CHAPTER 7

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

7.1 SUMMARY

The aim of the resent investigations was to grow good quality lead free single crystals. Well known perovskite ferroelectric sodium potassium niobate (KNN) crystals with Mn and Ta dopants were chosen for this study. The effect of dopants on the structural, electrical ad optical properties of the grown-crystals has also been studied. KNN is an important lead free piezoelectric crystal that belongs to ABO$_3$ family crystallizing in the orthorhombic structure. Lead free single crystals of sodium potassium niobate Na$_x$K$_{1-x}$NbO$_3$ were grown at three different phase boundary compositions (x = 0.17, 0.35, 0.50) by high-temperature solution method. Powder X-ray diffraction studies were carried out in order to confirm the structure of the grown crystals. The change in lattice parameters has been calculated. The crystal structure corresponding to the compositions x=0.17 and x=0.50 exhibit monoclinic and orthorhombic structures respectively. SEM and AFM studies reveal the morphological growth pattern of the sodium potassium niobate (KNN) crystals. The average step size decreases with the increase in concentration of potassium in KNN system. Dielectric studies were carried out on the KNN crystals using hp impedance analyzer. Dielectric loss is observed to decrease with increase in concentration of potassium in KNN crystals. The P-E hysteresis loops of different compositions of the KNN crystals show that the compositions with potassium concentration x =0.50 and
0.35 have maximum remnant polarization of about \( \sim 36 \mu \text{C/cm}^2 \) and 15.2 \( \mu \text{C/cm}^2 \) respectively and the corresponding coercive electric field were found to be 14 kV/cm and 11.2 kV/cm respectively. Piezoelectric coefficient \( \langle d_{33} \rangle \) for the compositions with potassium concentrations \( x = 0.50, 0.35 \) and 0.17 were found to be 72 pC/N, 63 pC/N and 52 pC/N respectively. Lead free piezoelectric single crystals of sodium potassium niobate \((K_{0.5}Na_{0.5})\text{NbO}_3\) (KNN) were grown by high-temperature solution method using two different fluxes; one with a mixture of NaF and KF and other with addition of \( \text{B}_2\text{O}_3 \) along with the mixture. In the study, the growth of KNN crystals without \( \text{B}_2\text{O}_3 \) flux and the same with \( \text{B}_2\text{O}_3 \) flux were compared. It was found that additions of small amounts of \( \text{B}_2\text{O}_3 \) lowered the melting temperature of the solid solution and enabled better dielectric properties. Phase analysis showed that all samples were crystallized in pure orthorhombic perovskite phase. The quality of the crystals was confirmed by Laue X-ray diffraction method. AFM morphological studies showed that the addition of \( \text{B}_2\text{O}_3 \) flux increased the roughness of the grown crystal. Further, addition of \( \text{B}_2\text{O}_3 \) flux slightly decreased the orthorhombic to tetragonal phase transition temperature \( \text{T}_{\text{O-T}} \) and the Curie temperature \( \text{T}_\text{C} \). The ferroelectric behaviour of KNN single crystal has been investigated at room temperature. The crystal grown using \( \text{B}_2\text{O}_3 \) flux exhibited a remanent polarization \( (P_r) \sim 32 \mu \text{C/cm}^2 \) and coercive field \( (E_c) \) of \( \sim 11.8 \text{kV/cm} \) whereas the crystal grown without the use of \( \text{B}_2\text{O}_3 \) flux had a remanent polarization \( (P_r) \sim 36 \mu \text{C/cm}^2 \) and coercive field \( (E_c) \) of \( \sim 14.6 \text{kV/cm} \).

Lead free piezoelectric single crystals of \((K_{0.5}Na_{0.5})\text{NbO}_3\) and 0.5 wt%, 1.0 wt% and 1.5 wt% \( \text{MnO}_2 \) doped \((K_{0.5}Na_{0.5})\text{NbO}_3\) (KNN) were grown by high-temperature solution method using \( \text{K}_2\text{CO}_3-\text{Na}_2\text{CO}_3 \) eutectic composition as flux with addition of small amounts of boron oxide for lowering the melting temperature. The effect of the manganese dopant on the dielectric properties, surface morphology and the domain structure were
investigated. Mn doping increases the dielectric constant and decreases the dielectric loss. A slight decrease in the orthorhombic to tetragonal phase transition temperature $T_{(O-T)}$ and Curie temperature $T_C$ has been observed in manganese-doped KNN single crystals. EDAX analyses identify the elements present in the grown crystals. From SEM and AFM analysis, the domain size of KNN–Mn crystal was found to be smaller than that of the pure KNN crystal. The ferroelectric behaviors of 1.5 wt% of Mn doped KNN single crystal has been investigated at room temperature. It exhibited good ferroelectric nature and remnant polarization (Pr) $\sim 28 \, \mu\text{C/cm}^2$ and coercive field (Ec) of $\sim 8.6 \, \text{kV/cm}$ which is smaller than that of the pure KNN crystal ((Pr) $\sim 32 \, \mu\text{C/cm}^2$ and (Ec) of $\sim 11.8 \, \text{kV/cm}$). Single crystals of sodium potassium niobate $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN) and 5 wt%, 10 wt% and 15 wt% tantalum oxide $\text{Ta}_2\text{O}_5$ doped KNN were grown by flux method. EDAX analyses identify the elements present in the grown crystals. The effects of doping on the dielectric properties and piezoelectric properties of the crystal were investigated. The remnant values have been calculated from the hysteresis loop. The results show that addition of tantalum oxide increases the piezoelectric coefficient $d_{33}$ and decreases the coercive fields $(E_c)$ of the KNN single crystals. The addition of tantalum oxide enables tantalum ions to go into the B-site of the $\text{ABO}_3$ perovskite structure of the KNN single crystal, substituting its niobium ions. Hence, the dielectric and piezoelectric properties were found to be enhanced. Scanning electron microscope (SEM) observations indicated that addition of tantalum oxide improves the microstructure of the KNN single crystal. The dielectric measurements show that orthorhombic-tetragonal and tetragonal-cubic phase transition temperatures of the 15 wt% doped single crystals have decreased when compared to the pure KNN single crystals and the transitions occur at $210^\circ C$ and $420^\circ C$ respectively. From the dielectric measurements, as decrease in Curie temperature has been witnessed. The crystals show diffused phase transition behaviour on Ta substitute. From the above results, it is concluded
that Mn and Ta doped KNN single crystals possess excellent properties suitable for devices applications.

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 $1 \times 10^{12}$ ions/cm$^2$, $1 \times 10^{13}$ ions/cm$^2$ and $5 \times 10^{13}$ ions/cm$^2$ at room temperature (RT). Another pristine sample was irradiated with lithium ions of fluence $5 \times 10^{13}$ ions/cm$^2$ at liquid nitrogen temperature (LNT) for comparison. The irradiated samples including the pristine sample were characterized by powder X-ray diffraction, dielectric and Raman studies. Powder X-ray diffraction studies confirmed the ion induced surface modification and it reveals decrease in the degree of crystallinity due to creation of lattice defects by the energetic implanted ions. Powder X-ray results show that the density of 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 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.

7.2 SUGGESTION FOR FUTURE WORK

In the present investigation, importance has been given to grow bulk single crystals of sodium potassium niobate. An attempt has also been made to enhance the ferroelectric properties by ion implantation and Fe and Cu doping. Crystal growth was carried out by high temperature solution growth technique which has limitation in size of the crystals. Growth of these technologically important crystals can be carried out by Top Seeded Solution Growth (TSSG) technique. Moreover Ta substitution makes the system congruently melting and hence the Czochralski technique may be also be tried. Single crystals of KNN have been grown with Ta content upto 15 wt %. Attempts can be made to grow other compositions. It is expected that the higher concentration of Ta will show tricritical phase transition behaviour. Higher concentration of Mn in KNN induces magnetic moment. Magntisation studies can be carried out on Mn doped KNN crystals.

Ion irradiation studies were carried out with one energies and species. The future work can be focussed at different energies using different ion species in order to improve the ferroelectric properties. Apart from Fe and Cu doping dopants like Rh, Zr and Co may also be tried to enhance the ferroelectric properties. Ferroelectric characterization studies like pyroelectric and piezoelectric measurement can be carried out to assess the suitability of this material for transducer and mechanical devices.
KNN crystals also possess photorefractive properties apart from ferroelectric properties. Special attention may be focussed on the photorefractive property studies for applications in optical communication.

The complete KNN-LiNbO$_3$ solid solution have been prepared in ceramic form and thes ceramics showed the non-linear dielectric maximum. Hence single crystal growth from LiNbO$_3$ side will give better understanding on non-linear dielectric maximum.

KNN single crystals can be subjected to inelastic neutron diffraction and temperature dependent Raman spectroscopic studies in order to elucidate the physics behind the diffused phase transition behaviours. The fundamental studies attempted here can be extended to new lead free based single crystals and also thin films.