

Growth, structural, optical, electrical and SHG studies of N-N' allylthiourea doped KDP single crystals

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Abstract

Potassium Dihydrogen Phosphate (KDP) crystals are one of the most popular crystals used for Non-linear Optical (NLO) applications. Pure KDP single crystals and KDP crystals doped with N-N' allylthiourea were grown by the method of slow evaporation from aqueous solutions. The grown pure and doped crystals were confirmed by X-ray single crystal and powder diffraction studies. The pure and doped crystals were characterized by FTIR spectroscopy studies. Absorptions of these grown crystals were analyzed using UV-Vis-NIR studies, and it was found that these crystals possess minimum absorption in the entire visible region. Nonlinear optical studies of pure and doped crystals were carried out and it reveals that the dopants have increased the efficiency of KDP crystals. Dielectric measurements were carried out along both the unique axis and perpendicular directions at various temperatures ranging from 40 to 150 °C. The dielectric constant and the dielectric loss values of N-N' allylthiourea doped KDP crystals were lower than the pure KDP crystals. Also, it indicates that 0.8 mole% N-N' allylthiourea addition to KDP leads to low permittivity value dielectrics. The results are discussed.

Key words: Crystal growth, NLO Materials, powder XRD, UV-Vis. studies, SHG efficiency, Dielectric study.

I. Introduction

Potassium dihydrogen phosphate (KDP) and ammonium dihydrogen phosphate (ADP) are nonlinear optical materials and have been used as optical modulation and frequency converters. Particularly, optical crystals with lower impurity and higher damage threshold are required for inertial confinement fusion. This material is successfully utilized in many kinds of optical devices such as non-linear optical elements, electro-optical polarizers, solid state detectors and transformers of radiation, operating in a broad spectral range from the middle infrared to the vacuum ultraviolet (VUV) spectral regions [1]. KDP and DKDP crystals are still the only nonlinear optical crystals which can be applied to laser radiation conversion in laser fusion systems. These crystals are required to have good optical property and high laser damage threshold [2]. It is important that dihydrogen phosphate crystals (in particular, KDP) are a very unique inorganic material with a high content of hydrogen ions (protons) in the crystal lattice. Generally, anion and cation impurities in the solution are adsorbed onto (1 0 1) and (1 0 0) faces of KDP crystal, respectively. This selectivity on impurity adsorption has been attributed to the orientations of anion (H_2PO_4^-) and cation (K^+ or NH_4^+) on the respective crystal faces [3, 4]. In particular, this impurity adsorption causes step-pinning, which affects the optical property due to the density of lattice defects [5].

KDP finds widespread use as a frequency doubler in laser applications and has been studied in great detail. Improvement in the quality of the KDP crystals and the performance of KDP based devices can be realized with suitable dopants. Because of its wide applications in technology, impurities in KDP crystals, including divalent and trivalent metal ions, are introduced and investigated to see the effects on optical, electrical and other physical properties; and also the effects on the crystal growing mechanism and face morphology [6–11]. Divalent and trivalent metal ions occupy mainly different locations. Trivalent metal ions are generally adsorbed on the surface layer, but in a specific study it is seen that trivalent Fe^{3+} ions occupy the FeO_4^{2-} site in the form of FeO_4^{2-} by compensating the charge deficiency via nearby potassium or hydrogen vacancy [9]. Some other groups, like dyes, are also introduced into KDP to see the effects on optical properties, growth mechanism and face morphology [12, 13].

In this present work, to analyze the influence of organic NLO based dopants on the non-linear optical property of KDP crystals, efforts were made to dope KDP with N-N' allylthiourea in different concentration. The effects of impurity atoms on the quality and performance of the material are analyzed. In the present investigation, the growth aspects of KDP and doped KDP have been studied. Bulk crystals of KDP and different concentration of N-N' allylthiourea doped KDP were grown by slow evaporation from aqueous solutions technique. The

structural, chemical, optical, mechanical and non-linear optical properties of the pure and N-N' allylthiourea doped KDP crystals were studied with the characterization studies such as powder XRD, FT-IR, UV-Vis, micro hardness and SHG measurements, respectively. The results for doped KDP are compared with the results of the pure KDP crystals and as well as the results available in the literature.

II. Experimental procedure

Analytical reagent (AR) grade Potassium dihydrogen phosphate (KH_2PO_4), and N-N' allylthiourea were purchased from Merck Chemicals. These compounds were used without further purification for the growth of pure and doped KDP crystals. A supersaturated solution of KDP powder is prepared in double distilled water. The solution is stirred long enough to ensure complete dissolution of the solute, and filtered using Whatmann 100 filter

paper to remove residual microscope particles. The saturated solutions were transferred to clean beakers covered tightly with polythene covers. Small holes were made on the cover for the proper evaporation of the solvent. The whole setup was kept in dust free area and closely monitored. The periods of growth ranged from 5 to 10 days depending upon the temperature of the surroundings and the concentration of dopants in KDP solution. After the completion of growth, crystals were harvested. Good quality optically transparent large size crystals were selected for carrying out experiments. To obtain the N-N' allylthiourea doped KDP crystals, KDP was doped with N-N' allylthiourea in the ratios 1:0.00 (pure KDP), 1:0.02, 1:0.04, 1:0.6, 1:0.08 and 1:0.10 was prepared in separate containers and the same procedure was followed as that for the preparation of pure KDP crystal. Figure 1 shows the photograph of the as grown pure and doped KDP crystals .

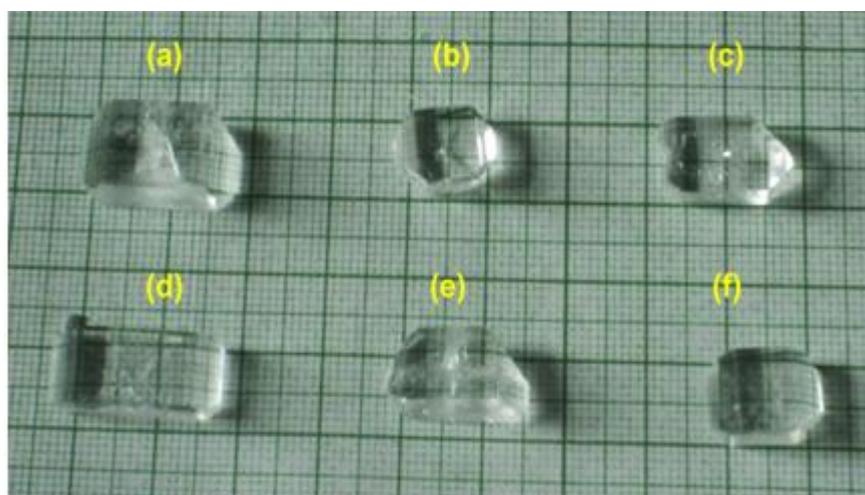


Figure 1. Photograph of the grown crystals (a) pure KDP (b) 2 wt.% N-N' allylthiourea doped KDP (c) 4 wt. % N-N' allylthiourea doped KDP (d) 6 wt.% N-N' allylthiourea doped KDP (e) 8 wt. % N-N' allylthiourea doped KDP and (f) 10 wt. % N-N' allylthiourea doped KDP single crystals

Powder X-ray diffraction analysis was performed to confirm the quality of the crystal and to identify the

cell dimensions using an automated PANalytical X-ray powder diffractometer with monochromated CuK_α radiation ($\lambda=1.54056 \text{ \AA}$) in the range of $15\text{--}65^\circ$ at a scan speed of $1^\circ/\text{min}$. The FTIR spectra of the grown crystals have been recorded in the range $400\text{--}4000 \text{ cm}^{-1}$ using a Perkin-Elmer spectrometer by KBr pellet method in order to study the presence of various functional groups. Optical absorption measurements were done at room temperature using a SHIMADZU UV-2400 PC spectrometer with a medium scan speed sampling interval of 0.5 nm in the wavelength range of $190\text{--}1100 \text{ nm}$. To confirm the nonlinear optical property, Kurtz and Perry powder SHG test [14] was carried out for the grown crystal using Nd:YAG Q-switched

laser which emits the first harmonic output of 1064 nm . Photodiode detector and oscilloscope assembly were used to detect the emitted light from the sample. The dielectric study on pure and doped KDP single crystals was carried on the prominent (100) face. The extended portions of the crystals were removed completely and the crystals more ground to proper thickness and polished. Each sample was electroded on either side with air-drying carbon ink coating so that it behaved like a parallel plate capacitor. A4279A, multi frequency LCR meter (Hawlett-Packard) was used to measure capacitance (C) and dielectric loss ($\tan\delta$) of the sample as a function of frequency.

III. Results and Discussion

The indexed diffraction pattern of pure and N-N' allylthiourea doped KDP crystal is presented in Figure 2. The unit cell parameters and the cell volume have been calculated by using unit cell software programme. The calculated cell parameters are given in Table 1. In addition, the spectrum contain sharp and strong peaks confirms the good

crystallinity of the grown crystals. The observed lattice dimensions are good in agreement with the reported literature values [15]. As the concentration of dopant increases from 0.2 wt. % to 1 wt. %, the XRD peaks are slightly shifted to lower angle side which confirms the incorporation of dopant into the host KDP crystal lattices. This leads to expand the unit cell volume of doped KDP crystals.

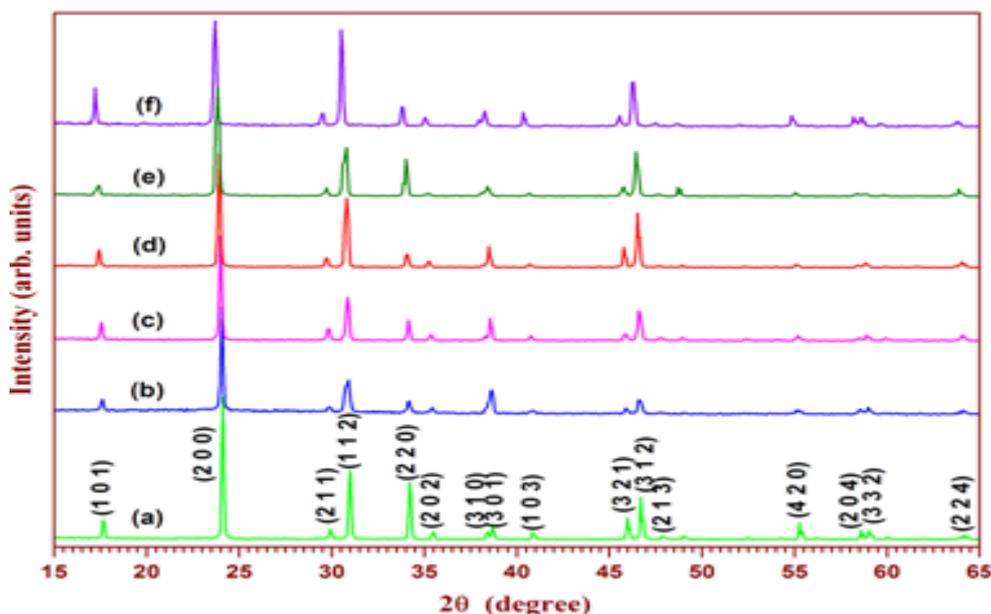


Figure 2. PXRD pattern of (a) pure KDP (b) 2 wt.% N-N' allylthiourea doped KDP (c) 4 wt. % N-N' allylthiourea doped KDP (d) 6 wt.% N-N' allylthiourea doped KDP (e) 8 wt. % N-N' allylthiourea doped KDP and (f) 10 wt. % N-N' allylthiourea doped KDP single crystals

The grown crystals were subjected to FTIR analysis to analyze the presence of functional groups quantitatively. The recorded spectra of pure and N-N' allylthiourea doped KDP crystals are shown in Figure 3. The observed vibrational frequencies and their assignments are listed in Table 2. Assignments were made on the basis of relative intensities, magnitudes of the frequencies and from the literature data [16–18].

The broad absorption band appeared at 3245, 3361, 3255, 3256, 3254 and 3250 were assigned to hydrogen bonded O–H stretching frequencies in pure KDP and different concentration N-N' allylthiourea doped KDP crystals. Its deviation from pure KDP to higher frequency in KDP doped with N-N' allylthiourea indicated clearly the interaction of dopants with P–O–H group of KDP and in reinforcement the bond between oxygen and hydrogen. This leads to the increase in the frequency of O–H stretching and confirmed the non-linear optical property of pure and doped KDP crystals at these sites in the crystal lattice. This property is also reflected in the P=O, P–OR, P–OH stretching and HO–P–OH bending vibrations (see Table 1). There is a broad strong absorption between 1500 and 1700

cm⁻¹ resulting from C-H stretching and O=P–OH stretching bands respectively. The present IR study on pure and doped KDP clearly indicates the effect of dopants on the crystal structure of pure KDP, which leads to the change in the absorption of IR frequencies and the nonlinear optical property of both the crystals.

Table 1. Calculated lattice parameter values for pure and doped KDP crystals from powder XRD. (* indicates lattice parameter value of pure KDP from JCPDS file No. 35-0807)

Sample name	Calculated Parameters		
	a=b Å	c Å	V Å ³
KDP	7.4691	6.9854	389.69
	7.453*	6.974*	387.42*
KDP:0.02	7.4758	6.9987	391.14
KDP:0.04	7.4914	7.0115	393.49
KDP:0.06	7.4821	7.0416	394.23
KDP:0.08	7.5043	7.0452	396.85
KDP:0.10	7.5185	7.0528	398.67

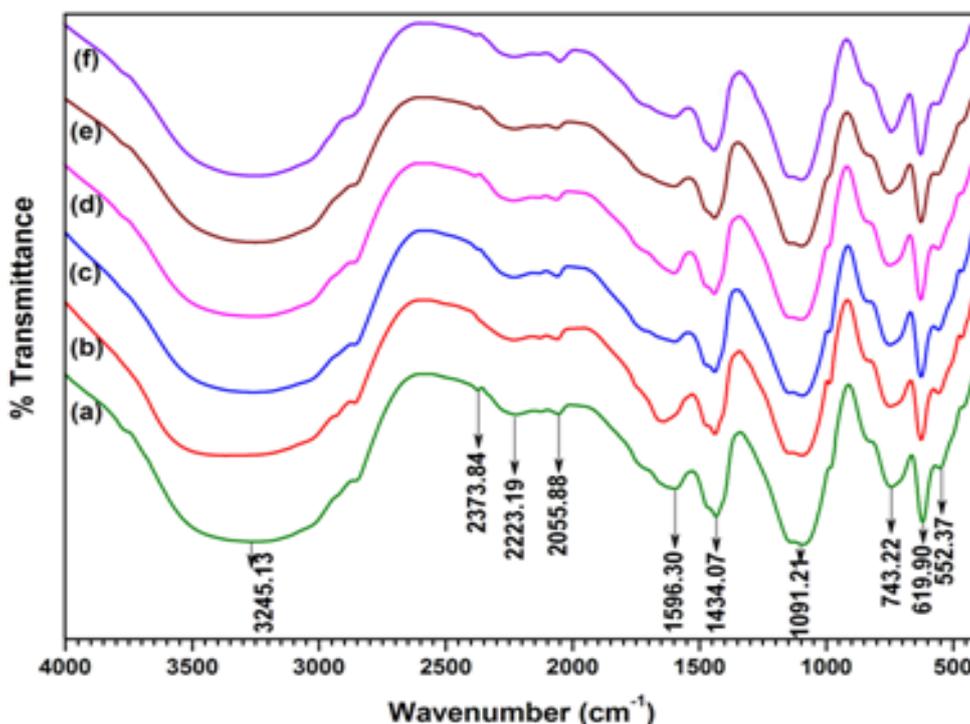


Figure 3. FTIR spectrum of (a) pure KDP (b) 2 wt.% N-N' allylthiourea doped KDP (c) 4 wt. % N-N' allylthiourea doped KDP (d) 6 wt.% N-N' allylthiourea doped KDP (e) 8 wt. % N-N' allylthiourea doped KDP and (f) 10 wt % N-N' allylthiourea doped KDP single crystals

Table 2. Observed IR frequencies (cm^{-1}) of pure KDP and KDP doped with N-N' allylthiourea.

Wave number (cm^{-1})						
Pure KDP	KDP:0.02	KDP:0.04	KDP:0.06	KDP:0.08	KDP:0.10	Assignment
3245	3361	3255	3256	3254	3250	P-O-H bending of KDP
2374	2379	2381	2385	2385	2390	O-H stretch
2223	2226	2224	2224	2223	2226	O-H,N-H stretch
2055	2054	2054	2056	2057	2055	N-H stretch
1596	1635	1590	1592	1593	1598	O=P-OH stretching
1434	1433	1434	1434	1434	1434	C-H stretch
1091	1088	1088	1092	1090	1089	P=O stretching
-	985	979	982	980	987	P-OR stretching
743	742	742	743	743	743	N-H wag 1° , 2° amines
620	619	619	619	620	619	N-H stretch
552	551	551	551	555	552	HO-P-OH bending
-	461	459	449	451	454	N-H Torsional oscillation

The UV-Visible absorbance spectra were recorded in the wavelength region 200–1100 nm. Figure 4 shows the absorbance and transparency in the visible spectral range of the samples. The crystal is highly transparent in the entire UV, Visible and near IR region. The large transmission in the entire visible region enables it to be a good candidate for electro-optic and NLO applications [19,20]. As clear from the Figure 4, optical absorbance is decreasing or transparency is increasing with doping from 0.02 to 0.10 wt. %. The UV absorption edge for the grown pure KDP crystal was observed to be around 268 nm. The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of electrons [21]. The optical absorption coefficient (α) was calculated from the transmittance using the following relation,

$$\alpha = \frac{2.303 \log(\text{absorbance})}{t}$$

where A is the absorbance and t is the thickness of the crystal. Owing to the direct bandgap, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies ($h\nu$):

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

where E_g is optical bandgap of the crystal and A is a constant. The plot of variation of $(\alpha h\nu)^2$ vs. $h\nu$ is shown in inset of Figure 4 and E_g is evaluated by the extrapolation of the linear part [22]. The band gap is found to be 4.63, 4.84, 5.14, 5.32, 5.69 and 5.48 eV for KDP:0.00 (pure KDP), KDP:0.02, KDP:0.04, KDP:0.06, KDP:0.08 and KDP:0.10 crystals respectively. As a consequence of wide band gap, the grown crystal has large transmittance in the visible region [23].

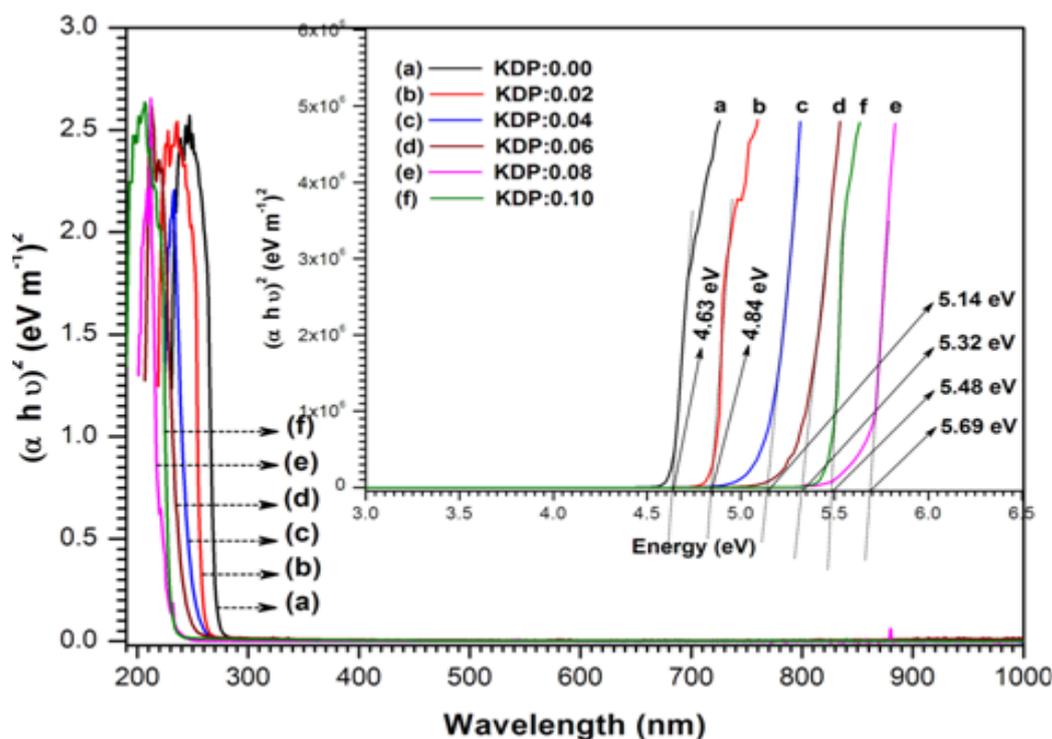


Figure 4: UV-Vis. absorbance spectrum of pure and N-N' allylthiourea doped KDP single crystals. The inset shows the determination of bandgap energies for the respective crystals.

The second harmonic generation signal in the pure and doped KDP crystals are examined by the Kurtz powder technique [14]. A high intense beam from the Nd:YAG laser with the wavelength of about 1064 nm is allowed to be incident on the samples. The SHG signal generation was confirmed by the emission of green radiation from the crystals. From the analysis it is found that the SHG output relative efficiency is 9.1, 11.2, 12.8, 14.1 and 17.6 mJ/pulse for the KDP:0.02, KDP:0.04, KDP:0.06, KDP:0.08

and KDP:0.10 crystals respectively. Comparing the above values with reference to that of KDP (SHG output relative efficiency 8.3 mJ/pulse), the measured SHG efficiency for different concentration of N-N' allylthiourea doped KDP sample was found to be about 1.1 (KDP:0.02), 1.3 (KDP:0.02), 1.5 (KDP:0.02), 1.7 (KDP:0.02) and 2.1 (KDP:0.02) times greater than that of KDP.

The dielectric characteristics of the material are important to know the transport phenomena and the

lattice dynamics in the crystal. It also gives the information about the nature of atoms, ions, bonding and their polarization mechanism in the material. Pure and N-N' allylthiourea doped KDP single crystals cut in to rectangular dimension was subjected to dielectric study. The experiment was carried out in the frequency range 1 kHz – 1 MHz and the temperature range 40–150 °C. The dielectric constant and AC electrical conductivity of the crystals have been calculated using the relations,

$$\epsilon_r = \left(\frac{A_{\text{air}}}{A_{\text{crys}}} \right) \left(\frac{C_{\text{crys}} - C_{\text{air}} \left(1 - \frac{A_{\text{crys}}}{A_{\text{air}}} \right)}{C_{\text{air}}} \right)$$

where C_{cry} is the capacitance with crystal (including air), C_{air} is the capacitance of air, A_{cry} is the area of crystal touching the electrode and A_{air} is the area of electrode.

$$\sigma_{\text{ac}} = \epsilon_0 \epsilon_r \omega \tan \delta$$

where ϵ_0 is the permittivity of free space ($8.85 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$), ω is the angular frequency ($\omega = 2\pi f$; $f = 1, 10, 100$ and 1000 kHz in the present study) and $\tan \delta$ is the dielectric loss factor.

The variation in dielectric constant, dielectric loss and AC electrical conductivity of pure KDP and N-N' allylthiourea doped KDP crystals is depicted as a function of temperature (40 to 150 °C) and as a function of frequency (100 Hz to 1 MHz) in [Figure 5a-f](#). From the plots it is observed that the dielectric constant, dielectric loss and AC conductivity increase with increasing temperature. The dielectric constant

and dielectric loss decreases with increasing frequency and the AC conductivity increases with increasing frequency. The dielectric constant values for N-N' allylthiourea doped KDP crystals are lower than the pure KDP crystals. Dielectric studies furnish a great deal of information regarding the dielectric constant that arises from the contribution of different polarizations, namely electronic, ionic, atomic, space charge, etc., developed in the material subjected to the electric field variations. The dielectric constant is found to be high at lower frequency and decreases exponentially with applied frequency from 100 Hz to 1 MHz ([Figure 5d](#)). The large dielectric constant at low frequency for the crystals in the present study is due to the presence of space charge polarization arising at the grain boundary interfaces [24] whereas, the N-N' allylthiourea doped KDP crystal has low dielectric constant as compared to pure KDP crystals due to high molecular polarizability of the N-N' allylthiourea in the lattice. The variation of dielectric loss with logarithmic frequency ([Figure 5e](#)) indicates the low value of dielectric loss at higher frequency which suggests that the sample has enhanced optical quality which is of vital importance for non-linear optical materials. The conductivity is high for higher frequencies at a given temperature ([Figure 5f](#)) confirming polaron hopping in the crystals [25, 26]. It is clear from the figure that conductivity increases as the temperature increases. This increase in conductivity could be due to the reduction in the space charge polarization at higher frequencies. The low values of dielectric constant and loss at higher frequencies reveal the good optical quality of the grown crystals with less defects [27], which are the desirable property of the materials to be used for various optical and communication devices [27].

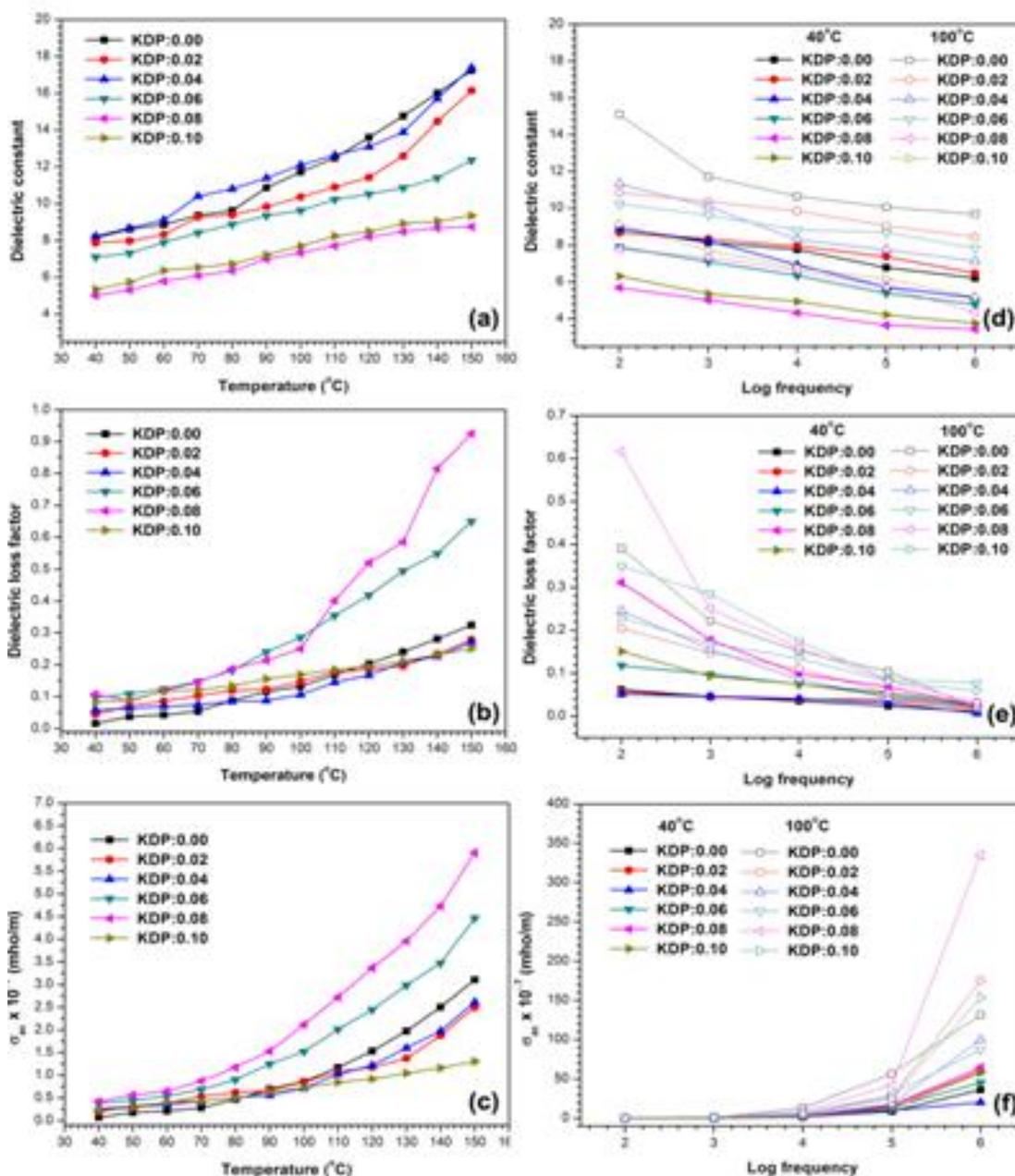


Figure 5: Temperature dependence of electrical parameters such as (a) dielectric constant (b) dielectric loss factor, (c) AC conductivity for the temperature range of 40 to 150 °C at a constant frequency (1 kHz) and frequency dependence of electrical parameters such as (d) dielectric constant (b) dielectric loss factor, (c) AC conductivity for the frequency range of 100 Hz to 1 MHz at 40 °C and 100 °C temperatures.

References

- [1] V.G. Dmitriev, G.G. Gurzadyan, D.N. Nikogosyan, Handbook of Nonlinear Optical Crystals, Springer, Berlin, New York, 2000.
- [2] D. Xu, D. Xue, *J. Rare Earth* 24 (2006) 228.
- [3] D. Xu, D. Xue, H. Ratajczak, Morphology and structure studies of KDP and ADP crystallites in the water and ethanol solutions, *J. Mol. Struct.* 740 (2005) 37–45.
- [4] X. Xu, X. Sun, Z. Wang, G. Xu, Z. Shao, Z. Gao, Supernormal optical characteristics in doped quaternary ammonium salt KDP crystals, *Opt. Mater.* 23 (2003) 409–414.
- [5] E.A. Salter, A. Wierzbicki, T. Land, Ab initio studies of stepped (1 0 0) surfaces of KDP crystals, *Int. J. Quant. Chem.* 100 (2004) 740–745.
- [6] H. Koga, K. Hukuda, *J. Phys. Soc. Jpn.* 25 (1968) 630.

- [7] A. Otani, S. Makhisima, J. Phys. Soc. Jpn. 26 (1969) 85.
- [8] T.A. Eremina, N.N. Eremin, V.A. Kuznetsov, T.M. Okhrimenko, N.G. Furmanova, E.P. Efremova, V.S. Urusov, Crystallogr. Rep. 47 (Suppl. 1) (2002) 76.
- [9] N.Y. Garces, K.T. Stevens, L.E. Halliburton, M. Yan, N.P. Zaitseva, J.J. DeYoreo, J. Cryst. Growth 225 (2001) 435.
- [10] J. Podder, J. Cryst. Growth 237 (2002) 70.
- [11] S. Seif, K. Bhat, A.K. Bata, M.D. Aggarwal, R.B. Lal, Mater. Lett. 58 (2004) 991.
- [12] N.Y. Garces, K.T. Stevens, L.E. Halliburton, S.G. Demos, H.B. Radousky, N.P. Zaitseva, J. Appl. Phys. 84 (1) (2001) 47.
- [13] S. Hirota, H. Miki, K. Fukui, K. Maeda, J. Cryst. Growth 235 (2002) 541.
- [14] S.K. Kurtz, T.T. Perry, J. Appl. Phys. 39 (1968) 3798.
- [15] Fernando Loretta, T. Josephine Rani, P. Selvarajan, S. Perumal and S. Ramalingom, World Journal of Science and Technology 2011, 1(3): 01-06
- [16] S.H. Kim, B.H. Oh, K.W. Lee, C.E. Lee, Phys. Rev. B 73 (2006) 134114.
- [17] S. Koval, J. Kohanoff, R.L. Migoni, E. Tosotti, Phys. Rev. Lett. 89 (2002) 187602.
- [18] M. Rak, N.N. Eremin, T.A. Eremina, V.A. Kuznetsov, T.M. Okhrimenko, N.G. Furmanova, F.P. Efremova, J. Crystal Growth 273 (2005) 577.
- [19] P. Rajesh, P. Ramasamy, Physica B 404 (2009) 1611.
- [20] P. Rajesh, P. Ramasamy, J. Cryst. Growth 311 (2009) 3491.
- [21] N. Tigau, V. Ciupinaa, G. Prodana, G.I. Rusub, C. Gheorghies, E. Vasilec, J. Optoelectronics Adv. Mater. (6) 211.
- [22] A.K. Chawla, D. Kaur, R. Chandra, Optical Mater. 29 (2007) 995.
- [23] D.D.O. Eya, A.J. Ekpunobi, C.E. Okeke, Academic Open Internet J. 17 (2006).
- [24] S. Ishwar Bhat, P. Mohan Rao, A.P. Ganesh Bhat, D.K. Avasthi, Surf. Coat. Technol 158 (2002) 725.
- [25] A. Vijay, A. Hiremath, Venkatraman, Bull. Mater. Sci. 26 (2003) 391.
- [26] V.L. Mathe, K.K. Patankar, M.V. Kothale, S.B. Kulkarni, P.B. Joshi, S.A. Patil, Pramana J. Phys. 58 (2002) 1105.
- [27] C. Balarew, R. Duhlew, J. Solid State Chem. 55 (1984) 1.