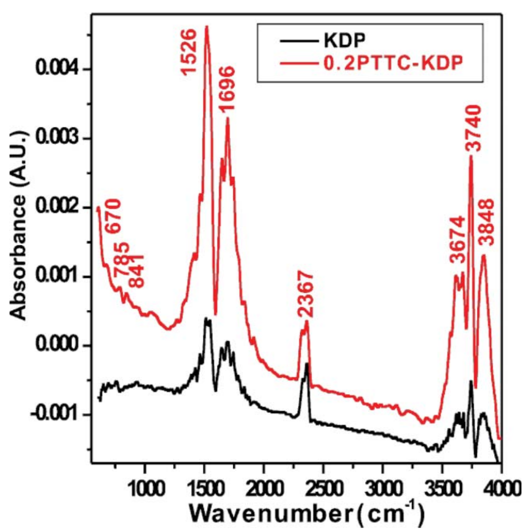

Figure 2. FT-IR spectrum of pure and doped KDP.

Table 2. Observed IR frequencies (cm^{-1}) of pure KDP and PTTC doped KDP.

Pure KDP	Doped KDP	Assignment
693	670	P–Cl stretching
—	785	P–O–C stretching
—	841	C-Cl Stretching
1532	1526	C=C stretching
1695	1696	NH_2 bending
2364	2367	Phosphorus acid and ester O–H stretching
3678	3674	O-H asymmetric stretching
3743	3740	O-H stretching
3841	3848	O-H stretching

The recorded transmittance spectrum is as shown in Figure 3(a), it reveals that PTTC doped KDP (89%) crystal is optically transparent than KDP (88%) in entire visible region with cutoff wavelength 300 nm. The enhanced optical transparency of PTTC doped KDP crystal shows prominence of material for designing NLO devices. The relation used to evaluate optical band gap is

$$E_g = 1240/\lambda \tag{1}$$

where, λ is the lower cut off wavelength [20]. From the transmittance spectrum value of λ was evaluated and found to be 242 nm for doped KDP. The magnitude of the band gap energy was found to be 5.12 eV for doped KDP crystal, which is desirable in NLO applications [8]. The propagation of light through crystal medium as refractive index is determined by using formula

$$n = [1/T + (1/T - 1)] \tag{2}$$

where, T is Transmittance. The reflectance is calculated by using formula

$$R = (n-1)^2/(n+1)^2 \tag{3}$$

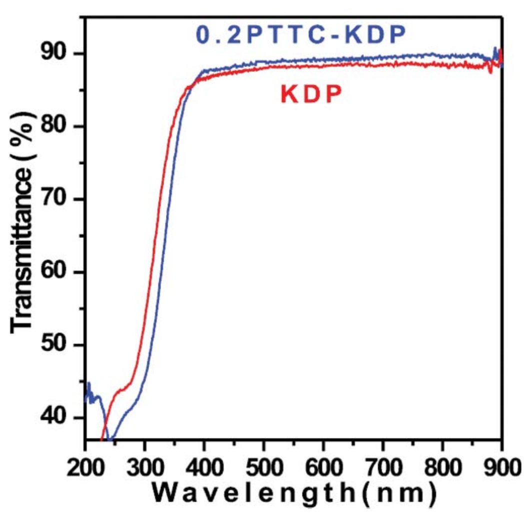

Figure 3. Transmittance spectrum.

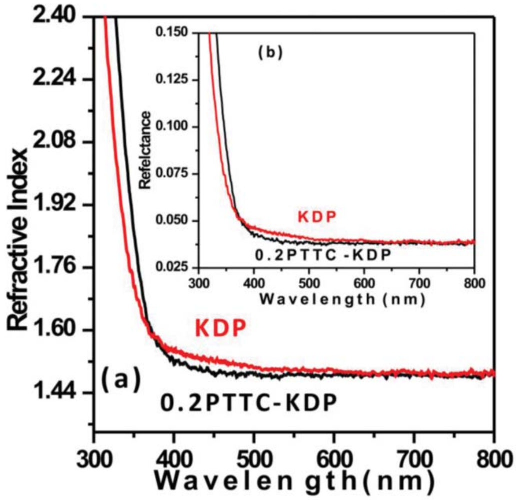

Figure 4. (a) Refractive index and (b) reflectance vs. wavelength.

The plots refractive index and reflectance vs. wavelength is as shown in Figure 4(a) and (b) respectively. The high transmittance, lower refractive index and reflectance in entire visible region are the most desirable properties for antireflection coating in solar thermal devices [20]. The optical conductivity ($\sigma_{op} = \alpha nc/4\pi$) increases with increase in photon energy shows grown crystal have applications in information processing and computing [21]. The graph of extinction coefficient and optical conductivity of 0.2 mol% PTTC doped KDP in response to photon to energy is depicted in Figure 5(a) and (b) respectively. The lower value of extinction coefficient and high value of optical conductivity confirms very less time response to electron ejection from surface of grown crystal. The lower value of extinction coefficient and higher optical conductivity suggest suitability of doped crystal in the conversion efficiency and integrated optical applications [22].

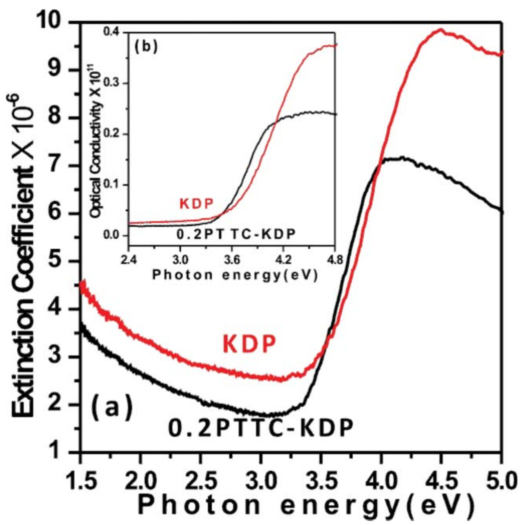

Figure 5. (a) Extinction coefficient vs. E and (b) optical conductivity vs. E.

Table 3. SHG analysis data.

Doped KDP crystal	SHG efficiency	Reference
0.5 mol% FA	1.09	[3]
1 mol% FA	1.13	[3]
0.1mol% PTTC	1.01	Present study
0.2 mol% PTTC	1.24	Present study
KDP	1.0	Present study

3.3.2. NLO studies

The Kurtz–Perry powder test [23] was performed to determine second harmonic efficiency of grown crystal. The crystals 0.1, 0.2 mol% PTTC doped KDP and pure KDP was powdered with a uniform particle size and then packed in a micro capillary of uniform bore and exposed to laser radiations. The powder sample was illuminated by Q switched Nd-YAG laser operating at 1064 nm having input beam energy of 4.7 mJ/pulse, repetition rate of 10 Hz and pulse width of 10 ns. The green light emission from the powdered sample at the output confirms the nonlinear behavior of the subjected samples. The measured output signals for 0.1 and 0.2 mol% doped KDP crystals were 116 mV and 141 mV, respectively and that of KDP was 114 mV. The 0.2 mol% PTTC doped in KDP has SHG efficiency 1.24 times higher than that of pure KDP crystal. The comparative study of second harmonic efficiency is shown in Table 3.

3.3.3. Z-scan studies

The third order nonlinear susceptibility is measured by using Z-scan experimental technique for 0.2 mol% PTTC doped KDP crystal. The crystal of low defects of thickness 0.6 mm is used to record the open and closed transmittance data. The experimental spectral configuration used for Z-scan in the present study is shown in Table 4. The filtered beam of He-Ne laser of wavelength ($\lambda = 632.8$ nm) is incident on a crystal through convex lens and the crystal position is varied along the beam of focused path that is along Z direction.

The laser beam was focused to a waist radius of 3.3 mm with the help of convex lens of focal length 30 mm. The crystal is varied along Z direction and the transmittance spectrum as a close and open aperture has been recorded on photo detector placed at far distance. By analyzing above spectrums, the values of the nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) are calculated. The closed aperture Z-scan graph is shown in Figure 6 and it is observed that peak to valley confirms negative nonlinearity of doped material. Also from above observation the refractive index change is negative for doped KDP crystal, exhibiting self-defocusing effect which has applications in optical night vision sensor devices [24]. The difference between the normalized peak and valley transmittance and

Table 4. Experimental spectral configuration of z-scan setup.

Laser beam wavelength (λ)	632.8 nm
Lens focal length (f)	30 mm
Optical path distance (z)	85 cm
Beam waist radius (w_a)	3.3 mm
Aperture radius (r_a)	2 mm
Sample thickness (L)	0.60 mm
Intensity at focus (I_0)	26.50 MW/m^2

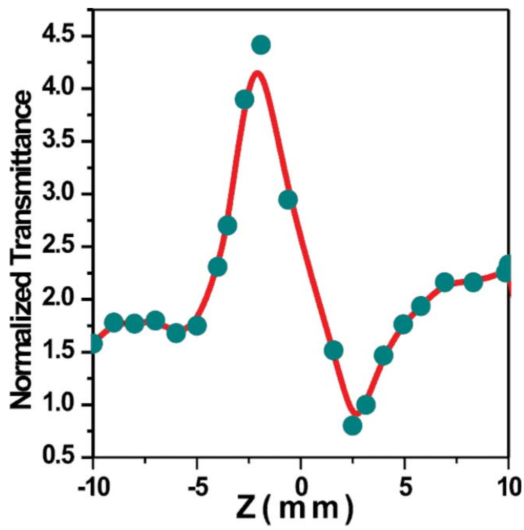

Figure 6. Close aperture curve.

nonlinear refractive index n_2 are calculated by using formulas

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}\,|\Delta\phi| \text{ and } n_2 = \frac{\Delta\phi}{KI_0L_{eff}} \tag{4}$$

where, $\Delta\phi$ is phase shift at the focus and calculated from above equation and $S = [1 - \exp(-2r_a{}^2/\omega_a{}^2)]$ is the linear transmittance of the aperture. And $K = 2\pi/\lambda$, I_o is the incident intensity of laser beam at the focus (Z = 0) and the effective thickness of the sample $L_{eff} = [1 - exp\,(-\alpha L)]/\alpha$ is calculated by using equation depends on linear absorption coefficient (α) and L thickness of the sample used for analysis. The value of nonlinear refractive index n_2 is found to be 2.38×10^{-9} cm^2/W.

The normalized transmittance T as a function of the distance Z along optic axis with open aperture is shown in Figure 7 and reveals that material has saturable nonlinear absorption [25].The nonlinear absorption coefficient (β) was calculated using the equation

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0L_{eff}} \tag{5}$$

The value of nonlinear absorption coefficient β calculated from open aperture Z-scan curve 6.46×10^{-6} cm/W. The third order nonlinear susceptibility are expressed in terms of real and imaginary parts as shown by formulas

$$\mathrm{Re}\chi^{(3)}(esu) = 10^{-4}(\varepsilon_0 C^2 n_0{}^2 n_2)/\pi(cm^2/W) \tag{6}$$

$$\mathrm{Im}\chi^{(3)}(esu) = 10^{-2}(\varepsilon_0 C^2 n_0{}^2 \lambda\beta)/4\pi^2(cm/W) \tag{7}$$

where $\mathcal{E}_0$ is the vacuum permittivity, c is velocity of light in vacuum, n_o is the linear refractive index of the material.

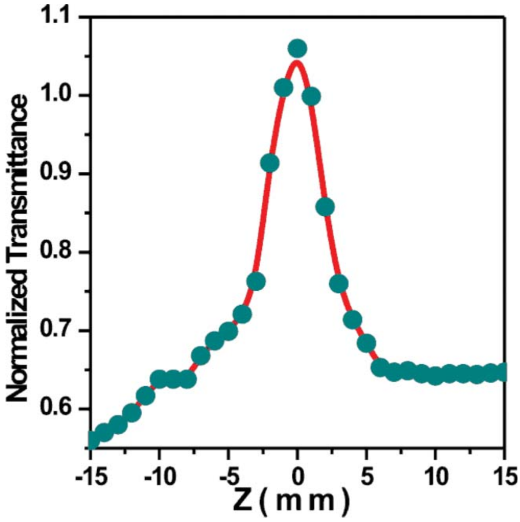

Figure 7. Open aperture curve.

Thus, we can easily obtain the absolute value of χ^3 using equation,

$$\chi^3(esu) = \sqrt{(\mathrm{Re}\chi^3)^2 + (\mathrm{Im}\chi^3)^2} \tag{8}$$

The magnitudes of the real and imaginary nonlinear susceptibility are 1.32×10^{-5} esu and 1.85×10^{-5} esu respectively. The third order nonlinear susceptibility (χ^3) of 0.2 mol% PTTC doped KDP crystal is 2.28×10^{-5} esu which is greater than that of KDP (8.34×10^{-14}) esu.

The Table 5 shows analysis of Z-scan parameters of doped KDP crystal and shows higher value of nonlinear susceptibility, suggest the doped KDP crystal has strong polarizing nature [26]. Thus magnitude of third order nonlinear parameters shows that PTTC doped KDP crystal is prominent third order nonlinear material [27–28].

3.3.4. Laser-induced damage threshold studies (LDT)

In view of NLO application laser damage threshold is very important parameter that defines the tendency of material to withstand at high power laser radiations [29]. A pulsed Q switched Nd:YAG laser incident with wavelength 1064 nm having laser beam diameter 1 mm with repetition pulse rate of 10ns. The polished crystal having thickness

Table 5. Comparison of nonlinear optical parameters n_2, β and χ^3.

Doped KDP crystal	$n_2(cm^2/W)$	β (cm/W)	χ^3(esu)	Reference no.
KDP	2.34×10^{-13}		3.72 × 10–14	[8]
1 mol% FA	-1.14×10^{-5}	1.16×10^{-7}	3.81×10^{-7}	[8]
1 mol% OA	2.25×10^{-5}	1.14×10^{-7}	1.90×10^{-7}	[8]
2 mol% MA	7.92×10^{-5}	8.99×10^{-8}	2.13×10^{-7}	[8]
0.2 mol% PTTC	2.38×10^{-9}	6.64×10^{-6}	2.28×10^{-5}	Present study

3 mm is mounted on crystal holder and placed at the focal point of the lens. The power of the laser ray was increased for every incident on crystal and the crystal surface was observed every time. Increase the power of incident laser radiation until the crystal surface was damaged. The damage spot on the crystal was clearly observed and at that radiation input laser energy density was recorded by power meter. The laser damage threshold of the grown crystal is calculated by using relation

$$I = E/\tau A \tag{9}$$

where, E is the input laser energy (mJ), τ is pulse width (ns) and A is the damaged circular area of the laser spot. The calculated value of laser damage threshold of 0.2 mol% PTTC doped KDP is found to be 2.08 GW/cm^2 which greater than KDP value 0.20 GW/cm^2 and urea 1.5 GW/cm^2. It is concluded that the PTTC doped KDP crystal is prominent material in the laser and optoelectronic applications [29].

3.4. Dielectric studies

The Agilent 4284-A LCR cube meter is used to measure the temperature dependent dielectric behavior of the doped KDP crystal in the temperature 30°C to 120°C range at the frequency of 100 KHz. The Figure 8 shows dielectric constant and it's response to temperature of pure and doped KDP crystal. From the graph, it is depicted that the dielectric constant of both pure and doped KDP crystal increases with increase in temperature. The dielectric constant of material is mainly due to the dipolar, ionic, electronic and space charge polarizations which are effective at lower frequencies [30]. The lower dielectric constant indicates the lower power consumption tendency of doped KDP crystal which is vital element for designing microelectronics devices, broad band electro-optic modulators and field of detectors [31].

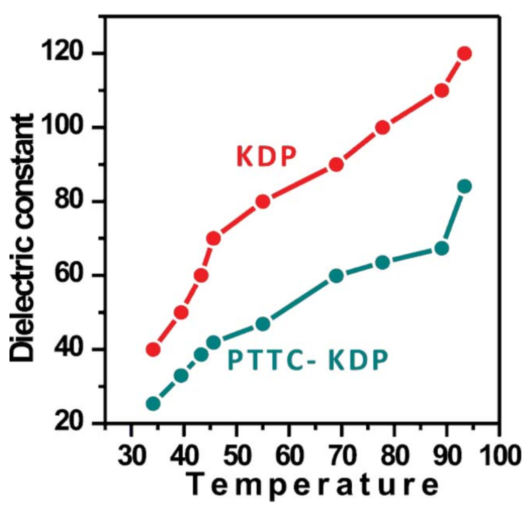

Figure 8. Dielectric constant vs. temperature.

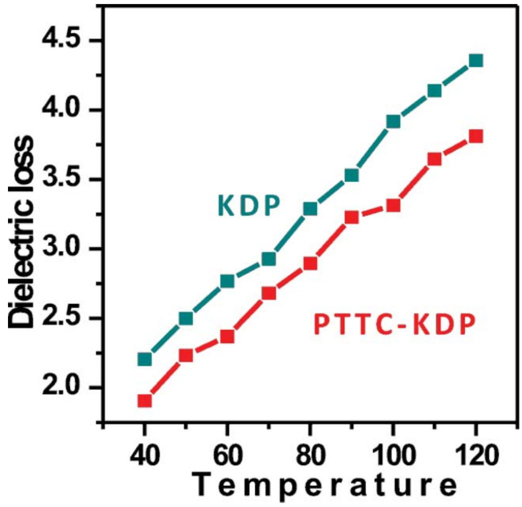

Figure 9. Dielectric loss vs. temperature.

The Figure 9 shows the variation of dielectric loss as a function of temperature. It is observed that dielectric loss increases with increase in temperature. Thus, lower dielectric properties of doped KDP crystal depict its suitability for fabrication of electro-optic and NLO devices applications [32].

3.5. Thermal studies

The thermal behavior of 0.2 mol% PTTC doped KDP crystal was studied by thermogravimetric analysis (TG) and differential thermal analysis (DTA) at a heating rate of 50 ml/min in the range of 20°C and 500°C in the nitrogen atmosphere. The Figure 10 shows testing of weight loss and thermal stability. The thermogravimetric (TG) and differential thermal analysis

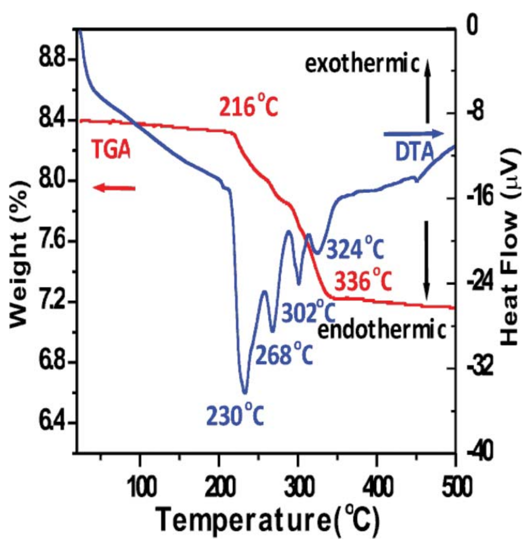

Figure 10. TG – DTA analysis.

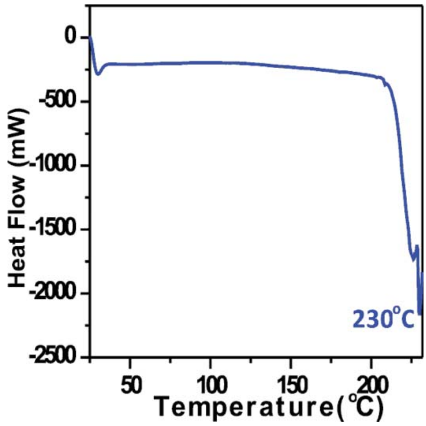

Figure 11. DSC analysis.

(DTA) analysis was carried out using Shimadzu DTG-60H. The analysis of TGA curve reveals that decomposition of doped crystal is started from temperature 216°C. The major weight loss of the doped KDP crystal is observed in the temperature range 216°C to 336°C hence there is no mass reduction or decomposition up to 216°C, In DTA curve the melting point of doped crystal is observed at 230°C. Also Differential Scanning Calorimeter (DSC) analysis of doped crystal was carried out by using Shimadzu DSC-60 as shown in Figure 11. The endothermic peak in DSC analysis at 230°C shows that melting point of potassium tetra thiourea chloride doped KDP crystal. The results of DSC analysis are match with the TG-DTA analysis and shows grown crystal have very good thermal stability, which has scope in NLO applications [33].

3.6. Micro-hardness studies

The Vickers hardness testing of 0.2 mol% PTTC doped KDP crystal is done by Shimadzu, HMV-2T microhardness analyzer. The mechanical strength of the doped KDP crystal was observed by applying loads of 25 g, 50 g and 100 g for constant indentation time 5 Second. The Vickers microhardness value was calculated using formula

$$H_\nu = 1.8544 \ \left(P/d^2\right) \tag{10}$$

where, p is the applied load (g) and d is the average diagonal length (mm) of the indentation mark [34]. The plot of Vicker's hardness (Hν) versus load (P) for doped KDP crystal is shown in Figure 12(a). From the profile, it is observed that hardness increases with load and up to 100 gm, no cracks have been observed, which is moderately harder. The relation between the load (p) and indentation diagonal length as (d) is given by Meyer's law as

$$\mathrm{p} \ = \ \mathrm{k}_1 \times \ \mathrm{d}, \tag{11}$$

where, n is Meyer index.

The graph is plotted between log p and log d, as shown in Figure 12(b), and n value is found to be 4.2. According to Onitsch criterion, the calculated n value suggests that the

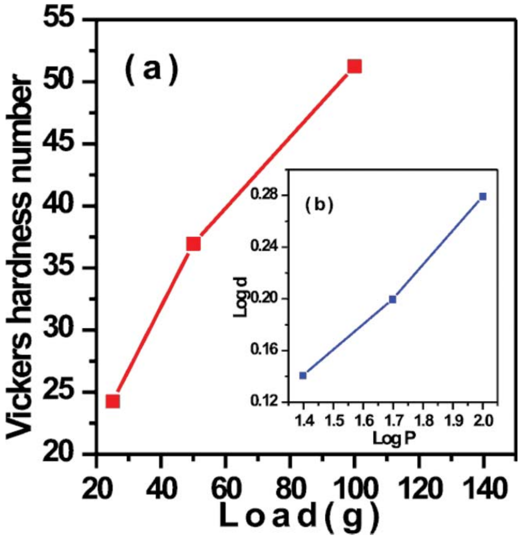

Figure 12. (a) Vickers hardness number vs. load; (b) Log p vs. Log d.

grown crystal belongs to soft material. The material constant ($k_1 = 13.74$) in above Meyer's law [34] and is determined from Figure 13. It is possibility of the material to change in elastic mode after every indentation so correction is applied to the d value and which is expressed by Kick's law as

$$P = K_2(d + x) \tag{12}$$

From above two equations Meyer's law and Kick's law we can assemble new equation as

$$d^{n/2} = (K_2/K_1)^{1/2} d + (K_2/K_1) X \tag{13}$$

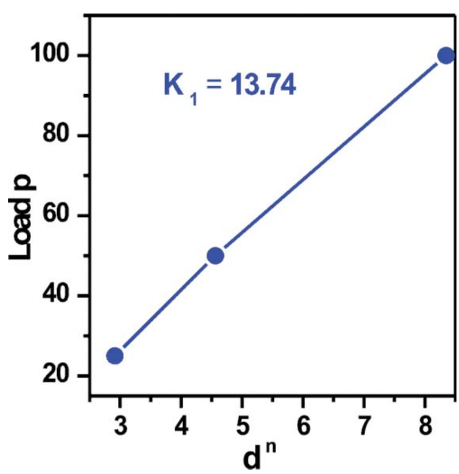

Figure 13. Load p vs. d^n.

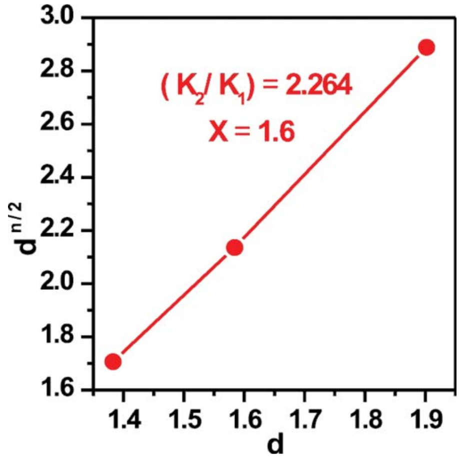

Figure 14. $d^{n/2}$ vs d.

If we plot d vs. $d^{n/2}$ graph reveals that it is straight line and the slope of it gives $(K_2/K_1)^{1/2}$ value and intercept is measure of (x = 1.6) value as shown in Figure 14. The interatomic bond strength between consecutive atoms of the crystalline lattice is interpreted by using elastic stiffness coefficient calculated by formula and depicted in Table 6.

$$C_{11} = H_v^{7/4} \tag{14}$$

The yield strength (σ_y) of the grown crystal was calculated by using formula $(0.1)^{n-2}$ H_ν /3. The fracture toughness K_c determines how much fracture stress is applied under uniform loading and is calculated by using formula

$$K_c = P/\ \beta_0 l^{3/2} \text{ for } 1 \geq d\ /\ 2 \tag{15}$$

where, β_0 is the indenter constant, equal to 7 for the Vickers's diamond pyramid indenter and the crack length (l) is the average of two crack lengths for each indentation. The Brittleness is the property tendency of a material to fracture or fail upon the application of a relatively small amount of force of a material, and is expressed in terms of the brittleness index (B_i) as

$$B_i = H_v/\ K_c \tag{16}$$

From the hardness parameters (Table 6) grown crystal has excellent mechanical properties and is well suited for device fabrication [35–37].

Table 6. Hardness parameters of PTTC doped KDP crystal.

Load P (gm)	H_v (Kg/mm^2)	σ_y (MPa)	C_{11} x 10^{14} (Pa)	K_c x 10^4 Kg $m^{-3/2}$	B_i x 10^3 $m^{-1/2}$
25	24.25	12.563	4.554	3.711	6.407
50	36.95	19.143	9.516	7.422	4.881
100	51.25	26.551	16.870	14.844	3.385

4. Conclusions

The thiourea metal complex, potassium Tetra thiourea chloride doped KDP crystal was grown by slow evaporation technique at room temperature. The crystal structure was confirmed through single crystal XRD. The optical study reveals that high transparency and improved optical parameters throughout visible region. The SHG efficiency of doped crystal is 1.24 times higher than that of KDP crystal. The Laser damage threshold value of PTTC doped KDP crystal was found to be 2.08 GW/cm^2. The third order nonlinear studies of the doped KDP crystal reveal that the strong defocusing nature. The third order nonlinear susceptibility (χ^3) of doped crystal is found to be 2.28×10^{-5} esu. The dielectric study of grown crystal depicts the lower value of dielectric constant and dielectric loss. The thermal study confirms that doped crystal is stable up to 230°C. Microhardness studies reveal that the grown crystal belongs to soft material category. The results suggest that doped crystal has applications in NLO, solar thermal devices, information processing and computing, microelectronic industry and optoelectronics device fabrication.

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