

# Studies on Au<sup>3+</sup> ION Irradiated Organic – Inorganic Nonlinear Optical (NLO) Single Crystal: 2-Amino-5-Nitropyridinium Dihydrogen Phosphate (2A5NPDP)

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**Abstract-** 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) a nonlinear optical (NLO) single crystal was irradiated using Au<sup>3+</sup> ion with various fluencies such as  $1 \times 10^{13}$  ions/cm<sup>2</sup>,  $5 \times 10^{13}$  ions/cm<sup>2</sup> and  $1 \times 10^{14}$  ions/cm<sup>2</sup>. Quality of Unirradiated and Irradiated crystals were studied using single crystal X-ray diffraction. Functional group of irradiated and pristine crystal was measured confirmed using FTIR. Optical properties of irradiated and pristine samples were measured and optical absorption decreases with increase of ion fluencies. Optical energy band gap of both the samples were calculated and it was found to be 3.14 eV, 3.07 eV, 3.08 eV and 3.09 eV for pristine and irradiated crystal of various fluences such as  $10^{13}$  ions/cm<sup>2</sup>,  $5 \times 10^{13}$  ion/cm<sup>2</sup> and  $10^{14}$  ions/cm<sup>2</sup> respectively. Mechanical properties of pristine and irradiated crystals were measured using Vicker's hardness test. Hardness of irradiated crystal was increased due to increase of density of lattice defects. The decrease of second harmonic generation (SHG) was due to higher ion fluence, which almost affected the noncentro symmetric packing of the molecular crystal. Dielectric constant increased with increase of ion fluencies. Damage created by swift heavy ion (SHI) was isolated from each other. This increased charge carries which increased the space charge polarization at low frequency. Morphology of the pristine and irradiated crystals was studied using scanning electron microscope (SEM). Surface of irradiated crystal was heavily damaged and degree of crystallinity decreased when ion fluencies increases. Second harmonic generation (SHG) of pristine and irradiated samples were also studied. Second harmonic generation (SHG) efficiency decreases. Thermal stability of irradiated single crystal increased with increase of ion fluencies. Impedance of pristine and irradiated crystal was also studied. Impedance of irradiated crystal was greater than the pristine sample. Photoluminescence and fluorescence spectral studies were also studied.

**Keywords-** Swift heavy ion irradiation, dielectric, thermal properties, 2-amino-5-nitropyridinium dihydrogen phosphate

## I. INTRODUCTION

Recent decades swift heavy ion (SHI) have been used to irradiate solids. Using irradiation process one can modify the structural, mechanical, optical, thermal and electrical properties of the materials. Ion irradiation plays a vital role in modification of engineering materials. Ion beam interaction has wide application such as industrial, technological and medical application for the compound formation, nanostructure, thin film, biological diagnosis etc. Swift heavy ion irradiation methods provide a highly controllable set of tool which can be used for investigation systematically at the atomic level. When an energetic ion beam interacts with solid or crystal, energy is transferred from ion to solid [1- 4]. Semiorganic crystals are new kind of materials which has interesting nonlinear optical properties [5- 7]. These hybrid materials combining the advantages of organic and inorganic crystals are built up by the anchorage of organic molecules into inorganic matrices through strong hydrogen bonds. Semiorganic crystals exhibit wide transparency range and bulk crystals morphologies. Donor –acceptor conjugated NLO materials, high molecular polarizability and acentric structure materials are used to build efficient NLO materials. The donor and acceptor groups are linked through conjugated rings, such as benzene or pyridine that are more used. Among various organic molecules, 2-amino-5-nitropyridine allow for the growth of numerous salts [8]. 2-amino-5-nitropyridine is a potential nonlinear optical candidate. 2-amino-5-nitropyridine 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 acts as a cationic bonding site, the nitro group as hydrogen acceptor and amino group as a hydrogen donor [9]. Using organic molecule of 2-amino-5-nitropyridine, a numerous salts were grown like 2-amino-5-nitropyridinium sulfamate (2A5NPS), 2-amino-5-nitropyridinium chloride (2A5NPCl), 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP), 2-amino-5-nitropyridinium hydrogen oxalate (2A5NPHO), 2-amino-5-

nitropyridinium bromide (2A5NPBr), 2-Amino-5-nitropyridinium tri-fluoro-acetate, 2-Amino-5-nitropyridinium Phenolsulfonate, 2-amino-5-nitropyridinium dihydrogen arsenate (2A5NDA), 2-amino-5-nitropyridinium nitrate (2A5NPN) and 2-amino-5-nitropyridinium- L-(+)- tartrate (2A5NPT) [10-19]. 2-amino-5-nitropyridinium sulfamate (2A5NPS) was grown and structure solved and its properties were reported [10, 20]. 2-amino-5-nitropyridinium hydrogen oxalate (2A5NPHO) was grown and structure also solved. Using sankaranarayan- Ramasamy (S-R) method, 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) was grown and properties were reported [21]. Mechanical, electrical and photoconductivity of 2-amino-5-nitropyridinium hydrogen oxalate (2A5NPHO), 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) and 2-amino-5-nitropyridinium nitrate (2A5NPN) were also reported [21-25]. 2-amino-5-nitropyridinium chloride (2A5NPCl) was grown using assembled temperature reduction method (ATR) and characterizations were reported [26]. In this research article, modifications in morphology, mechanical, optical, electrical, and thermal and NLO of irradiated 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) is reported.

## II. CRYSTAL GROWTH AND IRRADIATION

An organic- inorganic crystal of 2-amino-5- nitropyridinium dihydrogen phosphate (2A5NPDP) was grown using slow evaporation and Sankaranarayanan- Ramasamy (S- R) method. A good and quality single crystal from slow evaporation was used as a seed crystal to grow unidirectional bulk crystal in S-R method. A unidirectional bulk crystal was harvested for 60- 80 days. with dimensions 13 mm X 5 mm X 8 mm [21]. The polished single crystal which was irradiated using  $\text{Au}^{3+}$  ion is shown in fig. 1.



Fig.1. Polished NLO single crystal of 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP)

## III. $\text{Au}^{3+}$ ION IRRADIATION

In order to understand the reaction between solid and ion, those grown crystals were irradiated. A cut and polished single crystal was used for irradiation. 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) was irradiated using 3MV Tandam accelerator in National Centre for Accelerator based Research (NCAR), department of pure and applied physics, Guru Ghasidas Vishwavidyalaya (a

central university), at Bilaspur, Chhattisgarh. A metallic ion and source of negative ions by cesium sputtering (SNICS) of  $\text{Au}^{3+}$  was selected for irradiation. Using copper paste the as grown crystals were kept on the stainless steel sample holder. The as grown crystal was irradiated with three ion fluencies such as  $1 \times 10^{13}$  ions/  $\text{cm}^2$ ,  $5 \times 10^{13}$  ions/  $\text{cm}^2$ , and  $1 \times 10^{14}$  ions/  $\text{cm}^2$  with beam current of 1.55 A, 1.35 A, and 8 p nA respectively. Ion beam was scanned over a sample normal to its face for uniform irradiation at room temperature. A dosimeter was given to measure the radiation around the lab which was almost zero.

## IV. RESULTS AND DISCUSSION

2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) was irradiated by using  $\text{Au}^{3+}$  ion. When swift heavy ion (SHI) interacted with solid, it lost its energy continuously and changed its direction by colliding with solid. Fig.2. shows electronic and nuclear energy losses in 2-amino-5- nitropyridinium dihydrogen phosphate (2A5NPDP) NLO single crystal. It was noticed from the graph that, the electronic loss increases with increase of ion energy and nuclear loss decreased with increase of energy. Using SRIM software, maximum electronic loss was calculated and was found to be  $1.361 \times 10^1$  at 11 MeV. The mean project range was calculated and it was 2.98.

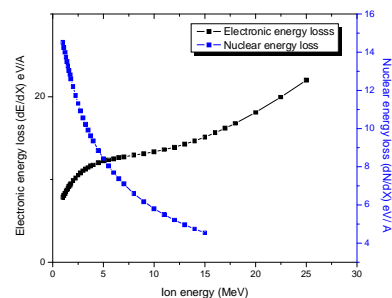


Fig.2. Electronic and nuclear energy losses of  $\text{Au}^{3+}$  ion energies in 2-amino-5-nitropyridinium dihydrogen Phosphate (2A5NPDP) NLO single crystal.

## Single crystal X-ray diffraction

Fig.4. shows X- diffraction pattern of pristine and  $\text{Au}^{3+}$  ion irradiated 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) single crystals.

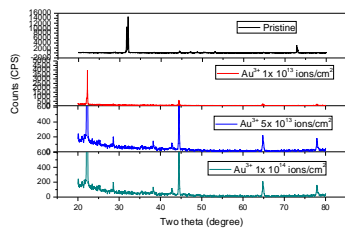


Fig.4. X- diffraction pattern of pristine and  $\text{Au}^{3+}$  ion irradiated 2-amino-5- nitropyridinium dihydrogen phosphate (2A5NPDP) NLO single crystals

It was clear from the X- ray diffraction patterns that, interaction of solid –ion, librated thermal energy that produced defects along the path of the ion. It is noticed from the X- ray diffraction pattern that intensity of irradiated crystal decreases with increase of ion fluencies. At fluencies of  $\text{Au}^{3+}$  ( $5 \times 10^{13}$  ions/ $\text{cm}^2$ ) almost all the peaks were vanished and intensity of (111), (211), (022), (122), (222) planes increased due to reordering and cross linkage of bands taking place. It was also observed from the X- ray diffraction pattern that, defects were formed and lattice was deformed. Lattice deformation was not in the entire crystal surface because deformation was taken place only in al small area that was around the ion paths. Peaks were observed at higher fluencies due to the unaffected planes in the irradiated crystal.

### Optical properties

Optical properties of 2-amino-5- nitropyridinium dihydrogen phosphate (2A5NPDP) was subjected to Perkin Elmer lamda 35 Uv- vis NIR spectrometer. Fig. 5 shows absorption spectra of pristine and irradiated semiorgaic crystal of 2- amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP). Lower cut off wavelength of pristine is 364 nm. It is revealed from the Uv-vis spectra that absorption of irradiated crystal increases with increase of ion fluencies. Maximum absorption are 356.1 nm, 357 nm and 357.7 nm for ion fluencies  $1 \times 10^{13}$  ions/ $\text{cm}^2$ ,  $5 \times 10^{13}$  ions/ $\text{cm}^2$  and  $1 \times 10^{14}$  ions/ $\text{cm}^2$  respectively. Both pristine and irradiated crystal has wide transparency window which is one of the additional key requirements for having efficient NLO character. The increase of absorption is due to excited electrons which are formed by vacancies and formation of additional defects centers. It is also noticed that there is no additional peak in the visible region. Due to insufficient energy that is observed by electrons from swift heavy ion (SHI) to move lattice to substitution. Transmittance of irradiated crystal decreases as ion fluencies increase. The decrease of transmittance of irradiated crystals is due to creation of defects. It is noticed from the spectra that the absorption spectra shifted towards shorter wavelength

(blue shift) with increase of ion fluencies. The change in the absorption may also be the creation of some intermediate energy levels due to structural rearrangements. Fig.6. shows Tauc plot of pristine and irradiated NLO single crystal of 2-amino-5 nitropyridinium dihydrogen phosphate (2A5NPDP). It is calculated from the graph that photon ( $h\nu$ ) of pristine is 3.14 eV which is equal to the band gap of the crystal ( $E_g = h\nu$ ). Band gap of irradiated samples with varied fluencies are 3.07 eV, 3.08 eV, and 3.09 eV. It is revealed from the graph that there is a change in the energy band gap. Swift heavy ion (SHI) irradiation produces point defects such as vacancies, anti-site defects and interstitial causing lattice damage. The change in the band gap may be understood through the creation of some intermediate energy levels. It is understood from the graph that optical properties of 2-amino-5-nitropyridinium dihydrogen phosphate(2A5NPDP) does not altered considerably by swift heavy ion(SHI)

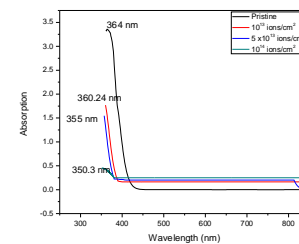


Fig.5. Absorption spectra of pristine and irradiated 2-amino- 5- nitropyridinium dihydrogen phosphate (2A5NPDP) NLO single crystal.

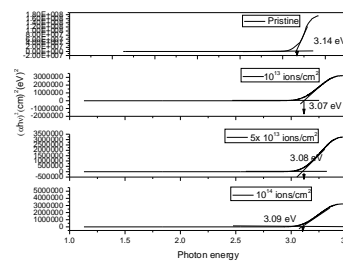


Fig.6. Tauc plot of pristine and irradiated NLO single crystal of 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP)

### Microhardness

Vicker's hardness ( $H_v$ ) test was carried out for pristine and irradiated 2-amino-5- nitropyridinium dihydrogen phosphate (2A5NPDP) crystal with varied fluencies at room temperature. Load was applied on the selected plane range from 25 g to 100 g. Fig.11 shows microhardness of pristine and irradiated semiorganic crystal of 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP). It is noticed from the graph that hardness of pristine and irradiated

crystal increases with applied load. It is also observed that hardness of pristine is lesser than the irradiated crystal. Hardness of irradiated crystal increases with increase of ion fluencies.

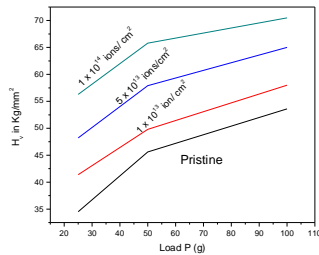


Fig. 11. Microhardness of pristine and irradiated 2- amino 5- nitropyridinium dihydrogen phosphate (2A5NPDP) NLO single crystal

Increase of hardness is due to increase in density of lattice defects caused by the passage of implanted ions through 2-amino-5- nitropyridinium dihydrogen phosphate (2A5NPDP) lattices. In an irradiated crystal a residual surface compression stress is produced in the irradiated surface layer because of increased density of lattice defects [23]. **Dielectric studies**

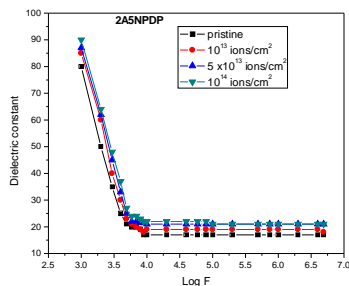


Fig. 14. Dielectric constant of pristine and irradiated 2-amino - 5- nitropyridinium dihydrogen phosphate (2A5NPDP) NLO single crystal

Electrical properties of dielectric constant and dielectric loss of pristine and irradiated crystals of 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) were studied. Fig.14. shows dielectric constant of pristine and Au<sup>3+</sup> ion irradiated NLO single crystal. It is observed from the graph that, dielectric constant increases at lower applied frequencies. High value of dielectric constant at lower frequencies is due to the contribution of space, electronic, ionic, and dipolar polarizations. Among these polarizations, Space charge polarization plays a vital role to get high dielectric constant at low frequency. The value of dielectric constant decreases with increase of applied frequency. This is because, after certain frequency the charge carriers cannot follow the alternation of AC electric field. It is also noticed from the graph that at low frequency, the dielectric constant of

pristine crystal is lesser than the Au<sup>3+</sup> irradiated crystals. The higher dielectric constant than the pristine could be attributed that, when solid is irradiated using swift heavy ion (SHI), ions are attached into a target material and they transfer energy to the target material until it loses energy completely. This transfer of energy from ion to solid results defects formation and disordering of the crystal structure. Defects are created along the ion tracks. This formation of defects increases the dielectric constant. It is elucidated from the graph that, dielectric constant increases with increase of ion fluencies. This might be explained that damage was created along the surface of the sample, when high fluence ion beam was irradiated. Damage created by swift heavy ion (SHI) was isolated from each other. It increased charge carriers which in turn increased the space charge polarization at low frequency.

### NLO test

A semiorganic single crystal of 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) of pristine and irradiated samples were subjected to second harmonic generation(SHG). Kurtz powder technique was used to measure second harmonic generation (SHG). A Q- switched Nd-YAG laser of 1064 nm was used as a primary source with an input power of 1.2 mJ/ pulse with repetition rate of 10HZ and pulse width of 10 ns. A convex lens of 20 cm focal length was used to collimate laser rays on the sample. Pristine and irradiated samples were powdered and filled in a microcapillary tubes. Photomultiplier tube was used to detect the green light and second harmonic generation(SHG) output of green laser (532 nm) light was seen on digital oscilloscope. SHG results revealed that, output of pristine was 45 mV and irradiated samples with varied fluencies ( $1 \times 10^{13}$  ions/cm<sup>2</sup>,  $5 \times 10^{13}$  ions/cm<sup>2</sup>, and  $1 \times 10^{14}$  ions/cm<sup>2</sup>) were 5 mV, 1 mV and 1 mV respectively whereas that of KDP was 22 mV. It is observed from the result that, when the samples are subjected to laser thermal diffusion comes to play and damage the crystal further. Spreading of thermal energy increases along the swift heavy ion (SHI) path, defects in the crystal surface also increases and second harmonic generation (SHG) efficiency decreases. The decrease of second harmonic generation (SHG) is due to higher ion fluence, which almost affected the noncentro symmetric packing of the molecular crystal. Swift heavy ion (SHI) irradiated crystals too contain many defects.

### Scanning electron microscope (SEM)

Scanning electron microscope used to study on morphology, crystal orientation and etc. Fig.15.(a, b, c, &d) shows SEM image of pristine and irradiated NLO single crystal of 2-amino-5-nitropyridinium dihydrogen phosphate

(2A5NPDP). It is noticed from the pristine SEM image that, the semiorganic crystal has leniently distributed grains. It looks like a smooth surface. In irradiated crystals, the roughness of the surface increases with increase of ion fluencies from  $1 \times 10^{13}$  ions/cm<sup>2</sup> to  $10^{14}$  ions/cm<sup>2</sup>.

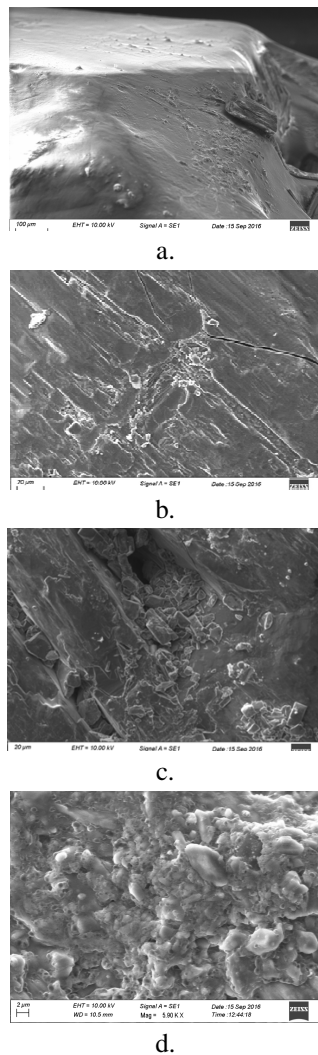


Fig. 15. SEM image of pristine, Au<sup>3+</sup> ion irradiated 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) NLO single crystal (a. Pristine, b.  $1 \times 10^{13}$  ions/cm<sup>2</sup>, c.  $5 \times 10^{13}$  ions/cm<sup>2</sup>, d.  $1 \times 10^{14}$  ions/cm<sup>2</sup>)

Craters were formed in the irradiated crystals. This is due to shock waves produced in the solid. When swift heavy ion (SHI) was bombarded with solid, Shock waves were produced which created crater in the crystalline surface [19]. It is also observed from the SEM image that, some changes or modifications in the crystal orientation were due to swift heavy ion (SHI). At  $5 \times 10^{13}$  ions/cm<sup>2</sup> fluence, bud like produced along with roughness of the surface. It is also found at higher fluence cracks were produced on the surface of crystal sample and also valley like structures were formed at ion fluence  $10^{14}$  ions/cm<sup>2</sup>. Surface of crystal was heavily

damaged and degree of crystallinity decreases when ion fluencies increase.

## Fluorescence

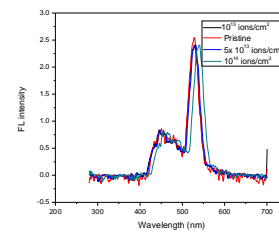


Fig. 16. Fluorescence spectra of pristine and irradiated 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) NLO single crystal.

Fluorescence study was carried out for as grown pristine and Au<sup>3+</sup> ion irradiated 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) NLO single crystal. Fig.16. shows fluorescence spectra of pristine and irradiated NLO single crystal, which was carried out at room temperature. It is observed from the spectrum that, as grown pristine sample shows high luminescence intensity at 528 nm. Energy band gap was calculated using conversion, wavelength to energy relation  $E_g = 1.24/\lambda \dots \text{eV}$ . The energy band of pristine was calculated and it is 2.34 eV from the wavelength 528 nm. This emission of (528 nm) green light is due to  $\pi$ - $\pi^*$  transitions. 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) NLO single crystal emits green radiation which is an excellent candidate for nonlinear applications and device fabrications. It is also observed from the luminescence spectra that, intensity peak of ion irradiated NLO single crystal decreases with increase of ion fluences. It is also revealed from the spectra that, intensity of irradiated crystals is less than that of unirradiated crystal. It is noticed from the spectra that there is a change in the peak position, when ion fluences are increased from  $10^{13}$  ions/cm<sup>2</sup> to  $10^{14}$  ions/cm<sup>2</sup>. The decrease of intensity than the unirradiated sample is due to the effect of ion irradiation in the crystal lattice. Swift heavy Ion (SHI) irradiation creates defects in the crystal and which is rich at high ion fluence. Rich defects are due to high ion fluence that affect the irradiative transitions in which crystal loses its luminescence property. It is also observed from the fluorescence spectra that intensity of peak decreases and shifting of peak with increase of ion fluence. This is due to exchange of electron between F and F<sup>+</sup> centers, which were released from the conduction band. The decrease of intensity peak is due to the formation of new defects by swift heavy ion (SHI) irradiation.

## Thermal analysis

Thermogravimetric (TG) and differential thermal analysis (DTA) gives information about phase transition, water of crystallization and different stages of decomposition. TG and DTA were carried out for pristine and irradiated of orthorhombic NLO single crystal of 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP). A pristine sample was started to decompose at 179<sup>o</sup>C, which already was reported[21]. Au<sup>3+</sup> ion irradiated single crystal with different fluencies (1 x10<sup>13</sup> ions/cm<sup>2</sup>, 5 x 10<sup>13</sup> ions/ cm<sup>2</sup>, and 1 x10<sup>14</sup> ions/ cm<sup>2</sup>) were decomposed with weight loss was little more than the pristine at 183<sup>o</sup> C, 185.5<sup>o</sup> C and 186<sup>o</sup> C respectively. There was no endothermic peak observed before decomposition which is the melting point of crystal system. Increase of thermal stability was due to the decrease of degree of crystallinity. It was also noted that thermal stability increased with increase of ion fluences. This was due to increase of defects with increase of ion fluencies. Fig.17(a, b, &c). shows thermogravimetric (TG) and differential thermal analysis (DTA) which gives information about phase transition, water of crystallization and different stages of decomposition of irradiated crystals.

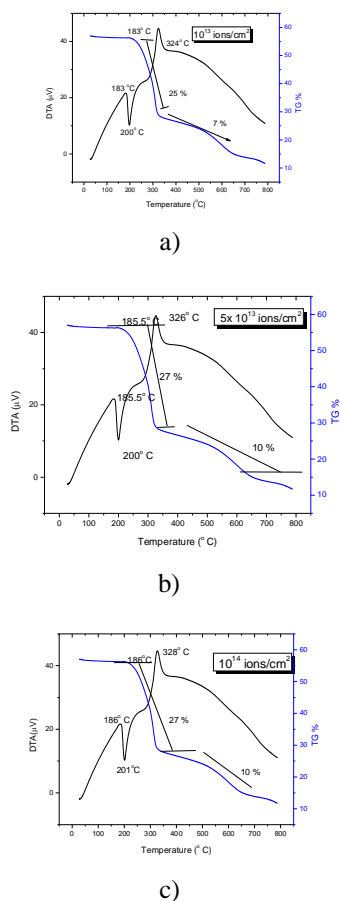


Fig.17. TG/DTA of irradiated NLO single crystal of 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP), a) 10<sup>13</sup> ions/cm<sup>2</sup> b) 5 x 10<sup>13</sup> ions/cm<sup>2</sup> c) 10<sup>14</sup> ions/cm<sup>2</sup>

**Impedance Analysis**

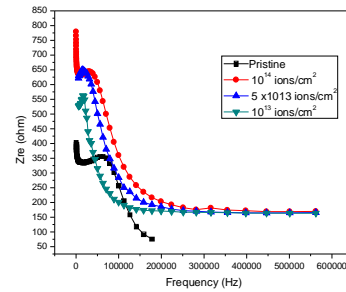


Fig. 18. Plots of real part of impedance with frequency for pristine and irradiated 2- amino -5- nitropyridinium dihydrogen phosphate (2A5NPDP) NLO single crystal

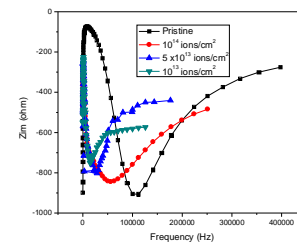


Fig. 19. Plots of imaginary part of impedance with frequency for pristine and irradiated 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) NLO single crystal

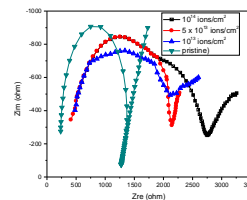


Fig. 20. Nyquist's plots for pristine and irradiated 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) NLO single crystal

Electrical properties of impedance of semiorganic crystal of 2-amino-5- nitropyridinium dihydrogen phosphate (2A5NPDP) NLO single crystal of pristine and Au<sup>3+</sup> ion irradiated studied using complex impedance spectroscopy. Complex impedance was analyzed at room temperature. The frequency dependent properties of materials is represented as a complex impedance Z\*, which is Z\* = Z' - jZ'', where Z' and Z'' are real and imaginary components of impedance respectively. Fig. 18 and fig.19. Show a frequency response of real (Z') and imaginary (Z'') parts of impedance. It is observed from the graph that impedance decreases with increase of applied frequency. High value of impedance at low frequency indicates that polarization is more due to space charge. In real part impedance decreases with increase of applied frequency up to certain frequency value afterwards it is independent. It is also revealed from the graph that the value of impedance

increases with  $\text{Au}^{3+}$  ion fluences. It is noticed from the graph that the impedance of irradiated crystal is greater than the pristine sample. This is due to the formation defects which were created by  $\text{Au}^{3+}$  ion with fluence of  $10^{13}$  ions/cm<sup>2</sup>,  $5 \times 10^{13}$  ions/cm<sup>2</sup> and  $10^{14}$  ions/cm<sup>2</sup>. Fig.20. shows Nyquist's plot of pristine and  $\text{Au}^{3+}$  ion irradiated 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) NLO single crystal. A semicircle is seen in pristine and as well as  $\text{Au}^{3+}$  ion irradiated crystal due to bulk effect of the sample. A combination of capacitor and resistor create bulk effect in the samples. It is also noticed from the Nyquist's plot that bulk resistance of irradiated crystal increased more than the pristine crystal. It is also revealed from the graph that bulk resistance increases with increase of ion fluences from  $10^{13}$  ions/cm<sup>2</sup> to  $10^{14}$  ions/cm<sup>2</sup>. The bulk resistance and grain boundary resistance were calculated from the intercept of the semicircle arc on the real axis and peak of the semi circle respectively. Tab.2 shows bulk resistance and grain boundary resistance of pristine and irradiated crystal.

S.No	Ion fluence ions/cm <sup>2</sup>	Bulk resistance (Ohm)	Grain boundary resistance (Ohm)
1	Pristine	1200	848
2	$10^{13}$	1750	1250
3	$5 \times 10^{13}$	2000	1250
4	$10^{14}$	2750	1289

Table.2. Value of bulk and grain boundary resistance of both pristine and irradiated NLO single crystal of 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP)

## V. CONCLUSION

2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) was irradiated by using  $\text{Au}^{3+}$  ion. swift heavy ion (SHI) interacts with solid, it loses its energy continuously and changes its direction by collision with solid. It is observed from the X-ray diffraction pattern that, defects were formed and lattice was deformed. Lattice deformation is not in the entire crystal surface because deformation was taken place only in a small area that is around the ion paths. Functional group of pristine and  $\text{Au}^{3+}$  ion irradiated 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) NLO single crystals were analyzed and confirmed using FTIR. It is revealed from the Uv-vis spectra that absorption of irradiated crystal decreases with increase of ion fluencies. The change in the absorption may also be the creation of some intermediate energy levels due to structural rearrangements. Optical energy band gap of both the samples were calculated and it was found to be 3.14 eV, 3.07 eV, 3.08 eV and 3.09 eV for pristine and irradiated crystal respectively. Hardness of irradiated crystal increases with increases of ion fluencies. Increase of hardness

is due to increase in density of lattice defects caused by the passage of implanted ions through 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) lattices. It is elucidated from the dielectric studies that, dielectric constant increases with increase of ion fluencies. This is due to damage that is created along the surface of the sample, when high fluence ion beam was irradiated, Damage created by swift heavy ion (SHI) was isolated from each other, which increased charge carriers. SEM reveals that the surface of irradiated crystal was heavily damaged and degree of crystallinity decreases when ion fluencies increases. Second harmonic generation (SHG) of pristine and irradiated samples were also studied. Second harmonic generation (SHG) efficiency of irradiated crystal decreases. The decrease of second harmonic generation (SHG) is due to higher ion fluence, which almost affected the noncentro symmetric packing of the molecular crystal. It is observed from the photoluminescence a spectrum that, as grown pristine sample shows a high luminescence intensity at 528 nm. This emission of (528 nm) green light is due to  $\pi$ - $\pi^*$  transitions. 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) NLO single crystal emits green radiation which is an excellent candidate for nonlinear applications and device fabrications. The decrease of luminescence intensity was more than the unirradiated sample which was due to the effect of ion irradiation in the crystal lattice. Rich defects due to high ion fluence affect the radiative transitions in which crystal losses its luminescence property. Decrease of fluorescence was due to exchange of electron between F and F<sup>+</sup> centers, which were released from the conduction band. It is noticed from the thermal studies that, thermal stability increases with increase of ion fluencies. This is due to increase of defects with increase of ion fluencies. Increase of impedance of irradiated crystal is more than the pristine which is due to the formation defects that was created by  $\text{Au}^{3+}$  ion with fluence of  $10^{13}$  ions/cm<sup>2</sup>,  $5 \times 10^{13}$  ions/cm<sup>2</sup> and  $10^{14}$  ions/cm<sup>2</sup>. It is also revealed that bulk resistance increases with increase of ion fluences.

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