Abstract

Perovskites (ABO_3) are the class of materials where slight distortion in the crystallographic structure leads to a drastic change in the physical properties such as ferroelectricity, ferromagnetism, ferroelasticity, etc. Out of these, ferroelectrics are the materials that exhibit diverse functionality and find enormous applications in sensors, actuators, transducers, energy harvesters, memory devices, etc. Nowadays, the field of nearly all these applications is dominated by lead-based ceramic systems. However, the adverse environmental concerns associated with the lead-based ferroelectric materials imposed by their toxic nature have intensified the search for lead-free alternatives. In this regard, 'A' and 'B' site-modified perovskite barium titanate ($BaTiO_3$)-based solid solutions have emerged as highly appealing technologically important lead-free candidates due to their potential to exhibit various tunable crystallographic structural phase transitions leading to different phase boundaries, and the relaxor ferroelectric behaviour. The term phase boundary comprises the polymorphic and morphotropic phase boundaries, where the free energy barrier between the coexisting phases (long-range ordered) gets reduced, facilitating the easy polarization rotation phenomenon to realize the high electromechanical responses. The polarization rotation phenomenon occurs when the phase transitions are ferroelectric-ferroelectric in nature and corresponds to different directions of polarization. These ferroelectric phases are described by the freezing of zone center (Γ_4^-) phonon mode belonging to the high symmetry cubic phase, whose amplitude determines the magnitude of the intrinsic contribution in the ferroelectricity present in the material. On the other hand, the fascinating properties of relaxor ferroelectrics are driven by the exotic polar nano-regions (short-range ordered) existing in the average cubic phase. The main characteristic feature of the relaxor is the existence of a broad phase transition temperature which is often beneficial since it leads to an increase in the thermal stability of the physical responses of the system and hence makes

the materials operational over a wide range of temperatures. Thus, the physical properties are highly sensitive to the crystallographic phases of the materials, and the macroscopic (long-range) as well as microscopic (short-range) atomic ordering plays a crucial role in predicting the suitability of the maerial for various application purposes.

Thus owing to the idea of relaxor ferroelectrics driven by short-range ordering (polar nano-regions), first, we have developed a lead-free perovskite-based solid solution $(Ba_{1-x}Ca_x)(Sn_{0.11}Zr_{0.05}Ti_{0.84})O_3$; BCSZT*x* ($0 \leq x \leq 0.20$), exhibiting relaxor ferroelectric behaviour in an average cubic structure. X-ray diffraction measurements for all the compositions have shown a simple cubic phase with $Pm\overline{3}m$ space group. Despite having a centrosymmetric cubic phase, a slim hysteresis loop has been observed via PE loop measurements. This contrapositive behaviour was explained via Raman spectroscopic measurements which reveals the presence of local ordering in the macroscopic cubic matrix, corresponding to the 'A' and 'B' sites. The cooperative behaviour of 'A' and 'B' site off-centered (local) atoms leading to microscopic polar symmetry in the macroscopically cubic matrix is held responsible for the relaxor ferroelectric nature of BCSZT*x* ceramics. Owing to the aforementioned contrapositive behaviour, BCSZT*x* ceramics exhibit a high value of dielectric constant. Eventually, we have observed a decisive role of Ca^{2+} dopant at the 'A' site in BCSZT*x* system leading to the enhancement in the relaxor ferroelectric behaviour and hence dielectric properties. The presence of a slim hysteresis loop, along with broad and diffuse dielectric nature, makes these ceramics a potential candidate for energy storage applications.

Further, in order to explore the evolution of crystallographic phases as a function of temperature for relaxor ferroelectric system BCSZT*x*, we have carried out temperature-dependent X-ray diffraction and Raman spectroscopic studies for one of the important compositions, *viz.,* BCSZT15. The Rietveld refinements performed on temperature-dependent X-ray diffraction data revealed a single cubic ($Pm\overline{3}m$) phase for 248 K $\leq$ T $\leq$ 448 K, while the coexistence of the disordered cubic (*Pm*$\overline{3}$*m*) phase with the ordered rhombohedral (*R*3*m*) phase for 100 K $\leq$ T $\leq$ 223 K. The results of temperature-dependent X-ray diffraction analysis in conjunction with Raman spectroscopic studies reveals the overall crystallographic structure of BCSZT*x* ceramics. Further, the evolution of lattice parameter, and unit cell volume corresponding to the cubic (*Pm*$\overline{3}$*m*) phase show a saturation as a function of temperature, revealing the presence of an electrostrictive-like effect in the material, making the composition suitable for actuators.

Subsequently, in order to study the role of inter-ferroelectric phase boundary, *i.e.,* the coexistence of ferroelectric phases (with long-range atomic arrangements), driven by component freezing of three-dimensional polar (Γ_4^-) phonon mode corresponding to the center of cubic Brillouin zone, we have fabricated another scientifically enriched and technologically important $BaTiO_3$-based eco-friendly functional material $(Ba_{0.92}Ca_{0.08})(Zr_{0.05}Ti_{0.95\text{-}x}Sn_x)O_3$; BCZTSn*x* ($0 \leq x \leq 0.10$) via solid-state reaction method. The combined X-ray diffraction, Raman spectroscopic analysis, and temperature-dependent dielectric studies have revealed the presence of several crystallographic phase transitions with coexisting phases, *viz.,* *P*4*mm*→(*P*4*mm* + *Amm*2 + *R*3*m*)→(*Amm*2 + *R*3*m*)→*R*3*m*→(*Pm*$\overline{3}$*m*+*R*3*m*), as a function of Sn(*x*) content. These crystallographic phases, *viz., P*4*mm*, *Amm*2, and *R*3*m* results due to component(s) freezing of Γ_4^- phonon mode (belonging to *Pm*$\overline{3}$*m* space group), with order parameter directions (0,0,a), (a,a,0), and (a,a,a) leading to ferroelectric polarization along $\langle 001 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions, respectively. The BCZTSn*x* ceramic system corresponding to Sn(*x*) = 0.025 exhibits a significant reduction in the coercive field (E_c) with an enhancement in ferroelectric polarization (P_r) in comparison to the composition having Sn(*x*) = 0. The enhancement in ferroelectric polarization for Sn(*x*) = 0.025 has been attributed to the inter-ferroelectric three-phase (*P*4*mm* + *Amm*2 + *R*3*m*) coexistence, which is further explained by the enhancement in the amplitudes of ferroelectric phonon modes (calculated using the symmetry mode analysis technique) corresponding to orthorhombic and rhombohedral phases. The existence of a high ferroelectric polarization and low coercive field makes the above composition (Sn(x) = 0.025) an eco-friendly candidate for various ferroelectric devices.

Finally, we have extended our studies and synthesized the solid solutions having higher Sn content, *i.e.,* BCZTSnx ($0.125 \leq x \leq 0.25$). The X-ray diffraction studies inferred a long-range cubic phase with $Pm\overline{3}m$ space group for all the compositions. However, Raman spectroscopic studies have revealed the presence of rhombohedral-like short-range ordering in contrast to the cubic phase inferred from X-ray diffraction analysis. Owing to the presence of short-range ordering driven polar nano-regions, the dielectric studies have shown broad peak with a relaxor ferroelectric nature. Further, the dielectric peak broadening and the relaxor nature increases with increase in Sn(x) content. Like the lead-based relaxors, *e.g.,* $Pb(Mg_{1/3}Nb_{2/3})O_3$, where the relaxor nature appears due to random electric fields driven by the charge disorder, the relaxor ferroelectricity in BCZTSnx is attributed to the random stress fields. The random stress field in BCZTSnx ceramics is attributed to the disordered distribution of Sn^{4+} cations corresponding to 'B' sites, effectively disrupting the long-range correlated O-Ti-O chain leading to a relaxor ferroelectric behaviour.

Thus, overall, the thesis is focused on the role of long-range ordered inter-ferroelectric phase boundaries (driven by freezing of zone center phonon modes associated with the $Pm\overline{3}m$ space group) and short-range atomic ordering in tuning the dielectric and ferroelectric properties of lead-free perovskite-based functional materials suitable for various technological applications.