CHAPTER 6

SWIFT HEAVY ION IRRADIATION STUDIES ON SODIUM POTASSIUM NIOBATE SINGLE CRYSTALS

6.1 INTRODUCTION

Environment friendly lead free piezoelectric materials are of great interest due to its vast applications in sensors, actuators, piezoelectric motors, transducers, etc. (Bindner et al 1998). The solid solution of sodium niobate–potassium niobate (KNN) is an environmental friendly material, having good piezoelectric characteristics and hence most popular among all the lead free piezoelectric materials (Brozel 1997). The sodium niobate–potassium niobate (KNN) synthesized at a composition that may lead to formation of morphotropic phase boundary (MPB) that can exhibit high electromechanical coupling coefficients, easier poling process and has good ferroelectric properties. Egerton & Dillion 1959 showed the existence of MPB in the solid solutions of sodium niobate and potassium niobate at a composition around 50:50.

SHI irradiation technique induces non-equilibrium states in matter (Moretti et al 1991), that cannot be created by substitutional impurities or doping or by heat treatment methods. It has been observed that SHI irradiation technique with ion beam energies in the order of MeV to GeV induces transient heating, point defects, local structural transformations, columnar defects, sputtering, etc. These defects are useful to control and alter the properties of piezoelectric materials for specific applications. Thus, in the
swift heavy ion irradiation process, a high density of defects are created along the linear ion track inside the material that directly affects the conductivity of the material. Irradiations of energetic charged particles on the surface of the crystal normally result in modification of surface features such as formation of craters, hillocks, etc. in nano dimensions. Irradiation studies in ferroelectric materials significantly modify the dielectric properties with respect to its fluence level and the temperature of the irradiated crystals (bubesh et al 2008). Suppression of ferromagnetic property and the Curie temperature was observed in rare earth manganite when irradiated with heavy ions. This technology has gained momentum in the recent past due to its ability to precise control and tailor make the material to suit the dielectric and piezoelectric properties for any specific application. This technology of heavy ion irradiation can be used for the fabrication of non-leaky wave guides using ferroelectric materials, which allows diffractionless propagation of light. Irradiation of the energetic heavy ions that moves inside the material undergo inelastic scattering producing a trail of excited or ionized atoms. As the energetic heavy ions traverse through the material, some of the atoms get dislodged from its position in the crystal lattice thereby creating defects in the crystal. The change in the density of defects results in changing the properties of the material largely at the surface of the material. If the energy of the irradiating ions are higher, then, their penetration into the material will be greater or vice versa. Ion-beam technology have already made breakthrough in current silicon technology for communications, surface hardening and materials engineering (Hiroaki et al 1992). Low energy ion bombardment can also be used for a variety of thin film applications such as ion beam etching and patterning of surfaces and assisting deposition and growth of thin films on suitable substrates. In addition, it finds wide variety of applications in semiconductor technology such as doping and formation of buried layers in semiconductors and insulators at controlled depth. Using irradiation modified lithium niobate, waveguides were fabricated by Kolarova et al (1998) and
Binder et al (1998). Related work with other materials such as $\text{KTiOPO}_4$ were carried out by Zhang et al (1993), Wang et al (1998) and Binder et al. (1998). Defect and ionization studies by implantation on the perovskite oxides were reported by Meldrum et al (1998), Kotomin and Popov (1998). Implantation of the He ions on barium titanate and the possible fabrication of waveguides and variation in refractive index were reported by Moretti et al (1991). Defects and dislocation formation due to electron irradiation were analyzed by Buck (1995) for ferroelectric materials. Indium phosphate single crystals were irradiated at room temperature (RT) and at liquid nitrogen temperature (LNT) with different fluences of $140 \text{ MeV Kr}^{10+}$, $390 \text{ MeV Xe}^{21+}$ and $600 \text{ MeV Au}^{30+}$ ions and the results showed that InP was much more radiation resistant to swift heavy ion irradiation at LNT than at RT (Costantini et al 2000). In the case of KNN crystals, the pristine samples themselves have a high concentration of intrinsic defects. Irradiation increases the defect density thereby changing the crystal properties such as Curie temperature, dielectric loss (which in turn affects the conductivity values) and the piezoelectric coefficient values. In the present work, KNN single crystals were grown using KF-NaF flux and subjected to a lithium ion irradiation. The pristine samples were irradiated with lithium ions of fluences $1\times10^{12}$ ions/cm$^2$, $1\times10^{13}$ ions/cm$^2$ and $5\times10^{13}$ ions/cm$^2$ at room temperature (RT). Another pristine sample was irradiated with lithium ions of fluence $5\times10^{13}$ ions/cm$^2$ at liquid nitrogen temperature (LNT) for comparison. The irradiated samples including the pristine sample were characterized by X-ray diffraction, dielectric, piezoelectric and Raman studies.

6.1.1 Advantages of Ion Irradiation

The unique characteristic of the ion irradiation are

(i) Mass separation techniques can be used to obtain a monoenergetic and highly focused beam of the desired
atoms free from contamination. Thus a single machine can be used for a widely variety of elements. Furthermore, the process of irradiation is carried out under high vacuum conditions and therefore, in an inherently clean environment.

(ii) Wide range of does from $10^{12}$ to $10^{17}$ ions/cm$^2$, can be delivered to the target and controlled to an accuracy of ± 1% in this range. Ion irradiation has uniform surface coverage of dopants unlike the dopant incorporation during diffusion.

(iii) Ion irradiation provides independent control of dose and penetration depth. Many types of dopant profiles can be obtained by controlling the energy and dose of multiple implants of the same or different elements.

(iv) Ion irradiation can be used for the controlled deposition of charge in a specific region of the material.

(v) Li ion beam is monitored as a current so that the number of irradiated ions can be calculated accurately.

(vi) The depth of the irradiation is controlled by the ion energy and hence a judicious choice of energy and dose can develop desired impurity profile beneath the surface.

(vii) The choice of irradiation ion is not limited and different ions may be placed at different depths.

(viii) Irradiation may be made at low temperatures.
6.1.2 Disadvantages of Ion Irradiation

(i) The equipment is highly sophisticated and expensive and hence the technology is relatively uneconomical compared to diffusion

(ii) Another apparent disadvantage of ion irradiation is the many atoms in the target are displace. This radiation damage is undesirable and sophisticated thermal cycles with electron beam or laser have to be developed to remove the damage without diffusing the implanted ions.

However this technology, inspite of the above disadvantages, is one of the important techniques as far as device fabrication is concerned especially in the field of semiconductors, biomaterials and insulators. Ferroelectric materials, generally insulators, show significant property changes for the ion dose between $10^{14}$ and $10^{16}$ ions/cm$^2$ (Townsend et al 1987). The property changes in insulators include refractive index, birefringence, optical dispersion, thermoluminescence, phase transition temperature, dielectric constant, electrical conductivity, pyroelectric, piezoelectric and electro optic coefficients (Townsend et al 1987).

6.2 ENERGY TRANSFER DURING IMPLANTATION

During irradiation, ions transfer energy to the target at the rate of 1 keV per micron by combination of electronic excitation and nuclear collisions. Below 500 keV, nuclear collisions are important and lead to displacement of lattice ions via secondary collisions and cascades of displacements. The stopping power is a function of energy, mass and atomic number (E,M,Z). Theoretical estimation of the stopping power requires accurate value of the interaction potential between the ion and target atom.
The nuclear stopping power can be described by energy parameter, $E_f$, scaled by the terms $M$ and $Z$ as

$$E_f = 0.8853a_0M_2E$$

$$Z_1Z_2e^2(Z_1^{2/3}+Z_2^{2/3})^{1/2}(M_1+M_2)$$

(6.1)

Where $a_0$ is the Bohr radius and $e$ is the electronic charge. Similarly the ion ranges can be scaled to an universal parameter

$$\rho = 4\pi(0.8853a_0)^2M_1M_2NR$$

(6.2)

$$Z_1^{2/3}+Z_2^{2/3})^{1/2}(M_1+M_2)$$

(6.3)

Where $N$ is the atomic density and $R$ is the path length.

Electronic stopping power is proportional to the ion velocity for low energy implants. At higher energies (> MeV) the electronic stopping cross section falls and the target becomes more transparent to the ions.

6.3 PENETRATION RANGE

There are two basic mechanisms by which energetic ions upon entering into the target can be brought to rest. The first of these is by energy transfer to the target nuclei. This causes deflection of the projectile ions and also dislodging of the target nuclei from their original sites. This is known as nuclear stopping ($S_n$) and is given by

$$S_n = 1/N(dE/dx)_n$$

(6.4)

Where $N$ is the density of the target atoms.

Nuclear stopping results in physical damage in the form of point as well as line defects. Another stopping process is by the interaction of ions
with both bound and free electrons in the target. This gives rise to the transient generation of hole-electron pairs as energy is lost by the moving ion. The electronic stopping ($S_e$) is given by

$$S_e = \frac{1}{N} \frac{dE}{dx}$$  \hspace{1cm} (6.5)$$

$$\frac{dE}{dx} = N[S_n(E) + S_e(E)]$$  \hspace{1cm} (6.6)$$

where $N$ is the density of atoms in the target material. If the total distance travelled by the ions before coming to rest is $R$ (range), then

$$R = \int_0^R dx = \frac{1}{N} \int_0^{E_0} \frac{dE}{[S_n(E) + S_e(E)]}$$  \hspace{1cm} (6.7)$$

Where $E_0$ is the initial ion energy.

### 6.4 45 MeV $^7$Li ION IRRADIATION STUDIES

Good quality KNN single crystals with polished surface were used after cleaning with ultrasonically and acetone to remove the residual polishing surface damage. The dimensions of KNN samples are ~ 5 X 5 mm$^2$ with thickness of ~ 0.8mm. The KNN single crystals were irradiated at RT with $^7$Li ions of 45 MeV at current density of 3 pnA/cm$^2$ of various fluencies with $1 \times 10^{13}$, $5 \times 10^{13}$ and $1 \times 10^{14}$ ions/cm$^2$ at RT and $5 \times 10^{13}$ ions/cm$^2$ using the facility linear accelerator at Inter University Accelerator Centre, New Delhi, India. To avoid charge pileup, the beam current was maintained as ~ 10nA for implantation and 0.5 nA for irradiation processes. The lattice damage induced by ion irradiation is considered to be the main reason for change surface damage. There are two different types of damage (Ishikawa et al 2006) produced by ion irradiation near surface damage generated by electronic stopping, which induces and increase in extraordinary refractive index and at the end of ion track, and damage correlated to nuclear collision cascades, which decrease the extraordinary refractive index values. The
electronic energy loss, nuclear energy loss contributions and the beam range of 45MeV Li ion in KNN samples were theoretically calculated using the simulation code SRIM-2008. The as grown KNN crystal has been characterized by single crystal X-ray diffraction studies by using Bruker AXS Kappa Apex2 CCD Diffractometer equipped with graphite-monochromated Mo Kα radiation (k = 0.71073 Å). The structural modifications due to irradiation of KNN single crystals have been carried out by powder X-ray diffraction studies using BRUKER D8 Advance X-ray diffractometer. Surface morphology of the gold coated sintered samples was studied by scanning electron microscopy (S-3400). The atomic force microscopy (AFM) measurement was carried out with a PARK XE-100 instrument and analysis was carried out using software available with the AFM. The AFM images have been analyzed by the same 500 x 500 nm² magnifications. The AFM measurements have been performed in non-contact mode for both trace and retrace information at the room temperature having silicon tip. The variation of dielectric constant with temperature at frequencies 100 Hz was determined from room temperature to 500°C using Agilent E4980A impedance analyser for the silver electrode samples. The Raman studies of as grown and irradiated KNN single crystals have been carried out using BRUKER Raman spectrometer.

6.4.1 SRIM Calculation

The energy derivative functions of the electron and neutron are given by $S_e = \frac{dE}{dx}_e$ and $S_n = \frac{dE}{dx}_n$ respectively. These functions are a measure of the energy lost by the Li ions in the crystal lattice as they penetrate through the crystal. The functions were calculated using the standard SRIM 2000 simulation program (Ziegler et al 2003) and are plotted as a function of energy values of the irradiating Li ions interacting with KNN single crystal that is shown in Figure 6.1. The ionic energy loss function $S_\delta$ increases as the ion energy increases and peaks [ $S_\delta \sim 56$ eV/Å ] at 2 MeV and
then it decreases with further increase in ionic energy. Whereas, the nuclear energy loss function $S_n$ values are found to be constant and very low that is negligible and may be ignored. This implies that the Li ions deposit all their energy into the single crystal during its penetration into the crystal. The energy imparted by the ions may induce electronic excitations of the atoms in the crystal lattice. It is known from literature that the Li ion requires energy above a threshold value to produce columnar defects or amorphization. Using Szene’s model, the threshold value can be estimated for ferroelectric materials. Since KNN crystal also belongs to the same class of ferroelectric materials, the estimated threshold value was found to be 12 keV/nm. Irradiation with Li ions would pass through a depth that is proportional to the energy of the ions and embed into the crystals. It was observed from the calculations that the variation of energy with depth is not much significant. Therefore, irradiation with 45 MeV $^7$Li ions has generated only clusters of defects or strain in the single crystals and generation of columnar defect is neglected.

![Figure 6.1](image.png)  
**Figure 6.1** Electronic and Nuclear energy loss of 45 MeV Li ion as a function of energy in KNN single crystal

### 6.5 X-RAY DIFFRACTION STUDIES

The powder X-ray diffraction studies have been carried out on all the irradiated samples and one pristine sample are shown in the Figure 6.2. All the grown pristine and irradiated KNN single crystals confirm the
orthorhombic structure and the intensity of the XRD peaks decreases with increase in ion fluency level that may be attributed to the creation of lattice damage in KNN single crystals. The decrease of peak intensity with ion fluency is due to amorphization. After ion irradiation, the lattices have a high degree of disorder due to nuclear collisions between the irradiated ions and target ions and between recoil-recoil the knock-one of the host ions. This result suggests that the point defects such as broken bonds produced at higher fluencies in the irradiated samples cause the decrease in the peak intensity. Similar results were also obtained in the case of high energy 200 MeV Ag$^{14+}$ irradiated Si (Singh et al 2000) and high energy heavy ions (Xe$^{15+}$ & Au$^{13+}$ ions) irradiated TiO$_2$ thin films (Ishikawa et al 2006). In the case of irradiation with the fluencies of 5 x 10$^{13}$ ions/cm$^2$ at LNT the intensity of the peaks were slightly decreased. At liquid nitrogen temperature creation of defects due to irradiation is less compared to room temperature. It clearly shows that the radiation induced defects is a temperature dependent phenomenon.

Figure 6.2  Powder X-ray diffraction pattern of pristine KNN single crystal and 45 MeV $^7$Li ions irradiated KNN single crystals with different ion fluences
6.6 SURFACE MORPHOLOGY

High-energy heavy ion irradiation usually results in the creation of clusters on the surface of ferroelectric crystals. The SEM investigation showed that Li ions with energy 45 MeV have created higher density of surface defects corresponding to the highest fluence used \(5 \times 10^{13} \text{ ions/cm}^2\), while for same energetic ions with lower fluence levels of \(1 \times 10^{12} \text{ ions/cm}^2\) and \(1 \times 10^{13} \text{ ions/cm}^2\), comparatively lower density of surface defects was observed in Figure 6.3. and the defect production rate due to irradiation at LNT was found to be lower than that of RT.

The structure of the observed defects crucially depends on the electronic stopping power of the incident ions near the surface. As Li ions are smaller and lighter ions, the surface damage created due to their irradiation is much lower when compared to other types of ions such as oxygen and argon (Townsend et al 1987). Projected range of the Li ions was higher as it can penetrate easier to deeper to more distances than other ions in creation of controlled defects.

The ability of the AFM to create three-dimensional micrographs with resolution down to nanometer scale has made it as an essential tool for imaging surfaces before and after SHI irradiations. It is a non-destructive characterization technique used to measure the quantitative surface roughness. The passage of SHI induces developing process very rapidly, as such it is difficult to observe during or immediately after their occurrence. However it could be identified with the formation of damage on crystals, shape and structural of defects. AFM surface pictures of the pristine KNN single crystals and irradiated (with RT and LNT) with various fluencs are shown in Figure 6.4. The effect of irradiation of 45MeV \(^7\)Li ions on the surface is visible from the change in the surface morphology for different fluencies. It is observed that clusters are formed due to irradiation which might have been
formed by the partial amorphization process (Trinkaus & Ryazanov 1995 and Costantini et al 2000) on the surface of the crystal. Due to the energy loss of the incident ions on irradiation, a very high hot regime was formed, which could result in the local melting of the host material. Due to melting of the host material at high temperatures followed by cooling partial amorphization take place and hence the cluster-like structures were observed. Similar results were obtained in the case of high energy 200 MeV Ag$^{14+}$ irradiated Si (Singh et al 2000) samples.

The Root Mean Square (RMS) values of surface roughness evaluated from the AFM data were 6.96 nm for the pristine sample and 50, 64 and 121 nm for samples irradiated at the fluence of $1 \times 10^{12}$, $1 \times 10^{13}$ and $5 \times 10^{13}$ ions/cm$^2$ respectively and the roughness of the irradiated crystal at LNT is lower compared to that of the crystal recorded at room temperatures. The irradiated KNN sample surface shows dramatic surface modifications distributed over the surface.

(a) ![SEM Image](image1) (b) ![SEM Image](image2)

**Figure 6.3 (Continued)**
Figure 6.3 Surface morphology of (a) unirradiated and irradiated KNN single crystals with 45 MeV Li ion of fluence (b) $1 \times 10^{11}$ ions/cm$^2$ (RT), and (c) $5 \times 10^{13}$ ions/cm$^2$ (RT) (d) $5 \times 10^{13}$ ions/cm$^2$ (LNT)

Figure 6.4 (Continued)
Figure 6.4 AFM images of surface features of (a) unirradiated and irradiated KNN single crystals with 45 MeV Li ion of fluence (b) $1 \times 10^{11}$ ions/cm$^2$ (RT), and (c) $5 \times 10^{13}$ ions/cm$^2$ (RT) (d) $5 \times 10^{13}$ ions/cm$^2$ (LNT)

6.7 DIELECTRIC STUDIES

Temperature dependent dielectric permittivities of unirradiated and irradiated KNN single crystals were measured by impedance analyzer. Figure 6.5 shows the dielectric permittivity of KNN single crystals before and after irradiation which exhibit a decrease in Curie temperature with increasing fluence levels. A slight decrease in Curie temperature from 422°C to 408°C was observed for the highest fluence level of $5 \times 10^{13}$ ions/cm$^2$ Li ion beam and decrease being lower for the irradiated crystal at LNT when compared to that at RT. The difference in the Curie temperature of the irradiated crystals depend on the incident ion energy and the penetration depth. The ion irradiation of ferroelectric materials is known to produce clusters of defects or columnar defects characterized by a distorted structure. In the distorted region, the electronic spectrum is expected to be modified and the mean free path of the electrons is reduced inducing greater scattering of electrons resulting changing Curie temperature. This is due to the creation of defects by the irradiated Li ions which lead to the flexibility of domain movement during
paraelectric to ferroelectric transition. The irradiation also reduces the intrinsic disorder in the crystal. Higher fluence creates more distortion in the crystal lattice and hence decreases the Curie temperature.

It is expected that heavy ion irradiation creates distortion in the oxygen site and may increase the dielectric loss. The dielectric loss increases on Li irradiation which implies that Li irradiation induces additional dipoles in the crystal. From the plot of dielectric loss ($\tan\delta$) as shown in Figure 6.6 it can be inferred that the dielectric loss increases with irradiation ion fluences. The dielectric loss of a material denotes quantitatively dissipation of the electrical energy due to different physical processes such as electrical conduction, dielectric relaxation, dielectric resonance and loss from non-linear processes. The total dielectric loss is the sum of intrinsic and extrinsic losses. The intrinsic dielectric losses depend on the crystal symmetry, ac field frequency and temperature. Extrinsic losses are associated with imperfections in the crystal lattice such as impurities, microstructural defects, grain boundaries, porosity, microcracks, order–disorder, random crystallite orientation, dislocations, vacancies, dopant atoms, etc. So, we can conclude that the increase in dielectric loss with irradiation ion fluence is mainly extrinsic.
Figure 6.5  Temperature dependence of dielectric permittivity of pristine KNN single crystal and 45 MeV $^7$Li ions irradiated KNN single crystals with different ion fluences

Figure 6.6  Temperature dependent of dielectric loss of pristine KNN single crystal and 45 MeV $^7$Li ions irradiated KNN single crystals with different fluences
6.8 RAMAN STUDIES

Raman spectroscopy that was suggested as a powerful tool to study the structural changes in the KNN-based single crystals. Raman spectroscopy can be used to study crystalline quality and also the nature of structural instabilities. Many scientists have investigated ABO$_3$ perovskite structure crystals through Raman spectral studies. In order to investigate the bonds between Nb and O ions in the NbO$_6$ units the Raman analysis has been done for all the samples. The observation plane of the all samples was an orthorhombic face. In the KNN, Raman modes can be ascribed to the internal vibrational modes of NbO$_6$ units, i.e., $n_1$ (A$_{1g}$), $n_2$ (E$_g$), and $n_5$ (F$_{2g}$). Of these vibrations, the first two modes are stretching and the last one is the bending mode. The Raman spectra for the crystals are shown in the Figure 6.7.

The Raman spectra analysis of pristine and irradiated KNN single crystals was carried out between 0-1000 cm$^{-1}$ and the most intense line appears at 123 cm$^{-1}$. This is evidently due to the A$_1$ mode because this is the intense peak generally observed in the Raman spectra of perovskite compounds (Van der Ziel et al 1974 and Hiroaki et al 1992). The next high intensity E and/or B$_2$(LO) mode is appearing at 675 cm$^{-1}$. In the Figures the Raman frequencies corresponding to A$_1$ and E and/or B$_2$(LO) modes increase and the curve are broadening with increase in the fluencies. Due to stress effect induced by SHI irradiation, cluster are formed in the top of KNN surface. The displacement in the position of the Raman A$_1$ and E and/or B$_2$(LO) modes can be attributed to the strain and lattice damage. The broadening of the Raman modes is closely related to the presence of structural defects to form amorphization on the irradiated surface or stress gradient in the scattering volume and is supported by our AFM results.
CONCLUSION

Powder X-ray diffraction analysis reveals decrease in the degree of crystallinity due to creation of lattice defects by the energetic irradiated ions and results show that the lattice defects created due to ion irradiation is lower at low temperature (LNT) when compared with that at room temperature. The cluster created by the ion radiation are clearly seen in the atomic force microscopy (AFM) images. The roughness of irradiated crystal increases with increasing ion fluences. The roughness of the irradiated crystal at LNT is lower compared to that of the crystal recorded at room temperatures. The SEM analysis confirm the same of that observed with AFM. The dielectric behavior indicate that the irradiated crystals show significantly higher dielectric loss when compared to the pristine sample. The behavior may be attributed to the destruction of the crystalline arrangement of atoms due to the bombardment of the energetic lithium ions on the surface that introduces lattice defects leading to deterioration in the electrical behavior. The Curie temperature is found to be 429°C for the pristine sample. The Curie temperature decreases slightly for the irradiated samples. The decrease being lower for the irradiated crystal at LNT when compared to that at RT. Raman
spectrum shows an intense band of NbO$_6$ modes and its peak intensity reduces with ion fluences. All the characterization methods adopted in the current study confirms the destruction of crystallinity in the irradiated crystals and the defects introduced by the irradiating ions at lower temperature (LNT) is lower compared to that at room temperature at different fluences.