Dielectric, Microhardness and Thermal Properties of Swift Ion \((\text{Au}^{3+})\) Irradiated NLO Single Crystal: 2-Amino-5-Nitropyridinium Sulfamate (2A5NPS)

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Abstract. An organic- inorganic NLO single crystal was grown using conventional and slow cooling method or ATR (Assembled temperature reduction method). Properties of as grown crystal were tried to modify using swift heavy ion \((\text{Au}^{3+})\) of various fluences ranging from \(10^{13}\) ions/cm\(^2\), to \(10^{14}\) ions/ cm\(^2\). Dielectric property of orthorhombic crystal was studied. It was noticed that, as ion fluence increases the dielectric constant of as grown material also increases. Hardness of the undamaged and swift heavy ion irradiated crystals was studied. It was concluded that the ability of resistance of deformation of swift heavy ion implanted crystal increases with increase of ion fluences. Thermal studies were carried out and it was observed that irradiated crystal exhibits increased thermal stability with increase of ion energy and this was owing to decreased degree of crystallinity.

1. Introduction
High energetic ion acts an important role in changing the characterization of materials such as surface, electrical, mechanical thermal etc. It entered deep into the crystals and creates a long and narrow amorphous region along its path [1].Crystals with swift heavy ion (SHI) result to the production of different defects in the crystal system which modifies the physicochemical properties of solids. The modifications are mostly dependent on the energy of SHI, incident ion mass and temperature in which the irradiation takes place. Ionization and excitation will be caused by heavy ion irradiation and sometimes atoms of target materials will be removed from their lattice [2-4].Swift heavy ion (SHI) interacts with the target materials and it loses its energy in two ways along its trajectory. Swift heavy ion losses its energy with the atomic electron of the target crystal and that is inelastic scattering. Heavy energetic ions loss its energy with the nuclei of the target atoms and it is called elastic scattering [5]. Energy is transferred from heavy energetic ion to crystals and materials. Specific effects are created where SHI transfer its energy to materials [6-7]. Sometimes the refractive index of the crystal changes significantly by SHI [8]. Swift heavy ion capable of breaking molecular bonds and produce damaged create defects in the solids [9]. The efficiency of luminescence increases due to point defects which created during irradiation that act as a colour centre [10-11]. Energetic heavy ion creates \textsuperscript{1}ambrosa@jrkumarphd@gmail.com
amorphization and the degree of crystallinity of the material gets changed when it interacts with target crystal [12-14]. In photonics technology NLO single crystals plays a vital role in fabrication devices. 2-amino-5-nitropyridine (2A5NP) has an attractive molecular structure. 2-amino-5-nitropyridine has nitro and amino group which act as an as an electron acceptor and electron donor respectively which stimulate nonlinear character in the crystal [15-18]. Because of this attractive molecular structure, 2-amino-5-nitropyridine (2A5NP) is used to construct NLO materials. It is a good choice for second order nonlinear optical (SONLO) applications [19-24]. Number of 2-amino-5-nitropyridine (2A5NP) derivative crystals such as 2-amino-5-nitropyridinium hydrogen oxalate, 2-amino-5-nitropyridinium chloride, 2-amino-5-nitropyridinium nitrate, 2-amino-5-nitropyridinium dihydrogen phosphate and 2-amino-5-nitropyridinium sulfamate were grown using conventional and slow cooling method [25-36]. Structural optical Properties of both undamaged and SHI irradiated 2-amino-5-nitropyridinium sulfamate NLO single were reported [37-38]. Electrical, mechanical, and thermal properties of both pristine and Au$^{3+}$ ion irradiated 2-amino-5-nitropyridinium sulfamate NLO single are reported in this research paper.

2. Experimental

2.1 Crystal growth

Conventional method (SET) was used to grow a semiorganic single crystal. Large size crystal of 2-amino-5-nitropyridinium single crystal was grown using temperature reduction method. 2-amino-5-nitropyridine and sulfamic acid were taken in equimolar (1:1) ratio and were dissolved in distilled water. In order to get homogeneous solution the mixture was stirred for 6 hours. Then the mixture was filtered using Whatman filter paper. To evaporate the water molecules, the filtered mixture was kept at room temperature. A colourless semiorganic single crystal was collected for 90 days [29].

2.1.2 Swift heavy ion (Au$^{3+}$) irradiation:

A metallic swift heavy ion (Au$^{3+}$) of varies fluences was used for irradiation with various beam current. Swift heavy ion scanned normal to the face of the crystal uniformly at room temperature. Metallic ion (Au$^{3+}$ with different beam current 1.55µA (1x 10$^{13}$ ions/cm$^2$), 1.35 µA (5 x 10$^{13}$ ions/cm$^2$) and 8 PnA (1x 10$^{14}$ ions/cm$^2$) were used or irradiation. At room temperature, a metallic ion (Au$^{3+}$) of 10.8 MeV was used for implantation [38].

3. Results and Discussion

3.1. Microhardness

Hardness is the resistance offered by materials to plastic deformation caused by indentation. Hardness of as grown crystals of pristine and SHI implanted crystals was measured using Vicker’s hardness tester The selected smooth surface of 2-amino-5-nitropyridinium sulfamate pristine and irradiated was used to measure the hardness at room temperature. The load was applied on the selected surface ranging from 25 g to 100 g. Four indentations were introduced in the sample of the same surface for each load. Both the diagonal lengths were measured in each indentation marked and the averages of eight diagonals were taken for calculations. Figure 3.1.1 shows the hardness of pristine and heavy ion implanted crystals. It is examined from the graph that both pristine and implanted crystal show linear behavior with applied load. Hardness of the undamaged and implanted crystals increases with applied load. It is also evident from the graph that hardness of the irradiated crystal is significantly larger than the pristine crystals. It is noted that hardness of the irradiated crystal increases with increases of ion fluences. This is due to certain amorphous formed in the irradiated samples. Least square fit method was used to calculated “n” hardening coefficients. According to Onitsch, the crystal is soft if the value of n is greater than 1.6 and the crystal is hard if the value of n is less than 1.6 [39]. Hardening co-efficient was found to be 2.2 for irradiated. So as grown crystals of 2-amino-5-nitropyridinium sulfamate belongs to soft materials. In order to understand stiffness and yield strength of plastic deformation of the pristine and irradiated, stiffness was determined using Wooster's empirical formula [40] and it is given by C$_{HV}$= Hv(7/4). Figure 3.1.2 and 3.1.3 shows stiffness and
yield strength of pristine and swift heavy ion irradiated crystals. It is understood from the graph that stiffness and yield strength increase with applied load. It is also elucidated that stiffness and yield strength of irradiated crystal is significantly larger than the pristine sample. It is noticed from the graph that stiffness and yield strength show linear behaviour with applied load. Stiffness and yield strength increase with increase of ion fluence from $10^{13}$ions/cm$^2$ to $10^{14}$ions/cm$^2$. Increase of binding force between ions and mechanical strength of Au$^{3+}$ ion with three different fluences is due to defects created in the crystal which makes the crystalline material into amorphous nature.

![Graph](image1.png)

**Fig.3.1.1** Hardness graph of pristine and Au$^{3+}$ ion irradiated 2- amino-5-nitropyridinium sulfamate (2A5NPS) NLO single crystal.

![Graph](image2.png)

**Fig.3.1.2** Stiffness graph of pristine and Au$^{3+}$ ion irradiated 2-amino-5-nitropyridinium sulfamate (2A5NPS) NLO single crystal.
Fig.3.1.3 Yield strength of pristine and Au\(^{3+}\) ion irradiated 2-amino-5-nitropyridinium sulfamate (2A5NPS) NLO single crystal.

3.2. Dielectric study

From graph (Fig. 3.2.1), it is observed that dielectric constant decreases up to a certain frequency range and remains constant. Dielectric constant is high at lower frequency due to ionic, electric, orientation and space charge polarization. The dielectric constant value is high for a swift heavy ion irradiated crystals than that of pristine sample. It also is noted that dielectric constant increases as ion fluence increase from \(10^{13}\) ions/cm\(^2\) to \(10^{14}\) ions/cm\(^2\). The increased dielectric constant in swift heavy ion irradiated crystals is the formation of defect along the ion trajectory. The metallic ion which is implanted in the orthorhombic crystals loses energy by elastic and inelastic collision. The crystal was damaged and the lattice was disordered by the swift heavy ion (SHI) which lost its energy in the form of collision. Irradiated ion which lose energy in the crystal in the form of collision which damage the crystals and disordering the lattice. The damaged zones are separated from each other as the ion produces a region of amorphous surrounded by regions containing defects. Dielectric constant increases as increase of ion fluences which produce lattice disorderness. Due to lattice disorderness more ions are activated which brings more interaction between ions results increase the capacitance and hence dielectric constant increases.

Fig.3.2.1 Dielectric constant of pristine and Au\(^{3+}\) ion irradiated 2-amino-5-nitropyridinium sulfamate (2A5NPS) NLO single crystal.
3.3 Thermal Analysis

TG and DTA analysis give information about physical phenomena, such as phase transition, oxidation, reduction and chemical phenomena including thermal decomposition. TG and DTA was studied for undamaged and SHI irradiated 2-amino-5-nitropyridinium crystals. It is observed from the graph (Fig. 3.3 a, b, c) that samples decompose in three different stages. A pristine sample was started to decompose at 195°C and an endothermic peak is absorbed in DTA cure at 195°C which confirm the melting point of undamaged sample. Au$^{3+}$ ion irradiated single crystal with different fluences (1 x 10$^{13}$ ions/cm$^2$, 5 x 10$^{13}$ ions/cm$^2$, and 1 x 10$^{14}$ ions/ cm$^2$) were decomposed with weight loss was little more than the pristine at 196$^0$ C, 196.5$^0$ C and 198$^0$ C respectively. There was no endothermic peak observed before decomposition which is the melting point of crystal system. Weight loss of pristine and irradiated sample increases with increase of temperature after melting of the crystal. Pristine and irradiated crystals decompose almost completely on or before 300°C. Thermal stability increased due to amorphous surface created after SHI irradiation. It is also noted that thermal stability increases with increase of ion fluences. This is due to increase of defects which are caused by increase of ion fluences.

![Graph 3.3 a)](image1)

**Fig.3.3 a)** Thermal analysis of 2-amino-5-nitropyridinium sulfamate (2A5NPS) NLO single crystal.

![Graph 3.3 b)](image2)

**Fig.3.3 b)** Thermal analysis of Au$^{3+}$ ion irradiated (10$^{13}$ ions/cm$^2$) 2-amino-5-nitropyridinium sulfamate (2A5NPS) NLO single crystal.
4. Conclusion
Orthorhombic unit of 2-amino-5-nitropyridinium sulfamate (2A5NPS) was grown using conventional evaporation method and Assembled Temperature Reduction (ATR) method. It was observed from the dielectric studies that Dielectric constant increases as increase of ion fluences which produce lattice disorderness. Due to lattice disorderness more ions are activated which brings more interaction between ions results increase the capacitance and hence dielectric constant increases. Microhardness of both pristine and irradiated was measured using Vicker's hardness test. It was concluded from hardness that hardness of the irradiated crystal increased with increases of ion fluences. This was due to certain amorphous formed in the irradiated samples. Stiffness and yield strength increased with increases of ion fluence from $10^{13}$ ions/cm² to $10^{14}$ ions/cm². Increase of binding force between ions and mechanical strength of Au$^{3+}$ ion with three different fluences was due to defects created in the crystal which made the crystalline material into amorphous nature. Thermal studies were carried out and thermal stability increased due to amphorphous surface created after SHI irradiation. It is also noted that thermal stability increases with increase of ion fluences. This is due to increase of defects which are caused by increase of ion fluences.
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