SWIFT HEAVY ION (Au^{3+}) IRRADIATED 2-AMINO-5-NITROPYRIDINIUM CHLORIDE (2A5NPCl) NONLINEAR OPTICAL (NLO) SINGLE CRYSTAL

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Abstract:

A semi organic nonlinear optical (NLO) ingle crystal of 2-amino-5-nitropyridiniumChloride, was irradiated using Au^{3+} *ion with various fluencies such as* 1×10^{13} *ions/cm*^{2}, 5×10^{13} *ions/cm*^{2} *and* 1×10^{14} *ions/cm*^{2}. *Single crystal X-ray diffraction was studied to check the quality of unirradiated and irradiated crystals.. Functional group of irradiated and pristine crystal was measured confirmed using FTIR. Optical properties of irradiated and pristine samples also were measured and from the absorption spectra, it was noticed that absorption increased with increase of ion fluence due to capture of existing ion vacancies and there was no additional peak observed.*

Keywords: *Irradiation, optical, 2-amino-5-nitropyridiniumChloride, and semiorganic*

1. Introduction

Second and third order nonlinear effects lead to a variety of useful applications in laser technologies and photonics and in investigating non- linear optical (NLO) properties of many classes of potentially, technologically useful materials such as organics, organometallics, inorganic, organic- inorganic, and semiconductors. There has been growing interest in fundamental and scientific research in the area of molecule based non- linear optical (NLO) materials with large second and third order nonlinearities. In particular, second order non- linear optical (NLO) materials offer many attractions, such as non resonant ultrafast response times, low dielectric constant and intrinsic architectural tailorability. The inorganic non-linear optical (NLO) crystals posses relatively modest optical nonlinearity due to the lack of extended π-electron delocalization. Compared with inorganic counterparts organic non- linear optical (NLO) materials have large NLO coefficient due to the presence of delocalized π- electron system linking donor and acceptor which enhances the necessary asymmetric polarisability and synthetic flexibility but in general they have very poor thermal and chemical stabilities lower continuous wavelength radiation damage [1] and a poor optical transparency [2]. The search for new non- linear optical (NLO) materials with improved stability, and a wide transparency window has resulted in the development of the new class of materials called semiorganic. In semiorganic, polarisable organic molecules are stiochiometrically bonded inorganic host. It combines the advantage of both organic and inorganic materials. More recently, crystals combining the asset of semiorganic entities were developed [3]. One of the prominent chromophores for semiorganic materials and a successful outcome has been presented by 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) [4-7], 2-amino-5-nitropyridinium chloride (2A5NPCl) [8], and 2-amino-5-nitropyridinium sulfamate (2A5NPS) [9]. Using an outstanding chromophore and nonlinear optical material, the new structure of 2-amino-5-nitropyridinium hydrogen oxalate (2A5NPHO) was grown and structure solved [10]. The mechanical and electrical properties of 2-amino-5-nitropyridinium hydrogen oxalate were reported [11-13] An efficient NLO crystal of 2-amino-5-nitropyridinium sulfamate (2A5NPS) and 2-amino -5-nitropyridinium chloride (2A5NPCl) were grown by assembled temperature reduction method and it's optical, electrical, mechanical and thermal properties were reported [14-15]. Irradiations with energetic ion beams play a vital role in the field of defect studies in inorganic materials. The energetic ions lose their energy during their passage through the material. This energy is spent either in displacing atoms of the sample by elastic collisions or exciting the atoms by inelastic collisions. Low energy ions up to a few hundred KeV have been used in the modification of surface and interface. The loss of energy by the ions in exciting or ionizing the atoms by inelastic collisions is called as electronic energy loss. The irradiation may cause ionization or excitation and possibly displacement of atoms from their sites in the lattice of the materials [16-17]. Recent research interest is focused on the search of new semiorganic nonlinear optical (NLO) materials, as these materials share the advantages of both inorganic (high thermal and mechanical stability) and organic (broad optical frequency and second harmonic conversion efficiency) materials [18-27]. New uses of this technology are developing, and one promising field is that of optical materials. The need for higher transmission speeds and densities in communications is placing ever increasing demands on materials technology. Using heavy ions of high energetic beam, one can modify materials so that they can acquire desired optical, electrical, and mechanical properties. In many cases, ion irradiation causes dramatic change in the optical absorption and luminescent properties of insulators. Hence, In this chapter attempts were made on 2-amino-5-nitropyridinium chloride (2A5NPCl) with Au^{3+} ion of varying fluences.

2. Experimental procedure

2.1Crystal growth

2-amino-5-nitropyridinium chloride (2A5NPCl), a semiorganic crystal was grown from slow evaporation method. 1: 1 equimolar ratio of 2-amino-5-nitropyridine and hydrochloric acid was dissolved in distilled water and stirred well for six hours to get homogenous saturated solution.

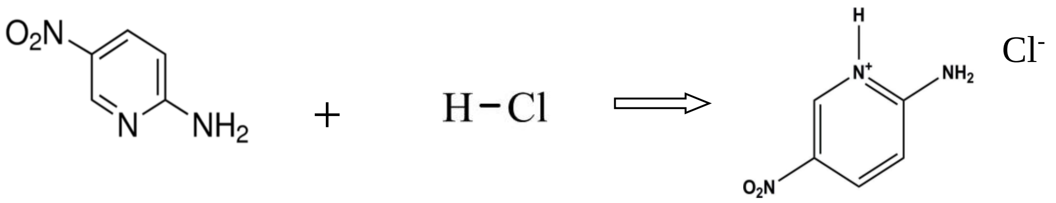

Fig. 2.1 Reaction scheme of 2-amino -5-nitropyridinium chloride (2A5NPCl)

The solution was filtered using whatman filter paper and kept at room temperature to evaporate. Nucleation of the crystal was formed after 60 days. Reaction scheme of 2-amino-5-nitropyridinium chloride (2A5NPCl) NLO single crystal is shown in Fig. 2.1. A good transparent coloured optical and defect free crystal was harvested for 120 days. The semiorganic crystal of 2-amino-5-nitropyridinium chloride (2A5NPCl) dimension of 7 × 3 × 2 mm^3 and 8 x 3x 2 mm^2 are shown in Figure 2.2 (a, b) respectively.

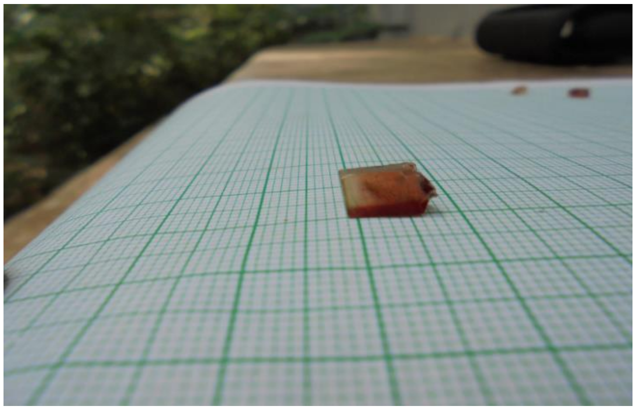

Fig.2.2 (a) Seed crystal of 2-amino-5-nitropyridinium chloride (2A5NPCl) NLO single crystal from slow evaporation

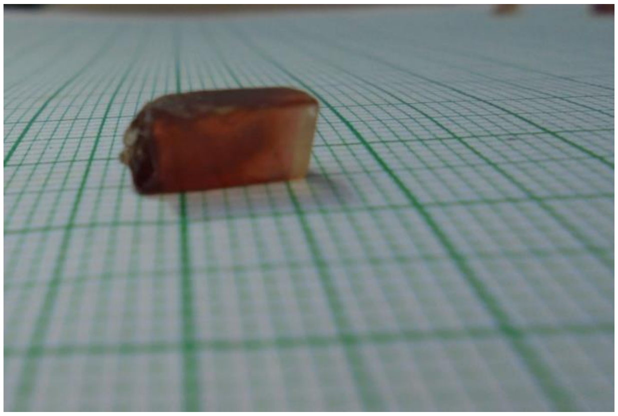

Fig. 2.2(b) Seed crystal of 2-amino-5-nitropyridinium chloride (2A5NPCl) NLO single crystal from slow evaporation

2.2 Solubility of 2-amino-5-nitropyridinium chloride (2A5NPCl)

The synthesized salt was used to measure the solubility of 2-amino-5-nitropyridinium chloride (2A5NPCl) in distilled water. A 250 ml glass beaker filled with 100 ml of distilled water was placed inside a constant temperature bath whose temperature was fixed at 30˚C. An acrylic sheet with a circular hole at the middle through which a spindle from an electronic motor placed over a sheet was introduced into the solution.

A Teflon paddle was attached at the end of the rod for stirring the solution. 2-amino-5-nitropyridinium chloride (2A5NPCl) salt was added in small amounts. The addition of the salt and stirring were continued till the formation of precipitate which confirmed the saturation of the solution. The solubility study of 2-amino-5-nitropyridinium chloride (2A5NPCl) was carried out by increasing the amount of 2-amino-5-nitropyridinium chloride (2A5NPCl) salt that dissolved in water at 30°C, 35°C, 40°C, 45°C, and 50°C. Fig. 2.3 shows the solubility of 2-amino-5-nitropyridinium chloride (2A5NPCl) in 100 ml of double distilled water at different temperatures. It is seen from the solubility curve that the solubility increases with temperature. The solubility of 2-amino-5-nitropyridinium chloride (2A5NPCl) was found to be 16.3 g/100 ml of water at 30°C.

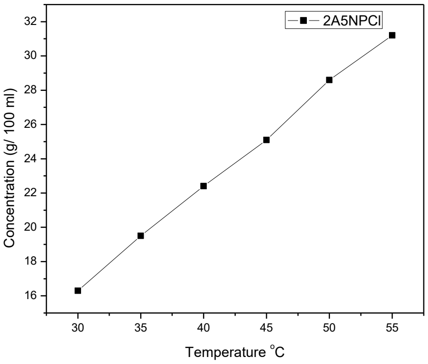

Fig. 2.3 Solubility of 2-amino -5-nitropyridinium chloride (2A5NPCl) NLO single crystal

2.3 Bulk crystal from assembled temperature reduction (ATR) method

Fig. 2.4 (a) As grown NLO single crystal of 2-amino -5-nitropyridinium chloride (2A5NPCl) from assembled temperature reduction (ATR) method

2-amino-5-nitropyridinium chloride (2A5NPCl) was grown as a bulk single crystal using Assembled temperature reduction (ATR) method to check its quality. A bulk crystal of 2-amino-5-nitropyridinium chloride (2A5NPCl) was harvested after 120 days. The size of the crystal is 30×20×20 mm^3.The grown crystal is shown in Fig. 2.4 (a) and 2.4(b). Bulk crystal was cut and polished for irradiation is shown in Fig. 2.5. The properties of 2-amino-5-nitropyridinium chloride (2A5NPCl), such as single crystal X- diffraction, FTIR, optical properties, microhardness and thermal properties have been reported [14].

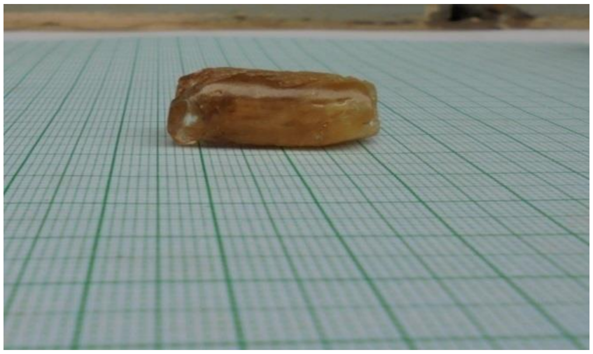

Fig. 2.4 (b) As grown NLO single crystal of 2-amino -5-nitropyridinium chloride (2A5NPCl) from assembled temperature reduction (ATR) method

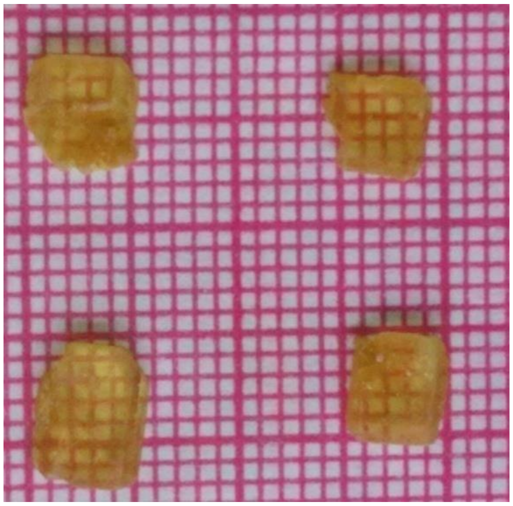

Fig. 2.5 Cut and polished crystal of 2-amino-5-nitropyridinium chloride (2A5NPCl) NLO single crystal

3. Au^{3+} ion irradiation

To know the importance of ions in material, 2-amino-5-nitropyridinium chloride was irradiated. 2-amino-5-nitropyridinium chloride was cut in 1mm thickness and polished for irradiation process. Au^{3+} ion was irradiated in National Centre for Accelerator based Research (NCAR) at Pure and Applied Physics Department, Guru Ghasidas Viswavidyalaya (a central university), Billaspur, Chhattisgarh using 3 MV Pelletron Tandem Accelerator. The cut and polished 2-amino-5-nitropyridinium chloride crystals were kept in a sample holder which is made up of stainless steel. Au^{3+} ion was irradiated at room temperature. Projected range of ion beam, electronic and nuclear loss was calculated using SRIM-2012. Swift heavy ion (SHI) of Au^{3+} was selected from a source of negative ions by cesium sputtering (SNICS). Au^{3+} ions of (10^{13}, 5 x10^{13} and 10^{14} ions/cm^2) different fluence irradiated on the semi organic samples. Energy of Au^{3+} ion was 10.8 MeV, 10.4 MeV and 10.8 MeV for 10^{13}, 5 x10^{13} and 10^{14} ions/cm^2 fluences respectively. The swift heavy ion (SHI) was scanned the samples normal to crystalline surface. Radiation was measured using dosimeter during the experimental work.

4. Result and discussion

4.1. Stopping and range of ions in matter (SRIM)

The projected range of swift heavy ion (SHI), electronic loss and nuclear loss were calculated using SRIM-2012. Swift heavy ion (SHI) was lost its energy, when it entered into the surface of the target atom. Incident energetic ion changed its direction by colliding with target atom. Projected range of swift heavy ion (SHI), electronic

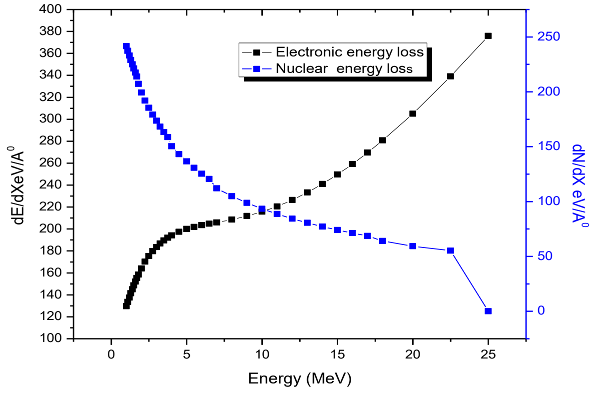

Fig. 4.1 projected range of ion Au^{3+} on 2-amino-5-nitropyridinium chloride (2A5NPCl) NLO single crystal

Ion Energy (MeV)	dE/dx Elec.	dN/dx Nuclear	Projected Range (µm)	Longitudinal Straggling(Å)	Lateral Straggling(Å)
10.00	1.259E+01	5.762E+00	2.90	2061	2090
11.00	1.287E+01	5.447E+00	3.21	2224	2274

Tab. 4.1 Electronic and nuclear energy losses and projected range for input incident Au^{3+} ion energies in 2-amino-5-nitropyridinium chloride (2A5NCl) single crystal

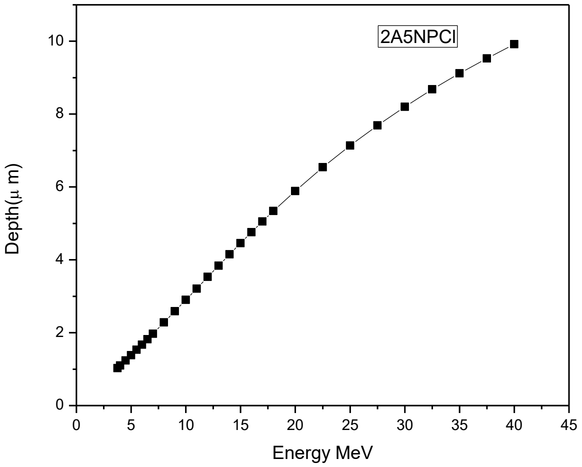

Fig. 4.2 Penetration depth of Au^{3+} ion in 2-amino-5-nitropyridinium chloride (2A5NPCl) NLO single crystal

loss and nuclear loss are presented in Tab. 4.1. Fig. 4.1 shows the electronic (dE/dx) and nuclear (dN/dX) energy losses. It is evident from the graph that electronic energy loss (dE/dx) increases with increase of ion energy (MeV), while nuclear energy ((dN/dx) loss decreases with increasing ion energy. It is also noticed from the graph that projected range of incident Au^{3+} ion is (R_P) 3.21 µm and straggle (δR_p) is 0.2274 µm. From these values, the modified surface thickness was calculated using the formula (R_P+ δR_p) and was found to be 3.4374 µm. Fig. 4.2 shows penetration depth of Au^{3+} ion in 2-amino-5-nitropyridinium chloride (2A5NPCl) NLO single crystal.

4.2. Single crystal X-ray diffraction

Pristine and irradiated samples of 2-amino-5-nitropyridinium chloride crystals were subjected to single crystal X-ray diffraction after swift heavy ion of Au^{3+} irradiation with different fluences. 2- amino-5-nitropyridinium chloride (2A5NPCl) is a monoclinic crystal system with a space group $P2_1$ and lattice parameters are a= 9.957Å, b= 7.384 Å, c= 4.821Å, β= 95.85^0 and Z= 2. The measured values were concordant with reported values by Horiuchi et al [28]. Density of 2-amino-5-nitropyridinium chloride was calculated from crystallographic data using ρ= MN/NV, where M is the molecular weight, Z is the number of molecules per unit cell, N is the Avogadro number and V is the volume of unit cell. Density was found to be $1.71 g/cm^3$. Fig.4.3. shows the Single crystal X-ray diffraction of pristine and irradiated crystals. The sharp nature of the peak indicated the good crystallinity of the grown crystal. It is revealed from the irradiated with different fluence (10^{13} ions/cm^2, 5 x10^{13} ions/cm^2 and 10^{14} ions/cm^2) pattern that decreased peak intensity and broadened the peak was due to defects. These decreased and broadening peak intensity shows occurrence of amorphization due to swift heavy ion (SHI). It was also noticed that the peak intensity decreases with increase of ion fluence. At higher fluence, SHI creates cluster of defects. So peak intensity decreases due to rich defects produced in the crystalline structure. Ion projected range is 3.21 μm. In this range large amount of energy would have been dumped into relatively small volume causing electronic and avalanche and subsequently extending the damage region in the crystal.

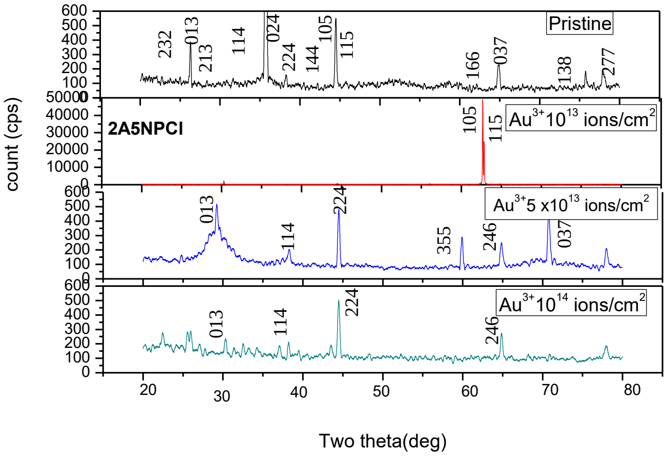

Fig. 4.3 Single crystal X-ray diffraction pattern of pristine and Au^{3+} ion irradiated crystals of 2-amino-5-nitropyridinium chloride (2A5NPCl) NLO single crystal

4.3 FTIR

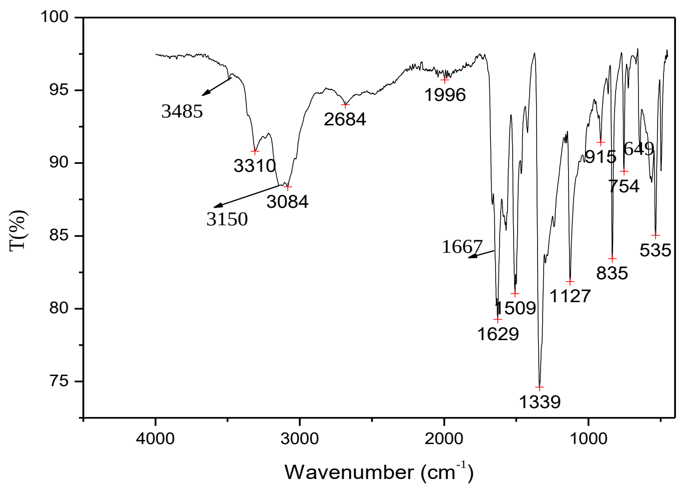

Fig. 4.4 FTIR spectral analysis of pristine 2-amino-5-nitropyridinium chloride (2A5NPCl) NLO single crystal

Pristine and irradiated samples of 2-amino-5-nitropyridinium chloride were exposed to FTIR spectrometer to analyse vibrational group in the grown crystals. FTIR spectral analysis of pristine 2-amino-5-nitropyridinium chloride (2A5NPCl) NLO single crystal is shown in figure 4.4. Strong and broad vibrational frequency observed at 3310 cm^{-1} and 3150 cm^{-1} indicate the presence of NH_2 asymmetric and symmetric modes. The symmetric and asymmetric vibrations of NO_2 occurred at 516 cm^{-1} and 1339 cm^{-1} respectively. These values are in good agreement with reported values by S. Dhanuskodi et al [19]. Aromatic asymmetric stretching vibration of 2A5NP$^+$ observed at 1648 cm^{-1}. The C-H out of plane and the vibrational frequency 649 cm^{-1} indicates the inorganic Cl$^-$. The measured FT-IR and reported

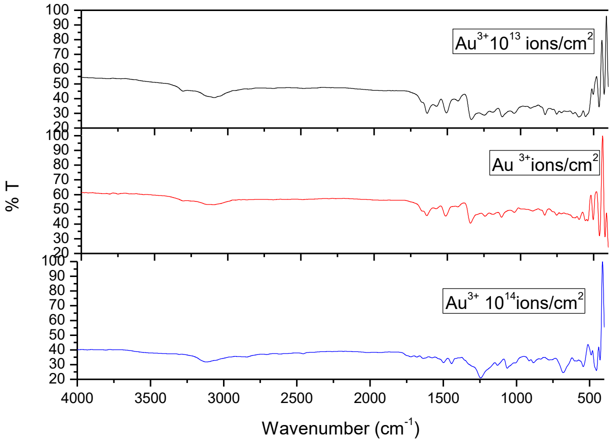

Fig.4.5 FTIR spectral analysis of Au^{3+} ion irradiated 2-amino-5-nitropyridinium chloride (2A5NPCl) NLO single crystal

Tab.4.2 The measured FTIR and reported values of 2-amino-5-nitropyridinium chloride (2A5NPCl) NLO single crystal

Reported Values (cm^{-1})	Measured values (cm^{-1})	Assignments
3296	3310	Asymmetric NH_2
3196	3150	Symmetric NH_2
1673	1667	C = N Asymmetric
1627	1629	N − H bending
1516	1509	Symmetric N − O
1352	1339	Asymmetric N − O
752	754	C − H out of plane pending
648	649	(N − H...Cl)

values are given in Tab. 4.2. It is noticed from the Fig. 4.5 that, appreciable peak or absence of peak from the pristine spectrum was observed after irradiation. When the sample is irradiated with MeV Au^{3+} ion, a large amount of energy is deposited in the system through electronic energy loss. This energy was used to break the bonds in target molecules. Vibrational frequency at 1223 cm^{-1} revealed that in- plane pending (C-H) vibrations are usually combined with pyridine (C-C) stretching mode. Vibration occurred at 3100 cm^{-1} is due to two C-H bonds in pyridine ring of the molecule. Bands observed at 531 cm^{-1} may be assigned to wagging and rocking modes of the nitro group.

4.4 Optical properties

Optical property of pristine and irradiated with different fluence (10^{13}, 5 x10^{13} and 10^{14} ions/cm^2) of 2-amino-5-nitropyridinium chloride was analyzed using UV-Vis-NIR analyzer. An optical spectrum of pristine and irradiated 2-amino-5-nitropyridinium chloride (2A5NPCl) is shown in Fig. 4.6. It is noticed from the absorption spectra that lower cut off value of pristine is 350.26 nm. The grown crystal almost has 99% of transmittance after the lower cut off wavelength. The absence of absorption in the region 350.26 nm and 800 nm is essential for the NLO materials. 2-amino-5-nitropyridinium is highly usable for second harmonic generation applications. Maximum absorption (λ_{max}= 350.26 nm) is due to the presence of conjugated double bond present in the sample. It is also noted from Fig.4.6 that the protonation of pyridine in the acid medium shortens the conjugated bond lengthens the C-NO_2 and shortens the conjugated bond lengths C=C, C=N and C-NH_2. This is due to alternation in the intra molecular charge transfer, ie.., NH being an electron- donor group in competition with the electron acceptor NO_2 group. The presence of the protonated N- heteroatom in the aromatic ring is believed to account for the inclination of the molecular transition dipole moment with respect to the nitro amino direction in the non protonated molecule. This protonation modifies the transparency of the original molecule [29]. It is also observed from the absorption spectra that absorption of irradiated crystal increases with increase of ion fluences. Absorption is very high at fluence of 10^{14} ions/cm^2. It is also noticed that absorption of pristine is lesser than the irradiated crystals. Increasing of absorption is due to higher concentration of defects [30] and the capture of excited electrons by existing ion vacancies in the irradiated 2-amino-5-nitropyridinium chloride (2A5NPCl). There is small change of absorption edge in the irradiated

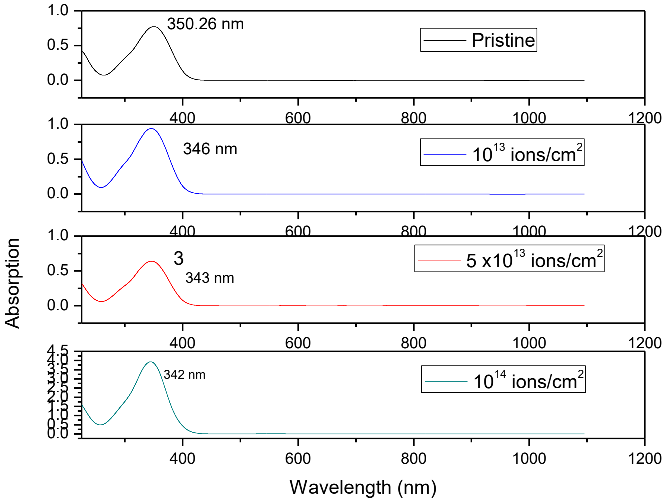

Fig. 4.6 Absorption spectra of Au^{3+}ion irradiated 2-amino-5-nitropyridinium chloride (2A5NPCl) NLO single crystal

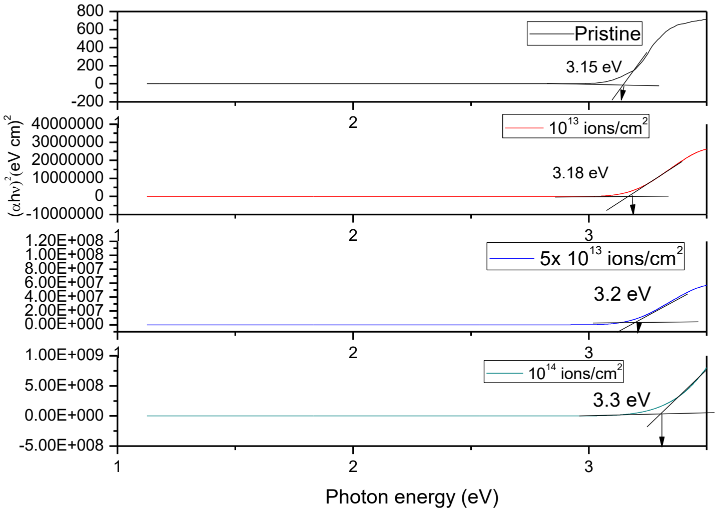

Fig. 4.7 Tauc's plot of pristine and Au^{3+}ion irradiated 2-amino-5-nitropyridinium chloride (2A5NPCl) NLO single crystal

crystals. lower cut off values are 346 nm, 343 nm, and 342 nm for Au^{3+} ion irradiated with three different fluence 10^{13} ions/cm^2, 5x 10^{13} ions/cm^2 and 10^{14} ions/cm^2 respectively. Both pristine and irradiated crystals have wide transparency window which is one of the additional key requirements for having efficient NLO character. Absorption edges were shifted towards shorter wavelength due to the formation of intermediate energy levels and change in structure after irradiation. It is also revealed that there is no additional peak absorbed in the spectra. This is due to the energy of the irradiated ion is not enough to move atoms from lattice to substitution. It is noticed that the surface of semiorganic crystal of 2-amino-5-nitropyridinium chloride (2A5NPCl) is not highly altered due to irradiation. Energy band gap of semiorganic crystals were calculated and using transmittance and absorption coefficient (α).

$$\alpha = A\left(Eg - hv\right)^{\frac{1}{2}}$$

where A is a constant, h is Plank's constant, E_g is the optical band gap and ν the frequency of the incident photons. Fig. 4.7 shows Tauc's plot. Energy band gap of pristine as well as irradiated samples were calculated and found to be 3.5 eV, 3.18 eV, 3.2 eV and 3.3 eV for pristine, 10^{13} ions/cm^2, 5x 10^{13} ions/cm^2 and 10^{14} ions/cm^2 respectively. Extinction coefficient (K) of the semiorganic crystal of 2-amino-5-nitropyridinium chloride (2A5NPCl) was calculated using

$$K = \frac{\lambda\alpha}{4\pi}$$

Fig. 4.8 shows extinction coefficient (K) of pristine and irradiated semiorganic NLO single crystal. It is understood from the extinction coefficient graph that there is loss of light due to interaction between incident light and electrons in pristine as well as

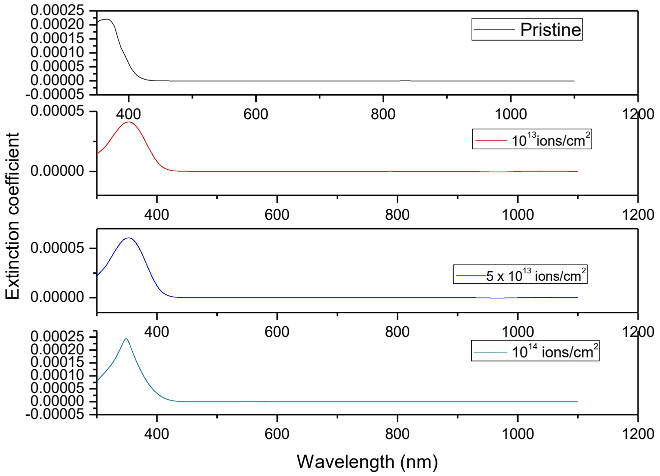

Fig.4.8 Extinction coefficient of pristine and Au^{3+}ion irradiated 2-amino-5-nitropyridinium chloride (2A5NPCl) NLO single crystal

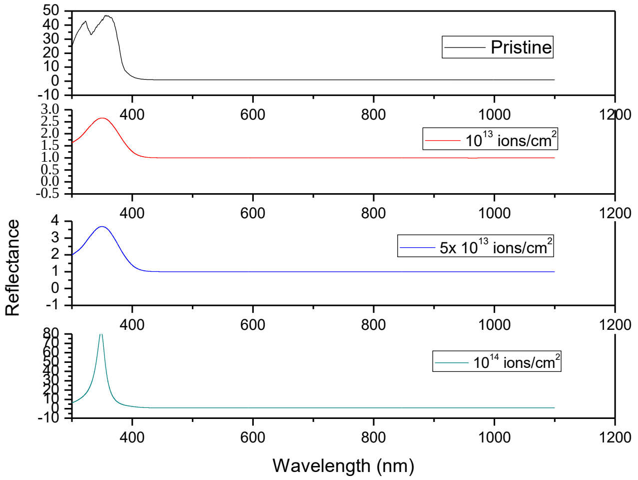

Fig. 4.9 Reflectance of pristine and Au^{3+}ion irradiated 2-amino -5-nitropyridinium chloride (2A5NPCl) NLO single crystal

Au^{3+} ion irradiated crystals. Fig. 4.9 shows reflectance of pristine and irradiated single crystals. It was calculated using

$$R = \frac{1+\sqrt{1+\exp(-\alpha t)+\exp(\alpha t)}}{1+\exp(-\alpha t)}$$

It is evident that reflectance of light decreases gradually with increase of wavelength and attains constant. Decrease of reflectance shows the higher transmittance of grown crystal of pristine and irradiated using three different ion fluences.

Conclusion

2-amino-5-nitropyridinum chloride (2A5NPCl) was grown from slow evaporation and Assembled Temperature Reduction (ATR) method. The grown crystal is a monoclinic with a space group P2$_1$ and lattice parameters are a = 9.957Å, b = 7.384 Å, c= 4.821Å, β= 95.85^0 and Z= 2. Semiorganic crystal of 2-amino-5-nitropyrodinium chloride (2A5NPCl) was irradiated with swift heavy ion of Au^{3+} with varied fluences (1x 10^{13} ions/cm^2, 5x 10^{13} ions/cm^2 and 1x 10^{14} ions/cm^2. It was subjected to the single crystal X-ray diffraction to study crystalline quality of the irradiated crystal. Crystalline quality decreased with increase of ion fluence because of the formation of defects produced after irradiation. It was also observed that crystal surface was not completely affected by swift heavy ion of 10.8 MeV. Functional group of irradiated crystal was measured. From the absorption spectra, it was noticed that absorption increased with increase of ion fluence due to capture of existing ion vacancies and there was no additional peak observed. It was due to the energy transferred by SHI was not enough to move atoms from lattice to substitution position.

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