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EFFECT OF DOPING ON ELECTRIC AND HARDNESS PROPERTIES OF AMMONIUM DIHYDROGEN PHOSPHATE SINGLE CRYSTAL

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ABSTRACT

The effect of ammonium chloride, ammonium malate, ammonium acetate, DL-malic acid, L-lysine monohydrochloride, Ni²⁺ and Oxalic acid on dielectric and microhardness properties of ammonium dihydrogen phosphate single crystals grown by the slow evaporation method has been investigated. Low dielectric losses were observed from the dielectric measurements for the doped ADP crystals. Vickers hardness measurements reveal the higher hardness of the doped crystals as compared to pure ADP crystal.

Keywords: Point of common coupling (PCC), reverse bias safe operating area (RBSOA), short circuit safe .

I. INTRODUCTION

Ammonium dihydrogen phosphate (ADP) is a nonlinear optical material having application in photonics for frequency mixing, parametric amplification and electro optical modulation. In the past decades, ADP and its counterpart potassium dihydrogen phosphate (KDP) have been widely studied with the aim to promote the crystal quality and the growth rate [1–4]. As a representative hydrogen-bonded material, ADP has also attracted extensive attention in the investigation of hydrogen bonding behaviors in crystal and the relationship between crystal structure and their properties [5–8]. Ammonium dihydrogen phosphate (ADP), a hydrogen bonded compound, belongs to isomorphous series of phosphates and arsenates that presents a strong piezoelectric activity. These molecular crystals exhibit low-temperature order–disorder phase transitions. Below 148.5K, ADP is antiferroelectric and belongs to P2₁2₁2₁ space symmetry group while above this temperature it becomes paraelectric having a 14/2d symmetry [9–11].

Optical transparency, hardness and dielectric constant are the basic properties of crystals. During ADP and KDP crystals growth, the metallic cations present in the crystals especially ones with high valency were considered to strongly affect the growth habit and optical properties of crystals [12]. The transmission window in the UV region and visible region enables good optical transmission of the second harmonic frequencies of Nd:YAG laser. So it is necessary to study the optical properties of the crystals. The micro-indentation test is a useful method for studying the nature of plastic flow and its influence on the deformation of the material. Also, the hardness of the crystal is dependent on the type of chemical bonding, which may differ along the crystallographic directions [13]. Hardness is one of the important deciding factors in selecting the processing (cutting, grinding and polishing) steps of bulk crystal in fabrication of devices based on the crystals. It is therefore important to study the mechanical properties of NLO crystals [14]. Dielectric constant is one of the basic electrical properties of the solids. Dielectric properties are correlated with the electro-optic properties of the crystals [15]. The measurement of dielectric constant and dielectric loss as a function of frequency and temperature is of interest both from theoretical point of view and from the applied aspects [16]. Studies on the temperature dependence of dielectric properties unveil useful information about structural changes, defect behavior and transport phenomena [14].

II. EXPERIMENTAL PROCEDURE

Crystal growth

The commercially available ADP used for growth after 2 times of recrystallization process. Single crystals were grown from aqueous ADP solution containing 1 mol% of ammonium chloride, Ammonium malate, Ammonium acetate, DI-malic acid, L-lysine monohydrochloride, Ni²⁺ and Oxalic acid separately using deionized water as a solvent by the slow evaporation technique. As literature confirms that 1 mol % of doping has resulted in higher growth rate and has enhanced the various properties of the crystal [17–20]. Single crystals of pure and doped ADP were grown by the slow evaporation technique. The filtered 500 ml saturated solution of ADP was taken in a 1000ml beaker. The beaker was closed with a porously sealed cover and the solution in the beaker was allowed to evaporate. Few days after, tiny crystals were seen in the beaker. After 25 days of growth transparent crystals were harvested.

III. RESULTS AND DISCUSSION

Dielectric Measurement

Dielectric properties are correlated with the electro-optic property of the crystals [21]. The magnitude of dielectric constant depends on the degree of polarization charge displacement in the crystals. The dielectric constant was measured using LCR meter. Two opposite surfaces across the breadth of the sample were treated with good quality silver paste in order to obtain good ohmic contact. Using the LCR meter, the capacitance of these crystals was measured for the frequencies 1 kHz at various temperatures. The dielectric constant of the crystal was calculated using the relation $\epsilon_r = C_{\text{crys}}/C_{\text{air}}$ where C_{crys} is the capacitance of the crystal and C_{air} is the capacitance of same dimension of air. Figure shows the variation of dielectric constants and dielectric losses with temperature at constant frequency 1 kHz. It is observed from the figure that the dielectric constant increases with increase of temperature for all the crystals. This is normal dielectric behavior of an antiferroelectric ADP crystal [22]. The dielectric constant of materials is due to the contribution of electronic, ionic, dipolar and space charge polarizations, which depend on the frequencies. At low frequencies, all these polarizations are active [23-26].

It is observed from the fig. 1 that the dielectric constant of the ammonium chloride [23], Ammonium malate [30], Ammonium acetate [31], DI-malic acid [36], L-lysine monohydrochloride [37], Ni²⁺ [25] and Oxalic acid [26] added ADP is higher compared to the pure ADP. The magnitude of dielectric constant depends on the degree of polarization charge displacement in the crystals. It is observed from the figures that dielectric loss is low for AmCl, AM, AA, DML, L-LMHCL, Ni²⁺ and oxalic acid added ADP crystals. It is also observed from the figure that the dielectric loss increases with increase in temperature. In comparing the dielectric losses of all the three doped crystals it is found that ammonium chloride added ADP crystals has highest dielectric constant [fig. (a)] and minimum dielectric loss [fig. (b)]. The low values of dielectric loss indicate that the grown crystals contain minimum defects [16-35]. Usually the dielectric losses fall into two categories, they are intrinsic and extrinsic. Intrinsic losses are dependent on the crystal structure and can be described by the interaction of the phonon system with the ac electric field. The ac electric field alters the equilibrium of the phonon system and the subsequent relaxation is associated with energy dissipation. These intrinsic losses set the lower limit of losses found in pure “defect-free” single crystals. Extrinsic losses are associated with imperfections in the crystal, e.g., impurities, microstructural defects, grain boundaries, porosity, microcracks and random crystallite orientation.

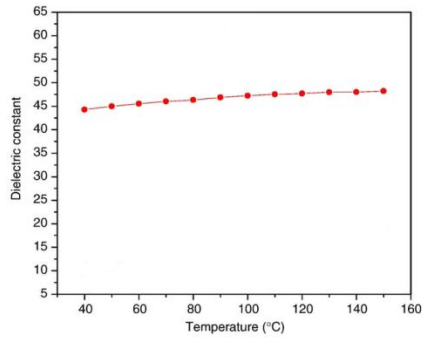


Fig (a) Temperature dependence of dielectric constant for ADP doped with 1mol% of AmCl.

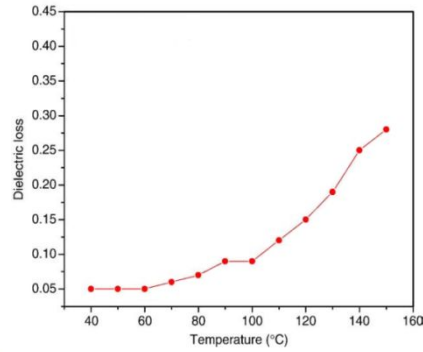


Fig (b) Temperature dependence of dielectric loss for ADP doped with 1 mol% of AmCl.

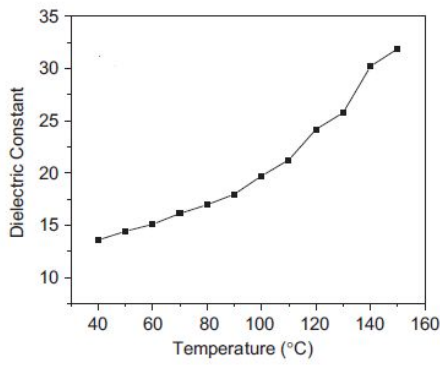


Fig (c) Temperature dependence of dielectric constant for ADP doped with 1 mol% of AM.

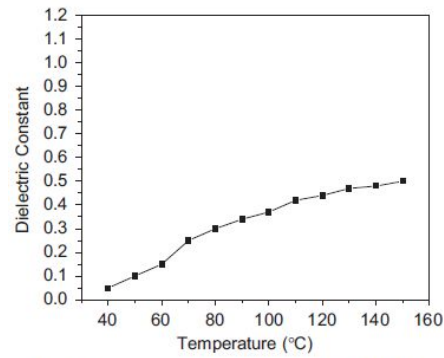


Fig (d) Temperature dependence of dielectric loss for ADP doped with 1 mol% of AM.

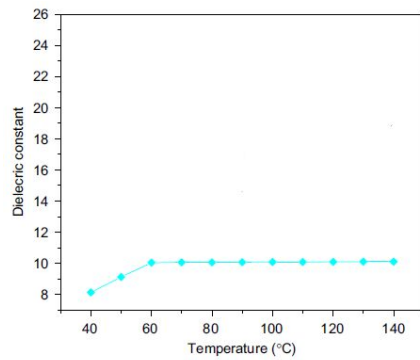


Fig (e) Temperature dependence of dielectric constant for ADP doped with 1 mol% of AA.

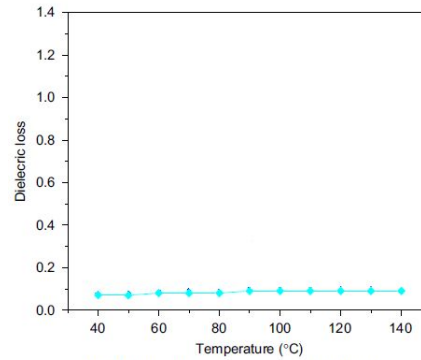


Fig (f) Temperature dependence of dielectric loss for ADP doped with 1 mol% of AA.

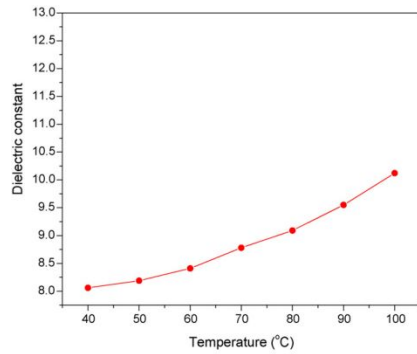


Fig (g) Temperature dependence of dielectric constant for ADP

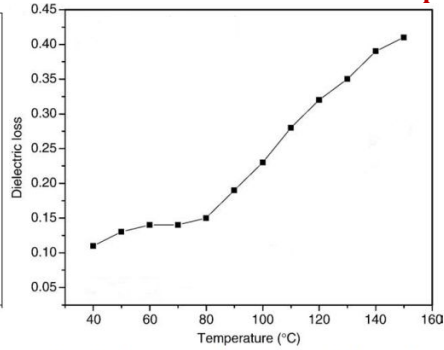


Fig (h) Temperature dependence of dielectric loss for pure ADP

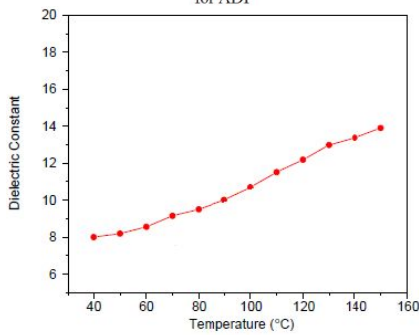


Fig (i) Temperature dependence of dielectric constant for ADP doped with 1 mol% of DML.

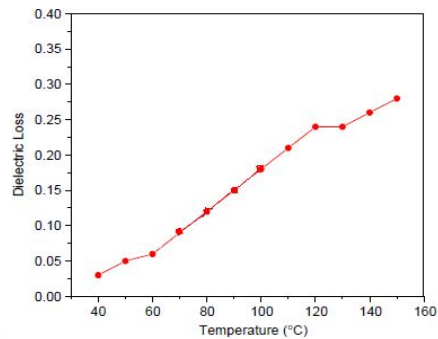


Fig (j) Temperature dependence of dielectric loss for ADP doped with 1 mol% of DML.

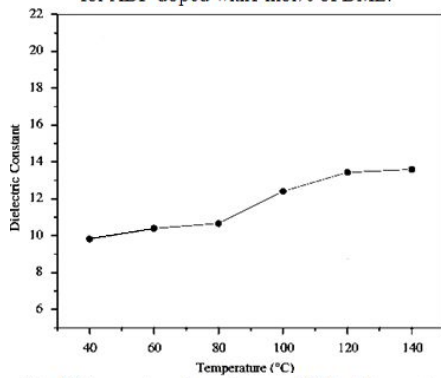


Fig (k) Temperature dependence of dielectric constant for ADP doped with 1 mol% of L-LMHCL.

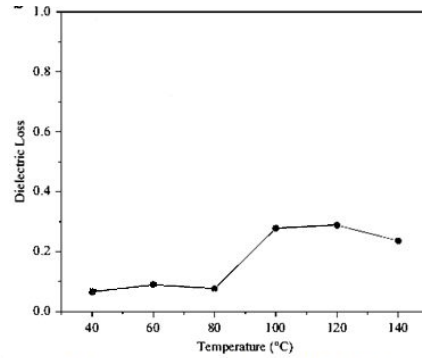


Fig (l) Temperature dependence of dielectric loss for ADP doped with 1 mol% of L-LMHCL.

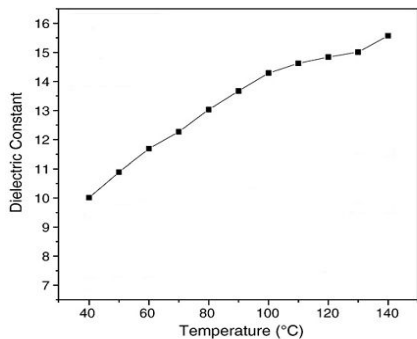


Fig (m) Temperature dependence of dielectric constant for ADP doped with 1 mol% of Ni²⁺.

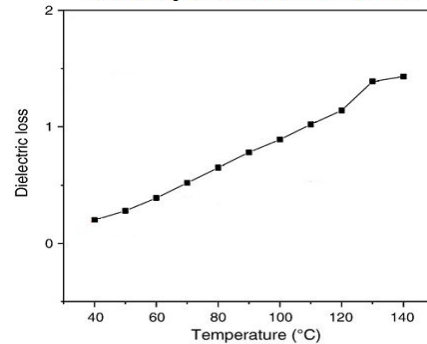


Fig (n) Temperature dependence of dielectric loss for ADP doped with 1 mol% of Ni²⁺.

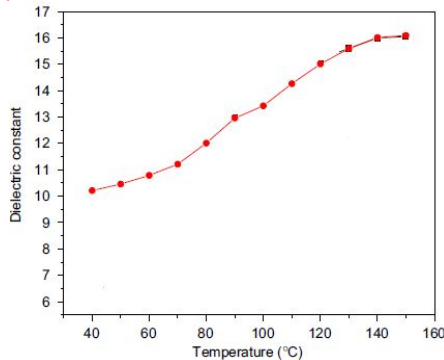


Fig (o) Temperature dependence of dielectric constant for ADP doped with 1 mol% of oxalic acid.

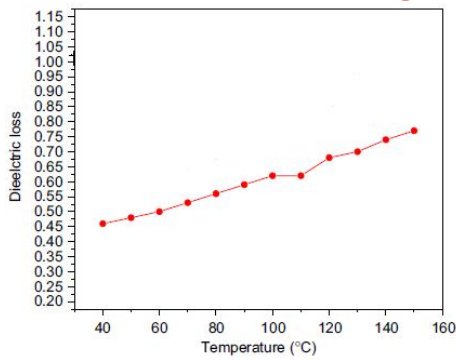


Fig (p) Temperature dependence of dielectric loss for ADP doped with 1 mol% of oxalic acid.

Fig 1: Temperature dependence of (a) dielectric constant for ADP doped with 1 mol% of AmCl (b) dielectric loss for ADP doped with 1 mol% of AmCl (c) dielectric constant for ADP doped with 1 mol% of AM (d) dielectric loss for ADP doped with 1 mol% of AM (e) dielectric constant for ADP doped with 1 mol% of AA (f) dielectric loss for ADP doped with 1 mol% of AA (g) dielectric constant for pure ADP (h) dielectric constant for pure ADP (i) dielectric constant for ADP doped with 1 mol% of DML (j) dielectric loss for ADP doped with 1 mol% of DML (k) dielectric constant for ADP doped with 1 mol% of L-LMHCL (l) dielectric loss for ADP doped with 1 mol% of L-LMHCL (m) dielectric constant for ADP doped with 1 mol% of Ni²⁺ (n) dielectric constant for ADP doped with 1 mol% of oxalic acid (o) dielectric loss for ADP doped with 1 mol% of oxalic acid.

The good quality crystals are needed for various applications not only with good optical performance but also with good mechanical behavior. Hardness is one of the important mechanical properties of the materials. It is used to measure the plastic properties and strength of a material [40]. Stillwel [41] defined hardness as resistance against lattice destruction. The good quality crystals are needed for various applications not only with good optical performance but also with good mechanical behaviour. A hardness study of the doped and undoped ADP crystal has been carried out and is reported. It is well known that microhardness is not only a mechanical characteristics but also it has been developed as micro structural investigations method due to fact that microhardness is sensitive to structural parameters as well as to mechanical characterization parameters (Yield stress, modulus of elasticity, some secondary transitions, etc.) The hardness of the material is defined as the resistance it offers to the motion of dislocations, deformation or damage under an applied stress. The general definition of indentation hardness, which relates to the various forms of indenters, is the ratio of the applied load to the projected area of indenters, is the ratio of the applied load to the projected area of indentations.

The indentation hardness was measured as the ratio of applied load to the surface area of the indentation. The suitable size of the grown crystal was selected for microhardness studies. Indentations were carried out using Vicker's indenter for varying loads. For each load (p), several indentations were made and the average value of the diagonal length (d) was used to calculate the microhardness of the crystals. Vicker's microhardness number was determined using $H_v = 1.8544p/d^2$. A plot drawn between the hardness value and corresponding loads is shown in Figures.

It is observed from the fig. 2 that Vickers hardness increases with increase in load for all the doped crystals and upto 100g no cracks have been observed, whereas, for pure ADP crystal cracks were observed at 100 g. This is shown in Fig. In AmCl added ADP crystal cracks have been observed above 100 g. This shows that for the grown crystal greater stress is required to form dislocation thus confirming greater crystalline perfection as compared to pure ADP. Similarly The addition of AM and AA has also enhanced the hardness of the crystal. For AA doped ADP crystal the crack is observed at 200g.

Hardness is the resistance offered by a solid to the movement of dislocation. Practically, hardness is the resistance offered by a material to localized plastic deformation caused by scratching or by indentation. Due to the application of mechanical stress by the indenter, dislocations are generated locally at the region of the indentation. It is also observed from the figures that the influence of crack formation on hardness was found to be higher for AmCl doped ADP crystal.

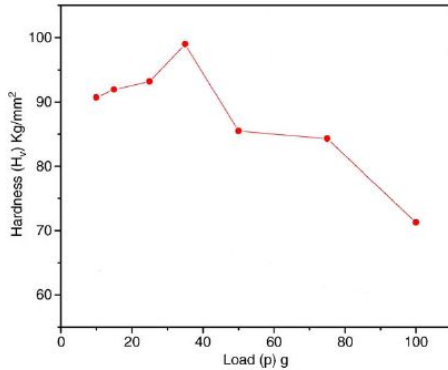


Fig (i) Vickers hardness plot of ADP doped with 1 mol% of AmCl

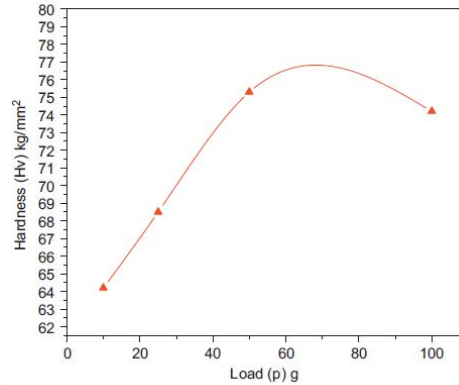


Fig (i) Vickers hardness plot of ADP doped with 1 mol% of AM

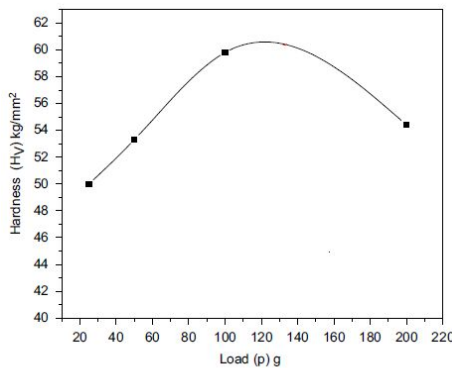


Fig (k) Vickers hardness plot of ADP doped with 1 mol% of AA

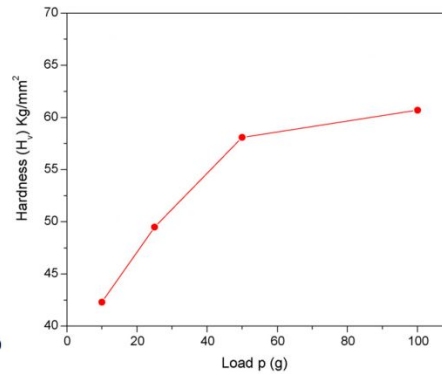


Fig (l) Vickers hardness plot of pure ADP

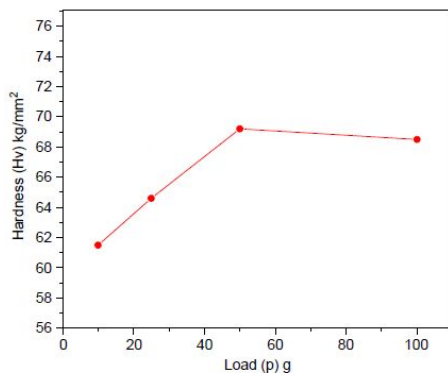
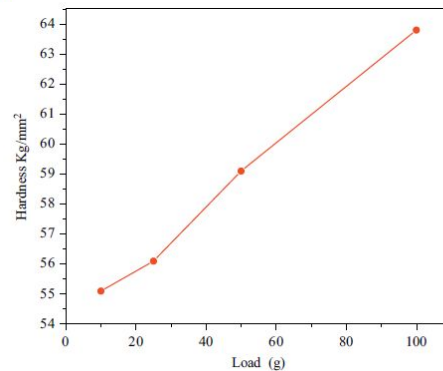
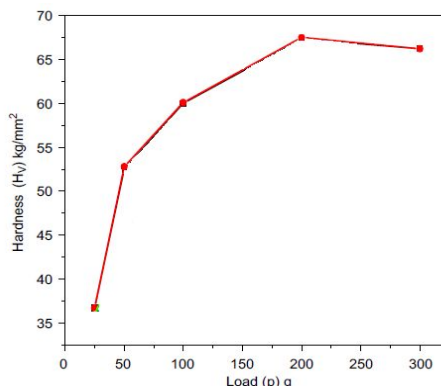


Fig (m) Vickers hardness plot of ADP doped with 1 mol% of DLM



Vickers hardness plot of ADP doped with 1 mol% of L-LMHCL



Vickers hardness plot of ADP doped with 1 mol% of oxalic acid

Fig 2 : Vickers hardness plot of (i) ADP doped with 1 mol% of AmCl (j) ADP doped with 1 mol% of AM (k) ADP doped with 1 mol% of AA (l) pure ADP. (m) ADP doped with 1 mol% of DMLI (n) ADP doped with 1 mol% of L-LMHCL (o) ADP doped with 1 mol% of oxalic acid.

IV. CONCLUSION

Good quality single crystals of ADP doped with 1 mol% of ammonium chloride, ammonium malate, ammonium acetate, DI-malic acid, L-lysine monohydrochloride, Ni²⁺ and Oxalic acid were grown by slow evaporation method. The dielectric study reveals that the doped crystals have high dielectric constant and low dielectric loss as compared to the pure ADP crystal. It is noted that the dopant in ADP has increased the hardness of the crystal and it is also observed that the mechanical strength of the crystals is good. It is concluded that the addition of 1 mol% of ammonium chloride, ammonium malate, ammonium acetate, DI-malic acid, L-lysine monohydrochloride, Ni²⁺ and Oxalic acid in the mother solution acts as a dopant and enhanced the electrical and mechanical properties of the crystals. This study will be useful to grow ADP crystals with enhanced properties

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