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Investigations on Non Linear Optical Crystal ADP Doped with Inorganic Compounds

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Abstract: Ammonium dihydrogen phosphate well known as ADP is a non-linear optical material having wide applications in non-linear and integrated optics. With appropriate dopants, the ADP crystals exhibit several properties. The behavior of these crystals in radiation fields is also of importance, for technology of the radiation induced formation of the optical wave guide (in these crystals). In the present work pure ADP and ADP doped with inorganic compounds like ferrous sulphate, Nickel chloride and Cuprium chloride have been investigated. Crystals were grown from supersaturated solution at room temperature by natural evaporation process. Grown crystals were characterized using X-ray diffraction and EDAX. The grown crystals were subjected to hardness studies to know the mechanical properties of NLO crystals which is essential for understanding the origin of laser induced damage in them. Hardness is calculated by Vicker's method. It has been observed that hardness increases in these crystals with load and the cracking has developed around 50gm. Dielectric constant and Dielectric loss is measured as a function of frequency. Study confirms the contribution of space charge polarization.

Keywords: NLO crystals, Microhardness,Dielectric constant, Dielectric loss, Polarization, SHG efficiency.

1. Introduction

In the last few decades, significant advances have been made in the field of non-linear optics and optical computing. Since the invention of the first laser, the frequency conversion of laser radiation in nonlinear optical (NLO) crystals has become an important technique widely used in quantum electronics and laser physics for solving various scientific and engineering problems. Use of NLO materials makes it possible to extend the optical frequency range from ultraviolet to infrared. Non linear optical crystal ammonium dihydrogen orthophosphate (ADP) has gained considerable importance in recent years because of its non-linear, ferroelectric, piezoelectric and electro-optic properties.

We have made an attempt to modify ADP crystals by adding inorganic compounds like ferrous sulphate, Nickel chloride and Cuprium chloride in definite ratios with the aim of discovering new useful materials for academic and industrial use. Present paper reports the studies of Vickers microhardness and dielectric constant of solution grown ADP crystals containing $FeSO_4$, $NiCl_2$ and $CuCl_2$.

2. Experimental

2.1 Crystal Growth

Single crystals were grown from super saturated solution at room temperature by natural evaporation process using AR grade samples of ADP, $FeSO_4$, $NiCL_2$ and $CuCl_2$.

ADP was added with $FeSO_4$, $NiCl_2$ and $CuCl_2$. Separately, each in definite molecular ratio, viz. ADP: X (X represents dopants added in one molar weight i.e. in 10:1 ratio).

Grown crystals were found to be transparent and exhibited **scalenohedral** (twelve sided polyhedron) morphology. Crystals with high transparency were used for microhardness and dielectric measurements.

The Grown crystals were characterized using X-ray diffraction and energy dispersive X-ray spectroscopy (EDAX). Data confirms that the impurities have entered into the lattice of the ADP

2.2 Dielectric Measurements

The extended portions of the crystals were removed completely and the samples were ground to proper thickness and polished. The final dimensions of the samples were about 1.5 to 2 sq.cm and 0.1 to 0.3 cm in thickness. Each sample was electroded on either side with air-drying silver paste so that it behaved like a parallel plate capacitor. A 4275A, Multi frequency LCR meter (Hewlett-Packard) was used to measure capacitance (C) and dissipation factor (D) of the sample as a function of frequency. The dielectric constant (ε_r) and dielectric loss (**tanδ**) were calculated from C and D using the relations,

$$\varepsilon_r = \frac{Cd}{A\varepsilon_o} \qquad \text{and} \qquad \tan\delta = D\,\varepsilon_r$$

Where,

C is the capacitance of the sample, **d** the thickness of the sample,

A area of the face in contact with the electrode and ε_o the permittivity of free space.

2.3 Microhardness Studies

Microhardness measurements were carried out using Zwick 3212 hardness tester fitted with a Vicker's diamond pyramidal indenter. All the indentation measurements were carried out on the freshly cleaved samples. The indentation was made varying a load from 5 to 25 gm and the time of indentation was kept at 10 sec. The indented impressions were approximately square. The crystal surfaces were indented at different sites. Diagonal lengths of the indented impression were measured during calibrated micrometer attached to the eyepiece of the microscope. Several indentations were made on each sample. The average value of the diagonal lengths of the indentation mark was used to calculate the hardness. The Microhardness is calculated using the expression [1]

$$\mathbf{H}=1.8544\ \mathbf{P/d^2}\ \text{Kg mm}^{-2}$$

Where, **P** is the applied load in **Kg** and **d** the average diagonal length of the Vickers impression in **mm** after unloading.

2.4 SHG Efficiency

The grown crystals of pure ADP and doped ADP were subjected to Kurtz second harmonic generation (SHG) test. A Q-switched Nd: YAG laser whose output was filtered through 1064nm narrow pass filter was used for the purpose. To measure the SHG efficiency, the powder of the samples were derived from the crystals grown with full morphology, which ensure homogeneity of the material. The input power of the laser beam was measured to be 6.6 mJ/pulse. Pure ADP was used as reference sample. Both the reference and test samples had uniform particle size of 30-50μm.

3 Results and Discussion

The variation of dielectric constant(ε_r) and dielectric loss (tan**δ**) at room temperature for ADP and ADP containing $FeSO_4$, $NiCL_2$ and $CuCl_2$.are shown in Figs 1 and 2. It is observed that the dielectric constant (ε_r) decreases with the increase in the frequency. Values of dielectric constant and dielectric loss at 100 kHz and 1 MHz frequency for pure ADP and ADP crystals containing $FeSO_4$, $NiCL_2$ and C_uCl_2 are given in Table 1**.** The dielectric constant of a material is generally composed of four types of contributions, viz ionic, electronic, orientational and space charge polarizations. At low frequencies all polarizabilities are operative hence and are high. As frequency increases one polarization mechanism after another is frozen out. The first to stop contribution to and is orientational compound, then the ionic and the lastly the electronic [2, 3].The dielectric loss (tanδ) is due to the resistive component that makes them loose, so that they dissipate some of the applied ac energy. tan**δ** in the present study was found initially to decrease with frequency and later almost a constant over a range of frequency for all the three dopants.

Fig.3 shows the variation of microhardness with indenter load. The microhardness increases with increase of indenter load (from 5 to 25g). With gradual increase of the applied stress, the elastic limit of the material can be exceeded and the specimen will not restore its original shape on removal of the stress.

Presence of $Fe^{3+,}$ Cu^+ and Ni^{2+} ions has resulted in decreased microhardness value.

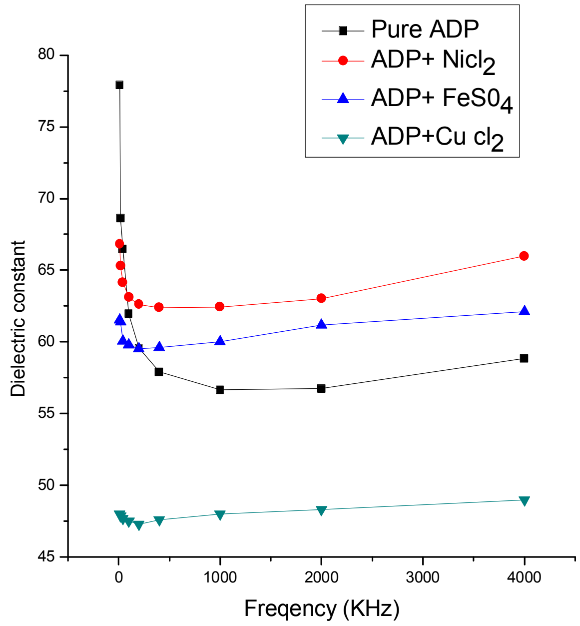

Fig1. Variation of dielectric constant with Frequency in pure and doped ADP crystals

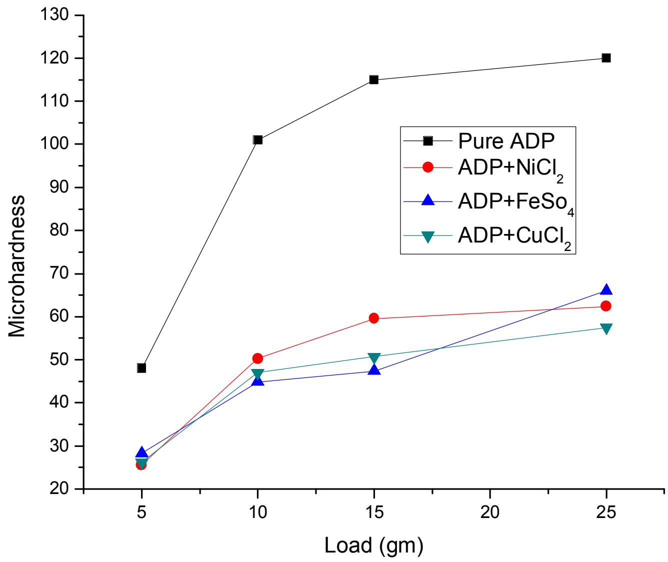

Fig3. Variation of microhardness with load in pure and doped ADP crystals

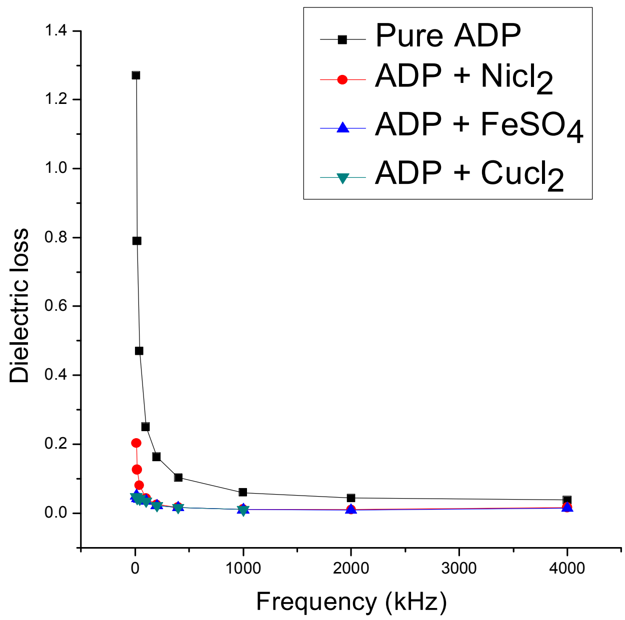

Fig2. Variation of dielectric loss with Frequency in pure and doped ADP crystals

Table1. Values of dielectric constant (ε_r) and dielectric loss (tan δ) of pure and doped ADP crystals

Sample	At 100 kHz		At 1 MHz	
	ε_r	**tan δ**	**ε_r**	**tan δ**
Pure ADP	61.94	0.25	56.66	0.06
ADP+$FeSO_4$	60.074	0.0047	60.125	0.0044
ADP+C_uCl_2	47.169	0.0069	47.169	0.0042
ADP+NiCl2	63.1	0.042	62.44	0.011

Table2.Work hardening number of ADP and ADP doped crystals

Sample	**Work hardening number (n)**
Pure ADP	**0.995**
ADP+ $CuCl_2$	**6.429**
ADP+ $FeSO_4$	**6.43**
ADP+ $NiCl_2$	**6.41**

Table3.SHG efficiency of pure ADP and doped ADP crystals.

Sample	**SHG efficiency with respect to ADP**
Pure ADP	**1.000**
ADP+ $CuCl_2$	**2.158**
ADP+ $FeSO_4$	**0.928**
ADP+ $NiCl_2$	**0.916**

The hardness or softness of the material can be determined by using Meyer's equation, $\mathbf{P=ad^n}$ where P is load in kg, d is diagonal length in mm and n is work hardening number. The n value tells us about the hardness or softness of the material [6]. A graph of **log p** versus **log d** has been plotted for pure ADP and doped ADP crystals. The slope gives the **n** value and the same are shown in the table2. The increase in **n** values of the doped ADP crystals confirms that, the material become soft on doping.

The SHG efficiency of ADP containing Cuprium chloride is found higher than pure ADP. It is surprising that the other metal additives $FeSO_4$, $NiCl_2$ are acting aspoison, not favoring SHG efficiency. In the present study the additives and host are in the molar ratio of 1:9.It is interesting to carry out the work at lower ratios to know exactly at what molar ratio the materials start nullifying the SHG efficiency and making the host crystal lose the NLO property. Definite conclusion regarding the result requires further work on phase matched efficiency of single crystals. The measured SHG efficiency of the crystal is as shown in the table.3

4. Conclusions

In summary, the ADP is turned out to be useful NLO device material for several reasons. It can be grown easily with suitable habit faces. It is transparent, so that phase matching for second harmonic and frequency mixing processes can be achieved well into the visible region. So higher efficiencies could be achieved by increasing the intensity of input signal. From the study of indentation hardness measurement in pure ADP and ADP containing FeSO4, NiCl2 single crystals, crystals have answered for different hardness values. Presence of $Fe^{3+,}$ Cu^+ and Ni^{2+} ions has resulted in decreased microhardness value. The hardness measurements may be useful in indicating the order of magnitude to be expected for the elastic constant in a new material. Dielectric constant and Dielectric loss decreases with frequency. Large value of dielectric constant at low frequencies in the present study confirms the purity of the sample, secondly, as due to the space charge polarization [4]. Values of hardness and dielectric constant in doped ADP crystals prove to be a useful candidature for many applications.

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