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EFFECT OF AMMONIUM THIOUREA CHLORIDE ON LINEAR AND NONLINEAR OPTICAL PROPERTIES OF KDP CRYSTAL

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Abstract : In present Investigation 0.1, 0.3 and 0.5 mol% Ammonium Thiourea Chloride (ATC) doped Potassium Dihydrogen Phosphate (KDP) crystal has been successfully synthesized by slow evaporation solution technique (SEST). The cell parameters of the doped crystals were determined using single crystal X-ray diffraction analysis and crystal belongs to Tetragonal (I) crystal system. The FT-IR spectroscopy was used to confirm the presence of various functional groups in the doped crystal. The optical transmittance and various optical parameters of the doped crystal were studied by using UV-Visible spectroscopy in the range of 200-900 nm. Mechanical hardness has been identified by Vickers micro hardness study and vital parameters were evaluated. The growth mechanism of the crystal was assessed by chemical etching studies. The second harmonic generation (SHG) efficiency was found to be 1.40 times of KDP crystal.

***Keywords*:** crystal growth; optical constant; optical device.

1. Introduction

In the field of photonic and optoelectronic technologies the new crystals with high second and third order optical nonlinearity has been attracted by crystal community. This Nonlinear (NLO) crystal fulfills the need of society by multilevel applications of nonlinear crystals.

The optical applications likeoptical storage, optical computing, optical information processing, optical power limiting, optical switching, antireflection coating, image manipulation and processing were achieved in NLO crystal by crystal engineering at the time of synthesis.applications.

The rapidly growing crystal fields are in laser technologies, frequency conversion devices, holographic memory, electro-optics modulation and photonics by second and third-order effects[1-4]. NLO crystals divides into organic, inorganic and semi-organic and have different significant characteristicsThe organometallic crystals have attracted the attention of researchers due to superior optical, dielectric and mechanical properties. The large dipole moment, ability to form metal ligands through hydrogen bonding effectively works to improve optical properties [5]. The optical property of the crystal was enhanced by the co-ordination of thiourea molecules with inorganic bits. The donor and acceptor electron system, formation of the hydrogen bonding throughout the crystal are key points in the growth of nonlinear optical (NLO) crystals. The researchers were attracted hygroscopic, centrosymmetricthiourea compound and metals to provoke frequency conversion properties [6]. Literature elucidates that thiourea metal complexes have interesting results shown in the optical industry due to their low UV cut-off wavelength and high NLO properties. In recent years, the number of thiourea metal complexes had grown enhanced optical properties than that of parent materials. Thioureametallic compounds reported in the literature are 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) and many more [7]. Ammoniumthioureachloride (ATC) is an interesting organometallic NLO crystal that orients with an orthorhombic structure [8]. Potassium dihydrogen phosphate (KDP) is a fundamental material in the field of nonlinear optical field due to its versatile and manifold crystalline nature. The different doping attempts were made in KDP crystal to improve various properties through molecular engineering technique [9-10].

The SHG efficiency of reported doping in KDP are bisthiourea copper complex (1. 2 times > KDP) [11], tetra thiourea potassium chloride (1.24 times > KDP) [12], thioureaammonium acetate (1.27 times > KDP) [13] and bisthiourea zinc chloride (1.65 times > KDP) [14]. In the current investigation an inventive report is put forward to Ammonium Thiourea Chloride doped (ATC) doped KDP crystal by imposing Single crystal XRD, FT-IR, UV-visible, second and third nonlinear optical, mechanical and etching studies to bring out the potential credibility in NLO device applications.

2. EXPERIMENTAL PROCEDURE

To synthesize the Ammonium (bis) thiourea chloride doped KDP (ATCKDP) complex starting material ammonium thiourea chloride (ATC) was prepared by taking thiourea and ammonium chloride in the 2:1 molar ratio. The mixture was dissolved in double distilled water whose conductivity is less than 1.0 µmhos in 3:1 M ratio. After stirring the mixture for fourhours, the prepared homogeneous solution was filtered by Whatman filter paper No. 1and kept for slow evaporation.

The good yield of thiourea (bis) ammonium chloride (ATC) was produced within fifteen days. The good crystals of ATC were used to produce fine microelements for further doping. The precisely measured 0.1, 0.3and 0.5 M% ATC was added gradually added in the separate beakers of supersaturated solution of the Potassium dihydrogen phosphate (KDP) in separate beakers and allowed to stir at a constant speed. The solution was constantly stirred for four hours to prepare the homogenous mixture of added reactants and filtered through 4µm membrane Whatman no. 1 filter paper and allowed to place in the clean rinsed beaker in a vibration-free atmosphere at room temperature. In the initial days, a large number of micro nucleates were formed which reduces the growth rate reflects on the uniform size of the crystal. In the recrystallization process purity was enhanced resulting in good quality crystals within two weeks. The picture of 0.5 M % ATCKDP crystal is shown in figure 1. Table 1 shows the optimized growth mechanism 0.5 of ATCKDP single crystal.

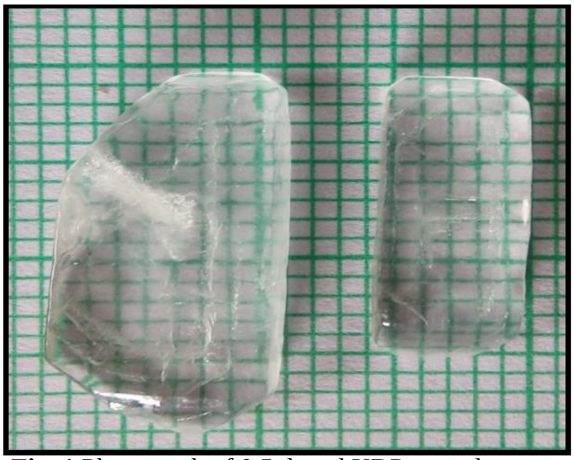

Fig. 1. Photograph of 0.5 doped KDP crystal

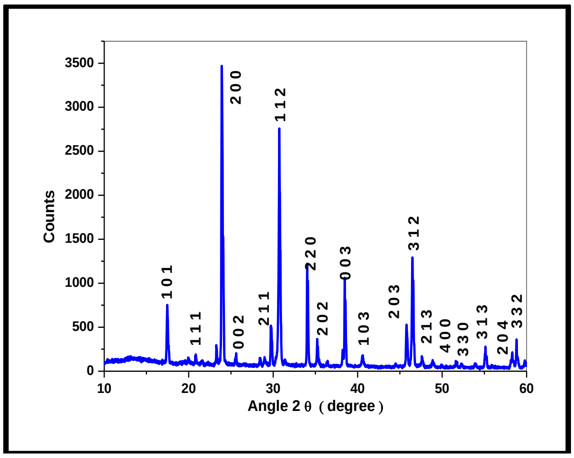

Fig. 2. PXRD pattern of ATCKDP crystal

Table 1 Growth mechanism of ATCKDP

Doped KDP	Parameter
Solvent used	Distilled H_2O
Molar ratio of thiourea and Ammonium Chloride	2:1
Molar ratio of ATC in KDP	0.1, 0.3 and 0.5
Size of grown crystal	1.8 × 0.9×0.5
Time of growth	2 weeks
Volume of crystal	391 cubic Å
Temperature	40°C

3. RESULTS AND DISCUSSION

3.1 SINGLE CRYSTAL XRD STUDIES

The well-phased crystal of 0.1 ATCKDP 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 ATCKDP confirms the tetragonal I crystal system. The determined lattice parameter values are a = 7.47 Å, b = 7.47 Å, c = 7.01 Å and α = 90^0, β = 90^0, γ = 90^0 crystal with volume 391 $(Å)^3$.

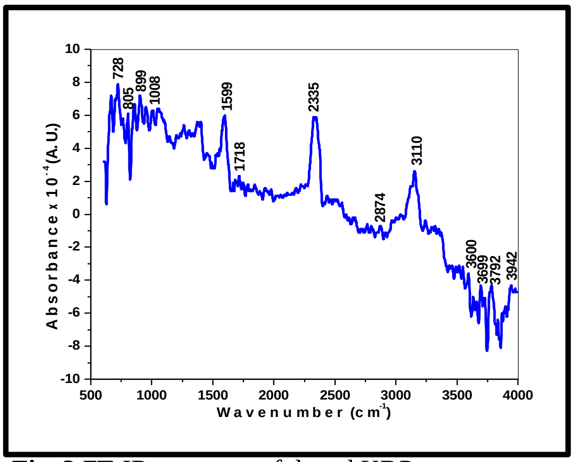

Fig. 3.FT-IR spectrum of doped KDP

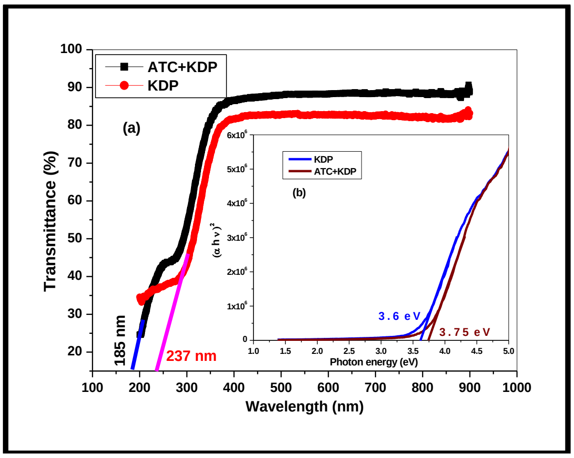

Fig. 4. A Plot a) wavelength vs. transmittance; b) Tauc's plot

3.2 POWDER XRD STUDIES

The good quality crystals of ATCKDP were finely grinded and subjected to powder x-ray diffraction (PXRD) analysis to ascertain crystalline nature. The typical diffractogram showing single crystal nature of grown crystal was depicted in figure 2. The Bruker Advance D8 X-ray diffractometer was used to record PXRD of 0.5 ATCKDP crystal within 2θ range of 10-70. It also confirms that the peaks have less width with high maxima shows that the grown crystals possess single crystalline nature. The sharp diffraction peaks also indicate that the doped crystal is free from impurities replies in fewer defects [15].

3.3 FT-IR SPECTRAL ANALYSIS

The incorporation of thiourea (bis) ammonium chloride in KDP was qualitatively analyzed by recording the FT-IR spectrum by using Bruker α-ATR spectrophotometer. The well-phased polished crystal of size 4×3×1.5 mm was used for the vibrational study. Figure 3 shows the plot of FT-IR spectrum; was recorded in the wave number range between 500 cm^{-1} to 4000 cm^{-1}. The C-Cl bond stretching vibration associated with ATC is observed at 728 cm^{-1}. The existences of KDP as P-O-C symmetric bond stretching vibration are attributed to 805 and 899 cm^{-1}. The P=O stretching is evidenced at wave number 1008 cm^{-1}. The O=P-OH bond stretching vibration is observed at 1599 cm^{-1}. The strong NH_2deformation is attributed to 1717 cm^{-1}. The absorption peak at 2335 $cm^{-1}$and 2874 cm^{-1} confirms the P-H and C-H stretching vibration. The peaks between 3600 to 4000 cm^{-1} appears due to O-H and N-H bond stretching vibrations [16].

3.4 SHG STUDIES

The Kurtz-Perry powder technique is used to study the frequency doubling of the 0.1,0.3 and 0.5 M % ATCKDP crystals owing to determine frequency conversion efficiency [17]. 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, 0.3and 0.5 M % ATCKDP and KDP were finely grinded. These uniform microgrannuals were sieved into micro-capillary and was exposed to a beam of Pulse energy 5.4μJ/pulse. The signals emitted from the sample were 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 voltage of the second order diffracted radiation beams were recorded and found the values 677 mV, 782 mV,833 mV and 594 mV for 0.1, 0.3 and 0.5 M % ATCKDP and KDP respectively. This shows that the 0.5 M % ATCKDP has a remarkable enhancement in the SHG efficiency than parent material KDP is due to higher polarizing ability, more electrons-phonon interaction, noncentro symmetric nature of crystal and enhanced charge transfer through ATC complex [18-19]. Table 2 shows a comparative chart of the SHG efficiency of doped KDP crystals with KDP (SHG Efficiency of KDP = 1 and ATC = 1.2) [7] found in the literature. It is observed that in the present case there is a massive enhancement in SHG efficiency. The 0.5 M % ATCKDP crystals may show better alternative in the frequency conversion and optoelectronic applications [18-20].

3.5 UV-VISIBLE TRANSMISSION STUDIES

The well-polished 1.5 mm thick crystal of 0.5 M % ATCKDP crystal was subjected to 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 900 nm range. The recorded spectrum of transmittance as a function of wavelength was depicted in figure 4 (a) and observed that the subjected crystal possesses optically transparency up to 85 % in the entire visible region and a lower cut-off wavelength at 185 nm. And figure 4(b) shows Tauc'splot which confirms the band gap energy value for the exposed crystal is 3.75eV. Table 3 shows a comparative chart for lower cut-off wavelength of the doped and undoped KDP crystals. The high value of transmittance and cut off wavelength strongly agrees for the suitability of the crystal in non linear optics for frequency conversion device applications.

Table 2 Comparative chart of SHG efficiency

Doped KDP Crystal	SHG Efficiency	Reference no.
CuT	1.2	[11]
PTTC	1.24	[12]
TAA	1.27	[13]
0.1 m% ATC	1.13	[Present]
0.3 m% ATC	1.31	[Present]
0.5 m% ATC	1.40	[Present]

Table 3 Comparative chart of cut off wavelength

Crystal sample	Cut off wavelength	Reference no.
CuT	200	[11]
PTTC	299	[12]
TAA	300	[13]
BTZC	299	[14]
KDP	237	[Present]
0.1 m% ATC	185	[Present]

Determination of optical parameters:

The optical properties of the crystal relates to the atomic structure, electronic band structure and electrical behavior. The various optical parameters are prerequisites for the selection of the crystal in non linear, optoelectronic and device fabrication [21]. In the present study different optical parameters such as optical transmittance (T in %), band gap energy ($E_g$ineV), cut off wavelength (λ_{co}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 been 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

$$\alpha = \frac{1}{d}\mathrm{Ln}\frac{1}{T}, \qquad (1)$$

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

$$\alpha h\nu = A(h\nu - Eg) \qquad (2)$$

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 4 (b) Tauc's plot and found E_g values for doped crystal is 3.75and that of KDP is 3.6 eV. This reflects the suitability of the doped crystal in optoelectronic applications [22].

Refractive Index and Reflectance:

The propagation of light through the medium of the material is a refractive index as shown in figure 5and was determined by using the above formula and found to be 1.7 in the entire visible region.

$$n = [\frac{1}{T} + (\frac{1}{T} - 1)] \qquad (3)$$

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

$$R = (n-1)^2/(n+1)^2 \qquad (4)$$

And, also from figure 5has a value 0.06 % in the entire visible region. The higher transmittance, band gap energy and lower reflectance of ATCKDP in the entire UV-vis region plays a crucible role in the antireflection coating in solar thermal devices [23].

Optical conductivity and Extinction coefficient:

The optical conductivity was calculated by using formula $\sigma = \frac{\propto nC}{4\pi}$, where, α is the absorption coefficient, n is refractive index and C is velocity of light and response to the photon energy is plotted in figure 6(a). The optical conductivity confirms the presence of a high photo response of the crystal [24].

This shows doped crystal has good matching properties for the use in optical information and processing purpose.

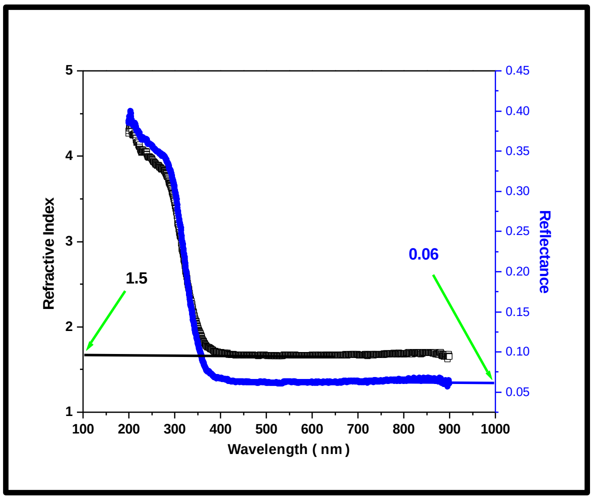

Fig. 5. A Plot of wavelength vs. refractive index

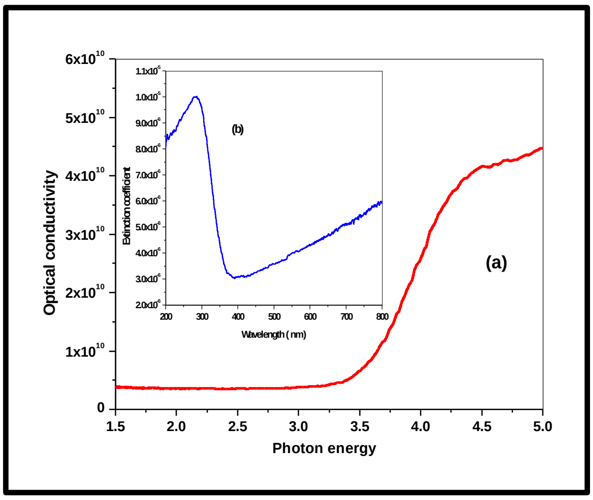

Fig. 6. A Plot of photon energy vs. a) opt. conductivity; and reflectance b) ext. coefficient

The formula $k = \frac{\propto\lambda}{4\pi}$ is used to determine the extinction coefficient and its response to wavelength is depicted in figure 6(b). The lower extinction coefficient facilitates less absorption of photons; vital for UV tunable laser, telecommunication applications [24-25]

4 CONCLUSIONS

Ammonium thiourea chloride doped potassium dihydrogen phosphate nonlinear optical crystal was grown by solvent slow evaporation technique. The unit cell parameters were calculated from powder single crystal X-ray diffraction pattern. The diffraction curve of the powder XRD results confirms the crystalline perfection of the crystal. The UV-visible studies employed within 200-900 nm confirmed the uplifting impact of ATC on optical parameters of KDP crystal. The optical transmittance of KDP and ATCKDP crystal is found to be 80% and 85% respectively. The SHG efficiency of ATCKDP crystal is 1.40 times that of KDP. The ATCKDP crystal with impressive linear and nonlinear optical properties might find suitable applications in antireflection coating in solar thermal devices, and optoelectronics device fabrication.

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