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Potassium Doping's Effect on Linear Optical Properties of L-PTCA Crystals

S. Shabnam Anjum[1], S.S Hussaini[2], R.N. Shaikh[2*]

[1]*Crystal Growth Research Laboratory, Milliya Arts, Science and Management science College, Beed-431122,Maharashtra, India.*
[2]*Department of physics, Milliya Arts, Science and Management Science College, Beed, Maharashtra, India.*
Email: raisshaikh9@gmail.com

The electro-optic potentials of pure and K-doped L-prolinium trichloroacetic acid crystals were revealed by analyzing their nonlinear optical properties. L-PTCA crystals are attracting considerable interest owing to their potential use in optoelectronic devices. The transmittance data were used to compute the optical band-gap values. Both the unaltered and potassium-doped L-PTCA crystals were found to have optical band gaps of 4.98 eV and 4.68 eV, respectively. Third-order NLO characteristics have also been reported. In this study, the nonlinear optical characteristics of pure and doped L-PTCA crystals were examined. The results of this study showed that the nonlinear optical properties of L-PTCA crystals could be significantly enhanced by doping with appropriate materials.
Keywords: L-PTCA, optical properties, Zscan, linear optical Optoelectronic application.

1. Introduction

Considering that organic materials are significant in many optical applications, researchers have investigated them [1–5]. To better understand a material's localized states, optical transition types, and electronic band structures, its optical properties must be understood. Crystals of L-prolinium trichloroacetic acid (L-PTCA) have several characteristics including robust thermal stability, low dielectric constant, and high optical transparency. Therefore, the L-PTCA crystals have various optical components. L-PTCA may be more suitable for a range of applications if K is added to enhance its optical and electrical characteristics [6]. In addition to being useful in photovoltaic and optoelectronic devices, chemical sensors, and nonlinear optical applications, L-PTCA is potentially beneficial [7]. The optical nonlinearity of L-PTCA is higher than those of other nonlinear optical materials, making it an ideal choice for applications in optical communication and optical sensing.

2. Experimental Procedure

High-purity l-proline and trichloroacetic acid were dissolved in water that was double distilled in equimolar ratios, resulting in L-prolinium trichloroacetic crystals. This solution was gently evaporated after being agitated for four to five hours and filtered. In a saturated solution of L-PTCA, potassium (K) doping was carried out by adding 0.1 mol of K. Evaporating K-L-PTCA slowly for two weeks produced transparent seed crystals.In this way; Crystals were formed by gradually evaporating the two types of L-prolinium trichloroacetic acid one doped with potassium and the other pure at normal temperature.

3. Results and Discussion

A. UV-Visible Study

A notable method of analysis for the linear optical study of materials is UV-Vis NIR spectroscopy. Using a UV-VIS spectrophotometer, pure and K-L-PTCA crystals were characterized within the 200–1100 nm range. The cutoff wavelength for the spectral assessment of the pure and K-L-PTCA crystal samples was 298 nm. As shown in Fig. 1, the transmittances of the pure and K-L-PTCA crystals were estimated to be 61% and 90%, respectively. The transmittance spectrum shows that the K-doped L-PTCA crystal has greater transmittance than the pure L-PTCA crystal. The increased transmittance of the K-doped L-PTCA crystal compared that with of the pure L-PTCA crystal is attributed to the presence of potassium ions, which enhance the optical properties of the crystal.

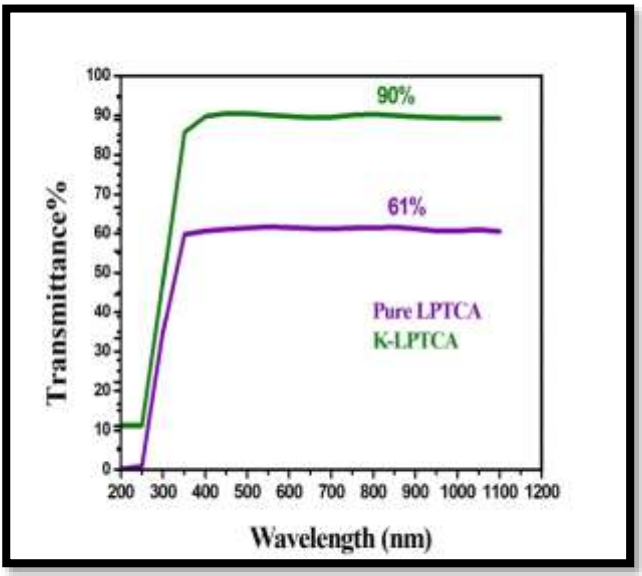

Fig.1.UV-VIS Spectral analysis of pure and K doped LPTCA.

B. Determination of Optical Constants

When it comes to the electrical band structures and the kinds of optical transitions that they reveal, the optical characteristics of a material are crucial. The optical absorption coefficient (α) was computed from transmittance (T) data using the following relation [8]:

$$\alpha = (2.303 \log 1/T)/t \qquad (1)$$

where t is the thickness of the material and T is the transmittance.

The spectrum of absorption was used to figure out the optical band gap, and the coefficient of optical absorption (α) towards the edge of absorption is determined by

$$\alpha = A\,(h\nu - E_g)^{1/2} \qquad (2)$$

where ν is the frequency, A is a constant, and Eg is the crystal's optical band gap.

The band gaps of the L-PTCA crystals, both pure and K-doped, were determined by plotting $(\alpha h\nu)^2$ versus photon energy (hν). The band gap Eg, which can be identified by estimating the linear part of the curve to the point $(\alpha h\nu)^2 = 0$, is depicted in Figure 2. And found to be 4.98 eV and 4.68 eV, respectively. Its promise as a potential opponent for electro-optic applications is demonstrated by its broadband gap [9].

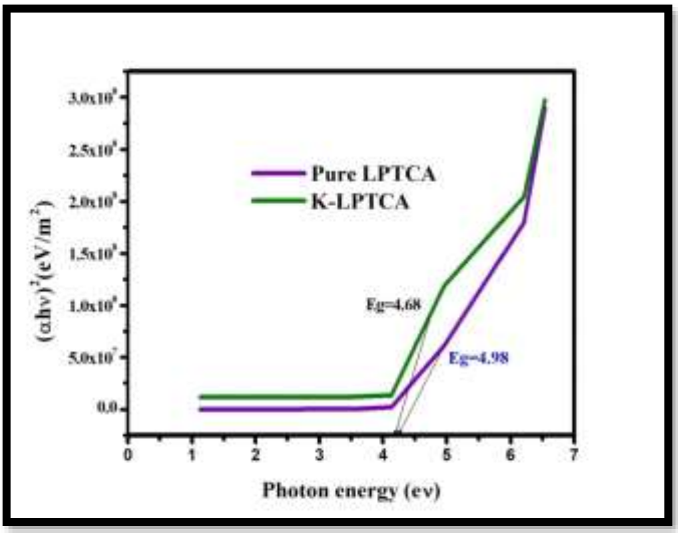

Fig.2 $(\alpha h\nu)^2$ vs. hν (eV)

The extinction coefficient K can be estimated in terms of absorption coefficient,

$$K = \frac{\alpha\lambda}{4\pi} \qquad 3$$

The absorption coefficient can be utilized to derive the extinction coefficient K. The amount of light that traverses the crystal is determined by the quantity of light reflected and absorbed along its optical path. Within the 200–1200 nm wavelength range, transmittance spectra were utilized to determine the refractive index n as a function of photon energy. The following formula can be used to obtain the reflectance (R) in terms of the refractive index (n) and absorption coefficient:

$$R = \frac{1 \pm \sqrt{\exp(-\alpha t) + \exp(\alpha t)}}{1 + \exp(-\alpha t)} \qquad 4$$

The given relation will be employed to calculate the refractive index n. –

$$n = \frac{-(R+1) \pm 2\sqrt{R}}{(R-1)} \qquad 5$$

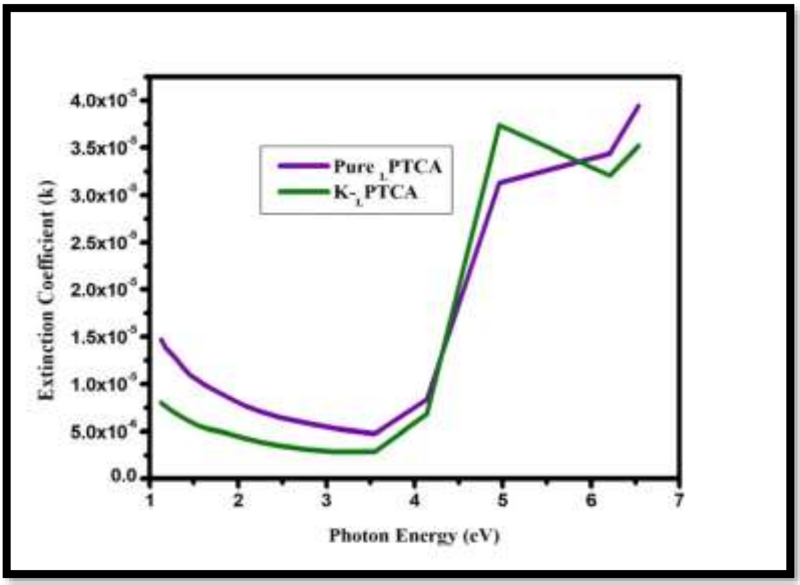

Fig.3 Extinction Coefficient vs. Photon energy (eV)

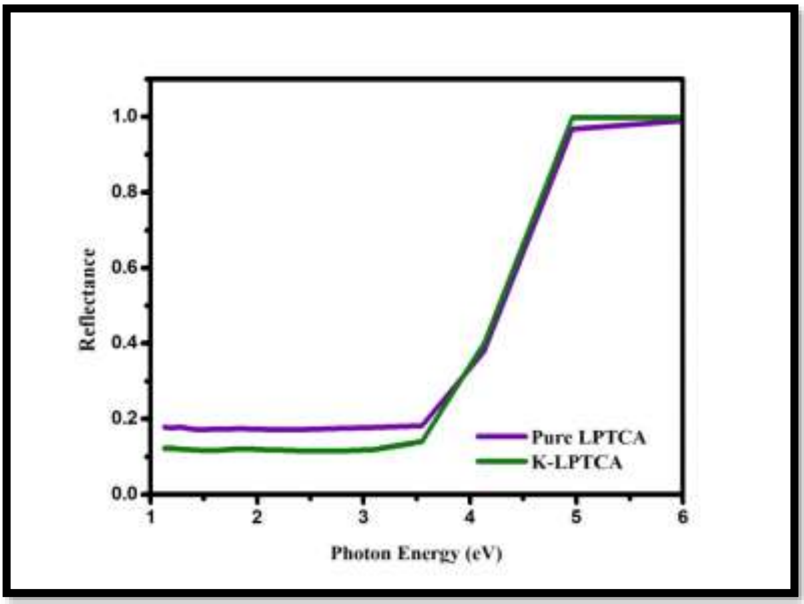

Fig.4 Reflectance vs. Photon Energy (eV)

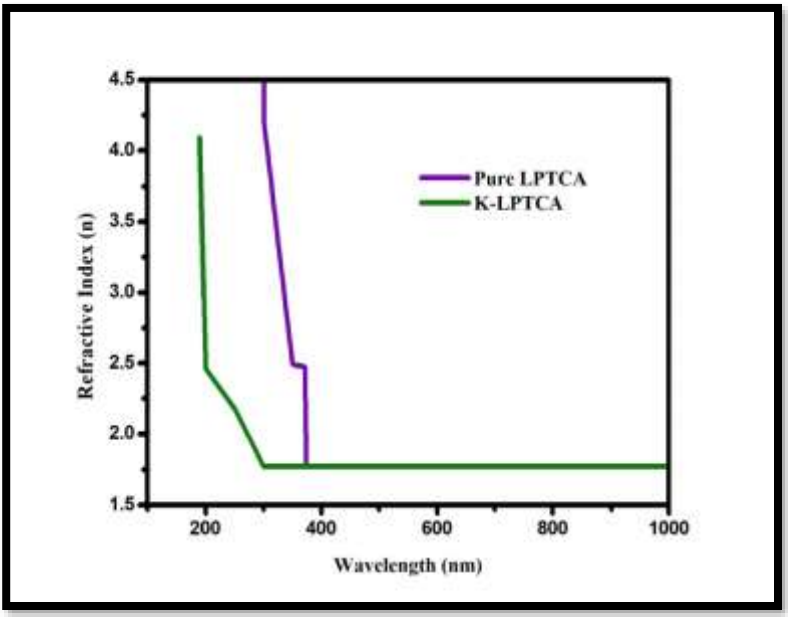

Fig.5 Refractive Index vs. Wavelength(nm)

Figures 3, 4, and 5 illustrate the changes in extinction coefficient, reflectance, and refractive index, respectively. The dependence of the reflectance and extinction coefficients on the absorption coefficient, which exhibits an increasing value with the photon energy, can be observed in Figures 3 and 4. K-doped L-PTCA crystals display the lowest absorption and a noticeably decreased index of refraction throughout the visible spectrum, which is an ideal characteristic for an antireflection coating in solar thermal systems [10].

It is evident from Fig. 5 that as the wavelength increased, the refractive indices decreased. At wavelengths between 250 and 400 nm, the refractive index (n) fluctuates from 1.75 to 2 and becomes saturated at wavelengths between 450 and 1000 nm. The examination of a material's frequency response to light rays is termed optical conductivity.

$$\sigma = \frac{\alpha n C}{4\pi} \qquad 6$$

Where light travels at a speed of C.

Figure 6 displays a curve of optical conductivity vs. photon energy. The extremely high photo-response behavior of the crystal was confirmed by the enormous magnitude of the optical conductivity of K-doped L-PTCA [10].

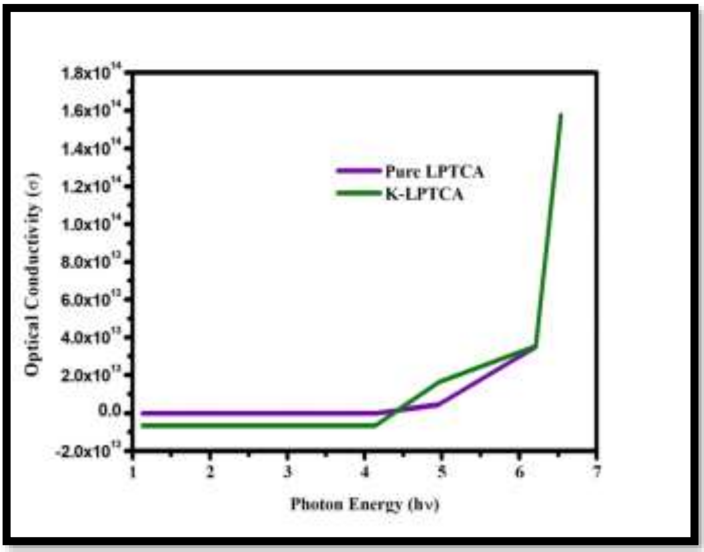

Fig.6 Optical Conductivity vs. photon energy (eV)

The given relation can be used to compute the electrical conductivity using an optical technique.

$$\sigma_e = \frac{2\lambda\sigma}{\alpha} \qquad 7$$

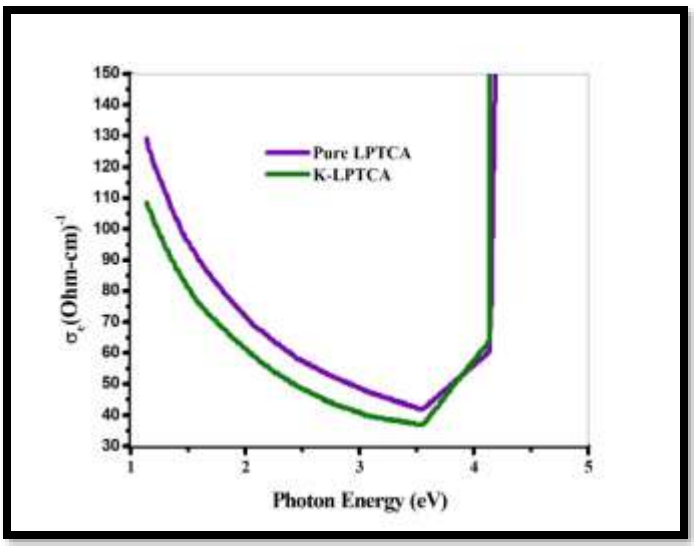

Fig.7— Electrical Conductivity vs. photon Energy (eV)

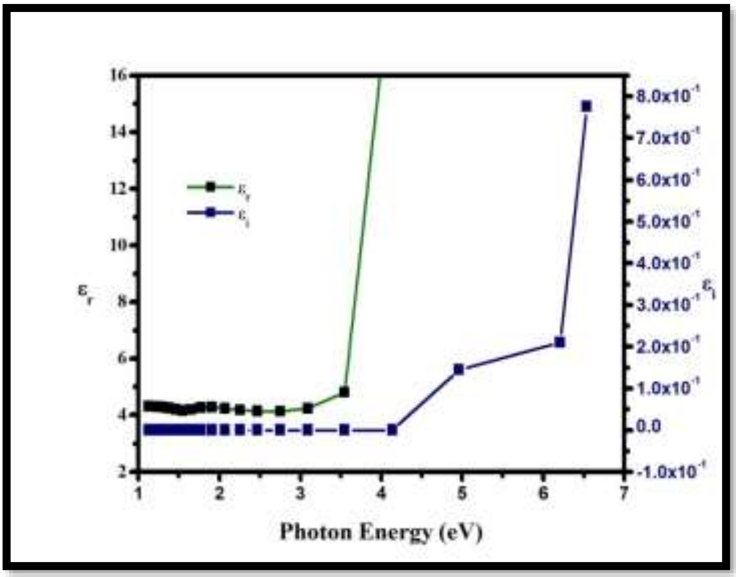

Fig.8 (a) Real & Imaginary dielectric const. vs. hν (eV) of pure LPTCA.

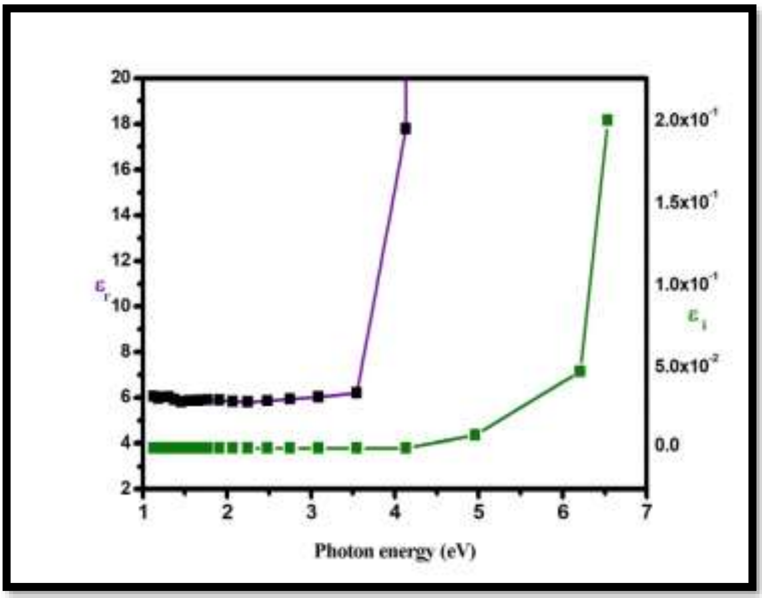

Fig.8 (b) Real & Imaginary dielectric const. vs. hν (eV) of cd doped LPTCA crystal

Figure 7 depicts the curve of the electrical conductivity versus the photon energy. As displayed in Figures 8(a) and 8(b), both the real and imaginary dielectric constants, εr and εi, can be determined by employing the following relations:

The graph indicates that when the photon energy increased, the dielectric constants of both the real and imaginary components increased simultaneously.

$$\varepsilon_r = n^2 - K^2 \quad 8$$

And

$$\varepsilon_i = 2nk \quad 9$$

C) Z-scan Analysis

The third-order nonlinear optical responses of pure $_L$-PTCA and K-doped $_L$-PTCA crystals were studied using a He-Ne laser and the Z-scan technique developed by Bahae et al. [11]. The experimental setup details are provided in Table 1, and the nonlinear refraction and absorption were analyzed using the close- and open-aperture Z-scan techniques, respectively. The Positive index of refraction was confirmed from the closed aperture transmittance data depicted in Figs. 9 and 10, which indicate that the self-focusing nature of the pre-focal transmittance valley is followed by the post-focal transmittance peak for both pure $_L$-PTCA and K-doped $_L$-PTCA. The absorption coefficient was negative for saturable absorption. The saturable absorption (SA) phenomenon of the $_L$-PTCA crystal is featured in the open-aperture transmittance data shown in Fig.10 [12-13]. The focused laser beam causes a thermal lensing effect, altering the crystal's refraction [14-15]. The nonlinear refractive index (n_2) of the K-doped $_L$-PTCA crystal ranged from 10^{-12} to 10^{-10} cm^2/W.

Table 1. Details of Z-scan Experimental setup

Parameter	Details	Notation
Gaussian beam wavelength (He-Ne)	632.8nm	λ
Focal length of Lens	30mm	f
Path length	85 cm	Z
Aperture Beam radius	3 mm	wa
Close Aperture radius	2 mm	ra
Incident intensity at Z=0	9.262 (MW/cm^2)	I_0

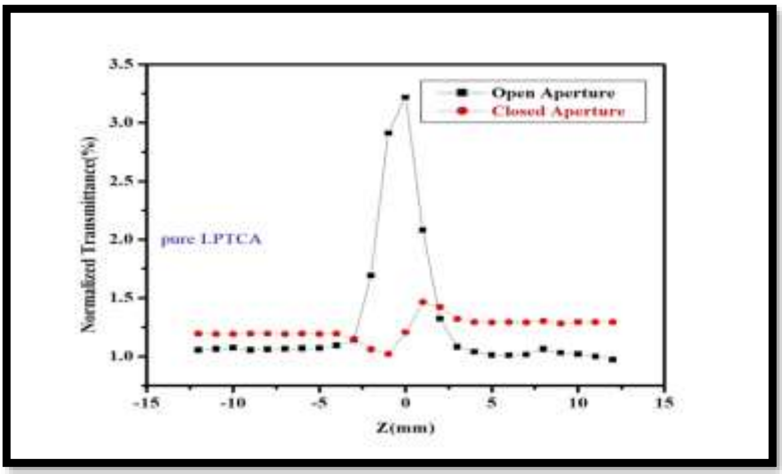

Fig.9. Zscan of Pure LPTCA

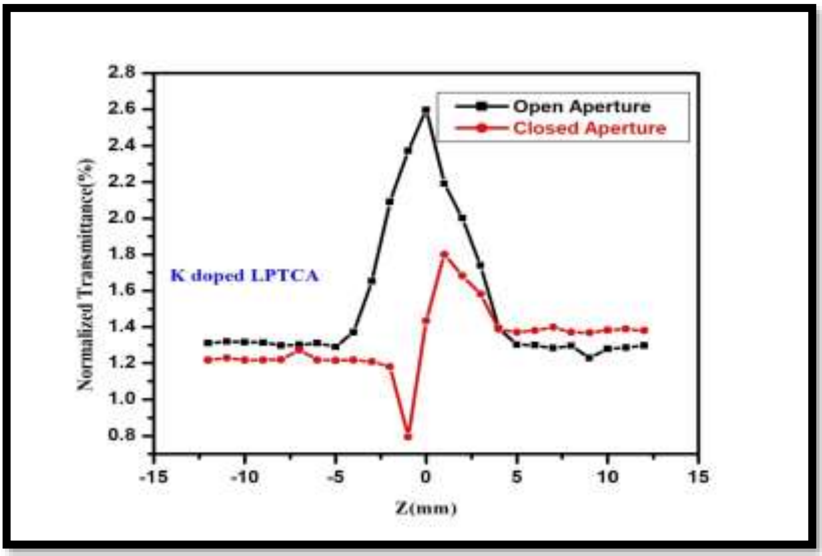

Fig.10. Zscan of K doped LPTCA

The purpose of the open-aperture Z-scan experiment is to determine the nonlinear absorption coefficient of the K-doped L-PTCA crystal. The low intensity of the laser beam causes linear absorption in the far-fields. However, the laser beam intensity at the focus is sufficiently high to cause nonlinear absorption, which leads to peak maxima or minima. The nonlinear absorption coefficient β can be calculated by measuring the single valley/peak transmittance ΔT. The value of β in the K-doped L-PTCA crystal was determined to be 10^{-6} cm/W in this investigation.

One of the appealing features of the K-doped L-PTCA crystal is its ability to generate high-power laser intensity, leading to various photonic effects. The crystal exhibits a saturable absorption effect (SA), which is attributed to the dominance of ground-state linear absorption over excited-state absorption [16-19]. This phenomenon is facilitated by charge delocalization over the pi-bonded network of the molecular system [20-21], as indicated by the χ3 value of the K-doped L-PTCA crystals, which is approximately 10^{-5} esu. Table 2 presents the TONLO (Third-Order Nonlinear Optical) properties of both the pure and K-doped L-PTCA crystals. Crystals exhibiting third-order nonlinearity properties possess the great potential for a wide range of applications. These include high-speed optical switching, advanced 3D optical data storage, effective photodynamic therapy, and efficient optical power-limiting devices [22].

Table 2. TONLO parameters

Sample	n^2 (cm²/W)	β (cm/W)	χ3 (esu)	Reference
Pure LPTCA	$6.19x10^{-12}$	$9.46x10^{-7}$	$4.27x10^{-6}$	[present work]
K doped LPTCA	$2.12x10^{-10}$	$9.63x10^{-6}$	$7.01x10^{-5}$	[present work]

4. Conclusions

The transmittance of the K-doped L-PTCA material increased from 61% to 90%, based on UV-visible spectral analysis. The K-doped L-PTCA's optical band gap is found to be 4.68 eV. These developed crystals also have high optical responsiveness and a low refractive index, both of which are important features for a variety of optical purposes. The produced K-doped L-PTCA crystals' optical properties exhibited remarkable potential, making them formidable competitors for electro-optic applications. All the conditions that are advantageous for photonic devices are shown by the optical constant. At 632.8 nm, the Z-scan analysis verified that the K-doped L-PTCA crystals constituted TONLO. At a magnitude of 7.01×10^{-5} esu, the K-doped L-PTCA crystal exhibits saturated absorption ($\beta = 9.63\times10^{-6}$ cm/W) and positive nonlinear refraction ($n_2 = 2.12\times10^{-10}$ cm^2/W). The crystal under consideration exceptional qualities i.e. favorable nonlinear refraction and saturated absorption, make it an ideal candidate for the advancement of ultrafast optical switching, particularly in the domain of 3D optical data storage, photodynamic treatment, and optical power-limiting devices.

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