SUMMARY AND CONCLUSIONS

9.1 Summary and conclusions
One of the fascinating aspects of the field of ferroelectric ceramics is its interdisciplinary nature. This aspect is also a source of difficulty for people working in this field. This thesis contains a description on ferroelectric ceramic, processing and physical properties like microstructure, structure and dielectric properties. It also covers the physics of swift heavy ion irradiation and its effect on the physical properties of selected compositions of strontium barium niobate and barium sodium niobate ferroelectric ceramics. Our aim in this thesis has been to investigate modification in the properties of ferroelectric ceramics.

The enormous increase in the number of known ferroelectric ceramics over the last two decades no longer makes it even remotely possible to attempt a comprehensive survey of the field. The thesis lay emphasis on the definition and physics of those microscopic properties of ferroelectric ceramics and modern techniques of measurements which enable such characterizations to be made. The fundamental theoretical principles are introduced without reference to specific materials and only the practically more important or best understood specific materials are discussed in detail.

The tetragonal tungsten bronze structured family of oxide ferroelectric covers a large number of compounds. There is a very extensive solid solution range with varying compositions between end members. The open nature of this structure permits a wide range of cations and anion substitutions without loss of ferroelectricity and basic structure.

The processing of ferroelectric ceramics have been done by the common methods adopted for the fabrication of ceramics. By far the most widely used method for the
preparation of polycrystalline ceramics is the sintering of consolidated powders. Powder consolidation forms the major processing step before the firing process in which the microstructure of the solid solution are developed. Polymeric binders play an important role in powder consolidation. Binder selection and burnout procedures remain largely empirical, however, for any forming method, careful manipulation of the powder characteristics and the consolidation parameters provides a useful approach for the optimization of uniformity of the green body microstructure.

We have considered a number of issues that are important to an understanding of the sintering procedures. Matter transport during the sintering of polycrystalline ferroelectric ceramics occur by diffusion, a thermally activated process. Diffusion can occur along different paths in the solid solution, giving rise to different mechanisms of diffusion such as lattice, grain boundary, surface and dislocation. Matter transport during sintering can be viewed in terms of the flux of atoms or in terms of the counter flow of vacancies. The flux of the diffusing species is driven by gradients in the chemical potentials or by gradients in the vacancy concentration.

The basic feature of the microstructural development in polycrystalline ceramics is examined. Simple models allow the derivation of equation for the kinetics of normal grain growth. Abnormal grain growth can not be explained in terms of the reduction of uniform grain boundary energy. It is believed to be due to local increases in the driving force or in the mobility of the grain boundary. However, simple models provide useful guidelines for the control of the microstructure during sintering. Excessive grain and abnormal grain growth must be prevented if high density ceramics with controlled grain size are to be fabricated. Improvements in particle packing in the consolidated powder form also leads to benefits in densification. Pores that are large compared to particle size are difficult to remove during sintering and therefore limit the final density achieved. Liquid phase sintering enhances densification through easier rearrangement of the grains and faster matter transport through the liquid. However, the liquid normally remains as a glassy grain boundary phase in the sintered product, which may lead to deterioration of properties.
X-ray diffraction studies on strontium barium niobate and barium sodium niobate emphasize that very significant information can be obtained by the diffraction method. The reciprocal lattice geometry is determined more readily using X-ray powder indexing programs. The structure of $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ over the composition range $0.35 \leq x \leq 0.75$ are studied. The results indicate that SBN is in the tetragonal phase belonging to the space group $C_{4v}^2-P_{4bm}$ over the composition range $0.47 < x < 0.75$ and in the monoclinic phase in the $0.35 < x < 0.45$ range. The volume and axial ratio corresponding to the unit cell of each composition are determined. The results show minor variations with compositions which are quiet common in ferroelectric polycrystalline samples. Computer programs are used for indexing powder diffraction pattern. The underlying physical principle of indexing is the reconstruction of the three dimensional reciprocal lattice the radial distribution of the length $d^\prime$ of the reciprocal lattice vectors.

The X-ray studies on BNN samples show distinct crystalline phase. The crystalline phase with tetragonal symmetry are found. Barium sodium niobate can form a large range of solid solution incorporating alkaline, alkali and rare earth ions. The calculated and observed values of the $d$-spacing are in good agreement which confirms the structure and symmetry. The absence of new peaks apart from tetragonal symmetry confirm the single phase nature. The relative intensities of (001) and (002) peaks are high when the concentration of neodymium increases. This points to the preferred orientation along the $c$ axis.

For the dielectric constant studies a measurement set up, consisting of a dielectric cell with a sample holder, which can be evacuated has been fabricated. The cells have been calibrated by measuring dielectric constants of known samples like perspex. The dielectric constant of SBN and rare earth modified solid solutions showed diffuse phase transitions. The phase transition in $[\text{Sr}_{0.61}\text{Ba}_{0.39}]_{4-2x}\text{Li}_{2+x}\text{Eu}_x\text{Nb}_{10}\text{O}_{30}$ and $[\text{Sr}_{0.61}\text{Ba}_{0.39}]_{4-2x}\text{Li}_{2+x}\text{Nd}_x\text{Nb}_{10}\text{O}_{30}$ samples showed diffuse nature in the ferroelectric to paraelectric transition. Similar results are obtained for neodymium modified barium sodium niobate, with diffuseness of the transition increasing with increase in neodymium. It is believed that the well known compositional inhomogeneities/fluactuations of different microregions on a scale of a few hundreds to a few thousand $\text{A}^0$ in these samples cause
these phenomena. These microregions possess different $T_c$'s because of compositional variations from one to another. A broad envelope of these local transitions, which are assumed to be sharp may lead to diffuse phase transitions in the system. For these solid solutions, the phase transition temperature often changes continuously with composition and rare earth addition into these systems. The transitions may be placed at optimum temperature by controlling heterogeneity deliberately in the solid solutions.

The power dissipation in these systems is directly proportional to the dielectric loss factor. One main advantage of ferroelectric ceramics as a dielectric is that the loss factor is small. The energy loss in these materials mainly arise from ion jump relaxation between two equivalent ion positions which is responsible for the largest component of the dielectric loss.

Effects of swift heavy ion irradiation on strontium barium niobate and barium sodium niobate ceramics are studied in this thesis. The basic physics underlying the penetration of energetic particles in to matter and the different energy loss mechanisms are examined. The theoretical distribution of ions irradiated on these materials are calculated using TRIM simulation program. An important parameter characterizing energy transfer of swift heavy ion to the target material is the energy loss $dE/dX$ ($eV/A^0$). The values of $dE/dX$ changes with ion species, its energy and the density of the target specimen. The maximum value of the energy loss parameter appear to be near the end of ion path, where the ion velocity is rather low. From the calculated results it is clear that the energy loss mechanism is mainly contributed by the electronic energy loss, rather than nuclear energy loss, which is very small at 100 MeV energy.

The range of ions in BNN by Fe$^+$ ion, calculated using TRIM is about 14 $\mu$m, which shows that irradiation is a surface phenomena. Similarly, the range of Si$^+$ ion in SBN, which is nearly 25 $\mu$m, shows that Si has more penetration power than Fe$^+$. The longitudinal and lateral straggling values obtained gives the second order of ion distribution in these materials.
Swift heavy ion irradiation as a tool to modify material properties has gained considerable attention in recent years. It can be used to introduce precise number of any ion species in to any substrate materials, irrespective of the doping solubility limits. The interaction of swift heavy ion with ferroelectric materials induces large mechanical stresses compositional modifications and defects in the materials. The microstructural analysis done by SEM studies have shown that the individual grains on the surfaces are deformed and some of the grain layer on the surface are removed due to sputtering.

Fe\(^+\) ion irradiation leads to changes in the X-ray diffraction spectra. A systematic shift in the patterns are observed in the spectra. The variations in the relative intensity at higher angles indicate the changes in the orientations of atoms with in the unit cell. The reduction in peak intensity of SBN samples indicates the partial amorphization of surface layers in the specimen.

The dielectric constant of BNN and BNN modified with neodymium are found to be affected after irradiation. The irradiation of BNN with Fe\(^+\) ions suppresses the dipole moment in the irradiated region by introducing defects in to the system. This is supported by the reduction in dielectric constant measured in BNN ceramic samples.

### 9.2 Scope for future work

For gaining more information regarding tuning or controlling the transition behavior and Curie temperature, we have to refine the basic ceramic preparation and sintering process. These physical properties depend strongly on structural and microstructural features of these systems. Structural aspects need to be considered when anomalous properties of these materials are encountered. The relaxor properties of these materials can be understood by frequency variation measurements at various temperature including their \(T_c\) values.

Swift heavy ion (SHI) irradiation is gaining more and more importance as a tool to modify physical properties, especially in thin films. One main advantage of SHI is that precise number of ions can be implanted at a required depth uniformly distributed across the sample surface. Swift heavy ion with the state of the art nuclear instrumentation have
opened up exciting possibilities for characterization and depth profiling of ferroelectric materials over a wide mass range, particularly for lighter elements. 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 (fluence) of ions can be precisely controlled, so that we can introduce specific number of ions or defects at a precise depth below the surface of substrate materials. There is scope for doing much more work in this area.