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Photoconductivity, Microhardness and Dielectric Studies of 2- Amino 5- Nitropyridinium Hydrogen Oxalate (2A5NPHO) Single Crystal

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Abstract

A good optical quality single crystal of 2- Amino 5- Nitro pyridinium Hydrogen Oxalate (2A5NPHO) was grown by using unidirectional solution growth method. Photoconductivity, Microhardness and Dielectric studies of 2- Amino 5- Nitro Pyridinium Hydrogen Oxalate (2A5NPHO) were carried out. KEITHLEY 480 picometer was used for photoconductivity studies of a triclinic crystal (2A5NPHO). Microhardness was measured by using Vicker's hardness tester. Dielectric studies were performed with help of HIOKI HITESTER model 3532- 50 LCR meter

INTRODUCTION

New materials exhibiting non linear optical (NLO) effects have been explored with view to develop opto- electrical devices for example optical modulator and frequency doubling devices [1]. Hence the search for efficient non linear optical (NLO) crystals is in fact that search for the polar crystals in which the macroscopic properties reflect the internal asymmetric molecular relationship. Such a crystal may have an external morphology with hemi hedral faces that have different chemical reactivity and physical properties, such as third order NLO activity in addition to pyro electric, pizzo electric and ferro electric effects [2]-[3]. 2- Amino 5- Nitro Pyridinium is a necessary raw material for preparing azo compounds which have been widely used as a colouring matter. 2- Amino 5- Nitropyridinium has an interesting molecular structure which has a nitro group as an electron donor and amino group as an electron acceptor and amino group as an electron acceptor. Further, the pyridine ring acts 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 nonlinear 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. It has also been used within hydrogen- bonded organic anionic networks, or as counterions in organic/inorganic salts. Moreover, 2- Amino 5-Nitropyridine can be adsorbed on silver sols or surface to be employed in surface enhanced Raman scattering experiments or electrochemical research [4]-[9]. Pyridine derivatives are important intermediates in organic synthesis, particularly in the synthesis of biologically active and medicinally important agents, for example in the synthesis of anti convulsant agents and antiviral agents. Compounds containing the imidazo pyridine ring system have been shown to exhibit antibacterial and anti- inflammatory properties [10]. Recently the study of 2- Amino 5- Nitropyridinium Dihydrogen Phosphate (2A5NDP) crystal has been presented by Morel et al, Anna puig- Molina et al and pericilla Jeyakumari et al have reported on the non linear absorption properties of a hybrid orgnic- inorganic crystal 2- Amino 5- Nitro pyridinium Dihydrogen Phosphate (2A5NDP). The non linear transmission measurements with nanosecond pulses are interpreted in terms of a three photon absorption that results from a two-step process followed by excited state absorption. Additionally the absorption property and their polarization dependence have been studied for several crystal orientations in the visible range of 450- 650 nm. Pericilla Jayakumari et al have synthesized and the molecular structure was elucidated by FT- IR, FT- Raman and FT- NMR. The bulk and powder second harmonic generation (SHG) measurements were carried out using Nd: YAG laser and its phase matching condition were determined. Anna Puig- Molina et al have interperated the topological analysis of the 2-Amino 5- Nitropyridinium Dihydrogen Phosphate (2A5NDP) and the experimental electron density distribution determined from X-diffraction data interpreted in terms of the Hansen &Coppenspsudoatom formalism. It has been found that the bond critical point property of the total experimental electron density fairely agrees well with ab initio Hartree- Fock calculations for the isolated ions [11] - [13]. Recently the new structure of 2- Amino 5- Nitropyridinium hydrogen selenate and 2- Amino 5-Nitropyridinium tetraoxido- rhenate(VII) monohydrate [14]-[15]. G. Anantha babu et al have prepared a noncentrosymmetric crystal of 2-Amino 5- Nitropyridinium Phenolsulfonate, the structural properties of these crystal have been analyzed by HXRD, FT- IR and spectral analysis. It was seen that 2- Amino 5- Nitro Pyridinium Phenolsulfonate seems to promising material for NLO applications. Single and multiple shot surface laser damage threshold were found to be GW/cm^{2}and 0.31 GW/cm^2 at 532 nm laser radiations respectively [16]. New second harmonic crystal 2- Amino 5- Nitropyridinium -L- (+) tartrate has been synthesized and crystal structure was determined by XRD analysis. The structure was solved by direct method using Multan 78 programme. The crystal data of 2-Amino 5- Nitropyridine –L- (+) tartrate showed the monoclinic system of space group $P2_1$ [17]. The crystal structure of 2- Amino 5-Nitropyridinium Acetophosphate confirms the possibility to design at request non-centrosymmetric structures based on the 2- Amino 5- Nitropyridinium polar chromophore. The non-centrosymmetry in this class of materials is mainly depedendent on the structure of the associated counter- anion. Layered anionic aggregates always favour non- centrosymmetrical organization of non- linear cations as evidenced by many crystal structure investigations [18]. The quadratic nonlinear optical efficiency of the 2-Amino 5- Nitropyridinium dihydrogen chloride crystal was studied. The quadratic coefficients were determined by second harmonic generation as d_{11} = 9 pm/V and d_{12} = 8pm/V. The effective coefficients obtained are d_{eff} = 5.1 pm/V for type I and d_{eff} = 9.7pm/V for type II. Following the gas-oriented model, the dimensions of the hyperpolarizability tensor b_{IJK} of the 2- Amino 5-Nitropyridinium were examined. Considering the arrangement of the organic and inorganic entities in the unit cell, the failure of the two- dimensional model can be due to the local electric field induced by the Cl^- anions [19]. In the present investigation, we have grown good optical quality and large size 2 Amino 5- Nitropyridinium Hydrogen Oxalate (2A5NPHO) single crystal by unidirectional solution growth method. We already reported the new structure of 2A5NPHO [20]. However, a few data on the microhardness, dielectric and photoconductivity properties of 2A5NPHO crystal has not been reported. In this present work we are processing our findings on the microhardness, dielectric and Photoconductivity properties of 2 Amino 5- Nitropyridinium Hydrogen Oxalate (2A5NPHO) single crystals.

PHOTOCONDUCTIVITY STUDIES

Photoconductivity serves as a tool to understand the internal processes in crystals and it is also widely used to detect the presence of light and measure its intensity in light – sensitive devices. Photoconductivity is an important property of solids by means of which the bulk conductivity of sample changes due to incident radiation. Photoconductivity is not an elementary process in solids. Photo detection technology is becoming more and more important in military applications, particularly in guided weapons and communication through fiber optics. Infrared developments are based on solid- state photonic devices. Further developments in these fields demand a good understanding of the basic principles of photoconductivity process. Photoconduction as the name suggest, includes the generation and recombination of charge carries and their transport to electrodes. Obviously, the thermal and hot carrier relaxation process, charge carrier statistics, effects of electrodes and several mechanism of recombination are involved in photoconduction. Above all every mechanism is a complicated one, and therefore photoconductivity in general is very complex process. In spite of the complexity of the photoconductivity process, it provides useful and valuable information about physical properties of materials and offer applications in photo detection and radiation measurement. Historically, the first photoconductivity was recorded in 1873 by W.Smith, who observed that the resistivity of selenium was decreased by radiation falling on it. According to this literature, this is very first experimental detection of photoconductivity.

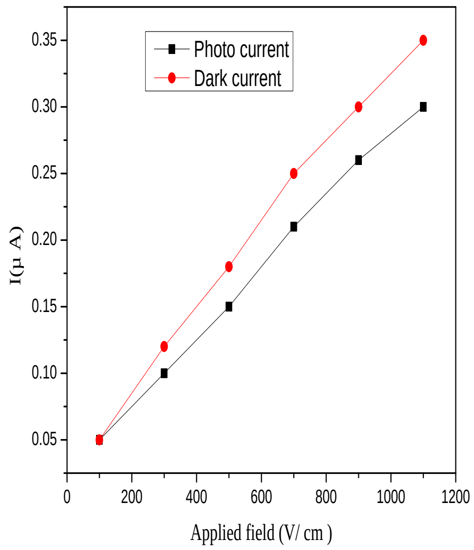

Figure 1: Photoconductivity studies of 2A5NPHO single crystal

The photoconductivity of 2- Amino 5- Nitropyridinium Hydrogen Oxalate (2A5NPHO) was measured using KEITHLEY 480 picometer. Initially, the sample was kept away from any other radiation. The dark current (I_d) of 2- Amino 5- Nitro Pyridinium Hydrogen Oxalate (2A5NPHO) was measured by connecting a DC power supply, picometer and the sample in series. The photo current (I_d) for the sample was calculated by exposing it to the radiation from a halogen lamp containing iodine vapour by focusing a spot light on the sample with the help of a convex lens. Initially the applied voltage was increased from 100 to 1800 V in steps 200 V and the corresponding dark current (I_d) was measured. Fig shows the variation of the dark current (I_d) and photo current (I_p) of the sample with applied field. From the graph both the dark current (I_d) and photo current (I_p) were seen to increase linearly with the applied field. For same applied field the photo current (I_p) is less than the dark current (I_d) which reveal that the negative photoconductivity behavior of the sample. This negative conductivity may be due to the reduction in number of charge carries in the presences of radiation [21]-[22]. The decreases in mobile charge carries during negative photoconductivity were also explained by stock man model [23]. Though the material shows negative photoconductivity for visible light radiation, the material is excited to create more charge carriers for intense beam laser.

MICROHARDNESS

Mechanical strength of the material plays a key role in the device fabrication. Vickers 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 crystals. The mechanical behavior of a crystal is of paramount importance in technological applications. The hardness measurement is treated as an efficient technique of providing information about the elastic, viscous, plastic and fracture properties. The microhardness measurements were carried out with the load range from 5 to 50 g on crystal surface using Vicker's hardness tester fitted with a diamond pyramidal indenter and attached to an incident light microscope. The Vicker'smicrohardness number (H_v) was calculated using the relation,

$$H_v = (1.8544\ P/d^2) \qquad (1)$$

Where P is the load and d is the diagonal length of the impression. Fig 2 shows the variation of load P with hardness number (H_v) for 2- Amino 5- Nitro Pyridinium Hydrogen Oxalate (2A5NPHO).

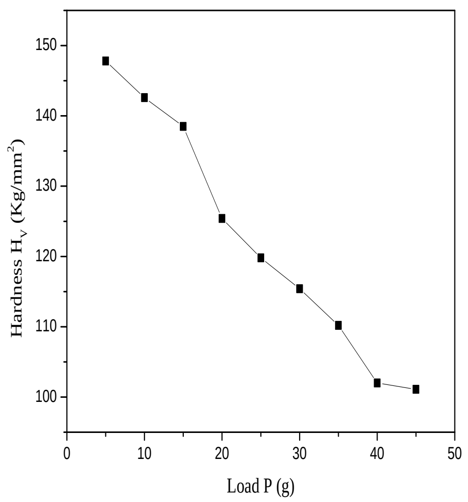

Figure 2: Variation of Vicker's Hardness of 2A5NPHO single crystal

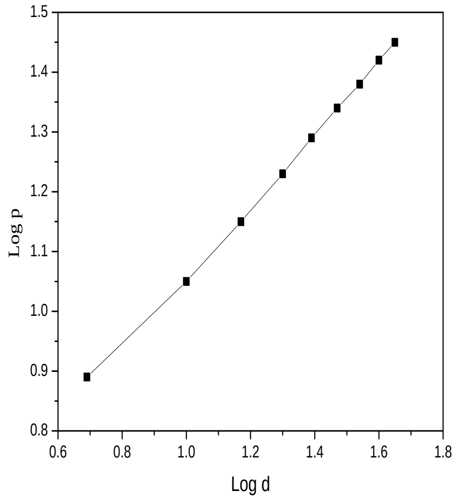

Figure 3: Log d Vs Log p of 2A5NPHO single crystal

It is evident from the graph that the hardness number of 2- Amino 5- Nitro Pyridinium Hydrogen Oxalate (2A5NPHO) decreases with increasing applied load. It is in good agreement with the concept proposed in literature [24]-[25]. According to Meyer's law, the relation connecting the applied load is given by

$$P = K_1 d^n$$

Where n is the Meyer index or work hardening and K is the constant for a given crystal. By plotting log p against log d, the value of work hardening coefficient was calculated as 1.4, which is less than 2, establishing the crystal to be a hard material [25].

DIELECTRIC STUDIES

Dielectric measurements were performed on a 2-Amino 5- Nitropyridinium Hydrogen Oxalate (2A5NPHO**)** single crystal using a HIOKI HITESTER model 3532- 50 LCR meter. The sample was placed inside a dielectric cell whose capacitance was measured at various temperatures for different frequencies. A sample of crystal having silver coating on the opposite faces minimize the edge effect and act as parallel plate capacitor for the sample. The dielectric constant and dielectric loss have been calculated using the equations (2) and (3)

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

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

Where d is the thickness of the sample, A is the area of the sample. The observations are made in the frequency range 50 Hz- 5 MHz at different temperatures.

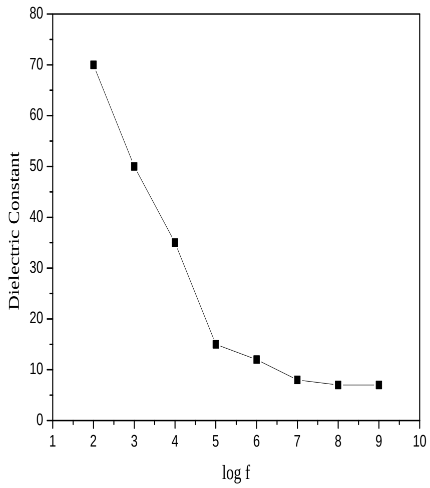

Figure 4: Log f Vs Dielectric Constant of 2A5NPHO single crystal

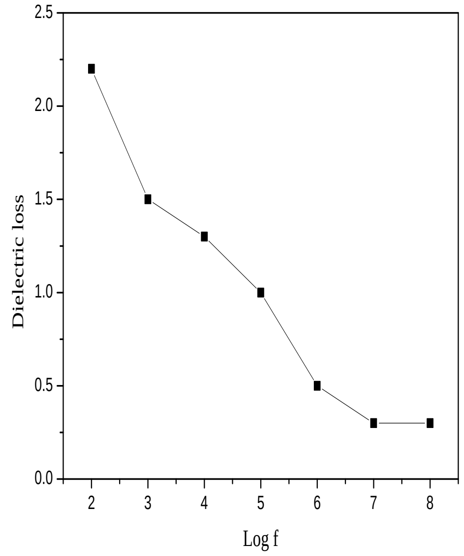

Figure 5: Log f Vs Dielectric loss of 2A5NPHO single crystal

Dielectric constant and dielectric loss measurements of 2- Amino 5- Nitropyridinium Hydrogen Oxalate (2A5NPHO) single crystal are shown in fig. 4 and fig.5. It is observed from the graph that the dielectric constant and dielectric loss decreases slowly with increasing in frequency and attains saturation at higher frequencies. The dielectric constant is due to the electronic, ionic, dipolar and space charge polarizations, which depend on the frequencies, and high dielectric constant of the crystal at low frequency is attributed due to space charge polarization [26]-[28]. In accordance with Miller rule [29] the lower value of dielectric constant at higher frequencies is a suitable parameter for the enhancement of SHG coefficient. The characteristic of low dielectric loss with high frequency for the sample suggests that the crystal posses enhanced quality with lesser defects and this parameter play a vital role for the construction of devices from non linear optical materials [30].

CONCLUSION

In this present work single crystal of 2-Amino 5-Nitropyridinium Hydrogen Oxalate (2A5NPHO) was characterized by microhardness, Dielectric and photoconductivity studies. Micrhardness indicates that 2-Amino 5- Nitropyridinium Hydrogen Oxalate (2A5NPHO) single crystal belongs to hard material. Photoconductivity of 2-Amino 5- Nitropyridinium Hydrogen Oxalate (2A5NPHO) single crystal confirms the negative conducting nature of the crystal. The dielectric study indicates that the 2-Amino 5-Nitropyridinium Hydrogen Oxalate (2A5NPHO) single crystal posses good optical quality with less defects.

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Dr. D. Prem Anand received M.sc, M.phil and Ph.D in physics from Madras University. He has been actively doing research from 2004. He has published research articles in national and international journal. He is working in the field of crystal growth and nanotechnology. He is now working as an assistant professor of physics at St. Xavier's College- Palayamkottai.

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