CHAPTER 6

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

6.1 SUMMARY

The objective of the present investigation was two fold. First one is to eliminate the twin formation in barium titanate and grow bulk single crystals. Second objective is to enhance the ferroelectric properties by ion implantation and doping.

Barium calcium titanate (BCT) single crystals with different concentrations of Ca have been grown by flux method. The butterfly twinned crystals were obtained for lower concentrations of Ca. The twinning was completely eliminated for higher Ca concentrations by adopting optimized growth parameters and bulk single crystals were obtained. The quality of the crystals was confirmed by Laue photograph. 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. Vein, spiral and hopper structures were observed by optical microscope. XPS studies confirmed the presence and also the valence state of calcium.

The spontaneous polarization values \( P_s \) for different concentrations of Ca have been calculated from hysteresis loops traced using Sawyer-Tower circuit. A decrease in \( P_s \) has been observed. The domain structure has been studied using atomic force microscopy (AFM) and 90° c- domains were observed. Dielectric constants were measured at different frequencies. From the dielectric measurements, an increase in Curie temperature \( T_c \) has been witnessed. The crystals show diffused phase transition behaviour on Ca doping. The dielectric constant decreases on increasing the...
Ca concentration. The refractive indices decrease as determined from transmission and absorption spectra.

Barium strontium titanate (BST) crystals have been grown with different concentrations of Sr. It was found that the twin formation could be reduced for low Sr concentration and bulk single crystals were obtained. Layer growth and vein structures were observed by optical microscopy. Single crystal X-ray diffraction studies were carried out and the crystal characteristics are reported. The single crystallinity of the crystal was confirmed by Laue X-ray diffraction. The change in lattice parameters and structure have been observed from powder X-ray diffraction analysis.

AFM was employed to study the domain structure of BST single crystals and 90° c-domains have been observed. The twin angle has been calculated and is compared with the lattice parameters. Hysteresis loops were traced and the spontaneous polarization values for different concentrations of Sr have been calculated. The $P_s$ values decrease on increasing the Sr concentration. The dielectric constant measurements show a decrease in dielectric constant and Curie temperature and for 30 mol.% of Sr, the Curie temperature falls below room temperature. A diffused phase transition behaviour was observed on Sr doping.

Ion implantation technique was used for material modification and also to improve the ferroelectric properties of BST single crystal. 120 MeV $^{28}$Si ions were implanted with a dose of $10^{12}$ ions/cm$^2$ on the BST crystals of Sr composition 20 and 30 mol.%. The surface features and the defects created on implantation have been studied by SEM. The domain patterns were observed by AFM and the twinning angles were also calculated. The phase transition studies from dielectric measurements indicated that the Curie temperature decreases on implantation. The dielectric constant and spontaneous polarization values increase and the phase transition becomes sharp.

100 keV He ions were implanted with a dose of $10^{17}$ ions/cm$^2$. The effect of implantation on ferroelectric properties was analyzed. He implantation enhances both
dielectric constants and the spontaneous polarization values. The Curie temperature is also shifted to higher temperature side.

Twin-free crystals of Ce and Nb doped barium strontium titanate were grown with optimized growth parameters. X-ray diffraction studies showed that the lattice parameters and c/a ratio increase and the system shifts towards tetragonal phase. XPS studies confirmed the 5+ state of Nb in Nb doped BST single crystal. Ferroelectric characterization studies showed that there is a considerable increase in dielectric constant and spontaneous polarization values on both Ce and Nb doping. The Curie temperature increases for Ce doping whereas it decreases for Nb doping. The nature of phase transition becomes sharp for both Ce and Nb doping.

6.2 SUGGESTION FOR FUTURE WORK

In the present investigation, importance has been given to grow twin-free bulk single crystals of barium titanate family. An attempt has also been made to enhance the ferroelectric properties by ion implantation and Ce and Nb doping. Crystal growth was carried out by spontaneous nucleation 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 Sr substitution makes the system congruently melting and hence the Czochralski technique may also be tried.

Ion implantation studies were carried out with two different 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 Ce and Nb doping, dopants like Rh, Zr and Co may also be tried to enhance the ferroelectric properties. Ferroelectric characterization studies like pyroelectric and piezoelectric measurements can be carried out to assess the suitability of this material for detector and mechanical devices.
BaTiO$_3$ family crystals also possess photorefractive properties apart from ferroelectric properties. Special attention may be focussed on the photorefractive property studies for applications in optical communication. Barium titanate shows semiconducting behaviour under reduced atmosphere and it will be of interest to study their semiconducting properties.