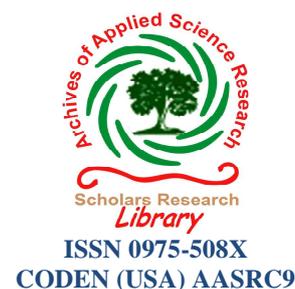




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Electrical properties of allyl thiourea doped KDP single crystals

M. Ugine Prince* and S. Perumal

Physics Research Centre, S.T. Hindu College, Nagercoil

ABSTRACT

Single crystals of pure and N-N'allyl thiourea doped KDP were grown successfully by slow evaporation technique. Allyl thiourea was added in four different weight percentages (2%, 4%, 6% and 8%). In order to improve the electrical characteristics of KDP crystal, a dopant was incorporated into the parent crystal. The pure and doped crystals were characterized by Fourier transform infrared spectroscopy (FTIR) analysis and electrical measurements. The capacitance (C_{crys}) and dielectric loss factor ($\tan \delta$) measurements were carried out to achieve an accuracy of $\pm 2\%$ using an systronic LCR meter (A) for a fixed frequency of 1KHz at various temperatures ranging from 40 - 150°C along a- and c- directions. Here, the results are discussed in the following section.

Key words: Crystal growth, electrical measurements.

INTRODUCTION

A second order nonlinear optics (NLO) is widely used to convert the frequency of coherent sources. Applications such as, laser based imaging, communication, remote sensing, and counter measures system require an improved nonlinear optical materials. A strong need continues to exist for lower cost, more efficient, higher average power materials for optical parametric amplifier operation and second harmonic generation (SHG) throughout the blue near UV spectral regions. Another area of growing need is materials for microelectronic industry with low dielectric constant value. The potassium dihydrogen phosphate (KDP) is the well known member of an important family of compound, where relevant nonlinear optical properties have made it, a widely used crystal in frequency converts, electro-optic switching and modulators, and applications such as second harmonic generation and optical parametric oscillations. Attempts have been made to dope KDP with inorganic additives to study the stability of the grown phase and compositional homogeneity of the existing crystal [1]. The SHG of KDP with the addition of

carbonates of Lithium Li, Sodium Na, Cesium Cs, and Rubidium Rb are reported by Rajasekaran [2]. The organic additives such as urea and thiourea were also doped in KDP and different properties were studied [2, 3]. The electrical conductivity measurements on KDP crystals added with urea and thiourea were reported [4], but no attempt is made on large scale to dope N-N' allyl thiourea into KDP. In our present work, we made an attempt to study the effect of N-N' allyl thiourea as dopant on the electrical properties of KDP.

MATERIALS AND METHODS

Analytical reagent grade (AR) samples of KDP (KH_2PO_4) and N-N' allyl thiourea (C_4H_8) along with double distilled water were used for the growth of single crystals by the free evaporation method. KDP was added with N-N' allyl thiourea in four different wt % viz. 2, 4, 6 and 8 wt %. Supersaturated aqueous solution of the salt (2.3 M) was prepared in a 100 ml beaker (corning glass vessel) and allowed to equilibrate at the desired temperature. The crystals were grown in the unstirred condition. In order to understand whether the added impurity has entered into the KDP lattice or not, we made the FTIR studies. Crystals with high transparency and large surface defect -free (i.e., without any pit or crack or scratch on the surface, tested with a travelling microscope) size ($>3\text{mm}$) were selected and used for the dielectric measurements. The capacitance (C_{crys}) and dielectric loss factor ($\tan\delta$) were measured using the conventional parallel plate capacitor method for fixed frequency using an LCR meter (Systronics make) at various temperatures ranging from 50-150°C along both the a- and c- directions while cooling the sample. The dielectric constant (ϵ_r) and the AC conductivity (σ_{ac}) were calculated in a way similar to that followed by Mahadevan and his co-workers [5-7].

RESULTS AND DISCUSSION

Figure 1 shows the sample crystals grown. Scalenohedral morphology is exhibited by all the crystals grown. All the crystals are found to be stable, colourless and transparent.

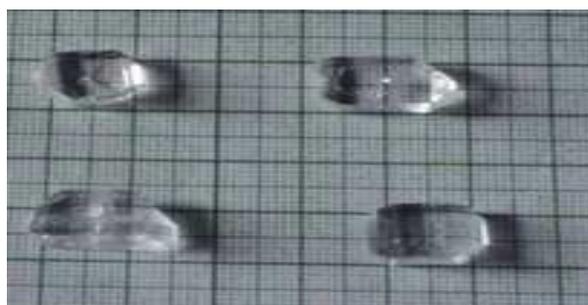


Figure1: Photograph of the sample crystals grown
[From left: Pure KDP and 2,4,6 and 8 wt % doped KDP]

Figure 2 shows the FTIR spectra of the grown crystals, which confirms the chemical composition of the grown crystals. The peak at 2250 cm^{-1} , 550 cm^{-1} confirms the presence of KDP, the peak at 3250 cm^{-1} , 2220 cm^{-1} , 1590 cm^{-1} , 1430 cm^{-1} confirms the presence of N-N' allyl thiourea, and the peak at nearly 1050 cm^{-1} and 750 cm^{-1} denote the complex formation between KDP and N-N' allyl thiourea.

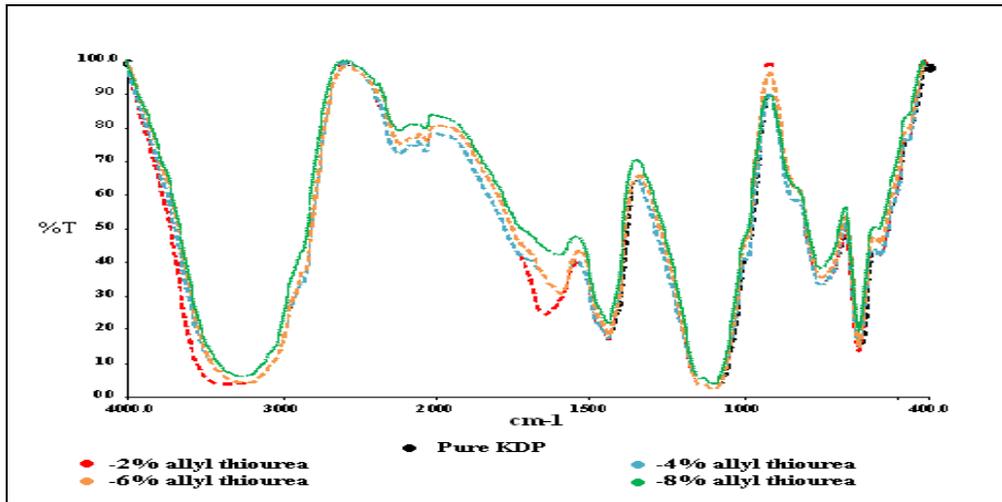


Figure 2: FTIR spectra of pure and doped KDP crystals

The dielectric constants observed in the present study are shown in figure 2a and 2b. The ϵ_r value is increased with the rise in temperature in the case of all five crystals grown in the present study. This is similar to that observed for pure and urea added KDP single crystals reported earlier [5]. Also, the dopant decreases the value of dielectric constant of KDP. This is due to the sulfur present in allyl thiourea, which produces more delocalization of electrons in KDP. According to Millers rule, reduction in ϵ_r favored the enhancement of nonlinear properties. Thus, the result also confirmed the enhancement of NLO properties of KDP by the addition of allyl-thiourea. Udupa et.al.[8] have explained that the decrease of ϵ_r with increase in temperature may be due to the dehydration process of water molecules (acquired during the growth). There is an ion dipole interaction between the dipole moments of water molecules and the effective lattice charges.

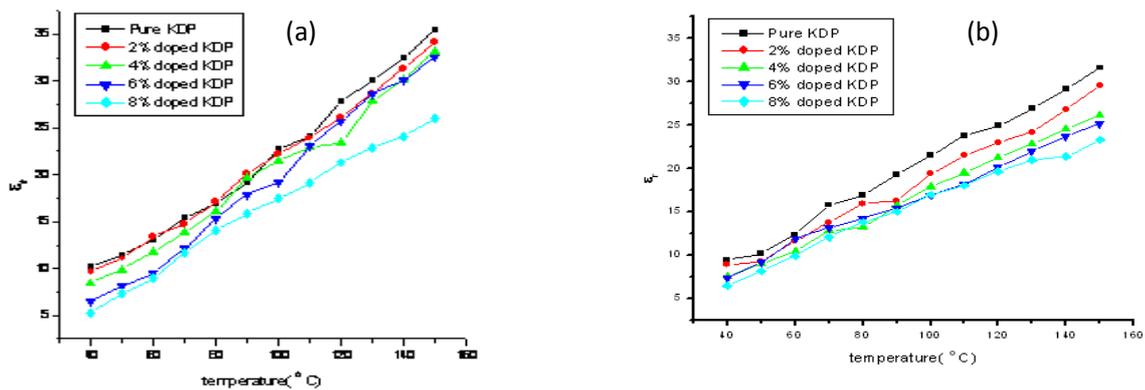


Figure 3: Variation of dielectric constant with temperature for pure and doped KDP at 1 kHz along a) a- and b) c-direction

The obtained $\tan \delta$ values in the present study are shown in figure 3a and 3b. The $\tan \delta$ values are found to increase with rise in temperature. Further, the low $\tan \delta$ values observed indicate that the grown crystals are of good quality.

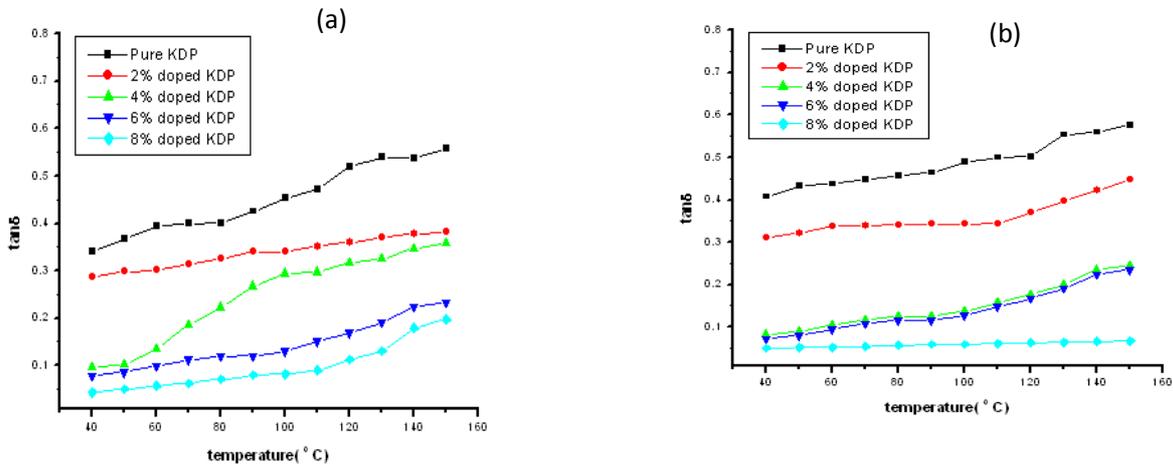


Figure 4: Variation of dielectric loss factor with temperature for pure and doped KDP at 1 kHz along a) a- and b) c-direction

The AC electrical conductivities (σ_{ac}) obtained are shown in figure 4a and 4b. The σ_{ac} values are found to increase with rise in temperature as in the case of ϵ_r and $\tan\delta$ values similar to that observed by Goma et al [7] for urea added KDP single crystals. The conduction in KDP is established to be protonic [9,10] mainly due to the anions [(H₂PO₄)⁻ ions] and not the cations [K⁺ ions]. A combination of the following two mechanisms may be considered. The first mechanism is identical to the conductivity mechanism in ice also containing hydrogen bonds. According to the second mechanism, conductivity is associated with the incorporation into the crystal lattice of impurities and the formation of corresponding defects in ionic crystals. The positive conduction may be accounted for by motion of protons accompanied by a D-defect (excess of positive charge). Migration of these defects may only modify electronic polarizations and may not change the change at an electrode [11].

It is interesting to note that impurity addition (with some concentrations) leads to a reduction of dielectric constant significantly and consequently leads to low ϵ_r – value dielectric material which is gaining more importance nowadays. Allyl thiourea may be considered to be a good choice. sulfur content of the impurity may be a considerable factor in choosing the impurity for reducing the ϵ_r value

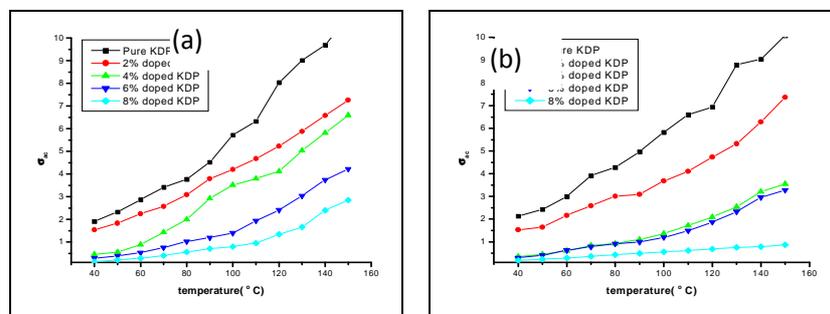


Figure 5: Variation of AC conductivity (x 10⁻⁷ mho/ m) with temperature for pure and doped KDP at 1kHz along a) a- and b) c- direction

CONCLUSION

Pure and allyl thiourea doped KDP crystals were grown from the solution by employing slow evaporation of the solvent. An external observation of the doped crystals shows no change in the morphology of the doped crystals. FT-IR Spectroscopy of the pure and doped KDP crystals confirms the expected doping of the allyl thiourea in the doped KDP crystals. Increasing the doping level in the KDP crystal decrease the values of electrical parameters viz ϵ_r , $\tan \delta$, and σ_{ac} which in turn improve the optical transparency. Thus, Allyl thiourea doped KDP crystals are useful for photonic and electro-optic device fabrication.

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