

INFLUENCE OF Au³⁺ SWIFT HEAVY ION ON DIELECTRIC, FLUORESCENCE, SCANNING ELECTRON MICROSCOPE, AND NONLINEAR OPTICS: 2-AMINO-5-NITROPYRIDINIUM CHLORIDE (2A5NPCl) SINGLE CRYSTAL

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ABSTRACT

The single crystal of 2-amino-5-nitropyridinium chloride (2A5NPCl) was developed using the assembled temperature reduction (ATR) technique and a slow evaporation solution. The crystal was cut for irradiation as it was growing. Cesium sputtering was used to choose a swift heavy ion (SHI) of Au³⁺ from a source of negative ions (SNICS). Au³⁺ ions of (10¹³, 5 x 10¹³, and 10¹⁴ ions/cm²) different fluence irradiated on the semi-organic samples. A luminescence study reveals that intensity decreased due to the loss of luminescence property of the material, which is caused by swift heavy ions (SHI). The formation of intermediate energy levels which converted the photon into phonon affected the radiative transition. Hence, the peak shifted and the intensity of the peak decreased. More ions were activated with lattice disorders at higher fluences, which boosted the activation of ion interactions. Capacitance increased due to this interaction of ions hence dielectric constant increased as increased the ion fluence 10¹³ ions/cm² through 10¹⁴ ions/cm². When a semi-organic 2-amino-5-nitropyridinium chloride (2A5NPCl) was exposed to high fluence radiation, pores, cracks, and roughness could all be clearly visible in the SEM along with the material's roughness. SHI significantly changed the surface of 2-amino-5-nitropyridinium chloride (2A5NPCl) at higher fluence. When compared to pristine, it was determined that the non-centro symmetric system in 2-amino-5-nitropyridinium chloride (2A5NPCl) was less impacted than in the other derivatives of the 2-amino-5-nitropyridinium families of crystals. Irradiated crystals' nonlinear optical properties were less than pristine; however, they were still higher than reference material KDP.

Keywords: 2-amino-5-nitropyridinium Chloride, Luminescence, Dielectric Constant, and the Non-Centro Symmetric System.

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INTRODUCTION

Energetic ions are effective means of altering the surface or large-volume architecture of solids. Based on its mass, nuclear charge, and kinetic energy, an ion can only cause modification inside a narrow surface layer, or it can pierce deep into the entire body and start producing lengthy and confined disarrayed regions across its trajectory.¹ Electronic energy loss refers to the energy lost when ions excite or ionize atoms through inelastic collisions. When the displacement of atoms caused by elastic collisions is minimal, it predominates at high energies.^{2,3} Because these materials have the advantages of both inorganic (increased thermal and Mechanical stability) and organic (broad photonic frequency and second harmonic high efficiency), recent research has focused on the discovery of brand new semi-organic nonlinear optical (NLO) materials.^{4,6} Understanding how various types of radiation influence solid-state materials, particularly NLO crystals, is a critical issue with application implications in radiation-rich environments. All optical devices can be developed using nonlinear optics with the hope of outperforming semiconductors in terms of performance. One can alter materials to give them the necessary optical, electrical, and mechanical properties by using heavy ions in a high-energy beam. A variety of effective

semi-organic crystals, including 2-amino-5-nitropyridinium sulfamate (2A5NPS), 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NDP), and 2-amino-5-nitropyridinium hydrogen oxalate (2A5NPHO), have been exposed to radiation and described.⁷⁻¹¹ The 2-amino-5-nitropyridinium chloride (2A5NPCl) nonlinear optical (NLO) single crystal that was bombarded with fast Au^{3+} heavy ions is the subject of dielectric, fluorescence, scanning electron microscopy (SEM), and nonlinear optics (NLO) researches in this study.

EXPERIMENTAL

Crystal Growth

A long evaporation process was employed to create a semi-organic crystal of 2-amino-5-nitropyridinium chloride (2A5NPCl). To create a homogeneous saturated solution, 2-amino-5-nitropyridine, and hydrochloric acid were mixed in deionized water in a 1: 1 equimolar ratio and continuously mixed for six hours.

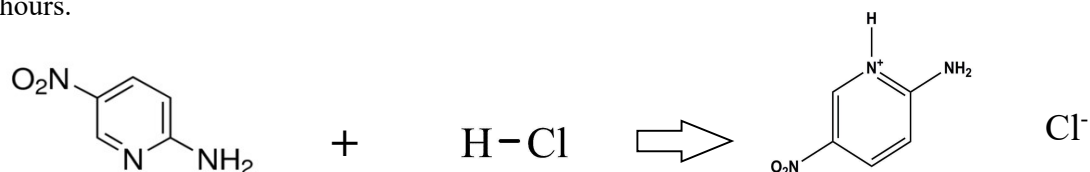


Fig.-1: Reaction Scheme of 2-amino -5-nitropyridinium chloride (2A5NPCl)

The Whatman filter paper was used to filter the solution, which was then allowed to evaporate at room temperature. After 60 days, the crystal began to develop its nucleus. The Figure depicts the reaction scheme of a 2-amino-5-nitropyridinium chloride (2A5NPCl). 2.1. For 120 days, a fine translucent colored optical and perfect crystal was collected, as shown in Fig.-2. Figure-3 depicts the cut and polished crystal used for radiation and it has already been reported.

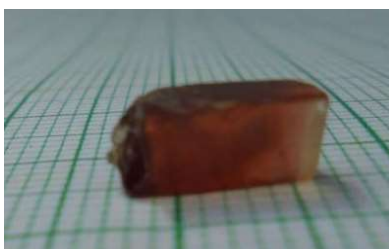


Fig.-2: Single crystal of 2-amino-5-nitropyridinium chloride (2A5NPCl) from slow evaporation

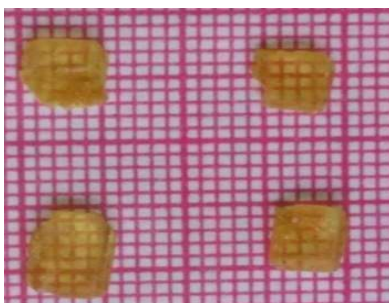


Fig.-3: Single crystal of 2-amino-5-nitropyridinium chloride NLO that has been cut and polished after being exposed to Au^{3+} ions

In a stainless-steel specimen holder, crystals of 2-amino-5-nitropyridinium chloride were placed. At room temperature, the Au^{3+} ion was exposed to radiation. The projected range of the ion beam and the electronic and nuclear loss was computed using SRIM-2012. Cesium sputtering was used to choose a swift heavy ion (SHI) of Au^{3+} from a source of negative ions (SNICS). Au^{3+} ions of (10^{13} , 5×10^{13} , and 10^{14} ions/ cm^2) different fluence irradiated on the semi-organic samples. The energy of Au^{3+} ion was 10.8 MeV, 10.4 MeV, and 10.8 MeV for 10^{13} , 5×10^{13} , and 10^{14} ions/ cm^2 fluences respectively. The swift heavy ion (SHI) scanned the samples normally to the crystalline surface. Radiation was measured using a dosimeter during the experimental work.

RESULTS AND DISCUSSION

Dielectric Study

Figure-4 illustrates the dielectric characteristics of the monoclinic system of pristine and irradiated samples. Opto-electronic device fabrication is dependent on the crystals' dielectric characteristics.¹² The dielectric measurements were conducted on a properly suitably sliced and polished NLO single crystal.

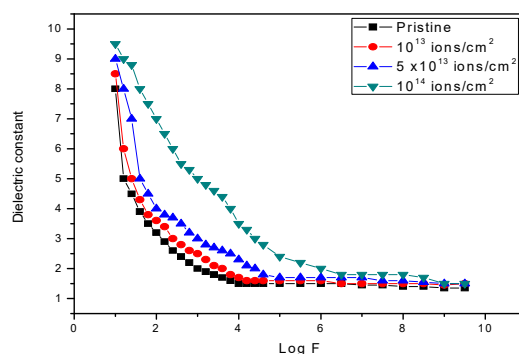


Fig.-4: Pristine and Au^{3+} -ion-irradiated 2-amino-5-nitropyridinium chloride (2A5NPCl) NLO single crystal dielectric constant

Using the equation, the dielectric constant was obtained:

$$\epsilon_r = Cd/\epsilon_0 A$$

Where A is the sample's area and d is the sample's thickness. The figure illustrates the dielectric constant of unaltered and irradiation specimens fall with rising applied frequency. Additionally, it is noted that pristine samples have a lower dielectric constant than irradiated samples. The increase of dielectric constant in irradiation crystal with three different ion fluences is due to the interaction of swift heavy ions with solid which creates a region of disorder with defects in the crystal lattice. Further, an increase in ion fluence creates an amorphous-containing region of defects and also isolates the amorphous region from each other. Many ions are stimulated with lattice disorders at greater fluences, which increases the reactivity of the ion-ion interaction.^{13, 14} As we increase the total number of ions from 10^{13} ions/ cm^2 to 10^{14} ions/ cm^2 , the dielectric constant rises as a result of the increase in capacitance caused by this ion interaction.

Fluorescence

At room temperature, 2-amino-5-nitropyridinium chloride (2A5NPCl) crystals, both unaltered and exposed to radiation, had their light emissions monitored. Fluorescence spectra of unaltered and irradiated crystals are shown in Fig.-5. For a virgin sample, the intensity peak reveals a noteworthy high-intensity band of about 529 nm may be attributed to π - π^* transitions due to collision between the ligand molecules and ultrafast heavy ion. It is also evident from the spectra that, the intensity peak of irradiated crystals decreases compared with the pristine sample. It's possible that the displacement of cations is what caused the intensity peak to decrease and the high-intensity peak to shift. High energetic ion irradiation is the cause of the lattice damage on the sample's surface. Due to the material's loss of luminescence, intensity diminishes. 2-amino-5-nitropyridinium chloride became a non-radioactive recombination center due to the Au^{3+} ion.

Scanning Electron Microscope (SEM)

The surface morphology of the virgin and the irradiated sample was examined using SEM (SEM). Figures 6–9 show SEM images of virgin and irradiated crystals. SEM image displays a similar hillock on the surface of the irradiation crystal. This is due to swift heavy ions which displaced the lattice on the surface of the crystal. It is also noticed that there are some morphological changes due to highly energetic ions. When a semi-organic sample was irradiated with high fluence, pores, cracks, and roughness were generated on the surface of the irradiated crystal.

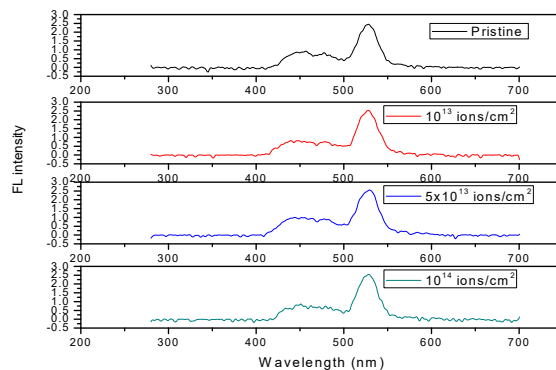


Fig.-5: Fluorescence of a 2-amino-5-nitropyridinium chloride (2A5NPCl) NLO single crystal that has been exposed to Au^{3+} ions and virgin conditions respectively.

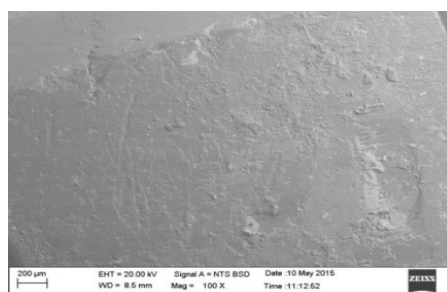


Fig.-6: SEM Picture of a single crystal of 2-amino-5-nitropyridinium chloride (2A5NPCl)

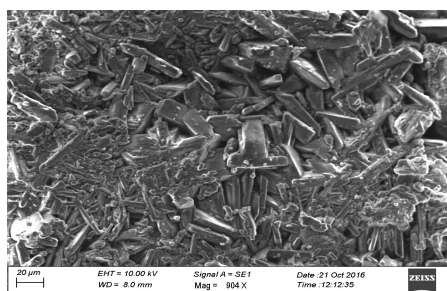


Fig.-7: SEM image of Au^{3+} ion-irradiated (10^{13} ions/ cm^2) 2-amino-5-nitropyridinium chloride (2A5NPCl) single crystal.

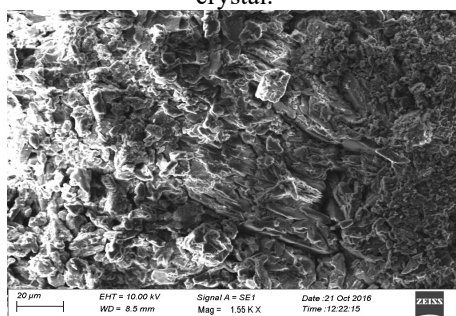


Fig.-8: SEM image of Au^{3+} ion-irradiated (10^{13} ions/ cm^2) 2-amino-5-nitropyridinium chloride (2A5NPCL) NLO single crystal

NLO Test

In order to measure nonlinear optical (NLO) properties, the Kurtz powder technique was used. Green laser light emission was used to evaluate output. When compared to KDP, 2-amino-5-nitropyridinium chloride (2A5NPCl) had an output intensity of 164 mV as opposed to 55 mV. Short wavelengths can be created using 2-amino-5-nitropyridinium chloride (2A5NPCl). This productivity is because of the large concentration of chromophores that can be seen in the herringbone building constructed with the

institution of 2-amino-5-nitropyridinium. It is a viable contender for frequency multiplication and a photonic oscillator. In comparison to 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) (145 mV) and 2-amino-5-nitropyridinium sulfamate (2A5NPS) (138 mV)¹¹, the output intensity of 2A5NPCl is found to be superior, and it is demonstrated to be favorable for the creation of short wavelengths up to 400 nm.

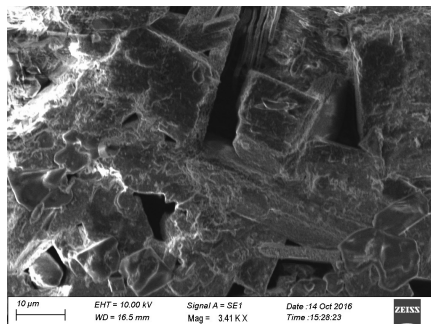


Fig.-9: SEM picture of Au³⁺ (10¹⁴ ions/cm²) irradiation - single crystal of 2-amino-5-nitropyridinium chloride (2A5NPCl)

The inorganic component's organization and other crucial elements affect how hyperpolarizabilities (ij) of the 2A5NP⁺ activity are modified. Irradiated crystals with nonlinear properties were examined using the Kurtz powder method similar to how we evaluated pristine samples. 125 mV, 118 mV, and 63 mV, respectively, are the output intensities of irradiated samples with ion fluences of 10¹³ ions/cm², 5x 10¹³ ions/cm², and 10¹⁴ ions/cm². It is noticed from the output value that there is a decrease of nonlinear property than the pristine but it is not less than reference material KDP. When compared to pristine, it can be seen that the noncentral symmetric system in 2-amino-5-nitropyridinium chloride (2A5NPCl) is less harmed than it is in the other derivatives of the 2-amino-5-nitropyridinium family of crystals.

CONCLUSION

Swift heavy ions of Au³⁺ were used to irradiate 2-amino-5-nitropyridinium chloride (2A5NPCl) at different fluences (1x 10¹³ ions/cm², 5x 10¹³ ions/cm², and 1x 10¹⁴ ions/cm²). Luminescence shows that the intensity decreased due to the material's loss of luminescence property, which was brought on by the swift heavy ions (SHI). The radiative transition was affected by the formation of intermediate energy levels that turned the photon into a phonon. As the ion fluence rose from 10¹³ to 10¹⁴ ions/cm², this ion interaction increased capacitance, which in turn raised the dielectric constant. SHI significantly changed the crystal's exterior of 2-amino-5-nitropyridinium chloride (2A5NPCl) at higher fluence. Irradiated crystals' nonlinear optical properties were less than pristine; however, they were still higher than reference material KDP.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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