

Dielectric Measurements on undoped and urea added DSHP Single Crystals

P. G. Praveen¹, Ayarine G. Dhas¹, R. Rakesh², N. Thangaraj³, and
N. Joseph John^{3*}

¹Department of Physics, Government Arts College, Ooty, Tamilnadu-643 002, India.

²Department of Physics, Sethupathy Government Arts College, Ramanathapuram, Tamilnadu-625 005, India.

³Department of Physics, Kamarajar Government Arts College, Surandai, Tamilnadu-627 859, India.

Corresponding Author: P. G. Praveen

Abstract: In recent years, nonlinear optical materials(NLO) have been of immense interest for their excellent applications in optical communication, second harmonic generation(SHG), optical communication, laser technology, optoelectronic technology and data storage technology etc. Disodium Hydrogen Phosphate is one such material which could be used for the above applications. It is an interesting and promising inorganic NLO material of phosphate group. It occurs in hydrated form and hence it has hydrogen bonding, as a result, DSHP is expected to have good nonlinear optical properties. Good quality transparent single crystals of pure and urea added Disodium Hydrogen Phosphate (DSHP) were successfully grown by slow evaporation method. Melting point of the grown crystals were measured. Electrical conductivity measurements were carried out at 1 kHz frequency at various temperatures ranging from 2 to 30°C by using the parallel plate capacitor method. The present study shows that the conductivity in DSHP crystals, for all the impurities considered, increases with the increase in temperature.

Key Words: Crystal growth, Characterization methods, Dielectrics, Electrical properties.

Date of Submission: 10-11-2018

Date of acceptance: 25-11-2018

I. Introduction

Disodium hydrogen orthophosphate (DSHP) is an interesting and promising inorganic NLO material of phosphate group [1-3]. Electrical conductivity is an elegant experimental tool to probe the structural defects and internal purity of crystalline solids. Most of the earlier investigations on alkali halides, rare earth tungstates, divalent vanadates, phosphates and oxalates, and other ferroelectric materials described the electrical conductivity in terms of electrons (or holes), polarons, impurities and thereby the mechanism of ionic conductivity was established on firm footing[4-14].

The electrical conductivity for ionic materials is found to be very low which may be due to the trapping of some carriers at defect sites. At a particular temperature, however, the Gibb's free energy of a crystal is minimum when a certain fraction of ions leaves the normal lattice. As the temperature rises, more and more defects are produced which, in turn, increase the conductivity[10]. In the high temperature (intrinsic) region, the effect of impurity on electrical conduction will not change appreciably whereas in the low temperature (extrinsic) region, the presence of impurity in the crystal increases its conductivity. The electrical conduction in dielectrics is mainly a defect controlled process in the low temperature region. The presence of impurities and vacancies mainly determines this region. The energy needed to form the defect is much larger than the energy needed to form the defect is much larger than the energy needed for its drift [15,16]. The conductivity of the crystalline material in the higher temperature region is determined by the intrinsic defects caused by the thermal fluctuations in the crystal.

Disodium hydrogen orthophosphate (DSHP) is one of the very good NLO materials of phosphate group. It belongs to heptahydrate class of monoclinic crystal system in the space group $P2_1/n$ having unit cell dimensions $a = 9.2432(4) \text{ \AA}$, $b = 10.9550(5) \text{ \AA}$ and $c = 10.4216(5) \text{ \AA}$ and $\beta = 95.651(1)^\circ$ hydrated crystal of this kind is expected to have hydrogen bonding, as a result, these crystals are expected to have good nonlinear optical properties. The NLO property of this material is confirmed by Nd:YAG laser[17]. DSHP crystals found a number of scientific applications and specific uses in the industry[18]. It is thermally stable up to 800°C but there is an internal weight loss due to water of crystallization at lower temperature. It is some times difficult, with the X-ray crystallographic studies to determine the molecular structure and the associated space group, in particular when the possible structures differ mainly in the hydrogen positions. The postulated disorder involves predominantly the protons that are distributed between two equally populated sites. It is found that there is a disorder in the phosphate group in sodium hydrogen phosphate [19, 20].

Effect of urea on growth, metastable zone width, induction time, nucleation parameters, dielectric parameters, lattice distortion etc., on some hydrogen phosphate single crystals were reported by several investigators[17-20]. Urea is a well known simple organic nonlinear optical(NLO) material. It is expected to occupy the interstitial positions (as no replacement of ions is possible) in DSHP crystal if added as impurity. It is also expected to disturb the hydrogen bonded materials.

A research programme has been planned in our laboratory to carry out a series of investigations on these materials at lower temperatures. As a part of our research programme we have grown higher quality DSHP single crystals and urea doped with five different concentrations by the slow evaporation method. The objective of the present work were to investigate the effects of urea doping on the normalized growth yield and dielectric properties of DSHP crystals. Herein we report the results obtained.

II. Experimental

Analytical reagent (AR) grade DSHP, urea and double distilled water were used for the growth of single crystals from aqueous solutions by using the procedure reported by John N. J. et al [1] . In the same way DSHP was added with urea in five different molar concentrations namely 1:0.002, 1:0.004,1:0.006, 1:0.008 and 1:0.010. The same molar concentration and temperature was maintained while preparing the doped crystals. The crystals were harvested after 20-30 days and shown in figure 1.



Figure 1: Photograph showing the pure and urea added DSHP crystals grown [From left are : pure, 0.2, 0.4, 0.6, 0.8 and 1.0 mole% urea added]

The melting point of the grown crystals was measured using a melting point apparatus (model : tempo 120). The sample crystals had a thickness about 4 mm and was polished for electrical measurements. Opposite faces of the sample crystals were coated with good quality graphite to obtain a good ohmic contact with the electrodes. The capacitance and dielectric loss ($\tan \delta$) were measured using the conventional two probe technique [24-29] at various temperatures ranging from 2 to 30°C using an LCR meter (Model APLAB) with frequency 1 kHz. The dielectric constant was calculated using the relation

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

where C_{crys} is the capacitance with crystal (including air), C_{air} is the capacitance of air, A_{crys} is the area of the crystal touching the electrode and A_{air} is the area of electrode. The AC electrical conductivity (σ_{ac}) was calculated using the relation $\sigma_{\text{ac}} = \epsilon_0 \epsilon_r \omega \tan \delta$ where ϵ_0 is the permittivity of free space(8.85×10^{-12} Farad/m) and ω is the angular frequency ($\omega = 2 \pi f$, $f = 1\text{kHz}$).

The resistance of the crystals were measured using a thousand meg ohmmeter. The observations were made while heating the sample. The dimensions of the crystals were measured using a traveling microscope . The DC conductivity (σ_{dc}) of the crystal was calculated using the relation $\sigma_{\text{dc}} = d / (RA)$ where d is the thickness of the sample , A is the area of the sample and R is the measured resistance.

III. Results and Discussion

All the crystals grown are found to be stable at room temperature, colourless, transparent and have well defined appearance. Since the temperature has not been completely kept constant during the growth of the crystals in the present work, there are morphological changes in the grown crystals. The melting point of pure DSHP crystal was found to be 35°C. This is in good agreement with the reported value[23]. The impurity added DSHP also melts at this temperature. Therefore, urea whose melting point is higher than DSHP [29] doesn't alter the melting point of the grown DSHP crystals.

The term dielectric applies to the material properties governing the interaction between matter and electromagnetic field. Induced or permanent electric polarization or magnetization of matter as a function of static or alternating electric, magnetic or electromagnetic field constitutes the dielectric properties of the material. The dielectric constant is one of the basic electrical properties of solids. Various polarization

mechanisms in solids such as atomic polarization of the lattice, orientational polarization of dipoles and space charge polarizations can be understood very easily by studying the dielectric properties as a function of frequency and temperature for crystalline solids [30-33]. These investigations help in detecting the structural phase transitions taking place in solids when abrupt changes in dielectric properties are observed. Particularly the presence of a dielectric between the plates of a condenser enhances the capacitance. The effect makes material with dielectric constant useful in capacitor technology.

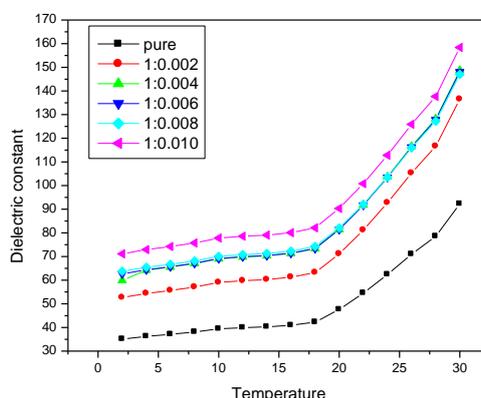


Figure 2: Variation of dielectric constant with temperature

The ϵ_r values obtained for the grown crystals for 1 KHz frequency in Figure 2. The dielectric constant increases with the increase in temperature for both the frequencies. Variation of ϵ_r with temperature is generally attributed to the crystal expansion, the electronic and ionic polarizations and the presence of impurities and crystal defects. The variation of ϵ_r at low temperature is mainly due to the expansion and electronic and ionic polarization. At higher temperatures, the increase is mainly attributed to the thermally generated charge carriers and impurity dipoles [35].

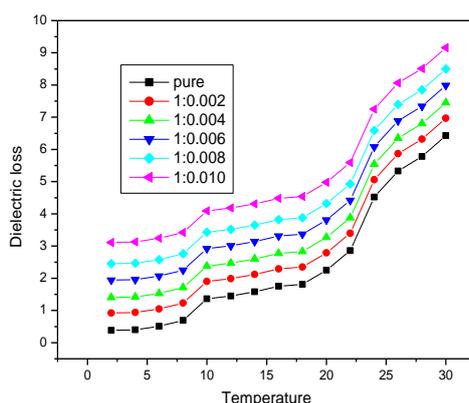


Figure 3. Variation of dielectric loss with temperature

The dielectric loss tangent ($\tan \delta$) is the imaginary part of dielectric constant and determines the lossiness of the medium. Similar to dielectric constant low loss tangent results in fast substrate while large loss tangent results in a slow substrate [37]. The dielectric loss values obtained for the frequency for 1 KHz in Figure 3. It increases with the increase of temperature. This may be attributed to the movement of halide ions in random directions. Since the dipoles of larger relaxation times are not able to respond to the higher frequencies, the ϵ_r and $\tan \delta$ are low at higher frequencies. This is due to the space charge polarization, which depends on the purity and perfection of the grown crystal. The low value of dielectric loss at high frequency can be taken as a proof for the good optical quality of the grown crystals.

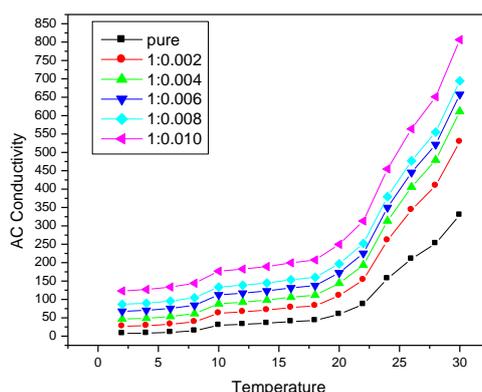


Figure 4 Variation of AC conductivity with temperature

The AC electrical conductivity (σ_{ac}) values obtained for all the six crystals for the two frequencies are provided in Figure 4. The AC electrical conductivity increases with increase in temperature and show no systematic variation with impurity concentration as in the case of dielectric constant and dielectric loss values. The reason may be due to the movement of halide ions in random directions, because of the ion-ion correlation which brings about the disorder [38,39]. The electrical conduction in dielectrics is predominantly a deformity controlled procedure in the low temperature region and the nearness of polluting influences and opening chiefly decide this locale. The deformity fixation will increment exponentially with temperature and therefore the electrical conduction additionally increments with respect to temperature. The σ_{ac} decreases with the increase of concentration of LA in TTCC matrices. The values obtained for σ_{dc} are presented in Figure 5. The DC conductivity also increases with the increase in temperature. The conductivity of the grown crystals just about demonstrates a direct association with temperature. The influence of the temperature on conductivity can be clarified by considering the versatility of charge bearers in charge of bouncing. As temperature builds the portability of bouncing particles additionally increments which thus tend to expand the conductivity.

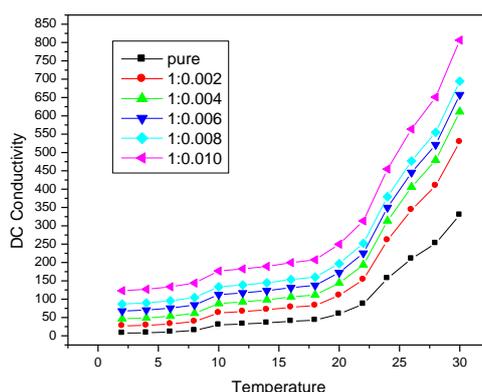


Figure 5: Variation of DC electrical conductivities with temperature

IV. Conclusions

Single crystals of undoped and urea doped disodium hydrogen orthophosphate (DSHP) were grown by the slow evaporation method. The grown crystals are transparent and with well defined external appearance. Melting point measurement indicates that the impurity doesn't alter the melting point. Capacitance and dielectric loss tangent ($\tan \delta$) measurements were carried out for the grown crystals at various temperatures ranging from 2 to 30 °C using an LCR meter with frequency 1 kHz. Dielectric constant and AC electrical conductivity were determined from the measured capacitance and $\tan \delta$ values. DC electrical conductivity was also measured at various temperatures. The dielectric constant, $\tan \delta$, σ_{ac} and σ_{dc} are found to increase with increasing temperature for both the frequencies.

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IOSR Journal of Applied Physics (IOSR-JAP) is UGC approved Journal with SI. No. 5010, Journal no. 49054.

P. G. Praveen. "Dielectric Measurements on undoped and urea added DSHP Single Crystals." IOSR Journal of Applied Physics (IOSR-JAP) , vol. 10, no. 6, 2018, pp. 21-25.