IOSR Journal Of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 12, Issue 6 Ser. III (Nov. – Dec. 2020), PP 11-17
www.Iosrjournals.Org

Optical Traits of Thiourea Metal Complex (TMC) on Potassium Dihydrogen Phosphate (KDP) Crystal for NLO Applications

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Abstract
Present research work exhibit perfect reinforcing in different optical parameters of thiourea metal complex (TMC) on potassium dihydrogen phosphate (KDP) crystal. The pure and TMC doped KDP crystals were grown by slow evaporation solution technique. The optical traits of the doped crystal have been systematically examined by UV-visible spectral analysis within the wavelength range of 200-800 nm. This investigation presents the detail study of optical properties transmittance, band gap, refractive index, reflectance, extinction coefficient, optical conductivity, real dielectric constant and imaginary dielectric constant of TMC doped KDP crystal. The Kurtz-Perry powder test has been employed to determine the enhancing effect of thiourea metal complex on the second harmonic generation (SHG) efficiency of KDP crystal and it found to be 1.78 times reference material.

Keywords: *Slow evaporation method; Non linear optics; optical studies; TMO.*

Date of Submission: 27-11-2020 Date of Acceptance: 11-12-2020

I. Introduction

The interaction of light with crystal is explained by phenomenon non linear optical (NLO) showing interest from last few decades by the researchers. The optical 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 and third-order effects in crystals has fulfilled many more needs of today's industry and society [1-4]. The organometallic crystals have attracted the attention of researchers due to 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 and acts as matrix modifier [5]. The higher transmittance of the crystal is a key factor to enhance the optical properties achieved by the co-ordination of thiourea molecules with inorganic bits. The researchers are attracted to the derivatives formed by hygroscopic, centro symmetric thiourea compound and metals to provoke frequency conversion properties [6]. Literature evidences that TMC have interesting results in the optical storage industry due to its low UV cut off wavelength and high NLO properties. The zinc thiourea sulphate (ZTS) is found to be an interesting organometallic NLO crystal which orients with orthorhombic structure [7]. In recent years, these materials were doped in KDP so as to achieve higher transmittance and SHG efficiency [8-14].

In current investigation an inventive report is put forward which deals to explore the most improving optical properties of ZTS doped KDP crystal. This investigation presents the detail study of optical properties transmittance, band gap, refractive index, reflectance, extinction coefficient, optical conductivity, real dielectric constant and imaginary dielectric constant of ZTSKDP crystal.

II. Experimental procedure

To synthesize the thiourea (tris) Zinc Sulpahte doed KDP (ZTSKDP) complex initially material thiourea and zinc sulphate were dissolved in double distilled water whose conductivity is less than 1.0 µmhos in 3:1 M ratio to produce thiourea (tris) zinc sulpahte. After stirring the mixture for four hours homogeneous solution was filtered and kept for slow evaporation. The ZTS crystal was found according to reaction

$$3CS(NH_2)_2 + ZnSO_4 \longrightarrow Zn[CS(NH_2)_2]_3SO_4.$$

The good yield of thiourea (tris) zinc sulpahte (ZTS) was collected and made fine microelements for further crystal growth. The precisely measured 0.1 M% and 0.2 M% ZTS was added gradually in the discrete beakers of supersaturated solution of the Potassium dihydrogen phosphate (KDP) and allowed to stir at a constant speed with optimum electric jerks. The solution was constantly stirred for six 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. In the initial days a large number of micro nucleates were formed which reduces the growth rate reflects on the size of the crystal. In the recrystallization process purity enhanced resulting in good quality crystals within a period of two weeks. The 0.1 M % ZTSKDP crystal is as shown in figure 1.

Fig. 1. Photograph of 0.1 ZTSKDP crystal

III. Results and discussion

3.1 SHG Studies

The Kurtz-Perry powder technique is used to study the frequency doubling of the 0.1 and 0.2 M % ZTSKDP crystals owing to determine frequency conversion efficiency [15]. 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 finely grinding good quality crystals of 0.1, 0.2 M % ZTSKDP and KDP converts into uniform microgrannuals and sieved in micro-capillary and was exposed by a beam of Pulse energy 5.4 µJ/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 1055mV, 1026 mV and 594 mV for 0.1, 0.2 M % ZTSKDP and KDP respectively. This shows that the 0.1 M % ZTSKDP have 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 organometallic ZTS complex [16-17]. The 0.1 M % ZTSKDP crystals may show better alternative results in the frequency conversion and optoelectronic applications [18-19].

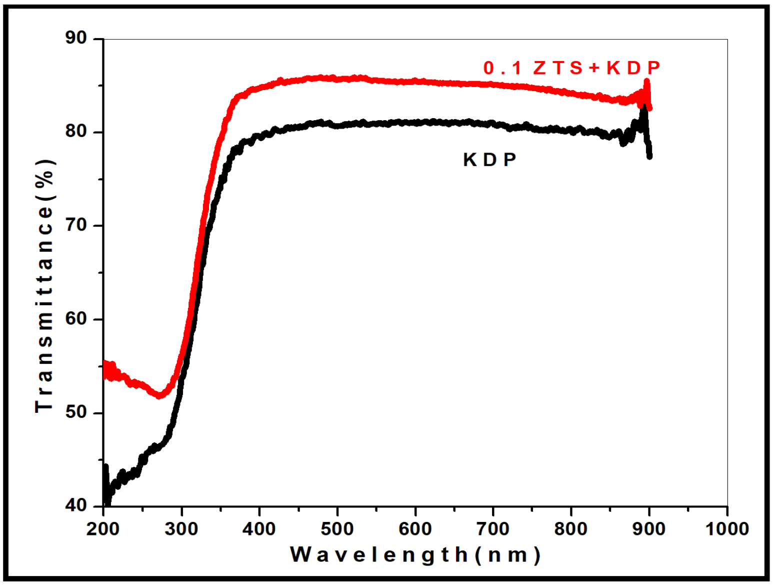

Fig. 2. Plot of Wavelength vs. transmittance;

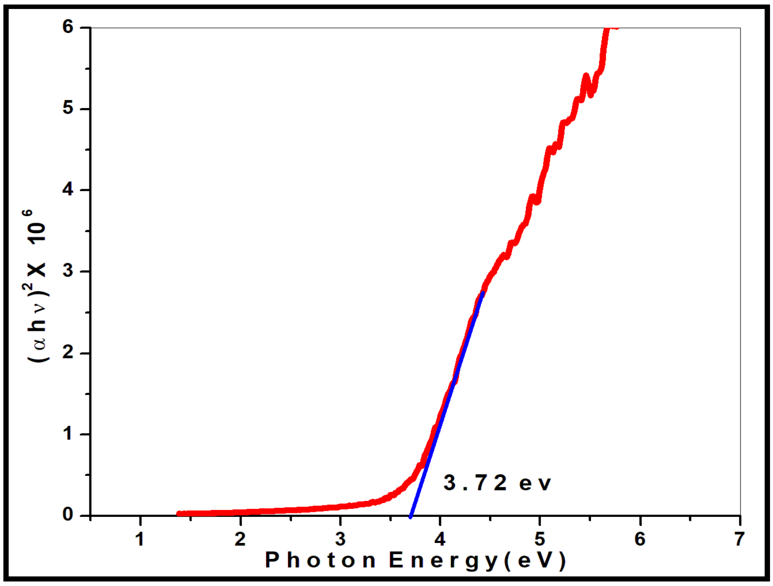

Fig. 3. Tauc's plot

3.2 UV-visible transmission studies

The well-polished 2 mm thick crystal of 0.1 M % ZTSKDP 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 2 and subjected crystal possesses optically transparency up to 85 % in the entire visible region and lower cut off wavelength at 285 nm. And figure 3 shows Tauc's plot and confirms the band gap energy for the exposed crystal as 3.72 eV. 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 behavior. 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 ($E_{g\ in}$ eV), 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 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

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

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

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

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 Tauc's plot and found to be 3.72 eV. This reflects the suitability in of the subjected crystal optoelectronic applications [21].

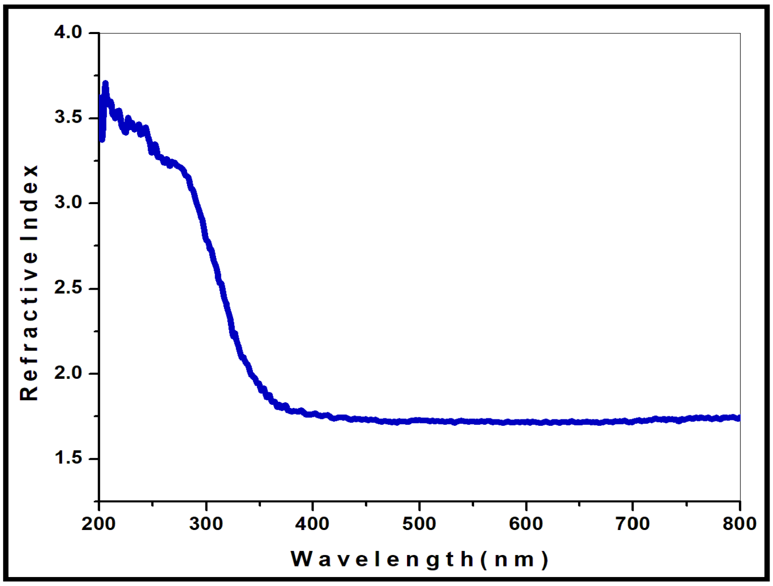

Fig. 4. Plot of wavelength vs. refractive index

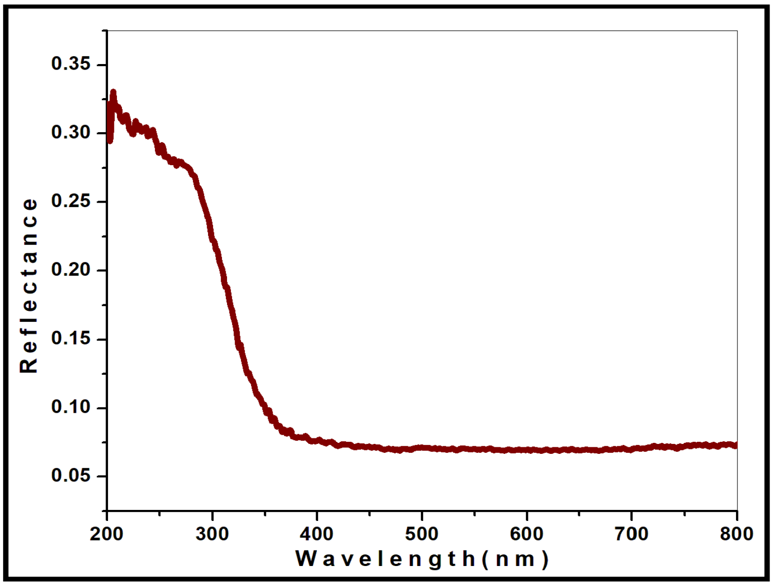

Fig. 5. Plot of wavelength vs. reflectance

Refractive Index and Reflectance:

The propagation of light through the medium of the material is a refractive index as shown in figure 4 and was determined by using the above formula and found to be 1.7 in the entire visible region.

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

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

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

And, which is observed from the figure 5 has value 0.06 % in the entire visible region. The moderate values of refractive index and optical band gap suggest that the material has the required transmission range for NLO application. The high value of transmittance and band gap energy and lower values of reflectance of ZTSKDP in the entire UV-vis region plays a crucible role in the antireflection coating in solar thermal devices [22].

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. 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 $k = \frac{\propto\lambda}{4\pi}$ is used to determine the extinction coefficient and its response to wavelength is depicted in figure 7 and shows that it depends on wavelength. The lower extinction coefficient facilitates less absorption of photons; vital for UV tunable laser, telecommunication applications [23].

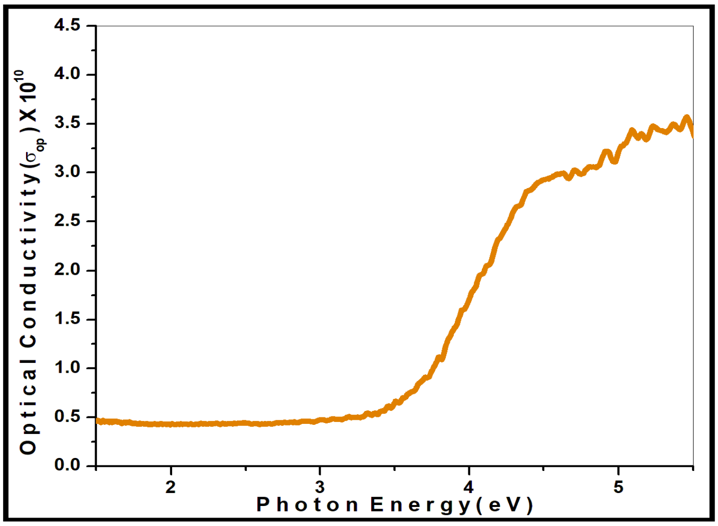

Fig. 6. A Plot of photon energy vs. opt. conductivity;

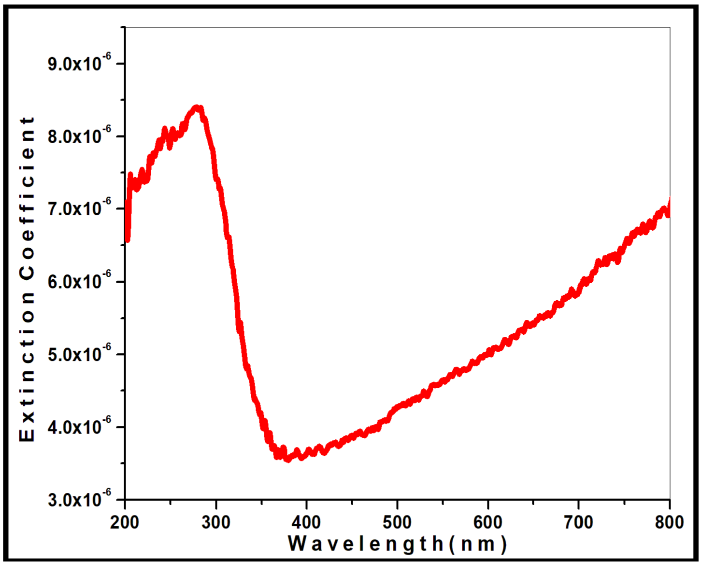

Fig. 7. Plot of photon energy vs. ext. coefficient

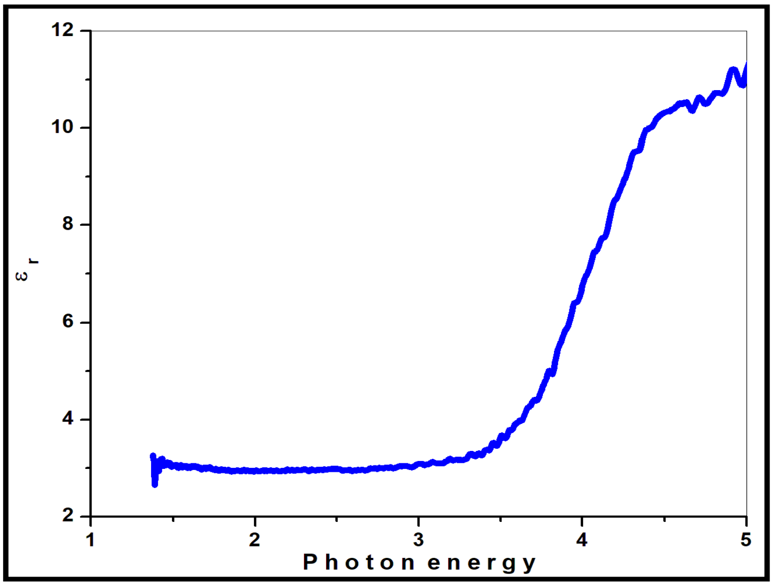

Fig. 8. Plot of photon energy vs. real dielectric constant

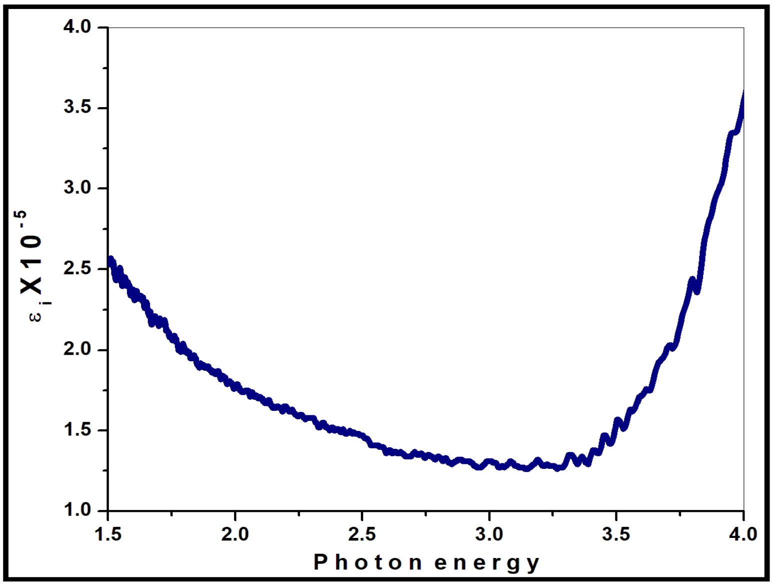

Fig. 9. Plot of photon energy vs. imaginary dielectric constant

Real and Imaginary Dielectric Constant:

The real part dielectric constant (ε_r) and imaginary part dielectric constant (ε_i) can be calculated from the following relations $\varepsilon r = n^2 - k^2$ and $\varepsilon i = 2nk$. The figure 8 and 9 shows the response of real and imaginary dielectric constant to the photon energy. The lower value of dielectric constant of the material is capable of producing induced polarization due to intense incident light radiation [24].

IV. Conclusions

The optical quality 0.1 M% ZTSKDP crystal was successfully grown by slow evaporation solution technique. 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 % ZTSKDP crystal is enhanced than ZTS and KDP crystals. The 0.1 M % ZTSKDP crystal with impressive optical properties might find suitable applications in designing distinct NLO devices.

Acknowledgment

The authors are also thankful to Prof. P.K Das, Department of Physical Chemistry, Indian Institute of Science (IISc), Bangalore, India for the SHG Test.

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Dr. S. S. Hussaini, et. al. "Optical Traits of Thiourea Metal Complex (TMC) on Potassium Dihydrogen Phosphate (KDP) Crystal for NLO Applications." *IOSR Journal of Applied Physics (IOSR-JAP)*, 12(6), 2020, pp. 11-17.