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Microhardness, Dielectric and Photoconductivity Studies of 2- Amino 5-Nitropyridinium Dihydrogen Phosphate (2A5NPDP) NLO Single Crystal

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Abstract

An orthorhombic (2- Amino 5 – Nitropyridinum Phosphate) semi organic crystals was grown using slow evaporation method. As grown crystals of 2A5NPDP was characterized by microhardness, dielectric and photoconductivity studies. Hardness value was measured by Vickers hardness. The study of dielectric constant was carried out by using HIOKI 3532-50 LCR HITESTER. The photoconductivity was also measured by using KEITHLEY 485 picometer.

INTRODUCTION

Recently the development of potential non linear optical (NLO) crystals, capable of generating green and blue laser light is of great importance for frequency conversion, optical data storage, optical amplifier, image processing, integrated data etc[1-2]. Non linear optics (NLO) has been an active field of research with advent of laser followed by the demonstration of harmonic generation in Quartz [3]. M aterials with very large second order non linear optical (NLO) susceptibilities have attracted a lot of attention because of their potential for high frequency electro- optic modulation [4-6], frequency conversion [7] and THz wave generation and Detection [8]. Molecules with delocalized π-electrons usually display a large NLO response which makes it most capable for variety of applications including optical communication, optical computing, optical information processing, optical disk data storage, laser fusion reaction and laser remote sensing [9]. Inorganic are highly resistant (Mechanically, thermally) owing to their ionic (or) covalent nature of inter molecular bonding while their figure of merit reaches a plateu exemplified by KTP [10] (deff~ 10^{-8}e.s.u) which may well be a ceiling. In contrast, while organic materials are often more fragile their non linearity may surpass by several orders of magnitude that of inorganic materials owing to the possible involvement of highly polarizable π -

electron system [11]. Organic materials show high NLO and susceptibility than the inorganic materials. Due to their poor chemical, thermal and mechanical stability, the organic crystals are currently limited in their industrial applications [12]. In order to overcome these difficulties semi organic materials have been proposed as a new approach for material with interesting non linear properties [13-15]. These hybrid materials combine the advantages of organic and inorganic materials. The efficient NLO are built from donor- acceptor conjugated molecules [16]. 2- Amino 5- Nitro Pyridine has an interesting molecular structure, which has a nitro group as an electron donor and amino group as an electron acceptor. Further, the pyridine ring act as a cationic bonding site, the nitro group as a hydrogen acceptor and the amino group as a hydrogen donor. Because of this special molecular structure, it has been commonly used as molecular building blocks of non linear optical materials, which have been the subject of very intensive studies in the last few years for their potential applicability in image processing and optical communications[17]. In this present work, 2 Amino 5- Nitropyridinium Dihydrogen Phosphate (2A5NPDP) was grown and their hardness, dielectric and photoconductivity measured.

1. Vickers Microhardness

The microhardness of a crystal is an important parameter to define the strength of its material. Mechanical strength of the materials plays a key role in device fabrication. It is a measure of the resistance, the lattice offers to local deformation [18].Shockley et al and Buckley pointed out that hardness of the crystal is obviously related to the crystal structure of the material (or) in other words, the pattern in which the atom are packed and the electronic factors operating to make the structure stable. Hardness is the only mechanical test that can be employed when the material is not available in substantial quantities. The hardness measurement is treated as an efficient technique of providing information about the elastic, plastic, viscous and fractures properties. Hardness is a measure of the resistance to permanent deformation. We have different methods for measuring hardness of materials. Among various methods, the most common method is the micro indentation and pyramid indenters are found to be best suited for hardness tests. A hardness tester fitted with a diamond pyramid indenter attached to an incident light microscope was used for study. The diamond indenter is in the form of a square pyramid, opposite faces of which make an angle $136^0$with one another. A pyramid indenter is suited for hardness test due to two reasons[19]. (i) The contact pressure for a pyramid indenter is independent of indent size and (ii) pyramid indenters are less affected by elastic release than other indenters. The indenter can be pressed on the sample under a load of 5, 10, 15, etc. gram. The base of the Vickers pyramid is a square and the depth of indentation corresponding to $(1/7)^{th}$ of the indentation diagonal. Hardness is generally defined as the ratio of the load applied to the surface area of indentation. Vickers hardness number (H_v) = load applied/ area of impression

$$H_v = P/ d^2 (2\sin (\alpha/2))$$

Where," p" is the load in kg and "d" is the diagonal length of the indentation mark in mm. α- is the apex angle of the indenter ($\alpha = 136^0$).

$$Hv = 2P\sin (\alpha/2)/d^2$$

$$Hv = 2P\sin (68^0)/d^2$$

$$Hv = 1.8544P/d^2$$

A variation of microhardness number (H_v) with applied load is shown in Fig. 1. It is evidence from the graph that the microhardness of 2 Amino 5- Nitropyridinium Dihydrogen Phosphate (2A5NPDP) increases with increase in the applied load. The increases in the microhardness values with increasing load are in agreement with the reverse indentation size effect (ISE). In order to find work hardening coefficient (n) a graph is plotted for log p against log d by least square method as shown in Fig.2. The work hardening coefficient (n) was found to be 2.2 by taking slope in the straight line portion of the graph. According to Onitsch, if 'n" is greater than 2 the microhardness will increase with an increase in the load. If "n" is less than 2 the microhardness will decrease with an increase in the load. The material is hard, if the value of "n" lies 1 to 1.6. The material is soft, if the value of "n" is greater than 1.6 [20]. Hence, we conclude that 2 Amino 5-Nitropyridinium Dihydrogen Phosphate (2A5NPDP) is soft material.

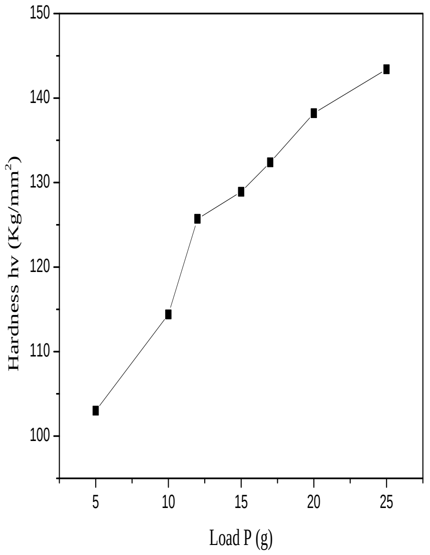

Fig.1 Variation of Vicker's hardness of 2A5NPDP

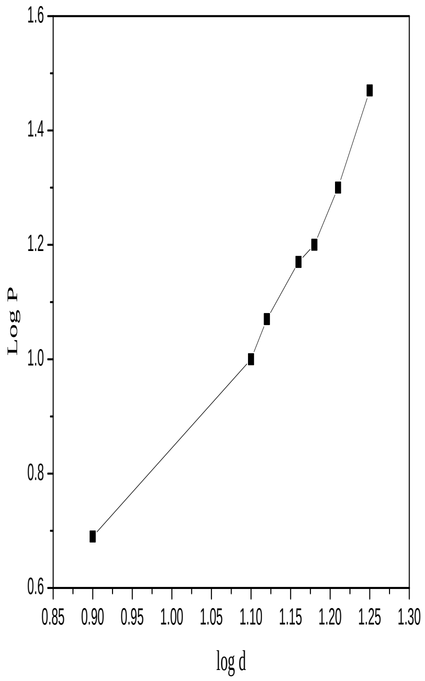

Fig.2 Log d Vs log p of 2A5NPDP

2. Dielectric characterization

A study of dielectric response gives information about lattice dynamics in the crystal [21]. The dielectric measurement is one of the useful characterizations of electrical response of solids and it gives information about the electric field distribution within the solid [22]. It is the measure of how easily a material is polarized in an external field[23]. Dielectric studies of 2 Amino 5-Nitropyridinium Dihydrogen Phosphate (2A5NPDP) was measured using HIOKI 3532-50 LCR HITESTER. The sample was mounted between the copper platform and parallel electrodes. In order to obtain good electric conduct between the crystal and the electrodes, the crystal faces are coated with silver paint. Proper care was taken that the silver paint does not spread to the sides of the crystal. The capacitance and the dissipation factor of the parallel plate capacitor were measured by the copper plate and electrodes having the sample. The dielectric constant and dielectric loss were calculated using the equations (2) and (3) respectively.

$\varepsilon = Cd/\varepsilon_o A$ ---------- (2)

$\varepsilon' = \varepsilon \tan(\delta)$ ---------- (3)

Where, C is the capacitance of the parallel capacitor, d is the thickness of the sample. A is the area of the sample and tan (δ)is the loss tangent of the crystal. The observations are made in the frequency range 100 Hz to 100MHz at different temperatures. The measurements were carried out in the temperature range room temperature- 150^0. Figure-3 shows the variation of dielectric constant with frequency of 2A5NDP. It is observed that the dielectric constant (ε_r) of 2- amino 5-nitroprydinium Dihydrogen phosphate (2A5NPDP) crystal decreases with increase infrequency. It was observed that the dielectric constant decreases slowly with increasing frequency and attain saturation at higher frequencies. The high dielectric constant of the crystal at low frequency is attributed due to the presence of all four polarizations such as electronic, dipolar, ionic and space charge polarization[24]. At low frequencies, all these polarizations are active. This behaviour is due to the fact that at lower frequency the dipoles are able to follow the applied field, whereas at higher frequency they are not [25]. At low frequencies the dipoles can easily switch alignment with the changing field. As the frequency increases the dipoles are able to rotate less and maintain phase with the field; thus they reduce their contribution to the polarization [26]. At lower frequencies, space charge polarization is predominant and hence the dielectric constant increases abnormally [27]. The dielectric constant increases in temperature. This is due to the presence of space charge polarization near the grain boundary interfaces which depends on the purity and perfection of the sample [28]. The lower value of dielectric constant at higher frequencies is a suitable parameter for the enhancement of SHG coefficient [29]. Figure- 4. shows the variation of dielectric loss withlow frequency for 2- Amino 5- Nitroprydinium Dihydrogen Phosphate (2A5NPDP) non linear optical crystal. It is noticed that the dielectric loss of 2A5NPDP decrease with increase in frequency. Low dielectric loss with high frequency for a given crystal suggest that the crystal possesses enhanced optical quality with lesser defects and this parameter is of its vital importance for the fabrication of nonlinear optical devices [30].

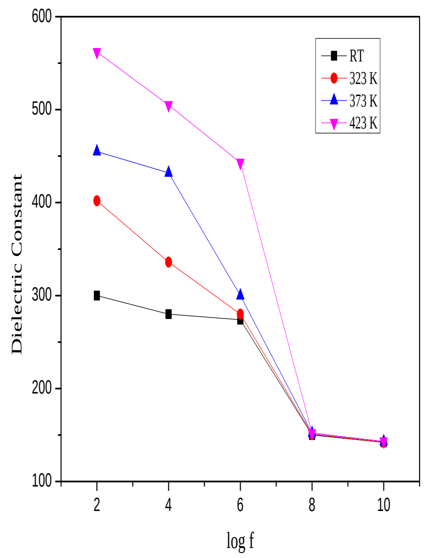

Fig.3 Effect of frequency on dielectric constant at different temperature of 2A5NPDP

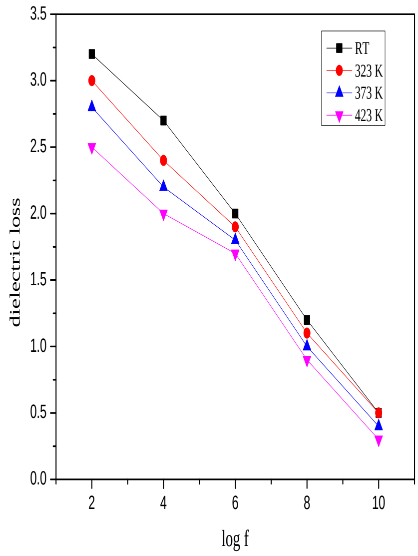

Fig.4 Effect of frequency on dielectric loss at different temperature of 2A5NPDP

3. Photoconductivity studies

Polished sample of 2-Amino 5- Nitropyridinium Dihydrogen Phosphate (2A5NPDP) was attached to microscope slide, and two electrodes of thin copper wire 1.14-mm diameter were fixed by the use of silver paint. The sample was connected in series to a DC power supply and a picometer (Keithley 480). The details of the experimental setup used are reported elsewhere [31]. The applied voltage was increased from 100 to 1800 V in steps of 100 V and the corresponding dark current was recorded. In order to record the photo current, the sample was than exposed to radiation from 100 W halogen lamp containing iodine vapour and tungsten filament. The emission spectrum of the halogen lamp observed to be a continuous one with wavelength range from 300- 1000 nm. The photo current was observed for the same range of the applied voltage. The field dependence of dark and photo current of 2-Amino 5- Nitropyridinium Dihydrogen Phosphate (2A5NPDP) was shown in Fig.5. It is evidence from the graph that both dark and photo current linearly increases for applying field. The photo current of 2-Amino 5- Nitropyridinium Dihydrogen Phosphate (2A5NPDP) leads the dark current, which reveals that the positive photoconductivity of the sample. This is due to generation of mobile charge carriers caused by absorption of photon [32].

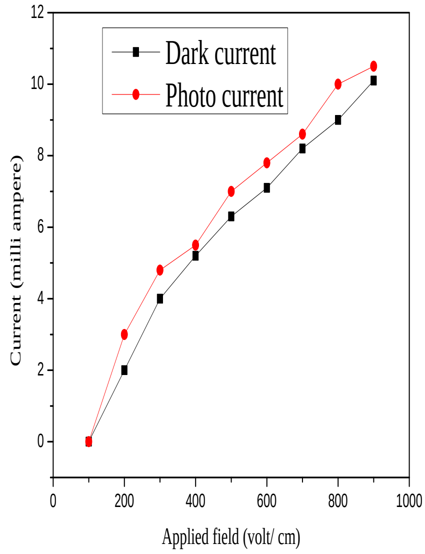

Fig.5 Photoconductivity studies of 2A5NPDP

CONCLUSION

In this present work single crystal of 2-Amino 5- Nitro Pyridinium Dihydrogen Phosphate (2A5NPDP) was characterized by microhardness, Dielectric and photoconductivity studies. Micrhardness indicates that 2-Amino 5- Nitro Pyridinium Dihydrogen Phosphate (2A5NPDP) NLO single crystal belongs to soft material. Photoconductivity of 2-Amino 5- Nitro Pyridinium Dihydrogen Phosphate (2A5NPDP) NLO single crystal confirms the positive conducting nature of the crystal. The dielectric study indicates that the 2-Amino 5- Nitro Pyridinium Dihydrogen Phosphate (2A5NPDP) NLO single crystal posses good optical quality with less defects.

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