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Structural, SHG and Dielectric Study of L-tryptophan Doped KDP 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. Most of the amino acids also exhibit NLO properties. The effect of doping of one of the amino acids, L-tryptophan, in KDP crystals has been investigated. Pure and L-tryptophan doped KDP crystals were grown by slow solvent evaporation solution growth technique. Good quality transparent crystals were obtained within 8 to 10 days. The powder XRD indicated the single phase nature of samples and the unit cell parameters were not altered much due to doping. The value of second harmonic generation (SHG) efficiency increased as the doping of L-tryptophan increased in KDP crystals. The variation of dielectric constant and dielectric loss with frequency in the range from 100 Hz to 100 kHz is reported. The dielectric constant and the dielectric loss of L-tryptophan doped KDP crystals were lower than the pure KDP crystals.

Keywords: Solution growth, Powder XRD, SHG study, Dielectric study.

1. Introduction and Experimental:

Potassium dihydrogen phosphate (KDP) single crystals have a high laser damage threshold, a large nonlinear optical coefficient, good structural and mechanical properties. KDP crystals find several device applications. The electro-optic effect in KDP is used to obtain phase and amplitude modulations [1]. KDP crystal based world's largest laser to generate UV beams has been demonstrated [2]. In order to get good quality crystals rapidly, many techniques have been introduced by several workers. As per one survey the market of NLO materials was $1.66 billion in 2009 and out of which KDP, ADP, and other crystals had share of $15.6 million [3].

Amino acids are interesting NLO materials for doping. They exhibit NLO property because they have a donor NH_2^+ acceptor $COOH^-$ and the intermolecular charge transfer is also possible. Modifications in optical and physical properties of KDP by doping of amino acids such as L-arginine [4], L-lysine [5] L-alanine [6] and L-theonine [7], have been studied. This communication is a part of extensive work which has been carried out to study the effect of doping of amino acids on different physical and optical properties of KDP crystal. The pure and L-tryptophan doped KDP crystals were grown by slow solvent evaporation technique and CHN analysis, FTIR and UV Vis spectroscopy of pure and doped KDP crystals were already reported earlier [8].

The aim of the present study is to investigate the effect of L-tryptophan (amino acid) in KDP crystal by employing various characterization techniques.

The doping of L-tryptophan into KDP was achieved by adding 0.3 wt. % and 0.4 wt. % of L-tryptophan in KDP solution prepared in double distilled water. The growth of pure and L-tryptophan doped KDP crystals were obtained by slow solvent evaporation method. The good quality and transparent were within 8 to 10 days. Figure-1 shows a photograph of 0.4 % L-tryptophan doped KDP crystal.

Fig. 1. Photograph of 0.4 % L-tryptophan doped KDP crystal.

The powder XRD was carried on PHILIPS X'PERT MPD system and the data were analyzed by software powder-X. Kurtz and Perry powder technique was employed to obtain the second harmonic generation (SHG) efficiency. The dielectric measurements were taken on Agilent 4274A LCR meter in the frequency range 100 Hz-100 kHz. The polished single crystal was placed between the two copper electrodes and thus a parallel plate capacitor was formed. The capacitance of the sample was noted for the applied frequency from 100 Hz to 100 kHz.

2. Results and Discussion:

Doping in crystalline materials has expected to modify the physical properties. Earlier, the growth and high frequency dielectric study of pure and thiourea doped KDP crystals [9], thermal, dielectric studies of pure and amino acid doped KDP single crystals [10] are reported.

2.1 Powder XRD:

Figures-2 show the powder XRD patterns of pure KDP and L-tryptophan doped KDP crystals. Powder XRD of pure and L-tryptophan doped KDP crystals reveal slight variation in the unit cell parameters and single phase nature of the sample and belong to tetragonal crystal system. It is also seen that there are no additional peaks present, but only change in the intensity of the peaks takes place, thus structure does not change by doping. The unit cell parameters are listed in Table 1.

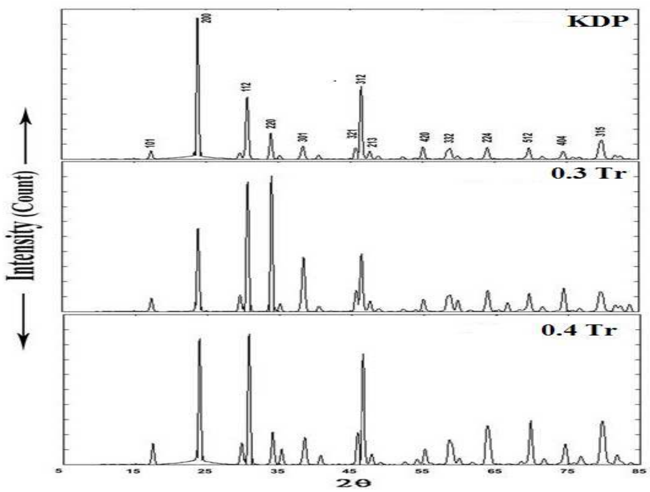

Fig. 2. Powder XRD patterns of pure and L-tryptophan doped KDP crystals

Table 1. Unit cell parameter and SHG efficiency data of pure and L-tryptophan doped KDP crystals.

Samples	Lattice Parameter (Å)		Cell Volume ($Å^3$)	SHG Efficiency
	a = b	c		
Pure KDP Crystal	7.457	6.976	387.9	1
KDP + 0.3 % L-tryp.	7.454	6.973	387.4	1.35
KDP + 0.4 % L-tryp.	7.454	6.973	387.4	1.54

2.2 SHG efficiency:

Kurtz powder method [11] was used by illuminating the powdered sample with fundamental mode (1064 nm) of a Q–switched Nd:YAG laser with input pulse of 2.7 mJ. For the Nd:YAG laser the fundamental beam of 1064 nm generates second harmonic signal of 532 nm. The SHG efficiency values are listed in Table 1. As the doping of L-tryptophan increases in KDP crystals, the SHG efficiency increases. The doping of L-tryptophan in KDP crystal is beneficial to increase SHG efficiency, thus L-tryptophan doped KDP crystals as good candidates for device application.

2.3 Dielectric Study:

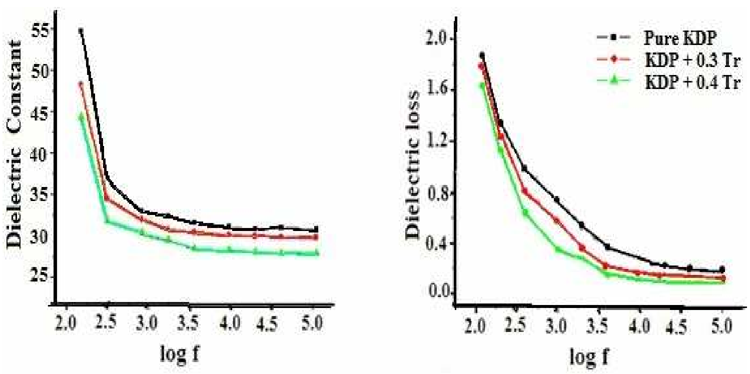

Fig. 3. Dielectric constant and dielectric loss verses *logf* for pure and L-tryptophan doped KDP crystals.

Figure 3 show the plots of dielectric constant (ε_r) and dielectric loss (tanδ) verses frequency for pure and L-tryptophan doped KDP crystals. The dielectric constant and dielectric loss have high values in the lower frequency region. The dielectric constant and the dielectric loss both decrease as the frequency increases and at high frequency region both remain almost constant, which is a normal dielectric behavior. The very high value of ε_r at low frequencies may be due to the contributions from all the four polarizations, namely, electronic, ionic, orientational and space charge polarizations. The electronic exchange of the number of ions in the crystals gives local displacement of electrons in the direction of the applied field, which in turn gives rise to polarization. As the frequency increases, a point will be reached where the space charge cannot sustain and comply with the external field and hence the polarization decreases, giving rise to diminishing values of ε_r. The dielectric constant and the dielectric loss of L-tryptophan doped KDP crystals are lower than the pure KDP crystals. The crystals with low dielectric constant lead to minimum dielectric losses as they possessed less number of dipoles per unit volume and hence L-tryptophan doped KDP crystals might be more useful for high speed electro-optic modulations as compared to pure KDP crystal.

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