Abstract

The search for the development of new materials of desired properties, both for sophistication and miniaturization, from the technological point of view, has been the motivating source and force of the present study. Ferroelectric materials are employed for the fabrication of many engineering components and thus play a considerable role in our life. Among the lead-free, environmentally friendly ferroelectric ceramics, solid solutions of barium calcium zirconate titanate $(Ba_{1-x}Ca_x)(Zr_{0.1}Ti_{0.9})O_3$ are promising. This widely investigated system exhibits interesting dielectric, piezoelectric and structural properties. The perovskite $(Ba_{1-x}Ca_x)(Zr_{1-y}Ti_y)O_3$ is of particular interest not only because it has structural phase transition but also because of morphotropic phase boundary (MPB) that occurs at a discrete composition (x) range. The MPB is an interesting area in the composition-property diagram, where physical properties are extremal. The composition-dependent dielectric anomaly makes MPB a very interesting region of study. The present thesis entitled '**Ferroelectric properties of Barium Calcium Zirconate Titanate $(Ba_{1-x}Ca_x)(Zr_{1-y}Ti_y)O_3$, near morphotropic phase boundary**' deals with the study of $(Ba_{1-x}Ca_x)(Zr_{1-y}Ti_y)O_3$, (x = 0.140- 0.160, y = 0.9), compositions. The study has been carried out in two parts; the bulk part, which explores the composition(s) near the morphotropic phase boundary in $(Ba_{1-x}Ca_x)(Zr_{1-y}Ti_y)O_3$ at x = 0.150 and y = 0.9; and the thin film part, which deals with the investigations on the optical and electrical measurements of the thin films of a single composition, with x = 0.155, near the MPB.

The first chapter of the thesis broadly introduces the subject, surveys the literature in the field and makes the foundation for the investigations presented in this report. The pellet samples of $(Ba_{1-x}Ca_x)(Zr_{0.1}Ti_{0.9})O_3$, $(0.140 \le x \le 0.160)$ were prepared using a solid-state reaction technique followed by double sintering. The preparation method, characterization (using XRD, SEM, EDX,

etc.) and dielectric measurement results have been described in **Chapter- 2**. Among the prepared samples, a break was noticed in the XRD peak shifting tendency indicating anomalous structural behaviour for the compositions with x = 0.150. Anomalous structural and dielectric behaviour indicated morphotropic phase boundary (MPB) in $(Ba_{1-x}Ca_x)(Zr_{1-y}Ti_y)O_3$, (x = 0.140- 0.160, y = 0.9), near the compositions with x = 0.150. The composition-dependent dielectric and structural response has been described in this chapter. The observed variation of the dielectric and structural properties, in a wide temperature range, from room temperature (RT) to 500 °C, has been measured on the compositions near MPB (near x = 0.150), which are described in **Chapter- 3**. The structural and dielectric anomaly was observed at the respective transition temperatures in all the prepared compositions. The observed dielectric anomaly, near transition temperature, has been associated with softening of the small-lying optical mode- the soft mode. At the transition temperature, the soft mode ceases, and the lattice observes a structural change, resulting in anomalous dielectric behaviour in the ABO_3-type ferroelectrics. Based on the soft mode theory, the observed results have been analyzed. Experimental observations were observed in fair agreement with the theoretical findings. Measurements of the piezoelectric properties of the compositions near the MPB, with x = 0.150, were carried out. The observed results have been presented in **Chapter- 4**.

In this age of miniaturization, thin film materials play a significant role in high-tech industries. Thin films have primarily been used in communication, optics, microelectronics, energy generation and conservation, and coatings of all types. Deviation from the corresponding bulk properties arises in the thin film material due to its thinness, distinct physical structure and high surface-to-volume ratio, which is a direct result of the growth process. The properties of oxide films are dramatically influenced by annealing, which makes them promising materials for industrial applications. Thin films were deposited on quartz for optical and silicon for electrical measurements by radio frequency (RF) magnetron sputtering of $(Ba_{0.845}Ca_{0.155})(Zr_{0.1}Ti_{0.9})O_3$ pellet target. The as-deposited $BCZT_{0.9}$ films were annealed at different temperatures in the ambient atmosphere. Prepared films were characterized by XRD- and optical-method. The film deposition and characterization method, observed optical properties and the underlying mechanisms have been discussed in **Chapter- 5**. The electrical measurements were carried out in the MIS (metal-insulator-semiconductor) arrangement. In **Chapter- 6**, the current-voltage (I-V); and **Chapter- 7**, capacitance-voltage (C-V) properties of the $(Ba_{0.845}Ca_{0.155})(Zr_{0.1}Ti_{0.9})O_3$ assisted MIS structures and the mechanisms responsible for the observed behaviour have been discussed. The composition-dependent dielectric and structural properties indicate the existence of a technologically important MPB region in $(Ba_{0.845}Ca_{0.155})(Zr_{0.1}Ti_{0.9})O_3$ system at x = 0.150. The measured temperature-dependent structural and dielectric properties have been associated with the soft mode, which softens at the transition temperature (T_c), and the lattice observes a structural change and leads to dielectric and structural anomaly at T_c. The enhanced piezoelectric properties near MPB show the remarkable potential of this system to replace lead-based systems. The measured electrical and optical characteristics of $BCZT_{0.9}$ thin films indicate the potential of the material and electronics applications. All the observed results and underlying mechanisms have been concluded in **Chapter- 8**. The observed properties indicate the exciting potentiality of the $(Ba_{0.845}Ca_{0.155})(Zr_{0.1}Ti_{0.9})O_3$ system for the development of tailor-made materials for industrial and technological applications.