Influence of Thiourea Metal Complex on Potassium Dihydrogen Phosphate for Optoelectronic Applications

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Abstract. Influence of 0.1 mole % Bis Thiourea Zinc Sulphate (BTZS) exhibits concrete reinforcing in optical and dielectric properties of Potassium Dihydrogen Phosphate (KDP). The pure and BTZS influenced KDP crystals have been grown by slow evaporation solution technique at room temperature. The structural and vibrational studies of the grown crystals have been studied by single crystal XRD and FT-IR technique respectively. The optical traits of the doped crystal have been analyzed by UV-vis spectral analysis within the wavelength range of 200-800 nm. The Kurtz-Perry powder test has been employed to determine the bisthiourea zinc sulphate on the second harmonic generation (SHG) efficiency of KDP crystal and it found to be 1.1 times higher than KDP. The dielectric and thermal behaviour has been analyzed for doped KDP crystal.

1. Introduction
The researcher and academicians were showing interest in the non linear optical (NLO) material from last few decades due to its fascinating materialistic properties. The NLO crystals study involves the interaction of light with the crystal resulted in the variation in the electromagnetic mechanism of the incident light. The most fascinating NLO applications of organic, inorganic and semi-organic crystals have a usage in the optical traits. These traits are optical storage, optical computing, optical information processing, optical power limiting, optical switching, antireflection coating, image manipulation and processes. The rapidly growing field in laser technologies, frequency conversion devices, holographic memory, electro-optics modulation and photonics by second order effects in crystals has fulfilled many more needs of today’s industry and society [1-4]. The organometallic crystals have superior optical, dielectric and mechanical properties. The large dipole moments, the ability to form metal ligands through hydrogen bonding effectively works to improve optical properties [5]. The optical properties of the subjected crystal enhanced during chemical reaction and due to the bonding of the thiourea and zinc sulphate. The donor and acceptor electron system and formation of the hydrogen bonding throughout the crystal enhances second harmonic efficiency due to engagement of centrosymmetric thiourea compound and metal component [6]. The thiourea metal complexes have applications in optical phenomenon due to its low UV cut off wavelength and high NLO properties. In Literature, the NLO zinc thiourea sulphate (ZTS) is found to be a versatile organometallic crystal [7]. The potassium thiourea bromide (PTB), bis-thiourea cadmium acetate (BTCA), copper thiourea chloride (CTC), bis-thiourea zinc acetate (BTZA), zinc thiourea chloride (ZTC), bis-thiourea cadmium chloride (BTCC) are some thiourea metal complexes found in the
The fundamental material in the NLO crystal category is potassium dihydrogen phosphate (KDP) due to its unique nature and properties. The different doping attempts were made into KDP crystal to improve various properties [9-10]. The enhanced SHG efficiency reported doped thiourea complexes in KDP are bis thiourea Copper complex [11], tetra thiourea Potassium chloride [12], thiourea Ammonium chloride [13] and bis thiourea zinc chloride [14]. In current research an investigation of BTZS in KDP is put forward, by imposing Single crystal XRD, FT-IR, UV-visible, Kurtz-Perry test, thermal and dielectric analysis to bring out the potential credibility in NLO device applications.

2. Experimental procedure
To synthesize the thiourea (Bis) Zinc Sulphate doped KDP (BTZSKDP) complex starting material thiourea and zinc sulphate were dissolved in double distilled water whose conductivity is less than 1.0 µmhos in 2:1 M ratio for to produce thiourea (Bis) Zinc Sulphate. After stirring the mixture for four hours homogeneous solution was filtered and kept for slow evaporation. The BTZS crystal was found according to reaction

\[2\text{CS(NH}_2\text{)}_2 + \text{ZnSO}_4 \rightarrow \text{Zn[CS(NH}_2\text{)}_2\text{]}_2\text{SO}_4\]

The good yield of thiourea (Bis) Zinc Sulphate (BTZS) was collected and made fine microelements for further crystal growth. The precisely measured 0.1 M% and 0.2 M% BTZS was added gradually in the distinct beakers of supersaturated solution of the Potassium dihydrogen phosphate (KDP) and allowed to stir at a constant speed. The solution was constantly stirred for five hours to prepare the homogenous mixture of added reactants. The solution was filtered through 4μm membrane filter paper and allowed to place in the clean rinsed beaker in a vibration-free atmosphere at room temperature. During the recrystallization process purity enhanced resulting in good quality crystals within a period of two weeks. The 0.1 M % BTZSKDP crystal is as shown in figure 1; also Table 1 shows the optimized growth mechanism 0.1 of BTZSKDP single crystal.

![Figure 1. Grown crystal of BTZSKDP crystal](image)

3. Results and discussion

3.1. Single crystal x-ray diffraction studies
The well-phased crystal of 0.1 BTZSKDP was subjected to single crystal x-ray diffraction studies. The study was carried out using Enraf Nonius CAD4-MV31 crystal X-ray diffractometer. The analysis of single crystal XRD of BTZSKDP confirms the tetragonal I crystal system. The determined lattice parameter values are \(a = 7.44\ \text{Å}, b = 7.44\ \text{Å}, c = 6.96\ \text{Å}\) and \(\alpha = 90^0, \beta = 90^0, \gamma = 90^0\) with volume 386 (Å)³.
3.2. Fourier transform infrared (FT-IR) spectral analysis

The incorporation of bis-thiourea zinc sulphate in KDP was qualitatively analyzed by recording the FT-IR spectrum for doped crystal by using Bruker α-ATR spectrophotometer. Figure 2 shows the plot of FT-IR spectrum; was recorded in the wave number range between 500 cm\(^{-1}\) to 4000 cm\(^{-1}\). The N-C-N bond stretching vibration associated with ZTS is observed at 570 cm\(^{-1}\). The absorption peak observed at 624 cm\(^{-1}\) corresponds to the C=S stretching vibration. The P=O and SO\(_3^-\) stretching is evidenced at wave number 1090 cm\(^{-1}\). The O=P–OH stretching absorption peak are observed at 1518 cm\(^{-1}\) in doped The C=N–OH bond stretching vibration is observed at 1717 cm\(^{-1}\). The strong P-H stretching vibration is attributed to 2349 cm\(^{-1}\). The absorption peak at 3070 confirms the N-H stretching vibration implies that the presence of thiourea molecule in the doped crystal. The peaks between 3732 to 4000 cm\(^{-1}\) appears due to O-H and N-H bond stretching vibrations [15].

Table 1. Optimized growth mechanism of BTZSKDP.

| BTZSKDP crystal Parameter | Value |
|---------------------------|------|
| Solvent used              | Double distilled water |
| Molar ratio of thiourea and Zinc Sulphate | 2:1 |
| Molar ratio of BTZS in KDP | 0.1 and 0.2 |
| Size of grown crystal     | 1.2 × 0.5 × 0.4 cm\(^3\) |
| Time of growth            | 2 weeks |
| Volume of crystal         | 386 (Å)\(^3\) |

Figure 2. FT-IR spectrum of doped KDP crystal

Figure 3. Plot of a) Wavelength vs. transmittance; b) Tauc’s plot

3.3 SHG Studies

The Kurtz-Perry powder technique is used to study the frequency doubling of the 0.1 and 0.2 M % BTZSKDP and KDP crystals owing to determine frequency conversion efficiency [16]. The fundamental Q-switched Nd:YAG laser beam of wavelength 1064 nm producing pulse width 6 ns with a repetition rate of 10 Hz interact with the subjected crystal. The good quality crystals of 0.1, 0.2 M % BTZSKDP and KDP converts into uniform microgranuals and sieved in micro-capillary and was exposed by a beam of Pulse energy 4.7μJ/pulse. The output signals emitted from the sample was focused on monochromator using a pair of lenses and collected by photomultiplier tube were displayed on CRO. The emission of the sharp green radiation of wavelength 532 nm confirms the second order nonlinearity of the subjected crystals. The output voltages of the second order diffracted radiation...
beams were recorded and found the values 124 mV, 84 mV and 114 mV for 0.1, 0.2 M % BTZSKDP and KDP respectively. This shows that the 0.1 M % BTZSKDP have remarkable enhancement in the SHG efficiency than parent material is due to higher polarizing ability, more electrons-phonon interaction, noncentrosymmetric nature of crystal and enhanced charge transfer through organometallic BTZS complex [17-18]. Table 2 shows a comparative chart of the SHG efficiency of doped KDP crystals with KDP [7]. The 0.1 M % ZTSKDP crystals may show better alternative results in the frequency conversion and optoelectronic applications [17-19].

Table 2. Comparative chart of SHG efficiency.

| Doped KDP Crystal | SHG Efficiency | Ref. |
|-------------------|----------------|------|
| CuT               | 1.2            | [11] |
| PTTC              | 1.24           | [12] |
| TAA               | 1.27           | [13] |
| BTZC              | 1.65           | [14] |
| 0.1 M % BTZS      | 1.1            | [Present] |
| 0.2 M % BTZS      | 0.7            | [Present] |

3.4 UV-visible transmission studies
The well-polished 2 mm thick crystal of 0.1 M % BTZSKDP crystal was subjected for UV-visible studies by using Shimadzu UV-2450 spectrophotometer. The crystal was placed in the holder and allowed to pass UV light of the wavelength 200 nm to 800 nm range. The recorded spectrum of transmittance as a function of wavelength was depicted in figure 3 (a) and subjected crystal possesses optically transparency up to 88 % in the entire visible region and lower cut off wavelength at 205 nm. And figure 3(b) shows Tauc’s plot and confirms the band gap energy for the exposed crystal as 4.8 eV. Table 3 shows a comparative chart of cut off wavelength of the doped and undoped KDP crystals. The higher value of transmittance and cut off wavelength strongly agree for the suitability of the crystal in non linear optics for frequency conversion device applications.

Determination of optical parameters:
The optical properties of the crystal relate to the atomic structure, electronic band structure and electrical behaviour. The various optical parameter values are prerequisites for the selection of the crystal in non linear, optoelectronic applications and in device fabrication [20]. In the present study different optical parameters such as optical transmittance (T in %), band gap energy (Eg in eV), cut off wavelength (λco in nm), absorption coefficient (α), reflectance (R), refractive index (n), optical conductivity (σ in S−1) and extinction coefficient (K) were calculated by using recorded optical transmission spectrum. The magnitude of transmittance values and cut off wavelength has already discussed and other optical parameters were determined as below.

Absorption coefficient and band gap energy:
To determine the optical band gap initially the optical absorption coefficient was calculated from the transmittance data by using relation

\[ \alpha = \frac{1}{d} \ln \frac{1}{T}, \]  

(1)

Where, T is the transmittance and d is thickness of the crystal. The Tauc’s plot shows the dependence of absorption coefficient (α) on the incident energy of photons (Eg) by the relation

\[ \alpha h\nu = A(h\nu - E_g) \]

(2)

Where, E_g is the optical band gap energy and A is constant. The photon energy E_g value is determined at an extrapolating onto the photon energy axis in the linear portion near the onset of the absorption edge as plotted in figure 3 (b) Tauc’s plot and found to be 4.8 eV. This reflects the suitability in of the subjected crystal optoelectronic applications [21].
Refractive Index and Reflectance:
The propagation of light through the medium of the material is a refractive index as shown in figure 4(a) and was determined by using the above formula and found to be 1.5 in the entire visible region.

\[ n = \left[ \frac{1}{T} + \frac{1}{T - 1} \right] \]  

(3)

Similarly, reflectance in terms of refractive index was evaluated by the relation

\[ R = \frac{(n - 1)^2}{(n + 1)^2} \]  

(4)

And, which is observed from the figure 4(b) has value 0.05 % in the entire visible region. The high value of transmittance and band gap energy and lower values of reflectance of BTZSKDP in the entire UV-vis region plays a crucible role in the antireflection coating in solar thermal devices [22].

Table 3. Comparative chart of cut off wavelength.

| Doped KDP Crystal | Cut off Wavelength (\(\lambda_{CO}\)) | Reference |
|-------------------|--------------------------------------|-----------|
| PTTC              | 299                                  | [12]      |
| BTZC              | 300                                  | [14]      |
| BTNN              | 299                                  | [20]      |
| BTZS              | 205                                  | [present] |

Optical conductivity and Extinction coefficient:
The optical conductivity was calculated by using formula \(\sigma = \frac{\alpha n C}{4 \pi}\), where, \(\alpha\) is the absorption coefficient, \(n\) is refractive index and \(C\) is velocity of light and response to the photon energy is plotted in figure 5(a). The optical conductivity confirms the presence of high photo response of the crystal [23]. This shows doped crystal has good matching properties for the use in optical information and processing purpose. The formula \(k = \frac{\alpha \lambda}{4 \pi}\) is used to determine the extinction coefficient and its response to wavelength is depicted in figure 5(b) and shows that it depends on wavelength. The lower extinction coefficient facilitates less absorption of photons; vital for UV tunable laser, telecommunication applications [23-24].

Figure 4. Plot of wavelength vs.
  a) refractive index; b) reflectance

Figure 5. Plot of photon energy vs.
  a) opt. conductivity; b) ext. coefficient
3.5. Thermal Studies

The thermogram of the 0.1 BTZSKDP crystal was used to study response to the temperature variations using Thermogravimetric (TG) and Differential Thermal (DTA) using detector DTG-60H in the temperature range of 25-500 °C at a heating rate of 10 °C/min in a nitrogen atmosphere. The well phased good quality crystal of doped crystal was crushed into powder form subject for thermal study. The sample weight used; 5.250 mg during the TGA process. The thermogram was illustrated in figure 6 and it is observed that decomposition of the sample starts at 65 °C and ends at 450 °C. During this process, 0.836 mg weight loss of the sample takes place which is around 15.9 % determined from the TGA curve. The major weight loss is produced from 208 °C to 352 °C. Also, it is confirmed from DTA curve initial loss at 229 °C, the sharp onset of the first endothermic fall occurs due to corresponding weak forces in the molecules and which is melting point of the doped material. The total decomposition of the material produced into another two stages at 266 °C and 305 °C. It is concluded from the thermal study that the ZTSKDP crystal has optimum thermal stability and may have applications in NLO and optoelectronic devices up to 229 °C temperature [13, 25].

![Figure 6. TGA-DTA analysis of 0.1 BTZSKDP](image)

3.6. Dielectric Studies

The good quality crystal of 0.1 M % BTZSKDP was subjected to study dielectric behaviour using Gwinstek LCR-819 meter. The measurements of capacitance were taken for the frequency range of 12 Hz to100 kHz for the subjected crystal at room temperature.

![Figure 7. Plot of Log f vs. dielectric constant](image)

![Figure 8. Plot of Log f vs. dielectric Loss](image)
Dielectric constant
The recorded data was used to calculate the dielectric constant (DC) of the subjected material by using formula

\[ \varepsilon = \frac{C \cdot d}{\varepsilon_0 \cdot A} \]  

(5)

Where C is the capacitance, d is the thickness and A is the area of crystal sample.

The response of the dielectric constant to the frequency was depicted in the figure 7 and decay observed in a lower frequency region above 100 Hz. The doping of thiourea metal complex makes superior quality than pure KDP. The DC value is mainly attributed to the charge delocalization among the crystal contributes to the frequency dependent electronic, ionic, dipolar space-charge polarizations. And the purity and lattice perfection of the crystal affects space charge polarization which is generally present in the low frequency domain [26].

Dielectric loss
The dielectric loss (DL) response to the frequency of the subjected crystal depicts in figure 8 and determined by using formula

\[ \text{Dielectric loss (Tan } \delta \text{)} = \text{Dissipation factor} \]  

(6)

The dissipation factor is measured using LCR meter along with the capacitance varied with frequency at room temperature. The DL is the dissipation of electromagnetic energy due to the heating of dielectric material when applied to the frequency dependent field. It can be parameterized in terms of either the loss angle \( \delta \) or the corresponding loss tangent (Tan \( \delta \)). The behaviour of the DL at lower frequencies have decaying response to the applied field cognates that there are less defects produced in the KDP crystal caused by doping [27]. The enhanced second order nonlinearity and optical parameters were assigned to lower magnitude of the dielectrics. This Miller theory holds well in the BTZSKDP crystal and founds its suitability in the frequency conversion and photonic devices [14, 28-30].

4. Conclusions
The optical quality 0.1 M% BTZSKDP crystal was successfully grown by slow evaporation solution technique. The single crystal XRD analysis confirmed the tetragonal structure. The presence of functional groups was confirmed by FTIR analysis. The enhancement in optical transmittance of KDP found due to the doping of ZTS. The high value of band gap energy and lower values of reflectance and refractive index of grown crystal plays crucible role in the antireflection coating in solar thermal devices. The SHG efficiency of 0.1 M% BTZSKDP crystal is enhanced than KDP crystal and found to be 1.1 times that of KDP. The thermal study reveals that the material is suited up to 229 °C for applications. The dielectric constant and dielectric loss was dropped to optimum value due to the presence of BTZS. The 0.1 M% BTZSKDP crystal with impressive optical and dielectric properties might find suitable applications in designing distinct NLO and photonic devices.

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