Chapter 7

Summary and future work suggestions

7.1 Summary

The 'A' and 'B' site-modified $BaTiO_3$-based solid solutions are getting continuous attraction as a potential replacement for toxic and hazardous lead-based ferroelectric materials. The enhancement in the physical responses of barium titanate ($BaTiO_3$) can be made by doping in two efficient ways; one of them is developing a relaxor ferroelectric nature via local random fields, and the other is tuning various phase transitions leading to polymorphic or morphotropic phase boundaries. Here, the relaxor-ferroelectrics are described by the short-range symmetry existing within the material, while the polymorphic and morphotropic phase transitions are governed by the long-range ordered ferroelectric phases, which appears due to the freezing of the ferroelectric Γ_4^- phonon modes associated with zone-center of the high symmetry cubic Brillouin zone. The freezing of Γ_4^- phonon mode shifts the atoms from their centrosymmetric position, thereby developing a ferroelectric phase in the material. Therefore, the physical properties can be enhanced significantly by tuning the atomic arrangements at short-range (local) and long-range (global) simultaneously.

In this regard, firstly, we have developed an 'A' site tunable eco-friendly relaxor ferroelectric material $(Ba_{1-x}Ca_x)(Sn_{0.11}Zr_{0.05}Ti_{0.84})O_3$; BCSZT$x$ ($0 \leq x \leq 0.20$), having cubic ($Pm\bar{3}m$) phase, but with the presence of ferroelectricity for all the compositions. The observed ferroelectric polarization was found to be driven by the correlated effect of locally off-centered atoms corresponding to 'A' and 'B' sites of the centrosymmetric cubic ($Pm\bar{3}m$) phase, which was confirmed via the PE hysteresis loop and Raman spectroscopic measurements. The cooperative behaviour of 'A' and 'B' site off-centered (local) atoms leading to short-range ferroelectric ordering in the average cubic matrix has been held responsible for the observed relaxor ferroelectric nature. The observed polarization and the dielectric relaxation have shown an enhancement with the increase in $Ca^{2+}(x)$ content via off-centering of Ca^{2+} cations due to its smaller ionic radii, which results in the increased strength of the dipoles corresponding to B(Ti^{4+}) sites. Moreover, we have discovered that the $Ca^{2+}(x)$ dopant works in a similar fashion as the lowering of temperature does in relaxors in terms of enhancing the number and interaction strength of the polar nano-regions. Owing to the diffuse nature of phase transition with a high value of dielectric constant, and a slim hysteresis loop, BCSZTx ceramics can act as a potential candidate for energy storage applications.

Subsequently, we have carried out temperature-dependent X-ray diffraction analysis corresponding to the composition BCSZT15 in conjunction with temperature-dependent Raman spectroscopic studies. Our analysis has revealed the existence of a single cubic ($Pm\bar{3}m$) phase for 248 K $\leq$ T $\leq$ 448 K, while the coexistence of cubic and rhombohedral ($Pm\bar{3}m$+$R3m$) phases for 100 K $\leq$ T $\leq$ 223 K. In addition, the evolution of the lattice parameter and unit cell volume has shown a saturation at low temperatures followed with the volume gain, revealing the presence of an electrostrictive effect in the material making BCSZT15 composition as an eco-friendly candidate for actuators.

Further, we have extended our studies to observe the effect of inter-ferroelectric phase boundary (coexistence of two or more long-range ordered ferroelectric phases), with the ferroelectric phases being driven by the component freezing of three-dimensional polar (Γ_4^-) phonon mode corresponding to the center (k = 0,0,0) of cubic Brillouin zone. Therefore, we have developed another scientifically enriched and technologically important barium titanate-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, and performed a detailed study of structure-property correlations. The combined X-ray diffraction, Raman spectroscopic studies, and temperature-dependent dielectric analysis have revealed a series of phase coexistence, *viz., P*4*mm* (Sn(x) = 0), $P4mm + Amm2 + R3m$ (Sn(x) = 0.025), $Amm2 + R3m$ (Sn(x) = 0.05), *R*3*m* (Sn(x) = 0.075), $Pm\bar{3}m$+*R*3*m* (Sn(x) = 0.10), and thereby stabilizing into a low symmetry rhombohedral (*R*3*m*) phase (isostructural to completely ordered low-temperature phase of $BaTiO_3$; where the microscopically ordered ferroelectric displacements coincide with the macroscopically ordered phase) at room temperature, as a function of Sn(x). These phases, *viz., P*4*mm*, *Amm*2, and *R*3*m* corresponding to polarization states $\langle 001 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$, are found to be driven by the component(s) freezing of the above-mentioned three-dimensional polar Γ_4^- phonon mode. Moreover, the amplitude of the Γ_4^- phonon mode corresponding to Sn(x) = 0.025 (calculated via symmetry mode analysis) has shown a peak value for the low symmetry *Amm*2 and *R*3*m* phases, which is further corroborated by a peak in the ferroelectric polarization inferred from PE loop measurements. Thus we find that the fabrication of a smart system with enhanced macroscopic polarization is linked with the high amplitudes of the ferroelectric phonon modes (Γ_4^-) at the microscopic level. Further, the presence of an inter-ferroelectric three-phase ($P4mm + Amm2 + R3m$) coexistence for Sn(x) = 0.025 has been believed to facilitate the easy polarization rotation between the coexisting phases, leading to a relatively high value of ferroelectric polarization and low coercive field. Moreover, due to the presence of an

inter-ferroelectric three-phase coexistence resulting in the high ferroelectric polarization and low coercive field, the smart composition Sn(x) = 0.025, may be a compelling lead-free candidate for ferroelectric device applications, *viz.,* ferroelectric memory devices, etc.

Lastly, we have explored the presence of a relaxor ferroelectric behaviour for higher Sn compositions in BCZTSnx; $(0.125 \leq x \leq 0.25)$. The X-ray diffraction studies revealed an average cubic ($Pm\bar{3}m$) phase for all the compositions, but the Raman spectroscopic studies have clearly revealed the presence of short-range ferroelectric-like ordering (polar nano-regions) existing in the average cubic matrix. As a consequence of the polar nano-regions in the cubic matrix, all these ceramics exhibits a broad dielectric permittivity peak with a non-relaxor nature for Sn(x) = 0.125, which transforms into a relaxor ferroelectric for Sn(x) = 0.15. With the further increase in Sn(x) content, the dielectric relaxational behaviour increases till Sn(x) = 0.25. Owing to the presence of a high dielectric constant with a relaxor ferroelectric nature, these ceramics can act as a potential candidate for various energy storage applications.

7.2 Future work suggestions

To have further insights into structure-property correlations, atomic pair distribution function analysis is required to precisely probe the local structures, bond angles, and inter-atomic distances for the compositions exhibiting the relaxor behaviour. Also, the temperature-dependent pair distribution function analysis needs to be carried out to observe the evolution of locally off-centered dipoles in the formation of polar nano-regions.

In addition, Landau-free energy calculations are required to calculate the energy barrier between the coexisting phases for the multi-phase regions. Also, the temperature-dependent symmetry mode analysis can be carried out to analyse the effect of amplitudes of frozen phonon modes on the variations in physical properties as a function of temperature.