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Electrical Conductivity Measurements on Pure and Magnesium Chloride Added Disodium Hydrogen Phosphate (DSHP) Single Crystals

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Abstract: In the present study we have grown pure and Magnesium Chloride added 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 indicates 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

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 [1,2] , rare earth tungstates [3,4], divalent vanadates [5], phosphates and oxalates [6,7], and other ferroelectric materials [8,9] 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 [10]. Heat plays a dominant role in the ionization of donar atoms and donar like traps when applied [11]. 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 [12,15]. 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. The a.c conduction in the high-temperature region seems to be connected with both electronic and ionic [13]. Electrical conductivity is affected by the structural changes [14].

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) A^o , b = 10.9550(5) A^o and c = 10.4216(5) A^o and β= 95.651(1) A^o 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[16]. DSHP crystals found a number of scientific applications and specific uses in the industry [17]. 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 phosphates [17,18, 21].

Magnesium chloride salts are typical ionic halides, being highly soluble in water. The hydrated magnesium chloride can be extracted frombrine or sea water. Its density is 2.32 g/cm^3 and has melting point 714°C [19]. Magnesium chloride consists of a large ionic lattice at room temperature. This means that it consists of layers of ions that are attached to one another via ionic bonds. Ionic bonds are bonds formed when one element gives an electron to another element. If you had one molecule of magnesium chloride, it would consist of one atom of magnesium and two atoms of chlorine. The two atoms of chlorine each give an electron to the atom of magnesium, forming an ionic bond. The lattice structure strengthens the ionic bonds between magnesium and chlorine [20].

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 Magnesium Chloride ($MgCl_2$) doped with five different concentrations by the slow evaporation method. The objective of the present work was to investigate the effects of Magnesium Chloride in the normalized growth yield and electrical studies. Here in we report the results obtained.

Experimental

Analytical reagent (AR) grade DSHP, Magnesium Chloride 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 [23,35] . In the same way DSHP was added with Magnesium Chloride 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.

Fig-1: Photograph showing the pure and Magnesium Chloride added DSHP crystals grown [From left are: 0.0 (pure DSHP), 0.2, 0.4, 0.6, 0.8 and 1.0 mole% $MgCl_2$ added]

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 [23-30]. 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 were 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. It has been found that dielectric constant and the dielectric loss both are highly dependent on frequency and temperature and also found to be increased with increasing concentration [22]. The capacitance and dielectric loss (tan δ) were measured using the conventional two probe technique [23-25] 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

$$\varepsilon_r = \frac{C_{cry}-C_{air}(1-(A_{crys}/A_{air}))}{C_{air}} \times (A_{air}/A_{crys}),$$

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 $\sigma_{ac} = \varepsilon_o \varepsilon_r \omega \tan \delta$ where ε_o is the permittivity of free space(8.85 x 10^{-12} Farad/m) and ω is the angular frequency ($\omega = 2 \pi f$, f = 100 Hz& 1kHz).

The resistance of the crystals was 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 = d / (RA) where d is the thickness of the sample , A is the area of the sample and R is the measured resistance.

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^{o}C. This is in good agreement with the reported value [23]. The impurity added DSHP also melts at this temperature. Therefore, Magnesium Chloride whose melting point is higher than DSHP [31] 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 [23].

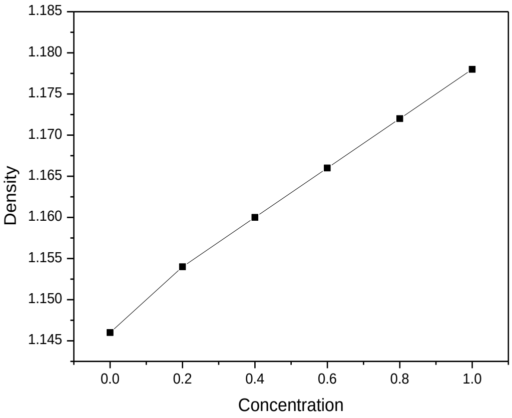

Fig-2: Variation of density with impurity

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 diploes and space charge polarizations can be understood very easily by studying the dielectric properties as a function of frequency and temperature for crystalline solids [32-33]. 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[34-35].

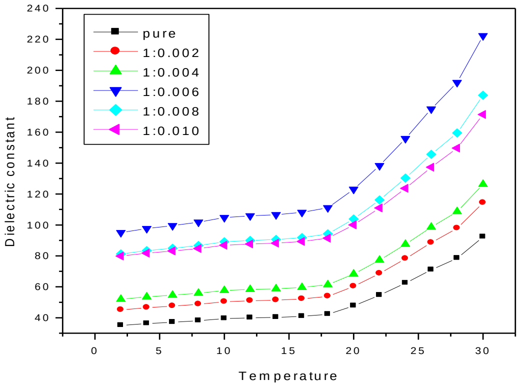

Fig-3a: **Variation of dielectric constant with temperature at 100 Hz**

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 [34,35]. At higher temperatures, the increase is mainly attributed to the thermally generated charge carriers and impurity dipoles.

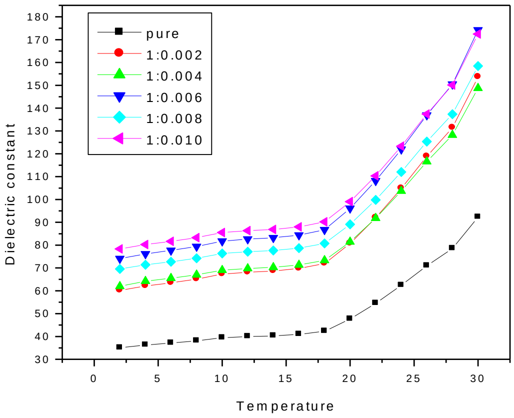

Fig-3b: **Variation of dielectric constant with temperature at 1 kHz**

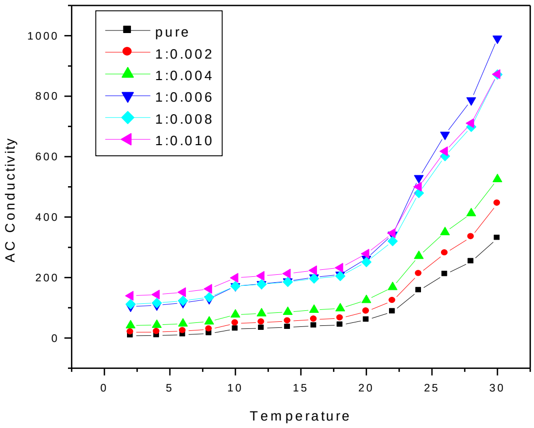

Fig-4a: Variation of dielectric loss with temperature at 100 Hz

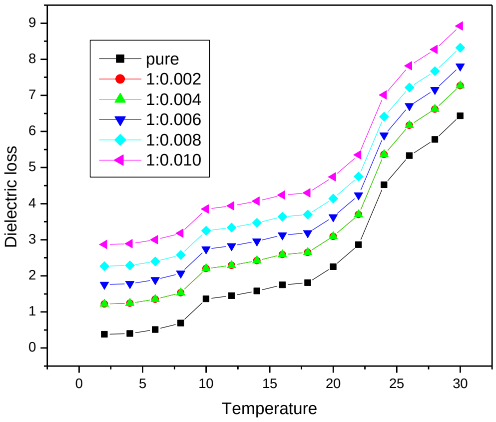

Fig-4b: Variation of dielectric loss with temperature at 1 kHz

The dielectric loss tangent (tan δ) is the imaginary part of dielectric constant and determines the loosiness of the medium. Similar to dielectric constant low loose tangent results in fast subtsract while large loss tangent results in a slow substract. 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 [36,37].

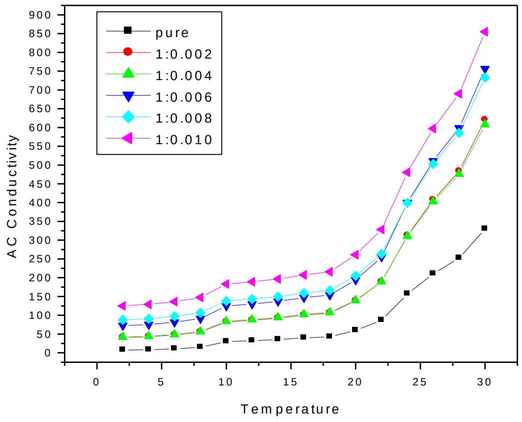

Fig-5a: Variation of AC conductivity with temperature at 100 Hz

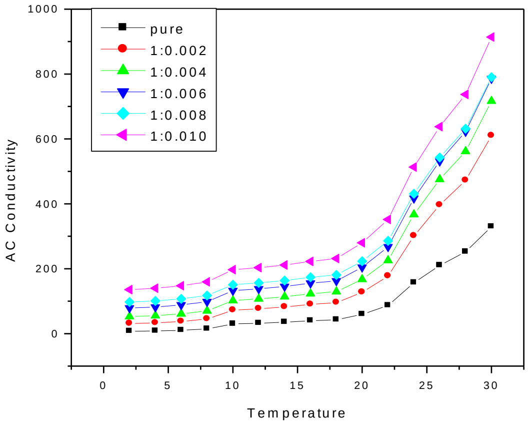

Fig-5b: Variation of AC conductivity with temperature at 1 kHz

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. The values obtained for σ_{dc} are presented in Figure 6. The DC conductivity also increases with the increase in temperature[38].

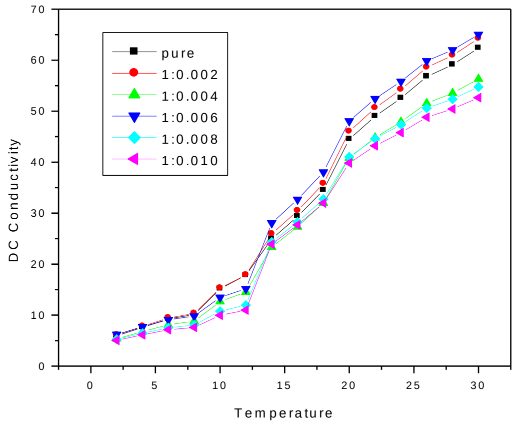

Fig-6: Variation of AC conductivity with temperature at 1 kHz

CONCLUSIONS

Single crystals of pure and magnesium chloride added 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 manganese chloride 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 δ) 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 δ values. DC electrical conductivity was also measured at various temperatures. The dielectric constant, tan δ, σ_{ac} and σ_{dc} are found to increase with increasing temperature for both the frequencies.

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