Chapter 7

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This piece of work adds a thrust in the direction of developing a new NBT-ST based piezoelectric ternary system which can turn out to be a potential lead-free alternative to the widely used PZTs with a number of future improvements. An in-depth understanding on the lead-free piezoelectric materials through extensive literature review has infused the impetus to design such a solid solution i.e. \((0.8-x) \text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3 - 0.2\text{SrTiO}_3 - x\text{BaTiO}_3, (0 \leq x \leq 0.10)\) that exhibits a morphotropic phase boundary as well as strong relaxor behaviour. Encouraging dielectric and piezoelectric properties are observed for this system close to the MPB composition. The dynamics of the PNRs, which is considered to be responsible for relaxor behaviour, is discussed in detail basing on the analysis of dielectric response of the ceramics using various empirical models. Modulus formalism is used to analyse the impedance spectroscopic data to further strengthen the perception on the thermal evolution and dynamics of the PNRs. In this chapter, the important findings are summarized based on the results and discussion of the preceding chapters. It also provides a thumbnail sketch to the future scope of work opening up new avenues in this field.

7.1 CONCLUSIONS

- A lead free ternary solid solution series, NBT-ST-BT was prepared by solid state reaction method at optimized calcination and sintering temperature of 800 °C and 1200 °C respectively for 4 h in air. The calcined powders were cold isostatically pressed at 200 MPa to obtain maximum density.

- XRD patterns of the ceramic powders confirmed pure perovskite phase with no traces of secondary phases. The ternary solid solution exhibited pseudocubic symmetry for low BT content (up to \(x = 0.02\)) while the structure gradually changed in to tetragonal and becomes prominent at \(x \geq 0.08\). This is evident from the (002) peak splitting into (002) / (020) in the range \(0.04 \leq x \leq 0.06\). This region also marked the co-existence of pseudocubic and tetragonal phases which may be attributed to the formation of an MPB. Further, the analysis of the lattice
parameters by ‘Celref’ software show an elongation along the c-axis above \( x = 0.04 \) which might be due to the occupation of ions of larger radii (Ba\(^{2+}\) and Sr\(^{2+}\)) at the A-site of the NBT lattice. The Lorentzian peak fitting of the Raman spectroscopic data also shows similar kind of anomalies in the fitting parameters at \( x = 0.04 \) which is evident of a structural change and morphotropic phase boundary.

- It is observed that the ceramic with \( x = 0.04 \) attains an optimum dielectric constant which is at par with some of the ternary systems available in literature (though less than the parent NBT-0.2ST). However, one of the vital results that could be obtained was an anomalous decrease in loss at the MPB composition below 300 °C. Similar kind of peculiarity was noticed in \( T_m, T_d, \varepsilon_m \) and \( \tan \delta_m \) values at 0.04BT.

- Evidences on the establishment of MPB were further strengthened when the electromechanical and piezoelectric properties were abnormally enhanced at MPB. A maximum \( d_{33}^* = 688 \) pm/V and \( S_{\text{max}} = 0.424\% \) was achieved for \( x = 0.04 \) at unipolar electric field loading of 6 kV/mm. Even the bipolar EFIS response at 6 kV/mm also exhibits an optimum strain of 0.372% at 0.04BT along with a decrease in \( S_{\text{neg}} \) value. Further it was also found that the values of \( E_c, P_r, P_m \) and the difference between them \( (P_m-P_r) \) as extracted from the P-E loops show a marked dependence on BT content. The \( E_c \) and \( P_r \) values decrease anomalously at \( x = 0.04 \) to 4.71 kV/mm and 2.18 \( \mu \)C/cm\(^2\) respectively. A large difference between the \( P_r \) and \( P_m \) was also noted leading to large strain response.

- Relaxor response is the second important novel feature exhibited by the solid solution under investigation along with MPB which brings in thermal stability of dielectric permittance. The temperature dependent dielectric curves show an increase in the relaxor behaviour in NBT-ST-BT solid solution with a diffuseness co-efficient rising up to \( \gamma = 2 \) at 0.10BT along with a frequency dispersion \( \Delta T_m (T_{m,1MHz} - T_{m,0.1kHz}) \) around 30 °C for all compositions. This is further supported by slim P-E loops. Such unique behaviour of the samples under study is related to the dynamics of PNRs in the range \( T_B \) to \( T_f \).
• From the point of view of analysing the relaxor behaviour and thermal evolution of the PNRs from $T_B$ to $T_f$, the dielectric data was inspected upon by fitting to various models like Curie-Weiss law, V-F law, Power law, and Cheng’s model in high and low temperature regime. The fitting parameters obtained from V-F law and power law in the interpretation of frequency dependence of $T_m$ reflected a better relaxation with increase in BT content. The values of activation energy ($E_a$) derived in this case suggested larger sized and less dynamic PNRs than those reported earlier. The two very crucial temperatures $T_B$ and $T_f$ were derived from Curie-Weiss fit and V-F fit of the experimental data. It was observed that $\Delta T (T_B, 1MHz - T_f, 1MHz)$ is maximum at 0.10BT giving an impression of maximum temperature stability of dielectric constant. Besides the fitting parameters obtained from the analysis of the relaxation behaviour in low and high temperature regime using Cheng’s model also provide information about the growth rate of the PNRs and their interactions.

• To have a better insight into the metamorphosis of the PNRs, it was further investigated by IS technique. The presence of highly polarisable entities for all the compositions were revealed by $M''(f)$ spectra. The size distribution and number density of PNRs decrease with addition of BT. Arrhenius plots of the relaxation times obtained from $Z''(f)$ and $M''(f)$ revealed three different regions of varying activation energies for 0.04BT, 0.06BT and 0.08BT. The different regions correspond to three separate temperature domains i.e. around $T_f$, $T_m$ and $T_B$ representing distinct relaxation processes. The activation energy calculated around $T_f$ (much below $T_m$) is less owing to greater interaction among the PNRs while for region around $T_m$ and further towards $T_B$, the values of activation energy increases indicating lesser interactions among them. The critical understanding on the existence of PNRs and a transition from long range conductivity to short range dielectric relaxation was analysed in detail in the case of 0.08BT sample. The present study may enrich the literature in the field of the evolution of PNRs and their co-relation with dielectric relaxation for ternary solid solutions; and motivate the researchers to adopt the IS technique for further investigation in this direction.
7.2 FUTURE SCOPE OF WORK

The present study may enrich the literature by achieving maximal functional properties in a newly developed solid solution at the morphotropic phase boundary. The study also adds new dimensions to impedance spectroscopy in analysing the evolution of PNRs and their co-relation with dielectric relaxation. The system needs to be intrigued by some additional measures before establishing them as a better lead free alternative and few of them are suggested below:

- The location of the exact position of the morphotropic phase boundary by compositional engineering may be performed to have a better introspection on the phase coexistence and property enhancements around MPB.
- Temperature dependent XRD may be carried out to observe the change in crystal structure with temperature. Surface analysis of the samples by HRTEM and electron diffraction may be carried out to observe the PNRs for better understanding of relaxor behaviour.
- From application point of view, some other figures of merit like $d_{33}$, $K_p$, $K_i$ etc may be derived experimentally to explore new applications of the investigated samples.
- Single crystals and nano ceramics may be prepared from the same composition to observe the behavioural changes and piezoelectric properties.