CHAPTER -8

STRUCTURAL AND DIELECTRIC MODIFICATION IN BNN AND SBN CERAMICS BY SWIFT HEAVY ION IRRADIATION

8.1 Introduction

Recently ion implantation has attracted much interest due to the possibility to modify or pattern the materials, to overcome the doping solubility limits, and to introduce virtually any element in the substrate materials. The interaction between incident ions and substrates cause effects directly connected to radiation damage, such as mechanical stresses, density and composition modifications, and consequent dielectric and optical property changes. In addition to these, it is possible to form new compounds (chemical interaction) which originate in regions with very large differences in the refractive index with respect to the substrate [1]. The implantation of metal ion is of particular interest because, depending on their reactivity with the substrate, metal colloids or compounds can be formed. Titanium silicide and titanium oxide compounds are observed in titanium implanted silica, whereas tungsten implantation in silica leads to the formation of metallic tungsten precipitates and tungsten oxides. On the other hand, implants of ions such as gold, silver, lead, copper and phosphorus induce the formation of colloids [2-4]. In recent years, ion implantation has attracted considerable attention as promising tool for the fabrication of special devices and structures, which require buried conducting or insulating layers [5].

Electronic energy in materials can be varied from tens of $eV / \AA^0$ up to a very high value of the order of 4000 $eV/\AA^0$ by choosing appropriate ions and their energies in the accelerator. This provides a remarkable flexibility and adequate opportunities to engineer properties of the materials to acquire desired electrical, optical or mechanical properties. A new area of intense research is now emerging, which is called "swift heavy
ions (SHI) in materials engineering and characterization" (SHIMEC). Some of the typical areas of research activities being pursued are engineering of electronic materials and devices, high $T_c$ superconducting materials, colossal magnetoresistance materials, ferroelectric materials, modification of surfaces and interfaces, and electronic sputtering by on-line ERD measurement.

8.2 SEM studies on swift heavy ion irradiated ferroelectric ceramics

Detailed studies have been made on BNN and SBN ceramic sample surfaces to elucidate the processes occurring during irradiation with swift heavy ion beams. After irradiation some of the surface layers of the ceramic grains get removed. SEM images reveal a wide variety of disorders within grains. The unirradiated sample surface contains grains with near spherical geometry. Surface effects produced by SHI irradiation have also attracted attention due to observed surface rippling, electronic imitation induced desorption of large molecules etc. There are possibilities of various new phases in materials and also to produce cylindrical channels of controllable diameter filled with the modified materials.

The irradiation of solids with swift heavy ions (SHI) has become one of the most important methods of near surface modification of solids. Here we study the microscopic processes involved in irradiation of ferroelectric barium sodium niobate (BNN) and strontium barium niobate (SBN) ceramics by swift heavy ion beams of different energies and species. Scanning electron microscopy is a unique technique for studying microscopic processes involved in irradiation of swift heavy ion irradiation of different species and energies.

High ion energy and normal incidence can result in permanent damage to the crystal surface of the specimen, which is visible in the microscope later. The specimens can also become very hot whilst being thinned. In the light of the above phenomena, we present the microstructural variation in BNN and SBN ceramics after irradiating with swift heavy ion.
8.2.1 SEM studies on BNN ceramics after irradiation with Fe$^+$ ions.

Surface effects produced by SHI irradiation have attracted attention due to observed surface rippling, electronic imitation induced desorption of large molecules etc. There are possibilities of creating various new phases in materials and also to produce cylindrical channels of controllable diameter (in the range of nanometers) filled with the modified elements or molecules.

Studies have been made on BNN ferroelectric ceramic sample surface to elucidate the process during the irradiation with swift heavy Fe$^+$ ions beam. After the irradiation it is observed that some of the polycrystalline grains on the surface layers of the sample are removed. SEM images reveal a wide variety of disorders within grains. Figure 8.1 (A) show the scanning electron microphotographs of Ba$_3$Na$_4$Nb$_{10}$O$_{30}$ showing the microstructure after irradiation with 100 MeV Fe$^+$ ions at a fluence of 10$^{13}$ ions/cm$^2$. When we compare the irradiated surface with pure sample surface, it is observed that there are significant microstructural changes. The pure sample surface contains grains with near spherical geometry. The main effects are the deformation of the initial grain geometry. The spherical grains on the surface are fragmented due to the shearing effect of the ion beams. The surface rippling leads to removal of some of the layers. From the micron marker on the photograph we get a clear indication of the dimensions of the deformed polycrystalline grain fragments. The grains are randomly oriented along the surface with irregular shape and varying size.

Figure 8.1 (B) shows the SEM photograph of Ba$_4$Na$_2$Nb$_{10}$O$_{30}$. The irradiation has an erosion effect on the grains. The contrast of the grain boundary separation is lost and the grains are found to be fused. The irradiation induced fragmentation is more manifested in Ba$_2$Na$_{1.5}$Nd$_{0.5}$Nb$_{10}$O$_{30}$ and Ba$_{1.8}$Na$_4$Nd$_{0.8}$Nb$_{10}$O$_{30}$ as shown in figures 8.1 (E) and 8.1 (F). Barium sodium niobate ceramics have grain boundaries and porous spaces separating individual grains from each other. The segregation of thermally activated impurities at grain boundaries promotes inter granular fracture along this
Figure 8.1 SEM images showing the microstructural changes after irradiation with 100 MeV Fe$^+$ ions with a fluence of $10^{13}$ particles per cm$^2$ of
(A) Ba$_4$Na$_3$Nb$_{10}$O$_{30}$  (B) Ba$_3$Na$_2$Nb$_{10}$O$_{30}$  (C) Ba$_{2.6}$Na$_{4.2}$Nd$_{0.2}$Nb$_{10}$O$_{30}$
(D) Ba$_{2.2}$Na$_{4.4}$Nd$_{0.4}$Nb$_{10}$O$_{30}$  (E) Ba$_2$Na$_{4.5}$Nd$_{0.5}$Nb$_{10}$O$_{30}$  (F) Ba$_{1.8}$Na$_{4.6}$Nd$_{0.6}$Nb$_{10}$O$_{30}$.
weakened path. Other causes of depletion at grain boundaries are formation of a precipitate or a continuous film at grain boundaries. The internal periodicity of an individual grain is lost at the grain boundary. The atoms at the interface are in a situation similar to those on the surface of a solid where bulk periodicity is lost. The smaller grains get deformed faster than the large grains, then the fragments dissociates from the surface. In larger grains, the irradiation induces sputtering of the atoms from the inner crystal lattice layers.

During irradiation with swift heavy ions, materials deform in such a way that thin grains or specimens expand perpendicular to the beam direction and have hammering effect in the beam direction. In thick or large grains this deformation leads to the generation of large mechanical stresses and, under off normal irradiation, to a shear flow. Since the range of 100 MeV Fe$^+$ ions in the above ferroelectric barium sodium niobate samples comes in the range 12-14 μm, many layers of grains deep inside the surface get deformed. The sputtered atoms or molecules get embedded on the porous spaces inside the surface.

8.3 Microstructural changes on SBN after Si$^+$ ion irradiation

Normally incident beam of 100 MeV $^{28}$Si$^+$ ions have been used for irradiation at room temperature. After completing irradiation the surface morphology of the samples were examined by scanning electron microscopy (SEM)

Typical SEM pictures show some kind of smoothening effect on the irradiated surface, though at submicron length scale. The surface modification is quantitatively expressed as the shear shift which is due to the displacement of near surface atoms resulting from irradiation. The shear shift in x (x-direction) is given by

$$x = \frac{6 \, R_p \, 1.16(1 + V) \, a \, (S \, \varphi) \, \sin \varphi \, \cos \varphi}{[3 \, e \, (5 \, - \, 4 \, v) \, pC]}$$

(8.1)

where v, a, p and C are the poisson numbers, thermal expansion coefficient, volume density and specific heat capacity of the material respectively. The value of C is
approximately given by $3K_B N_A / M$, where $K_B$ is Boltzmann constant, $N_A$ is the Avagadro number and $M$ is the molar weight of the material. The angle $\phi$ represents the tilt angle of the beam and $S_e$ represents electronic energy loss. For normal irradiation of a real (rough) surface, $\phi$ is given by the local variations in angle of incidence due to the roughness of the surface [6-9].

Figures 8.2 (A-F) show the microstructural changes on $\text{Sr}_{0.55}\text{Ba}_{0.45}\text{Nb}_2\text{O}_6$, $\text{Sr}_{0.5}\text{Ba}_{0.3}\text{Nb}_2\text{O}_6$ and $\text{Sr}_{0.47}\text{Ba}_{0.53}\text{Nb}_2\text{O}_6$ ceramics after irradiation with 100 MeV $\text{Si}^+$ ions at a fluence of $10^{13}$ particles per cm$^2$. Figure 8.2 A and 8.2 B show different surface areas of $\text{Sr}_{0.55}\text{Ba}_{0.45}\text{Nb}_2\text{O}_6$ sample with a magnification of 2500 times ($X$ 2500). In figure 8.2 A complete fragmentation of the surface layer is observed, where as in 8.2 B the fragmented layers are removed and part of the grains remain attached to lower layers. In figure 8.2 C we can observe the magnified ($X$ 5000) view of grain damage and fragmentation. This gives more details regarding the mechanisms undergoing during irradiation. The microstructural changes induced by irradiation are different for different areas on the same samples. This is due to the initial surface morphology and orientation of the surface grains and porosity. At regions where porosity is observed, the inner surface layers are damaged. Figures 8.2 D and 8.2 E show the irradiation induced changes on the surface of $\text{Sr}_{0.5}\text{Ba}_{0.3}\text{Nb}_2\text{O}_6$. Here the surface is highly damaged, creating partially amorphous layers in the irradiated region, the irradiation induces a smoothening effect on the surface. Figure 8.2 F shows the surface morphological changes induced by $\text{Si}^+$ ion on $\text{Sr}_{0.5}\text{Ba}_{0.3}\text{Nb}_2\text{O}_6$ after irradiation. Here part of the surface layers remains even after irradiation, while some of the surface grains are fragmented and get removed.

Similarly, figure 8.3 A shows the magnified image at $X$ 5000 for different regions on the same surface. Figures 8.3 B and C show the irradiated surface of $\text{Sr}_{0.45}\text{Ba}_{0.55}\text{Nb}_2\text{O}_6$, the surface grains are fragmented and removed leaving sub-micron particles on the observed surface. Figures 8.3 D, E and F show the surface morphology of $\text{Sr}_{0.43}\text{Ba}_{0.57}\text{Nb}_2\text{O}_6$ at different magnifications. Here the surface grains are fragmented due to mechanical stresses induced due to $\text{Si}^+$ ion irradiation. The irradiated surface shows sub-micron particles attached to the ferroelectric domains. Here the irradiation shows the
Figure 8. 2 SEM images showing the microstructural changes after irradiation with 100 MeV Si$^+$ ions with a fluence of $10^{13}$ particles per cm$^2$ of (A), (B) and (C) $\text{Sr}_{0.53}\text{Ba}_{0.47}\text{Nb}_2\text{O}_6$ (D) & (E) $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$; (F) $\text{Sr}_{0.47}\text{Ba}_{0.53}\text{Nb}_2\text{O}_6$ respectively.
Figure 8. 3 SEM images showing the microstructural changes after irradiation with 100 MeV Si⁺ ions with a fluence of $10^{13}$ particles per cm$^2$ of (A) Sr$_{0.47}$Ba$_{0.53}$Nb$_2$O$_6$; (B) & (C) Sr$_{0.45}$Ba$_{0.55}$Nb$_2$O$_6$; (D), (E) & (F) Sr$_{0.43}$Ba$_{0.57}$Nb$_2$O$_6$. 
thinning effect on the surface grains. The large grains are sputtered due to irradiation which removes the glassy grain boundaries. This makes the ferroelectric domain structure more visible compared to unirradiated samples.

The surface modifications that are observed by SEM are mainly due to electronic energy deposition process. Partial amorphization and colloid formation occur in the stopping region. These processes as well as ion implantation can well induce very large mechanical stresses, which could lead to the grain fragmentation and deformation. Since the range of 100 MeV Si\textsuperscript{+} ions in strontium barium niobate ferroelectric ceramics comes in the range 24-26 \( \mu \)m, the layers of grains with in this region inside the surface gets modified. The sputtered atoms, molecules and fragments may dissociate from the monolayers and occupy the porous spaces.

Figure 8.4 (A) and 8.4(B) shows the microstructural damages induced in \textit{Sr}_{0.4} \textit{Ba}_{0.6} \textit{Nb}_{2} \textit{O}_{6} ceramic samples after irradiation with 100 MeV Si\textsuperscript{+} ion at a fluence of \( 10^{13} \) particles/cm\(^{2}\). Random disorder in the irradiated surfaces are observed. The magnified image (x 5000) shows the fragmented submicron particles loosely distributed along the surface. In figure 8.4 (C) and 8.4 (D) and 8.4 (E), abnormal grains are observed in the microstructure of \textit{Sr}_{0.33} \textit{Ba}_{0.65} \textit{Nb}_{2} \textit{O}_{6}. The large grains with laminar striations can be seen, which are the ferroelectric domains formed with in a grain. The irradiation of 100 MeV Si\textsuperscript{+} ion induces modifications similar to etching effects on the surface grains. Some of the fragmented submicron crystallites can be observed attached to the surface layer. The irradiation induces sputtering of near surface layers of atoms of the large grains, removing the grain boundaries with glassy phases. The removal of glassy phase grain boundary increases the visibility of the domain structures.

For ion bombardment thinning, a collimated beam of energetic positive ions (Ar\textsuperscript{+} is usually employed, since it is inert and heavy) directed at any angle at a solid surface in a vaccum to cause atoms to be removed from the surface by the process of sputtering. Ion energies up to 10 KeV are used. The number of atoms removed, for each normally incident ion is called the 'sputtering yield' and varies from element to element. If the ion
Figure 8. 4 SEM images showing the microstructural changes after irradiation with 100 MeV Si$^+$ ions with a fluence of $10^{13}$ particles per cm$^2$ of (A) & (B) Sr$_{0.40}$Ba$_{0.60}$Nb$_2$O$_6$; (C), (D) & (E) Sr$_{0.35}$Ba$_{0.65}$Nb$_2$O$_6$. 
beam is incident at a glancing angle the rate of sputtering will be lower, but the bombardment tends to smooth out irregularities in the target surface by preferentially removing the high spots. In an ion-beam thinning apparatus a 3 mm disc of material preferably ≤ 50 μm thick is bombarded from both sides by narrow beams of argon ions, and is simultaneously rotated in its own plane about an axis through its center. Initially the ion beams can be incident at 45-90° to the surface, for a high thinning rate, but final thinning to perforation is carried out near glancing incidence eg. 10° to the surface, in order to produce a large area of thinned foil around the perforation.

Ion-beam thinning can be applied to a variety of difficult materials including ceramics, for which there would be no other means of thinning. It is a useful non-contact technique for specimen preparation, when used with discretion, and is ideal for preparing large thin areas of clean sample for high-voltage microscopy. Several variations on ion-beam thinning use chemical attack in addition to normal ion sputtering, in order to reduce the preparation time for certain types of specimen, principally semiconductors. In reactive ion-beam etching (RIBE) the inert gas used for sputtering is replaced by a gas which is chemically active in relation to the material to be thinned, eg. O⁺ is used in place of Ar⁺ [10].

Focused ion-beam machining: Focused beams of 80 KeV ions can be used for localized sputtering at a high rate, and micro-machining is possible. Since this also results in ionization and electron emission, a form of inspection by scanning ion microscopy is possible if the ion beam is scanned in a raster and the secondary electrons are detected. Used particularly for the examination of the detailed structures of microelectronics devices, focused ion beams (FIBs) can be used to isolate a chosen area of specimen and then thin it more gently for TEM examination [11].

8.4 X-Ray analysis on irradiated materials

Ion implantation has certain advantages over the standard method of ion incorporation into materials or substrates by diffusion at elevated temperatures. The main benefits stem from the fact that the energy and dose of the ions can be controlled, providing materials
with modified characteristics. The variation in physical properties is due to the implantation-induced crystal damage. The magnitude can be determined from many studies. These changes in physical properties depend on the lattice parameter (or inter planar d-spacing) in the damaged region. Therefore precise measurement of the lattice parameter (or inter planar d-spacing) is of importance; and X-ray diffraction is a direct method to achieve this. Modern X-ray diffraction techniques are highly sensitive to different types of lattice distortions arising in micron thick layers [12]. Experimental observations on the ion implanted LiNbO$_3$ for profile has a specific shape with a maximum at the end of the He trajectories, where the nuclear stopping mechanism is effective. Structural modifications introduced by electronic loss in a material range from displacive phase transitions in Ti to track formation in NiZr$_2$ alloys and metallic glasses [13, 14].

In the light of above phenomena, we present here structural modification in 100 MeV Fe$^+$ ion irradiated on BNN system and 100 MeV Si$^+$ ion irradiated on SBN system.

### 8.5 X-ray diffraction studies on BNN irradiated with Fe$^+$ ions

Swift heavy Fe$^+$ ion with 100 MeV energy irradiation leads to a specific transformation of the diffraction spectra, as revealed by a comparison of experimental data taken from virgin and as-implanted samples. A typical diffraction spectrum of an implanted sample consists of two parts: the main, narrow maximum from the non-implanted bulk region of the crystal and an extended structure (at smaller angles) from the damaged layer. The extended structure exhibits inhomogeneous lattice swelling of the damage layer, the swelling accumulating as the implantation dose, D, is increased. It should be stressed that the damaged layer remains in the crystalline state after the dose of 100 MeV Fe$^+$ ions /cm$^2$.

The structural variation induced by swift heavy Fe$^+$ ions has significant consequences on the physical properties. The structure of Fe$^+$ irradiated Ba$_3$Na$_4$Nb$_{10}$O$_{30}$ are analyzed by X-ray diffraction. Figure 8.5 shows the XRD pattern before and after irradiation. A systematic shift of the whole pattern towards the higher angle side is observed. Another significant change is the broadening of the peaks, manifesting the diffuse nature of the X-ray diffraction pattern, can also be seen. Line broadening of one
Figure 8.5 XRD pattern of $\text{Ba}_3\text{Na}_4\text{Nb}_{10}\text{O}_{30}$ before (B) and after (A) irradiation.

Figure 8.6 XRD pattern of $\text{Ba}_{2.2}\text{Na}_{4.4}\text{Nd}_{0.4}\text{Nb}_{10}\text{O}_{30}$ before (B) and after (A) irradiation.
of the major peaks at 32.3° is observed. Swift heavy ion (SHI) irradiation of materials provides a tool to modify various material properties such as physical, chemical and other, mainly through the inelastic energy transfer mechanisms. This is in contrast to the familiar elastic scattering of low energy ions causing direct lattice damage. Swift heavy ions can also produce lattice damage through inelastic scattering producing the trial of excited / ionized atoms, as it is clearly evident from the well known phenomena of ion track production in insulators. Experiments have shown that when the electronic energy loss exceeds a threshold value, SHI irradiation produces an amorphized zone along the ion (also known as columnar tracks) path in materials.

Figure 8.6 shows X-ray diffraction pattern of Ba$_2$Na$_4$Nd$_{0.4}$Nb$_{10}$O$_{30}$ sample. Comparing X-ray plots before and after irradiation, it is clear that higher order reflections increase in relative intensity ($I/I_0$). A systematic shift in the major peak positions towards higher angle is recorded. The shift in peak position reflects decrease in the lattice d-spacings due to changes in internal stress and may also be due to the incorporation of Fe$^+$ ions in the vacant lattice sites. There is considerable variation in the peak shape, which is evident from the full width at half maximum of the irradiated XRD pattern. This broadening can be explained in terms of grain size variation due to fragmentation of grains caused by heavy ion irradiation. The irradiation can well induce very large mechanical stresses, which could lead to the observed fragmentation. Another reason for line broadening may be due to the structural imperfection, which give rise to spread of intensity around each reciprocal lattice point. The increase in relative intensity of higher order reflections is entirely an irradiation related effect and independent of the material under study or their initial relative peak intensity.

Similarly, figure 8.7 shows the x-ray powder diffraction pattern of Ba$_{1.82}$Na$_{4.8}$Nd$_{0.8}$Nb$_{10}$O$_{30}$. Similar changes in pattern are observed. The absence of any new diffraction peaks indicates that no new phases are created due to irradiation.

The main effect of irradiation on BNN has been found to be the redistribution of the cations, which create a disordered tungsten bronze structure. The present studies
shows that partial amorphization of the material is sensitive to implanted ion and its energy. The irradiation region shows an obvious degradation of crystalline structure. Since ferroelectricity in oxide materials is strongly concerned with oxygen content, oxygen deficiency would directly result in degradation of ferroelectricity, and lead to destruction of crystal structure.

Numerous experiments show that above certain threshold values of the electronic stopping power $S_e$, high energy heavy ions are capable to amorphize crystalline insulators [15]. We assume the process to go on in the following way [16, 17]. Due to high $S_e$, the electrons around the ion trajectory are highly excited. As a result of electron-phonon interaction, a fraction of excitation energy is transferred to the host atoms close to the trajectory. The numerical solution of the heat flow equations clearly show [18] that this energy may be sufficient to raise the lattice temperature even above the melting point. In insulators the temperature increase $\Delta T$ is confined to a small cylinder along the trajectory and it lasts for a period of the orders of $10^{-12} - 10^{-11}$ seconds depending on the radius of this cylinder and the thermal diffusivity of the target. This short time interval is sufficient to destroy the lattice and the amorphous phase can be quenched as a result of the high cooling rate.

The removal of atoms from the surfaces can proceed through electronic processes. Energy deposition is followed by localization, whether of energy or momentum or both; ionic motions then lead to emission followed by processes in vapour phase [19].

The considerable increase in diffuse scattering observed after annealing at elevated temperatures is treated in terms of point defect clustering and the formation of extended defects. The variation in d-spacing profile will be maximum at the end of Fe$^+$ ion trajectories (ie at a range of 10-14 $\mu$m depth from surface), where the nuclear stopping mechanism is effective. This is due to the energy loss of the swift heavy ion on passing through the monolayers of BNN ceramics.
Figure 8. 7 XRD pattern of Ba$_{1.2}$Na$_{4.8}$Nd$_{0.8}$Nb$_{10}$O$_{30}$ before (B) and after (A) irradiation

Figure 8. 8 XRD pattern of Sr$_{0.53}$Ba$_{0.43}$Nb$_{2}$O$_{6}$ before (B) and after (A) irradiation
Heat treatment at elevated temperatures result in the annealing of the implantation-induced damage. Displaced atoms tend to return to their normal crystallographic positions with the corresponding occurrence of the pronounced modifications in the \( \delta d/d \) profiles. The main result consists of the observed decrease of the maximum \( \delta d/d \) value. Annealing is accompanied by defect clustering, which is revealed through the diffuse component arising in the diffraction spectra.

Due to inelastic energy transfer during ion irradiation, defects are introduced in a material directly by displacement of the lattice atoms and indirectly through de-excitation of the electronic subsystem. For swift heavy \( \text{Fe}^+ \) ions, the above regions of energy can be spatially separated. Processes initiated purely by energy transfer to lattice electrons and their subsequent de-excitation can be observed in regions nearest to the point of entry of such ions in the samples, separated from the ion stopping region. Such processes are called electronic energy loss or electronic stopping \( (S_e) \), as the ions lose energy through excitation of lattice electrons.

A general trend has now been established which connects electronic energy loss induced atomic movement in materials. All materials which show phase transformations under pressure (martensitic or displasive) get modified by ion irradiation, introduces stress field giving rise to displasive transformations. Atomic displacement by dissipation of electronic energy loss becomes a distinct possibility which under favourable conditions, could lead to defect structure formation [20].

8.6 Silicon ion induced structural variations in SBN ceramics

The irradiation of 100 MeV \( \text{Si}^+ \) ions in strontium barium niobate ceramics have significant effects on the lattice structure modification. Figure 8.8 shows the X-ray powder diffraction pattern before and after irradiation for \( \text{Sr}_{0.33}\text{Ba}_{0.45}\text{Nb}_2\text{O}_6 \). The diffraction pattern after irradiation is found to shift towards higher angle side. Therefore the lattice d-spacing is found to decrease correspondingly. Hence the irradiation decreases the lattice spacing. The intensity counts of all peaks are found to decrease generally. The intensity count corresponding to the major peak at 32.44° is reduced to
After irradiation the intensity of the higher order reflections increases, which is clearly evident from the appearance of highest intensity peak at 55.23°. The variations in the intensity of peaks reflects the change in relative atomic positions in the crystal lattice. The shift in major peak positions reflects the modification of the unit cell and lattice parameters. This modification in the structure is due to the large mechanical stresses induced due to irradiation.

Figure 8.9 shows the X-ray powder pattern before and after irradiation for Sr$_{0.47}$Ba$_{0.53}$Nb$_2$O$_6$. Here also the diffraction pattern after irradiation is found to shift towards higher angle side. The significant change is the appearance of two major peaks at 38.55° and 64.855°. The intensity of the major peaks are considerably reduced. The appearance of the two peaks indicates the formation of new phase in the Si$^+$ irradiated region. The variation in the intensity of original peaks reflects variations or rearrangement of relative atomic positions. The shift in 2θ values reflects the changes in the unit cell and lattice parameters which have undergone during irradiation.

Figure 8.10 shows the x-ray diffraction pattern before and after irradiation for Sr$_{0.35}$Ba$_{0.65}$Nb$_2$O$_6$. The diffraction pattern as a whole is found to shift to higher angle side. The major peak at 31.77° is found shifted to 32.415°. The corresponding lattice d-spacing decreases. The intensity of all major peaks are considerably reduced after irradiation. The appearance of major peak at 29.935° is the significant change on irradiation. The absence of new peaks indicates that no new compound phases are created. The major changes are relative ordering of the atoms in the unit cell, which is evident from the intensity variation. The shift in 2θ-values shows the significant changes in crystal structure and lattice parameter in the irradiated region.

The loss of crystallinity in ceramic materials due to irradiation with energetic ions has been studied earlier. The displacement dose required to induces amorphization in ceramics at room temperature has been found to vary by more then three orders of magnitude, depending on the type of material. Different criteria have been proposed to explain this wide variation in the susceptibility of ceramics to amorphization. These
Figure 8. 9 XRD pattern of $\text{Sr}_{0.47}\text{Ba}_{0.53}\text{Nb}_2\text{O}_6$ before (B) and after (A) irradiation

Figure 8. 10 XRD pattern of $\text{Sr}_{0.35}\text{Ba}_{0.65}\text{Nb}_2\text{O}_6$ before (B) and after (A) irradiation
criteria include bond-type, free energy of formation, and degree of structural freedom for the polytypes that describe the crystal stacking arrangement.

8. 7 Effect of Fe$^+$ ion irradiation on dielectric properties of BNN ceramics

8. 7. 1 Experimental details

Ferroelectric BNN ceramic samples were prepared by the conventional solid state reaction method as described in chapter 2. The dielectric characterization of all the samples has been performed using an impedance analyzer (HP 4192) in the temperature range 30$^0$C – 400$^0$C. The samples were then exposed to 100 MeV Fe$^+$ heavy ion beam of 15 UD Pelletron Accelerated at Nuclear Science Centre (NSC), New Delhi, with a fluence of 1 X 10$^{13}$ ions/cm$^2$. The ion beam induced dielectric property changes were studied after irradiation.

8. 7. 2 Results and discussion

The Fe$^+$ ion irradiation effects on the dielectric properties of BNN ceramic were analyzed by studying the changes in the values before and after irradiation. Figure 8.11 shows the variation of dielectric constant with temperature before and after irradiation for Ba$_3$Na$_2$Nb$_{10}$O$_{30}$. The plane curve shows the variation prior to irradiation where the dielectric constant ($\varepsilon_r$) shows a slight dip in the 100$^0$ C range. Beyond 150$^0$ C the $\varepsilon_r$ increases with temperature. The marked curve shows the changes in $\varepsilon_r$ after irradiation. Here the irradiation induces a smoothening effect on the temperature variation. The $\varepsilon_r$ variation shows a similar curved pattern as the original sample. The major effect is a reduction in dielectric constant throughout the temperature region of measurement. The measurements are limited to 400$^0$ C. The $T_c$ value is above the experimental temperature range.
Figure 8.11 Shows the temperature Vs dielectric constant of Ba$_4$Na$_2$Nb$_{10}$O$_{30}$ before and after irradiation.

Figure 8.12 Shows the temperature Vs dielectric constant of Ba$_3$Na$_4$Nb$_{10}$O$_{30}$ before and after irradiation.
Figure 8.12 shows the variation of dielectric constant with temperature before and after irradiation for Ba$_2$Na$_2$Nd$_{10}$O$_{30}$. The plane curve shows the variation of $\varepsilon_r$ with temperature in the 30 – 400$^\circ$ C range. The dielectric constant is found to decrease in the 50–150$^\circ$ C range, then increase gradually over higher temperatures. The marked curve shows behavior of $\varepsilon_r$ after irradiation. It shows a similar pattern with a reduction in dielectric constant. The variation is found to be more diffuse after irradiation. The transition temperature $T_c$ is found to decrease, which is evident from the slope of the curve for irradiated specimen.

Figure 8.13 shows the variation of $\varepsilon_r$ vs temperature for Ba$_{2.8}$Na$_{4.2}$Nd$_{0.2}$Nb$_{10}$O$_{30}$ before and after irradiation. Here we observe similar behavior in the temperature variation of dielectric constant. The basic difference after irradiation is the reduction in dielectric constant through out the temperature region of measurement. Another significant effect is the diffuse nature of the phase transition region. Since the $T_c$ covered a wide temperature region, it is said to exhibit relaxor behavior.

Figure 8.14 shows results of dielectric behavior for Ba$_{2.7}$Na$_{4.4}$Nd$_{0.4}$Nb$_{10}$O$_{30}$ before and after irradiation. Here the room temperature dielectric constant is found to increase after irradiation which is evident from the marked curve. The $T_c$ value is found to decrease, which is observed around 375$^\circ$ – 400$^\circ$ C. The variation at the transition region is more diffused when compared to the value before irradiation.

In Figure 8.15 the plane curve shows the dielectric constant versus temperature for Ba$_{2.5}$Na$_{4.5}$Nd$_{0.5}$Nb$_{10}$O$_{30}$. Here it shows the full phase transition behavior in the 30 – 400$^\circ$ C range, exhibiting the ferroelectric region, transition region and paraelectric region. Here the phase transition is diffused and is shifted to low temperature region due to the doping of Nd ions. The marked curve shows the irradiation induced effects. The dielectric constant is reduced through out the temperature region. The peak corresponding to transition is more smeared than the pure samples. Here the transition behavior is more complex which is evident from the tilt in the curve corresponding to high temperature region.
Figure 8.13  Shows the temperature Vs dielectric constant of \( \text{Ba}_{2.6}\text{Na}_{4.2}\text{Nd}_{0.2}\text{Nb}_{10}\text{O}_{30} \) before and after irradiation.

Figure 8.14  Shows the temperature Vs dielectric constant of \( \text{Ba}_{2.2}\text{Na}_{4.4}\text{Nd}_{0.4}\text{Nb}_{10}\text{O}_{30} \) before and after irradiation.
Figure 8.15 Shows the temperature Vs dielectric constant of $\text{Ba}_2\text{Na}_{4.5}\text{Nd}_{0.5}\text{Nb}_{10.9}\text{O}_{30}$ before and after irradiation.

Figure 8.16 Shows the temperature Vs dielectric constant of $\text{Ba}_{1.8}\text{Na}_{4.8}\text{Nd}_{0.8}\text{Nb}_{10}\text{O}_{30}$ before and after irradiation.
Figure 8.16 shows the variation of dielectric constant with temperature for Ba$_{1.8}$Na$_{4.6}$Nd$_{0.6}$Nb$_{10}$O$_{30}$. This range of temperature covers the full transition range. The irradiation on this material drastically reduces the dielectric constant. The transition behavior is more diffused covering a broad temperature region. In figure 8.17 the variation of $\varepsilon_r$ temperature for Ba$_{1.4}$Na$_{4.8}$Nd$_{0.8}$Nb$_{10}$O$_{30}$ is plotted. The plane curve shows the behavior for pure sample. The $T_c$ is found to be around 200$^\circ$C. Upon irradiation the transition temperature shifts to low temperature side as shown in the marked curve. The transition as a whole shift to the low temperature side. Here the difference in the room temperature $\varepsilon_r$ value before and after irradiation does not show much deviation, but at higher temperature it is very significant especially in the temperature region near $T_c$ and above.

![Graph showing temperature vs dielectric constant for Ba$_{1.8}$Na$_{4.6}$Nd$_{0.6}$Nb$_{10}$O$_{30}$ before and after irradiation.]

**Figure 8.17** Shows the temperature Vs dielectric constant of Ba$_{1.4}$Na$_{4.8}$Nd$_{0.8}$Nb$_{10}$O$_{30}$ before and after irradiation.

In the above cases the neodymium samples exhibit diffuse phase transition. The range of temperature over which the $\varepsilon_r$ makes a transition can normally be said to define the diffuseness of the ferroelectric–paraelectric transition. An explanation which can be offered for the relaxor behavior is that the Ba and Na ions do not order, so that across any trace in the crystal there are fluctuations in Ba:Na concentration. It is suggested that these statistical composition fluctuation leads to large fluctuations in the Curie temperature.
Table 8.1 shows the room temperature dielectric values of the samples before and after irradiation. There is an appreciable decrease in the room temperature dielectric constant values of the samples except for $\text{Ba}_{2.2}\text{Na}_{4.4}\text{Nd}_{0.4}\text{Nb}_{10}\text{O}_{30}$ whose room temperature $\varepsilon_r$ is found to increase slightly. The observed anomaly can be tentatively ascribed to the defect structure and chemistry induced in the above composition. This causes reduction in $T_c$ as well as shifting of the transition region to lower temperature region.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Room temperature dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before irradiation</td>
</tr>
<tr>
<td>1. $\text{Ba}<em>4\text{Na}<em>2\text{Nb}</em>{10}\text{O}</em>{30}$</td>
<td>100</td>
</tr>
<tr>
<td>2. $\text{Ba}<em>3\text{Na}<em>4\text{Nb}</em>{10}\text{O}</em>{30}$</td>
<td>92</td>
</tr>
<tr>
<td>3. $\text{Ba}<em>{2.8}\text{Na}</em>{4.2}\text{Nd}<em>{0.2}\text{Nb}</em>{10}\text{O}_{30}$</td>
<td>191</td>
</tr>
<tr>
<td>4. $\text{Ba}<em>{2.2}\text{Na}</em>{4.4}\text{Nd}<em>{0.4}\text{Nb}</em>{10}\text{O}_{30}$</td>
<td>164</td>
</tr>
<tr>
<td>5. $\text{Ba}<em>2\text{Na}</em>{4.5}\text{Nd}<em>{0.5}\text{Nb}</em>{10}\text{O}_{30}$</td>
<td>269</td>
</tr>
<tr>
<td>6. $\text{Ba}<em>{1.8}\text{Na}</em>{4.6}\text{Nd}<em>{0.6}\text{Nb}</em>{10}\text{O}_{30}$</td>
<td>310</td>
</tr>
<tr>
<td>7. $\text{Ba}<em>{1.4}\text{Na}</em>{4.8}\text{Nd}<em>{0.8}\text{Nb}</em>{10}\text{O}_{30}$</td>
<td>250</td>
</tr>
</tbody>
</table>

*Table 8.1* Room temperature dielectric constant before and after 100 MeV $\text{Fe}^+$ ion irradiation.

The ferroelectric properties of Nd-doped BNN samples are found to be modified after irradiation. The changes in the onset of the ferroelectric transition and decrease in the $T_c$ of the samples are evident from the above figures. The tetragonal tungsten bronze structured BNN ceramics is a relaxor ferroelectric due to fluctuations in the distribution of Ba, Na and Nd ions over the five fold and four fold tunnels in the structure. These dielectric property modifications after irradiation are accompanied by corresponding changes in the crystal lattice. The powder X-ray diffraction pattern of the irradiated samples show considerable variations. The intensity of the major peaks are considerably reduced which is accompanied by a broadening in the X-ray spectrum. These variations suggest deviations in the original crystal structure which is accompanied by induction of lattice strains. It is also assumed that partial amorphization is also induced on irradiation. These effects suppress the dipole moments with in the irradiated region. Hence a reduction in dielectric constant is generally observed. Since ferroelectricity in oxide materials are strongly concerned with oxygen content, oxygen deficiency would directly result in degradation of ferroelectricity, and lead to destruction of crystal structure. The
damage induced by ion implantation can result in point defects and clustered point defects. However, the implantation induced damage of crystal structure is sensitive to temperature variations.

8.8 References


