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Studies on optical, thermal, mechanical and dielectric properties of L-Cysteine doped KDP crystal to explore NLO device applications

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The amino acid L-Cysteine (LC) doped KDP crystal has been grown by slow evaporation technique. The cell parameters of grown crystal were determined by single crystal XRD analysis. The improved optical transparency and wide transmission range of LC doped KDP crystal has been investigated using UV-visible studies. The enhanced optical band gap of LC doped KDP is found to be 5.3 eV. The TG-DTA analysis was carried to examine the thermal stability of grown crystal. The mechanical stability of LC doped KDP crystal has been tested using Vicker's microhardness tester. The dielectric constant and dielectric loss of LC doped KDP crystal has been measured at varying frequency and temperatures. The SHG efficiency was determined using Kurtz-Perry powder test. The third order nonlinear optical parameters of LC doped KDP crystal were determined using Z-scan technique. The effective third order nonlinear susceptibility (χ3) of LC doped KDP is found to be 2.96×10^{-5} esu.

1. Introduction

In series of nonlinear optical (NLO) materials, potassium dihydrogen phosphate (KDP) is the first which still cites attention of many researchers due to its unbounded scope of applications in the field of optical switching, solid state lasers, second harmonic generation (SHG), optical parametric oscillators, telecommunication systems and photonics. The KDP is an ideal crystal material which crystallizes with tetragonal symmetry and possesses potential ferroelectric, piezoelectric and non linear optical properties [1-4]. The use of organic dopants like amino acids which cohabit polar nature (Zwitterionic form) in aqueous solution at normal pH modifies the crystallographic and chemical properties of host materials [5]. In recent past, many attempts had been made to evaluate the improved properties of KDP in presence of various dopants like amino acids and metal ions. The effect of L-arginine, L-histidine and glycine on UV-visible, thermal and dielectric properties of KDP has been explored by Suresh et al [6]. The investigation on nucleation kinetics of L-arginine, L-lysine and L-alanine doped KDP crystals have been successfully accomplished by K.D. Parikh et al [7]. The effect of L-alanine on structural, UV-visible, NLO, thermal, dielectric properties of KDP has been reported in literature [8-9]. The effect of L-glutamic acid and L-valine on performance of KDP crystal has been reported by Kumaresan et al [10]. The

effect of L-proline on growth and NLO properties of KDP has been investigated by Jagdish et al [11]. Of all the literature available on amino acid doped KDP crystals, no reports were found on studies of LC doped KDP crystal. L-cysteine is a sulfur containing amino acid; its chirality enforces non centrosymmetric crystal structure. We have already reported the effect of L-cysteine on optical thermal and mechanical properties of ADP crystal [12] and effect of L-cysteine on optical, electrical and thermal properties of ZTC crystal for NLO application [13]. This paper is first report to investigate the effect of L-cysteine on electrical, thermal, mechanical, linear and nonlinear optical properties of KDP crystal to explore its application for variety of NLO devices.

2. Experimental procedure

The amino acid LC was added in three different weight % in the super saturated solution of AR grade KDP. The homogeneous solutions were prepared by constant stirring for 7 h. The solutions were then filtered and kept for slow evaporation at room temperature. The good quality transparent seed crystals were harvested within 6–7 days. The salts of these three weight % LC doped KDP crystals were subjected to SHG test at Indian Institute of Science Bangalore and highest SHG efficiency was observed with 3 wt % LC doped KDP crystal powder;

hence the bulk crystal of the same with dimension $(26 \times 7 \times 6)$ mm^3 was grown by slow evaporation technique (Fig. 1).

Fig. 1. Photograph of 3 wt % LC doped KDP crystal

3. Results and discussion

3.1. Single crystal XRD

The cell parameters of grown crystal were determined using the Enraf Nonius CAD4 single crystal X-ray diffractometer. The LC doped KDP crystal belongs to the tetragonal crystal system and the slightly changed cell parameters are discussed in Table 1 [2]. The slight change in cell parameters might have been observed due to the successful incorporation of dopant in crystal lattice of KDP crystal.

Table 1. XRD data

Samples	a=b , c (Å)	V(Å)^3	Crystal system
KDP	7.44, 6.94	384	Tetragonal
KDP+LC	7.45, 6.96	386	Tetragonal

3.2. FT-IR spectral analysis

The FT-IR spectral analysis of LC doped KDP crystal was carried using the Bruker α-ATR spectrophotometer in the range of 600-4000 cm^{-1}. The recorder transmittance FT-IR spectrum of grown crystal is depicted in Fig. 2. The identified functional groups of LC doped KDP crystals are discussed in Table 2. The presence of phosphate group is confirmed by O=P-OH bending vibrations at 850 cm^{-1}. The SO_3 in phase stretching vibration of LC is evident at 1080 cm^{-1}. The absorption peak observed at 1280 cm^{-1} corresponds to the P=O bond stretching vibration. The C-C bending vibration is observed at 1398 cm^{-1}. The characteristic NH_2 bond scissoring of LC is evident at

1580 cm^{-1}. The absorption peak at 1768 cm^{-1} is attributed to the P-O-H bending vibration. Thus the identification of carbon, sulphur and nitrogen coordinated bond in present analysis confirms the incorporation of LC in KDP crystal.
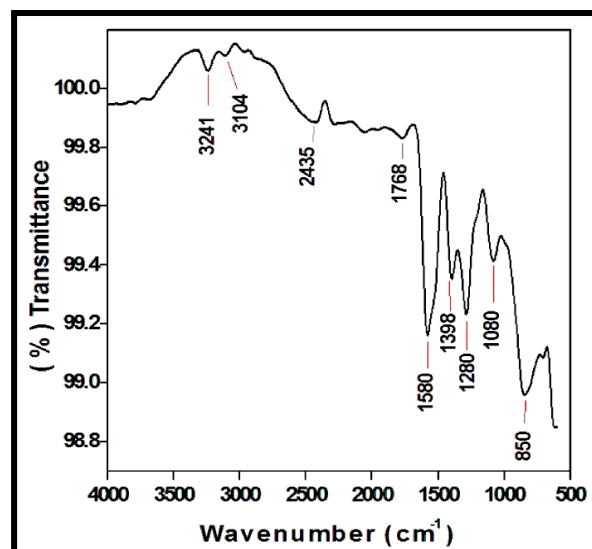

Fig. 2. FT-IR spectrum of LC doped KDP

Table 2. FT-IR assignments

Wavenumber (cm^{-1})		Assignments
KDP [8-9]	KDP+LC	
3239	3241	O–H stretching
3072	3104	O-H stretching
1750	1768	P–O–H bending
--	1580	NH_2 scissoring
--	1398	C-C bending
1279	1280	P=O stretching
--	1080	SO_3 stretching
878	850	O = P-OH bending

3.3. UV-visible studies

The UV-visible study of LC doped KDP crystal has been assessed in the range of 200-900 nm using Shimadzu UV-2450 spectrophotometer. The transmittance spectrum (Fig. 3) of 2 mm thickness crystal evidences the large transmission range of doped KDP crystal which might have been offered due to prominent n to π transitions offered by nitrogen group of LC [14]. The transparency of LC doped KDP crystal is above 75% in entire visible region which is suitable parameter for SHG transmission devices [15].
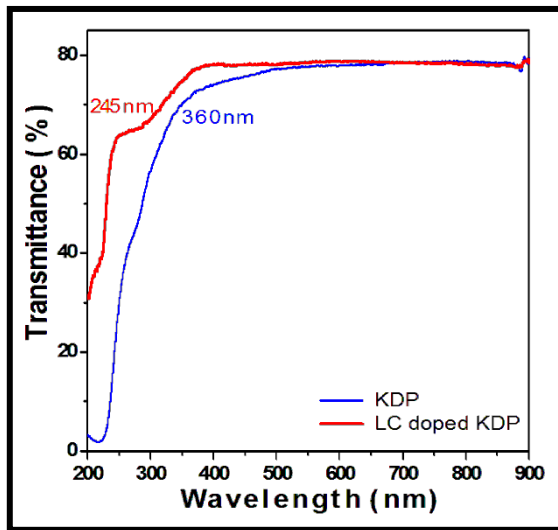
Fig. 3. UV-Visible spectrum

The transition of electron evidences the occurrence of direct band gap, which was evaluated using the relation $\alpha = A (h\nu - E_g)^{1/2}$ [15]. The optical band gap of pure and LC doped KDP crystal was determined using the tauc's extrapolation method as depicted in Fig. 4. The optical band gap of LC doped KDP is found to be 5.3 eV which is greater than pure KDP (5.1 eV). The wide optical band gap of LC doped KDP crystal suggests its prominence for optoelectronic applications [15-16].
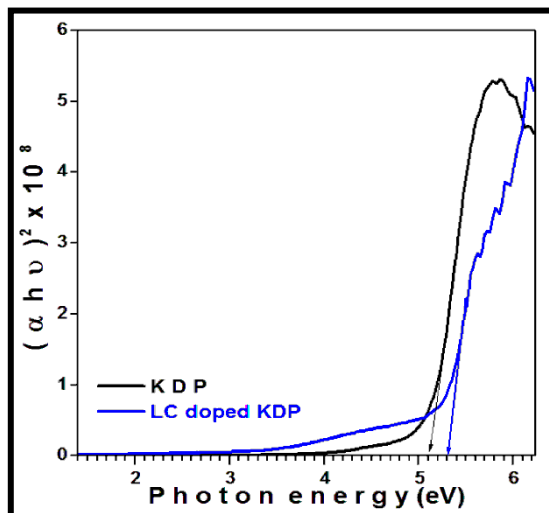

Fig. 4. Tauc's Plot

3.4. NLO studies

The second harmonic generation efficiency of pure and LC doped KDP crystal has been determined using the Kurtz-Perry powder technique [17]. The Q-switched Nd: YAG laser used for present studies operates at wavelength 1064 nm, having the repetition rate of 10 Hz and pulse width of 8 ns delivering the input energy of 2.8 mJ

pulse^{-1}. The grown crystals were finely powdered and tightly filled in a micro capillary tube of uniform bore. The prepared samples were illuminated by the Gaussian beam of Nd: YAG laser and the emergence of bright green light confirmed the second harmonic generation by LC doped KDP crystal. The corresponding output voltages recorded for pure and LC doped KDP crystals are 15.2 mV and 9.9 mV. The SHG efficiency of LC doped KDP crystal is found to be 0.65 times that of KDP which indicates its prominence for NLO application [18].

3.5. Z-scan studies

The third order nonlinear optical properties of LC doped KDP crystal has been investigated using the close and open aperture Z-scan technique developed by Sheikh-Bahae [19]. Gaussian beam of laser was focused using the convex lens on crystal of LC doped KDP (1.5 mm thickness) and allowed to translate along the Z direction. The translation of crystal along the Z direction causes the spatial distribution throughout the crystal surface causing the change in nonlinearity about the focus. The transmittance detected with closed aperture of detector placed at far field evidences the self-focusing or -defocusing ability of the material [19]. The closed aperture transmittance curve of LC doped KDP crystal shown in Fig. 5, indicates the peak to valley phase transition about the focus (Z=0), which is sign of positive refraction nonlinearity. The positive nonlinear refraction is the characteristic feature of material showing self-focusing tendency highly demanded for optical switching devices [20]. The optical kerr-lens mode locking effect is the effectively expressed in material with positive nonlinear refraction which is of vital importance for laser alignment systems and production of shorter pulses [21].
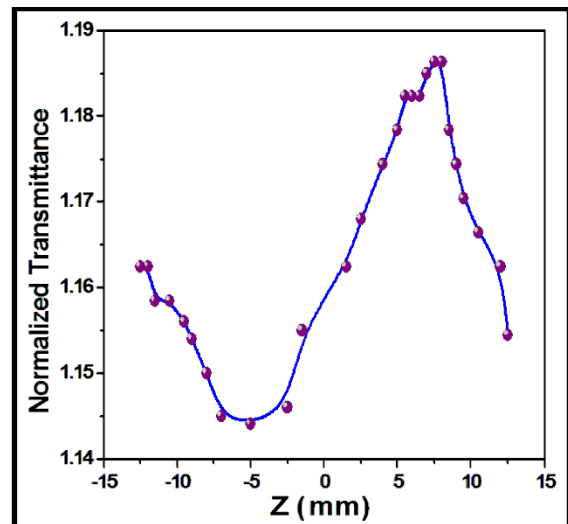

Fig. 5. Closed aperture Z-scan curve

The transmittance difference ΔT (peak to valley) and the nonlinear refractive index (n_2) of LC doped KDP

crystal has been evaluated using the relation quoted below [22],

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}|\Delta\phi| \qquad (1)$$

where S= $[1-\exp\ (-2r_a^2/\omega_a^2)]$ is the aperture linear transmittance, r_a is the aperture radius and ω_a is the beam radius at the aperture,

$$n_2 = \frac{\Delta\phi}{KI_0L_{eff}} \qquad (2)$$

where K = $2\pi\ /\ \lambda$ (λ is the laser wavelength), I_0 is the intensity of the laser beam at the focus Z=0, L_{eff} = [1-exp (-αL)]/α, is the effective thickness of the sample depending on linear absorption coefficient (α) and L is thickness of the sample. The nonlinear absorption coefficient (β) of LC doped KDP crystal was evaluated using the open aperture transmittance curve according to equation shown below [22],

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}} \qquad (3)$$

where ΔT is the one valley value detected in open aperture Z-scan curve. The third order nonlinear susceptibility of LC doped KDP crystal was calculated using the relations depicted below [22],

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

$$\text{Im}\ \chi^{(3)}(esu) = 10^{-2}(\varepsilon_0 C^2 n_0^2 \lambda\beta)\ /\ 4\pi^2(cm\ /\ W) \qquad (5)$$

$$\chi^3 = \sqrt{(\text{Re}\ \chi^3)^2 + (\text{Im}\ \chi^3)^2} \qquad (6)$$

where ε_0 is the vacuum permittivity, n_0 is the linear refractive index of the sample and c is the velocity of light in vacuum. The open aperture transmission curve of grown crystal is shown in Fig. 6, which indicates the saturable absorption of grown crystals.
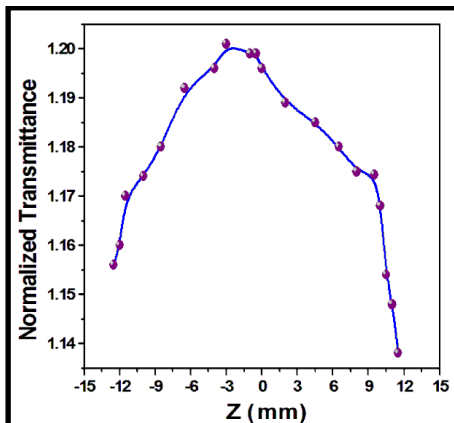

Fig. 6. Open aperture Z-scan curve

The nonlinear absorption coefficient of LC doped KDP crystal is found to be -7.2×10^{-6} cm/W. The third order nonlinear susceptibility (χ^3) is found to be 2.96×10^{-5} esu which is notably greater than pure and 1mole% FA (3.81×10^{-7} esu), MA (2.13×10^{-7} esu) and OA (1.9×10^{-7} esu) doped KDP crystals [23-25]. The higher order nonlinear effect of LC doped KDP crystal originates as a result of delocalisation of π electron cloud in molecular orbits due to influential optical field [26]. The optical details of the Z-scan setup and measured nonlinear optical parameters of the grown crystals are systematically arranged in Table 3. The figure of merit (FOM=$\beta\lambda$/n$_2$) value substantiates the suitability of doped KDP crystal for optical limiting and photonics applications [27] which is found to be 179.

Table 3. Optical detail of Z-scan setup and measured parameters

Laser beam wavelength (λ)	632.8 nm
Lens focal length (f)	12 cm
Optical path distance (Z)	115 cm
Spot-size diameter in front of the aperture (ω_a)	1 cm
Aperture radius (r_a)	4 mm
Incident intensity at the focus (Z=0)	3.13 MW/cm^2
Effective thickness L_{eff}	1.45 mm
Nonlinear refractive index (n_2)	2.538x10^{-12} cm^2/W
Nonlinear absorption coefficient (β)	-7.2 x 10^{-6} cm/W
Third-order nonlinear susceptibility (χ^3)	2.96 10^{-5} esu

3.6. Dielectric studies

The temperature dependent dielectric studies of LC doped KDP crystal has been evaluated using the HIOKI 3250 instrument using 1.3 mm crystal sample. The crystal surface of sample was smoothly silver pasted and placed between the copper electrodes for electrical contacts. The dielectric studies were recorded at different temperature ranging from 40 to 100^0 C with interval of 20^{0}C. Fig. 7 shows the variation of dielectric constant with variation of frequency. As temperature increases it favors high space polarization activity in material medium due to which dielectric constant of sample increases with rise in temperature [28]. The dielectric constant shows decreasing values with increasing frequency at all the temperatures which is ideal parameter necessary for microelectronics applications [29]. With reference to Millers law the lower dielectric constant is favorable parameter for the enhancement of SHG efficiency of the material [30]. The dielectric loss of LC doped KDP crystal increases with rise in temperature and decreases with increasing frequency as depicted in Fig. 8. The lower dielectric loss indicates high optical quality and less concentration of defects. The lower

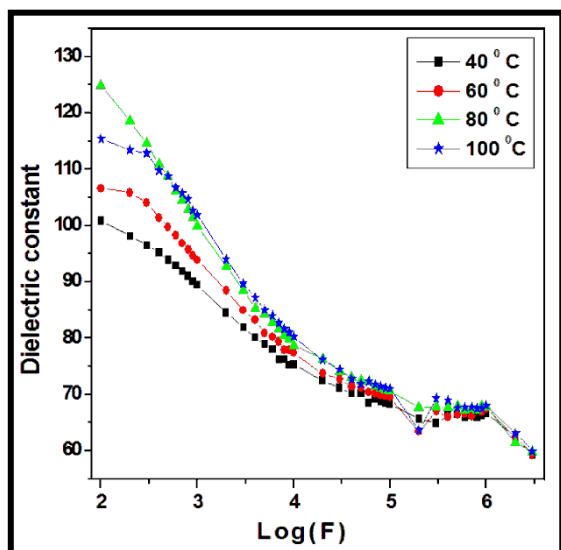dielectric properties of LC doped KDP are vital for NLO applications [30].

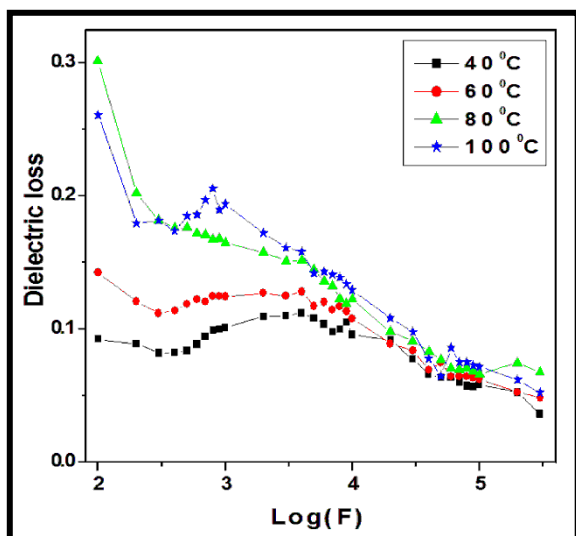*Fig. 7. Dielectric constant vs. Log F*

Fig. 8. Dielectric Loss vs. Log F

3.7. Thermal studies

The thermal behavior of LC doped KDP crystal has been investigated using the PerkinElmer Diamond thermal analyzer in a homogeneous nitrogen atmosphere at a heating rate of 20^0C/min. The simultaneous TG/DTA thermogram of LC doped KDP crystal is shown in Fig. 9. The recorded TGA curve revealed the two stage decomposition. The decomposition of LC doped KDP initiates at 197^0C and the further increase in temperature evidences the gradual decomposition of the compound. The DTA curve shows a strong endothermic peak at 226^0C representing the melting point of the grown crystal. The broad endothermic peak at 253^0C may be due to the

decomposition of volatile constituents like sulfur. The mild endothermic peak at 325^0C coincides with the final decomposition of LC doped KDP crystal. The melting point of LC doped KDP crystal is exclusively higher than glycine doped KDP crystal [5].
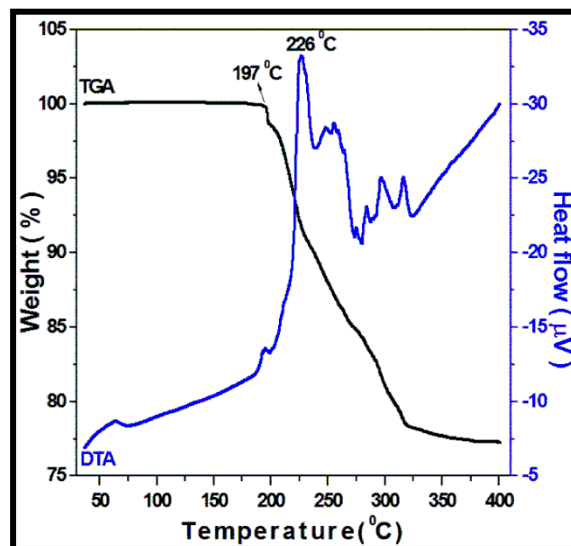

Fig. 9. TG-DTA curve of LC doped KDP

3.8. Microhardness studies

The mechanical strength of the grown crystal has been studied using the Vicker's microhardness intender varying the load from 10 to 200 g for a constant indentation period of 10 seconds. The grown crystal with smooth and dominant face was selected for microhardness studies. The average diagonal values of the indentations were recorded to evaluate the microhardness of the grown crystal. The Vicker's microhardness number was determined using H_v=1.8544 p/d^2 where, P is the applied load in kg and d is in mm. A plot of variation of hardness value and corresponding loads is shown in Fig. 10(a). The hardness number was found to be linearly increased over the entire range of applied load. Similar behaviour was reported in the L-proline doped KDP crystal [11]. The work hardening index of crystal was also calculated using the Meyer's law, which relates the load and indentation diagonal length: P= k.d^n, Where k is the material constant and n is Meyer's index. In order to calculate the value of 'n', the graph is plotted against log P versus log d (Fig. 10(b)), which gives a straight line, the slope of this straight line gives the value of 'n' and the 'n' was calculated to be 2.88. According to Onitsch 'n' should lie between 1 and 1.6 for harder materials and is greater than 1.6 for soft materials [31]. Thus the grown crystal belongs to the soft material category. The LC doped KDP crystal has good mechanical stability as compared to L-arginine doped KDP crystal (n=5.08) while it is lower than pure KDP [32].

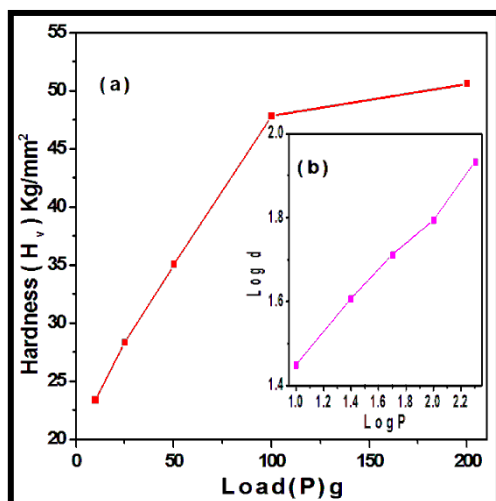*Fig. 10. (a) H_v vs. load   (b) log p vs. log d*

4. Conclusions

The single crystal of LC doped KDP was grown by slow evaporation technique. The single crystal XRD confirmed the tetragonal symmetry of grown crystal. The UV-visible studies of LC doped KDP crystal revealed the large range of transmission and the band gap was found to be 5.3 eV. The encouraging third order nonlinear parameters n_2 (2.53×10^{-12} cm^2/W) and χ^3 (2.96×10^{-5} esu) indicates the high polar nature of LC doped KDP crystal and vitalizes its importance for laser sensitive device applications. The grown crystal has good thermal stability up to 226^0C. The grown crystal exhibits lower dielectric characteristics imperative for microelectronic applications. Microhardness analysis reveals that grown crystal belongs to soft material category.

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