

Electrical Conductivity Measurements On Undoped And ADP Doped Disodium Hydrogen Phosphate (DSHP) Single Crystals

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Abstract : Electrical conductivity is an elegant experimental tool to probe the structural defects and internal purity of crystalline solids. In the present study we have grown undoped and ADP doped DSHP single crystals by the slow evaporation method from aqueous solutions at room temperature. Good quality transparent crystals have been obtained. Melting point and density measurements were done. Electrical conductivity measurements were carried out with two frequencies, 100 Hz and 1 kHz at various temperatures ranging from 2 to 30°C by using the parallel plate capacitor method. The present study indicate that the dielectric constant and AC and DC conductivities increase with increase of temperature.

Keywords : Crystal growth, Characterization methods, crystal structure, Dielectric constant, Dielectric loss, AC Conductivity, DC conductivity, Electrical properties, slow evaporation method .

Date of Submission: 12-11-2018

Date of acceptance: 26-11-2018

I. Introduction

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 [1-3], rare earth tungstates [4-7], divalent vanadates [8], phosphates and oxalates [9-11], and other ferroelectric materials [12,13] described the electrical conductivity in terms of electrons (or holes), polarons, impurities and thereby the mechanism of ionic conductivity was established on firm footing.

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 [14]. 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 hepahydrate 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 $\beta = 95.651(1) \text{ \AA}$ 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].

Ammonium dihydrogen orthophosphate (ADP), $(\text{NH}_4)\text{H}_2\text{PO}_4$, continues to be an interesting material both academically and industrially. ADP is a representative of hydrogen bonded crystals which possesses very good electro-optic and nonlinear optical (NLO) properties in addition to interesting electrical properties. Due to its interesting electrical and optical properties, structural phase transitions, and ease of crystallization, ADP has

been the subject of a wide variety of investigations. The demand for high quality large ADP single crystals increases due to their application as frequency conversion crystal in inertial confinement fusion [21]. ADP belongs to the scalenohedral (twelve faced) class of tetragonal crystal system and is isomorphous to KDP (potassium dihydrogen orthophosphate) [22].

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 Ammonium Dihydrogen Phosphate (ADP) doped with five different concentrations by the slow evaporation method. The objective of the present work was to investigate the effects of ADP in the normalized growth yield and electrical studies. Herein we report the results obtained.

II. Experimental

Analytical reagent (AR) grade DSHP, ADP 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 [21]. In the same way DSHP was added with ADP 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 undoped and ADP doped DSHP crystals grown [From left are : 0.0 (undoped DSHP), 0.2, 0.4, 0.6, 0.8 and 1.0 mole% ADP doped]

The melting point of the grown crystals was measured using a melting point apparatus (model : tempo 120). When the crystals are grown in the same container in some medium, there is a possibility that the dielectric constant and related properties are different for different crystals. It would be better if there is a possibility to estimate quantitatively the concentration level of impurity that is present in each crystal. Hence, in order to understand qualitatively at least whether the added impurity has entered into the lattice or not, we carried out the density measurement by using the floatation technique [21-25]. Carbon tetrachloride of density 1.594 g./cc and bromoform of density 2.890 g/cc were used for that purpose.

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 [26-29] at various temperatures ranging from 2 to 30°C using an LCR meter (Model APLAB) with two frequencies, namely 100Hz and 1 kHz. The dielectric constant was calculated using the relation

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

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 ($\omega = 2 \pi f$, $f = 100$ Hz & 1kHz). 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[21]. The impurity added DSHP also melts at this temperature. Therefore, ADP whose melting point is higher than DSHP [25] doesn't

alter the melting point of the grown DSHP crystals. Figure 2 shows the variation in density values obtained in the present study. For the impurity considered in the present study the observed increase of density of DSHP crystal caused by the impurities indicates that the impurity molecules have entered into the lattice of DSHP crystals. Moreover it can be seen that the density increases further with the increase in impurity concentration of the aqueous solution of DSHP used for the growth of crystals. The observed density value of DSHP compares well with that reported in the literature[21].

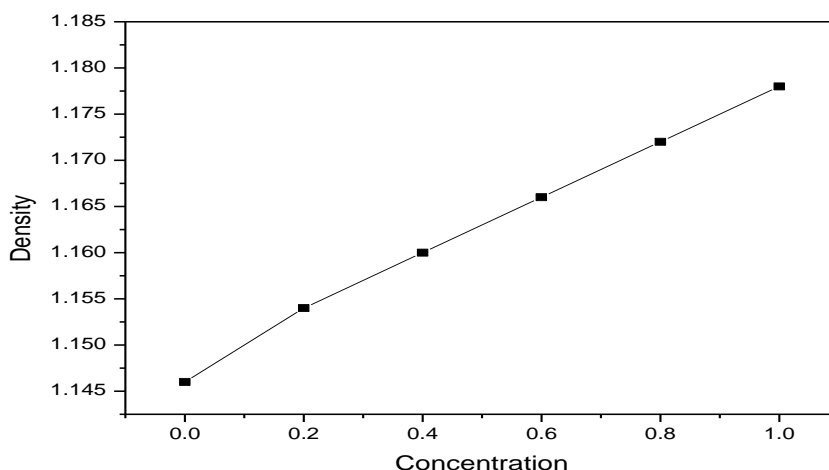


Figure 2 : Variation of density with impurity

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]. At lower frequencies at which all four types of polarizations contribute, the rapid increase in dielectric constant is mainly due to space charge and dielectric polarizations, which are strongly temperature dependent[34,35]. In the case of space charge polarization which is due to the accumulation of charges at the grain boundary, an increase in polarization results as more and more charges accumulate at the grain boundary with the increase in temperature. Beyond a certain temperature, the charges acquire adequate thermal energy to overcome the resistive barrier at the grain boundary and conduction takes place resulting in decreasing of polarization. This interfacial polarization occurs up to frequency of 1 kHz with possibly some contribution from the dipolar polarization also as the temperature increases. 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.

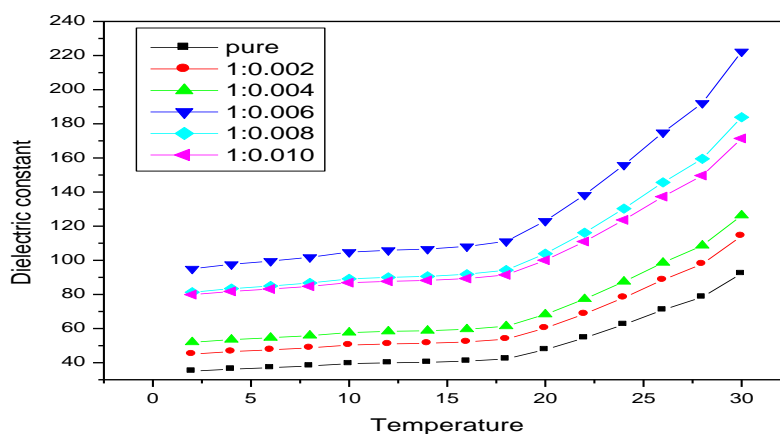


Figure 3a: Variation of dielectric constant with temperature at 100 Hz

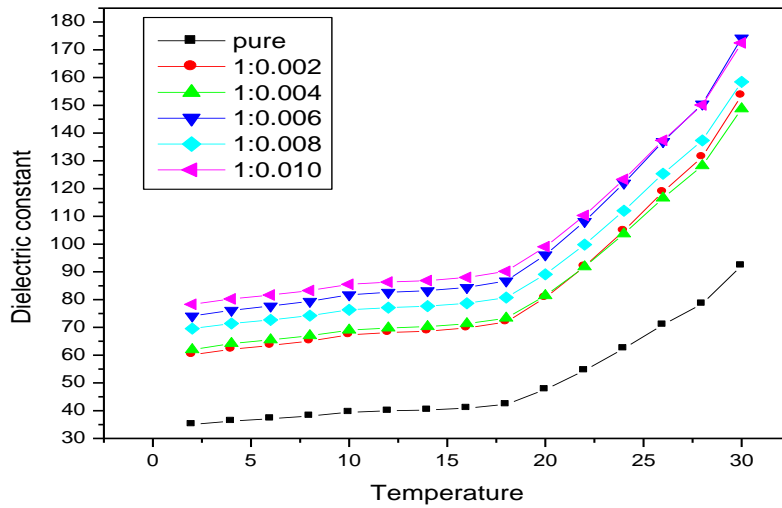


Figure 3b: Variation of dielectric constant with temperature at 1 kHz

The ϵ_r values obtained for the grown crystals for 100 Hz frequency is provided in Figure 3a and for 1 KHz frequency in Figure 3b. 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[36-39].

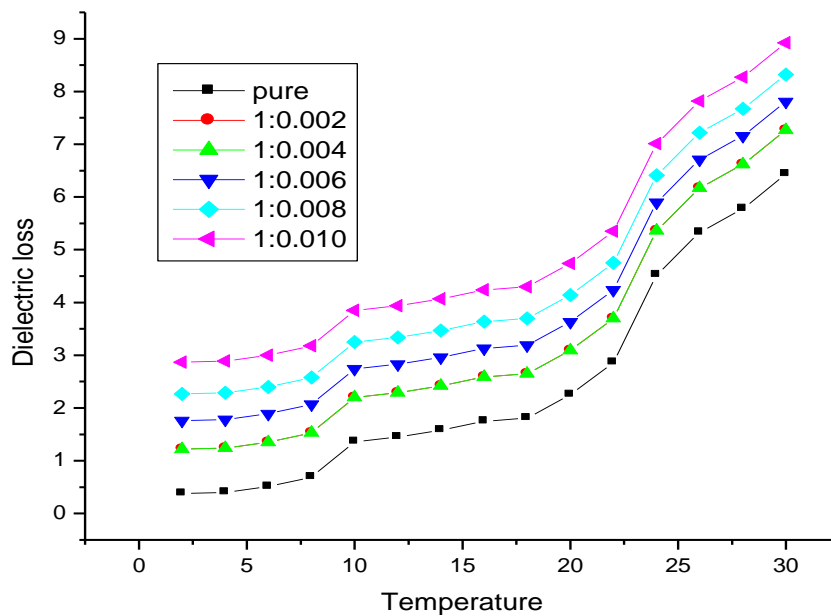


Figure 4a: Variation of dielectric loss with temperature at 100 Hz

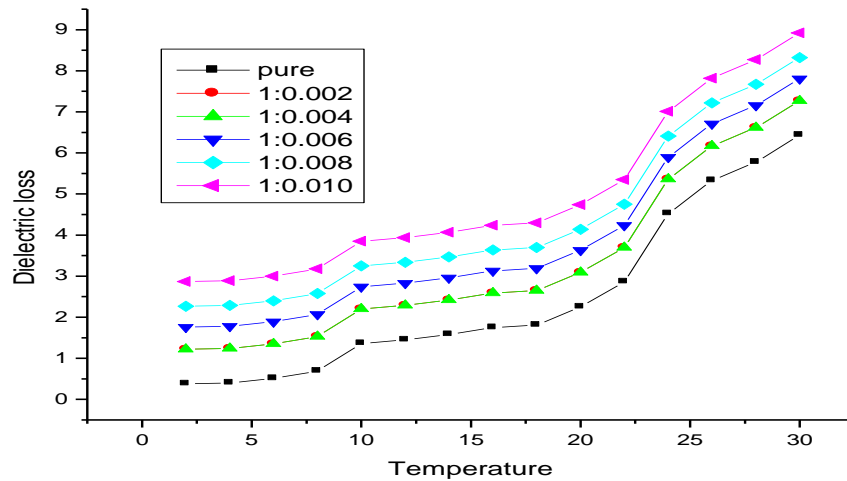


Figure 4b. Variation of dielectric loss with temperature at 1 kHz

The dielectric loss factor $\tan\delta$ represents the energy dissipation in dielectric system and it arises when the polarization lags behind the applied electric field. It is observed that dielectric loss is high at higher temperatures. It can be explained on the basis that at lower frequencies the trend in loss is due to space charge polarization and at higher temperature behavior of loss may be due to macroscopic distribution of charges [40,41]. Further, it can be explained by Shockley-Read mechanism. According to this mechanism, at lower and middle frequencies and at higher temperatures the impurity ions in the bulk crystal matrices capture the surface electron, causing the surface charge polarization at the surfaces. This process increases with increase in 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 [42-45]. The dielectric loss values obtained for the frequency 100 Hz is presented in Figure 4a and for 1 K Hz in Figure 4b. It increases with the increase of temperature. This may be attributed to the movement of halide ions in random directions.

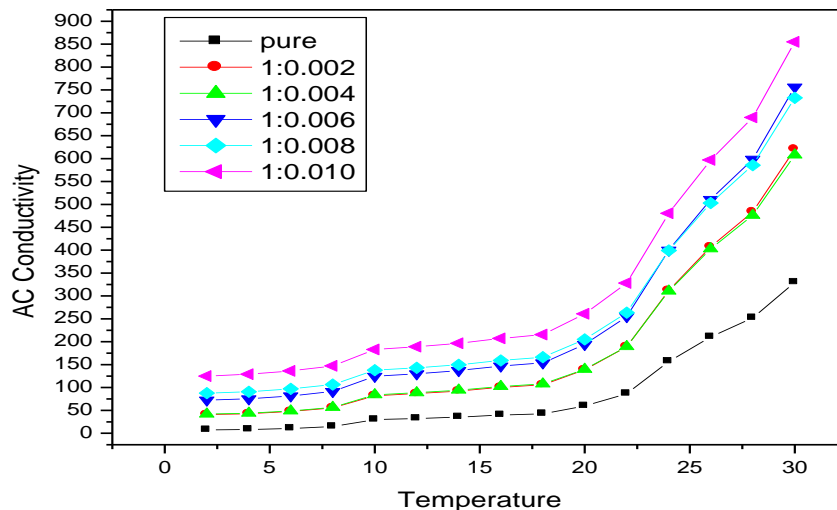


Figure 5a Variation of AC conductivity with temperature at 100 Hz

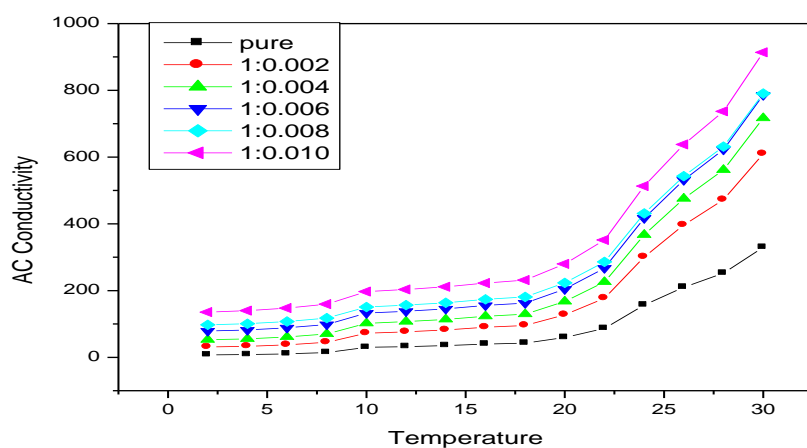


Figure 5b Variation of AC conductivity with temperature at 1 kHz

The AC electrical conductivity (σ_{ac}) values obtained for all the six crystals for the two frequencies are provided in Figure 5 a&b. 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 [46-47]. AC conductivity increases with the increase of temperature. This behavior can be explained on the basis that charge carriers are transferred between different localized states and trapped charges are liberated with the help of pumping force of the applied frequency [48,49]. The electron-hopping model explains the electrical conduction mechanism in which electron hopping between the lattice sites takes place. Consequently, the hopping frequency of charge carriers increases with the increase in frequency resulting in an increase in conductivity. Electrical conductivity increases with the increase in temperature due to the increase in drift mobility of the thermally activated charge carriers [50, 51].

The values obtained for σ_{dc} are presented in Figure 6. The electrical conductivity of a solid is due to the mobility of electrons or ions or ions or imperfections which are charged. In the case of semiconducting materials, the conductivity is due to the movement of electrons and holes. The DC conductivity also increases with the increase in temperature.

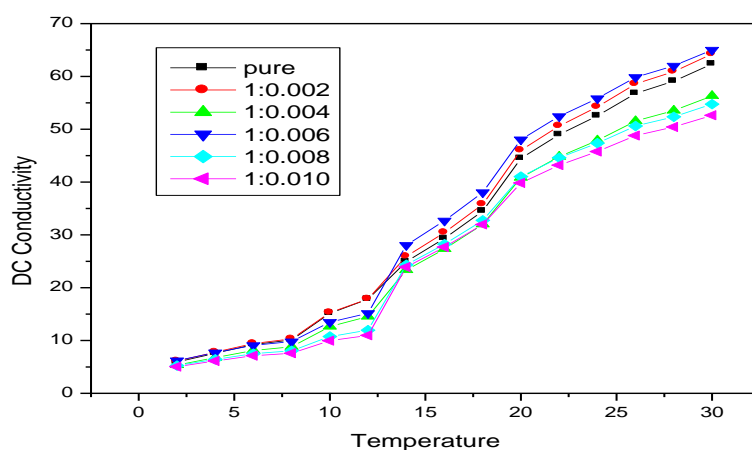


Figure 6: Variation of DC electrical conductivities with temperature

IV. Conclusion

Single crystals of undoped and ADP doped disodium hydrogen orthophosphate (DSHP) were grown by the slow evaporation method. The grown crystals are transparent and with well defined external appearance. Density measurements indicate that the ADP molecules have entered into the lattice of DSHP crystals. 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 frequencies of 100 Hz and 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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P. G. Praveen "Electrical Conductivity Measurements On Undoped And ADP Doped Disodium Hydrogen Phosphate (DSHP) Single Crystals "International Journal of Engineering Science Invention (IJESI), vol. 07, no. 11, 2018, pp 18-24