Chapter: 5

Low Temperature XRD and Dielectric Studies

Chapter-5

5.1 Introduction

The detailed study of the room temperature structure and electric field induced phase transformations in BMT-PT and BMZ-PT across the morphotropic phase boundary have been discussed in preceding chapters. In this chapter, we will discuss the result of low temperature XRD and dielectric measurements to investigate temperature dependent phase transitions below room temperature. The high temperatures frequency dependent dielectric studies, in ferroelectrics and piezoelectric mixed solid solutions show very large dielectric response due to their diffuse phase transition behaviour and relaxor nature [Bokov et al. (2006)]. Extensive research has been done on the MPB based solid solutions for dielectric characterisation at higher temperatures to understand the nature of phase transition in the vicinity of MPB. The high temperature XRD and dielectric characterisation for BMT-PT piezoceramics have been done by several authors [Chen et al. (2009); Leist et al. (2012); Randall et al. (2004); Moure et al. (2007)]. The paraelectric to ferroelectrics phase transition observed due to the anomalies found in the high temperature dielectric measurement is about 430ºC for BMT-PT in compositions close to MPB [Leist et al. (2012); Randall et al. (2004)]. Dielectric anomaly at ~620°C is also observed in some compositions of this system, which is attributed to the presence of $Bi_4Ti_3O_{12}$ phase in BMT-PT and defect inside the sample, as studied by thermal expansion [Moure et al. (2007), Randall et al. (2004)].

High temperature dielectric measurement has been done by earlier authors for BMZ-PT system also [Shabbir et al. (2007); Qureshi et al. (2007); Suchomel

et al. (2004); Pandey et al. (2014)]. High temperature dielectric anomaly for this system in the compositions close to MPB occurs around ~280ºC [Shabbir et al. (2007); Qureshi et al. (2007)]. The dielectric studies at cryogenic temperature for BMT-PT and BMZ-PT piezoceramics have not been done so far. The single crystal (1-x)$Pb(Mg_{1/3}Nb_{2/3})O_3$-x$PbTiO_3$ system [Lente et al. (2004)] have been reported to exhibit the dielectric relaxation below room temperature ~150k. There are two models viz. polarization fluctuations by chemical heterogeneities [Guo et al. (1990); Lente et al. 2004] and fractural cluster inside the normal ferroelectric domain [Viehland (2000); Priya et al. (2002)] to understand the origin of dielectric anomaly at cryogenic temperatures in this system. The dielectric anomaly at cryogenic temperatures is also reported in (1-x)$Pb(Ni_{1/3}Nb_{2/3})O_3$-x$PbTiO_3$ and is indirectly linked with a structural phase transition [Singh et al. (2007)] in the MPB compositions. However, this model will not explain the peak in dielectric relaxation below room temperatures for the cubic and tetragonal compositions that do not exhibit any structural phase transitions at cryogenic temperatures.

The present Chapter is devoted to the temperature dependent XRD and dielectric studies in selected compositions of BMT-PT and BMZ-PT piezoceramics below room temperature. The structure of BMT-PT for $x \leq 0.32$ is monoclinic phase with space group Pm, the structure is predominantly tetragonal with space group P4mm for $x \geq 0.40$, and the phase coexistence of monoclinic (space group Pm) and tetragonal (space group P4mm) phases is observed for the intermediate compositions with $0.33 \leq x \leq 0.40$ [Upadhyay et al. (2015)]. While in

case of BMZ-PT piezoceramics, it was shown that for the compositions with $x \leq 0.56$, the structure is cubic with space group Pm3m, the structure is observed to be predominantly tetragonal with space group P4mm for $x \geq 0.60$, and the phase coexistence of cubic (space group Pm3m) and tetragonal (space group P4mm) phases is observed for the intermediate compositions with $0.57 \leq x \leq 0.59$ [Pandey et al. (2014)]. Different compositions of BMT-PT and BMZ-PT piezoceramics across the MPB were selected to understand the difference in their dielectric and phase transition behaviour. For low temperature XRD studies, we have selected x=0.32 and x=0.35 compositions of BMT-PT. For the dielectric studies, we have selected x=0.32, 0.37 and 0.40 compositions of BMT-PT while x=0.55, 0.58, and 0.60 compositions of BMZ-PT. Low temperature XRD studies for BMT-PT do not show any splitting corresponding to any low temperature structural phase transformation. The dielectric permittivity measured at different frequencies around the cryogenic temperatures for BMT-PT and BMZ-PT solid solutions reveal Arrhenius type dielectric relaxation below room temperature.

5.2 Experimental details

Samples used in the present work were synthesised by the conventional solid state ceramic route as described in the chapter 2. For the temperature dependent powder XRD experiment of BMT-PT piezoceramics the sintered pellets were crushed into fine powder and annealed at 500^{o}C for twelve hours to remove the strains introduced if any during crushing. The temperature dependent dielectric measurements of sintered and then silver electroded pellets of BMT-PT and BMZ-PT piezoceramics at various frequencies from 1Hz to 1MHz were

carried out using a frequency-response analyzer (Novocontrol α-TB-Analyzer). The low temperature dielectric data were collected in closed sample cells. For cooling the sample down to 5K, a closed-cycle refrigerator with He-gas exchange attachment was used. Temperature-dependent capacitance data was measured with a heating rate of 0.8K/min in the range from 5K to 300K.

5.3 Results and discussion

5.3.1 Low temperature XRD studies for 0.68BMT-0.32PT

The evolution of powder X-ray diffraction patterns with varying temperature of the 0.68BMT-0.32PT ceramic in the temperature range 300K to 12K are shown in Fig. 5.1. As discussed in chapter 3, the room temperature structure of the BMT-PT piezoceramics for the composition with $x \leq 0.32$ is monoclinic with space group Pm. As can be seen from Fig. 5.1 there is no observable change in the XRD patterns of 0.68BMT-0.32PT piezoceramics on lowering the temperature from 300K to 12K. To illustrate more clearly, the evolution of XRD profiles for pseudocubic (110), (111) and (200) reflections are shown in Fig. 5.2 for BMT-PT piezoceramics with the composition x=0.32. We do not observe any clear signature of structural phase transition in diffraction pattern recorded below room temperatures. Neither the shift in the peak positions nor the broadening in peak is observed for all the reflections. Thus this material has negligible thermal contraction below room temperature in a wide temperature range of 12K to 300K.

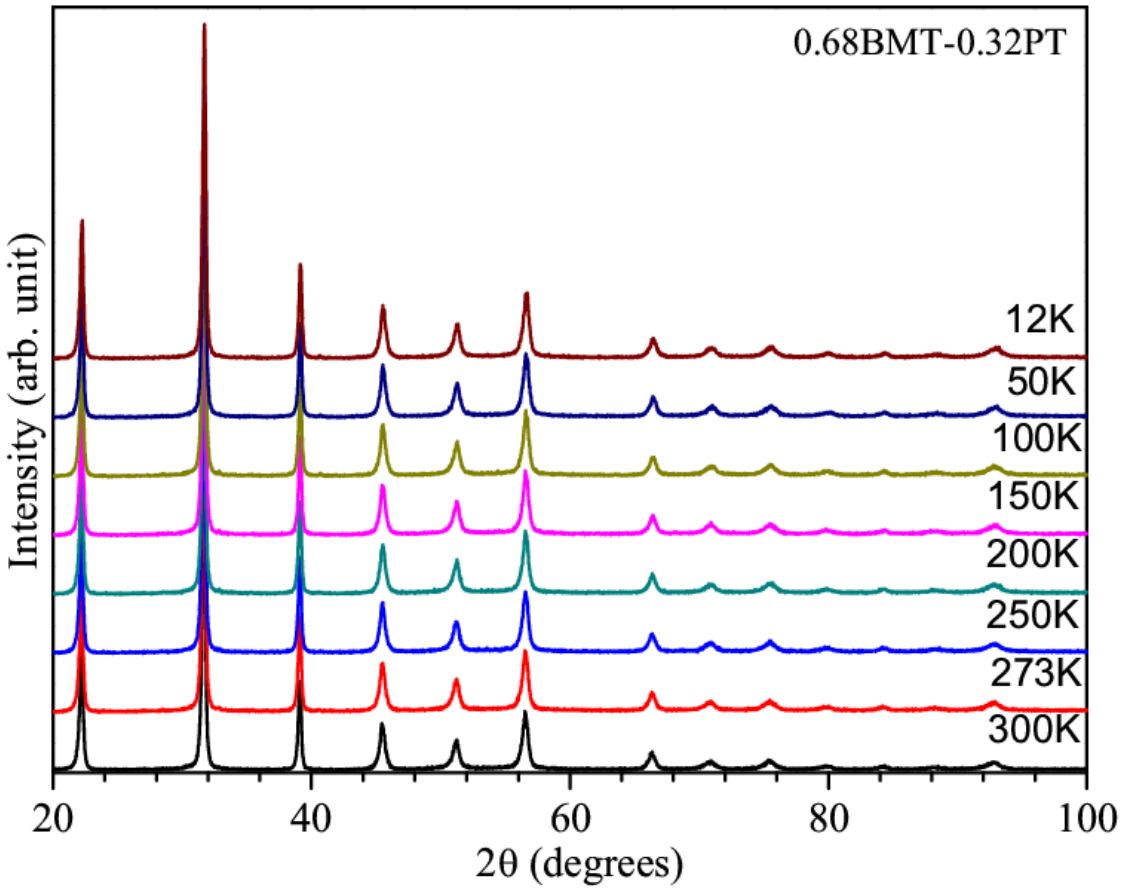

Fig.5.1 Evolution of XRD profiles for 0.68BMT-0.32PT piezoceramics with temperature.

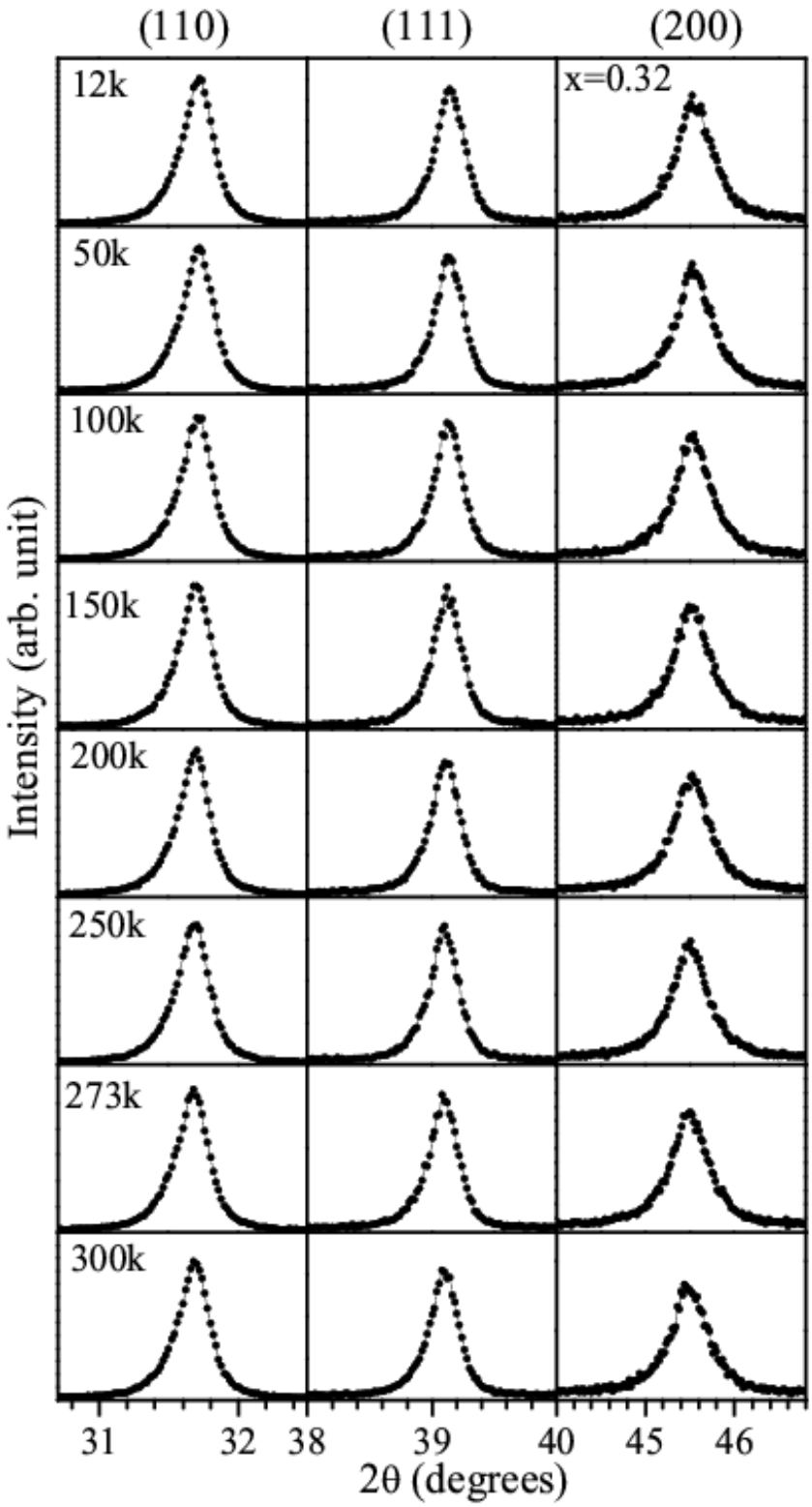

Fig.5.2 Evolution of pseudocubic (110), (111) and (200) XRD profiles for 0.68BMT-0.32PT below room temperature.

The Rietveld refinement of XRD data confirms that the structure of 0.68BMT-0.32PT piezoceramic is monoclinic phase with space group Pm for all the patterns below room temperature. Thus no structural phase transformation is observed below room temperature.

5.3.2 Low temperature XRD studies for 0.65BMT-0.35PT

Fig. 5.3 shows the evolution of powder X-ray diffraction patterns with varying temperature of 0.65BMT-0.35PT ceramics in the temperature range 300K to 12K. As can be seen from Fig. 5.3, the shapes of all the peaks do not exhibit any significant change on lowering the temperature in the temperature range from 300K to 12k. As discussed in chapter 3, the Rietveld refinement of XRD data confirms the structure for 0.65BMT-0.35PT piezoceramics to be coexistence of monoclinic (space group Pm) and tetragonal (space group P4mm) structures. For the better clarity, the evolution of XRD profiles for pseudocubic (110), (111) and (200) reflections with variation of temperature are shown in Fig. 5.4. As can be seen from Fig. 5.4, no significant change is observed for pseudocubic (110), (111), and (200) reflections on lowering temperature. The Rietveld refinement of XRD data for various temperatures also confirms that the room temperature structure of 0.65BMT-0.35PT piezoceramics does not change on varying the temperature below room temperature. The structure of 0.65BMT-0.35PT piezoceramics is coexistence of monoclinic (space group Pm) and tetragonal (space group P4mm) phases at cryogenic temperatures also. Similar to the composition with x=0.32, no shift in the XRD profile is observed on lowering temperature.

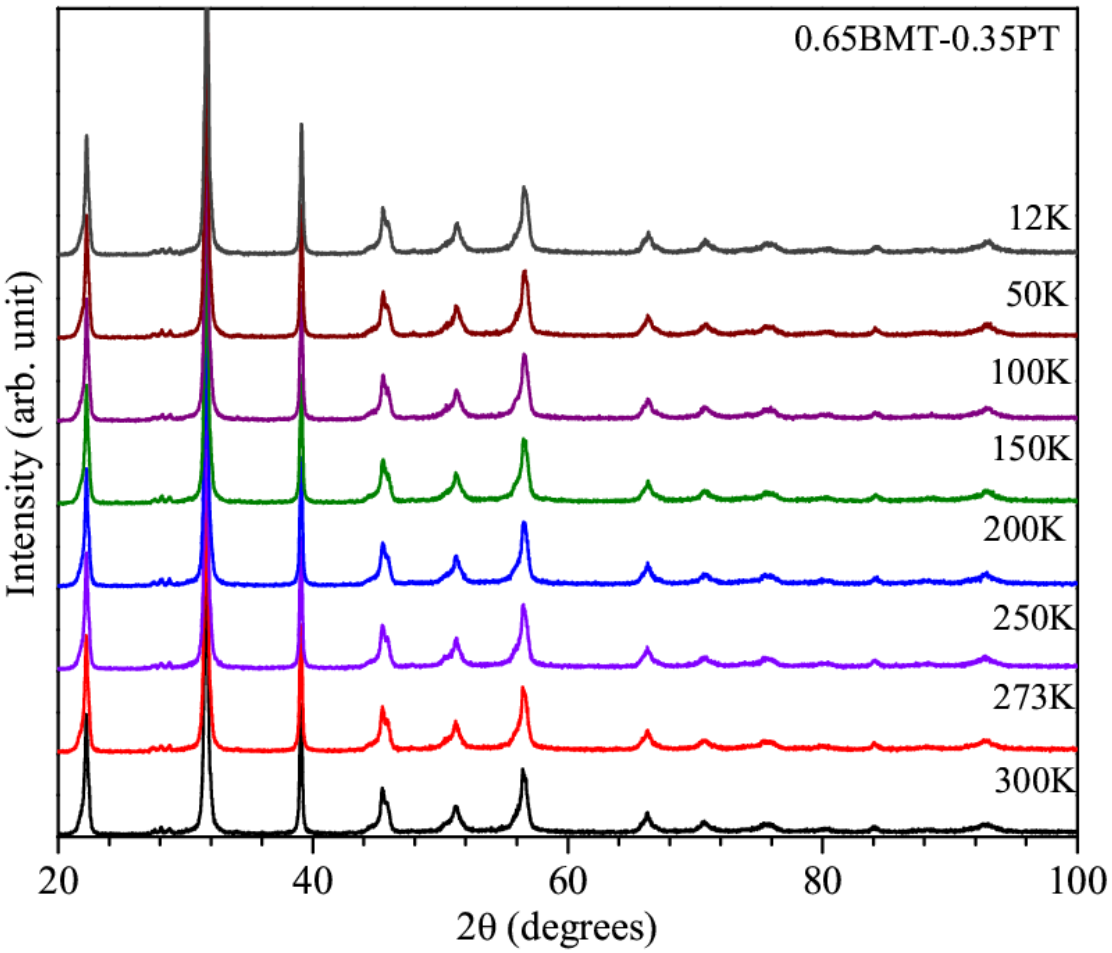

Fig.5.3 Evolution of XRD profiles for 0.65BMT-0.35PT piezoceramics with temperature.

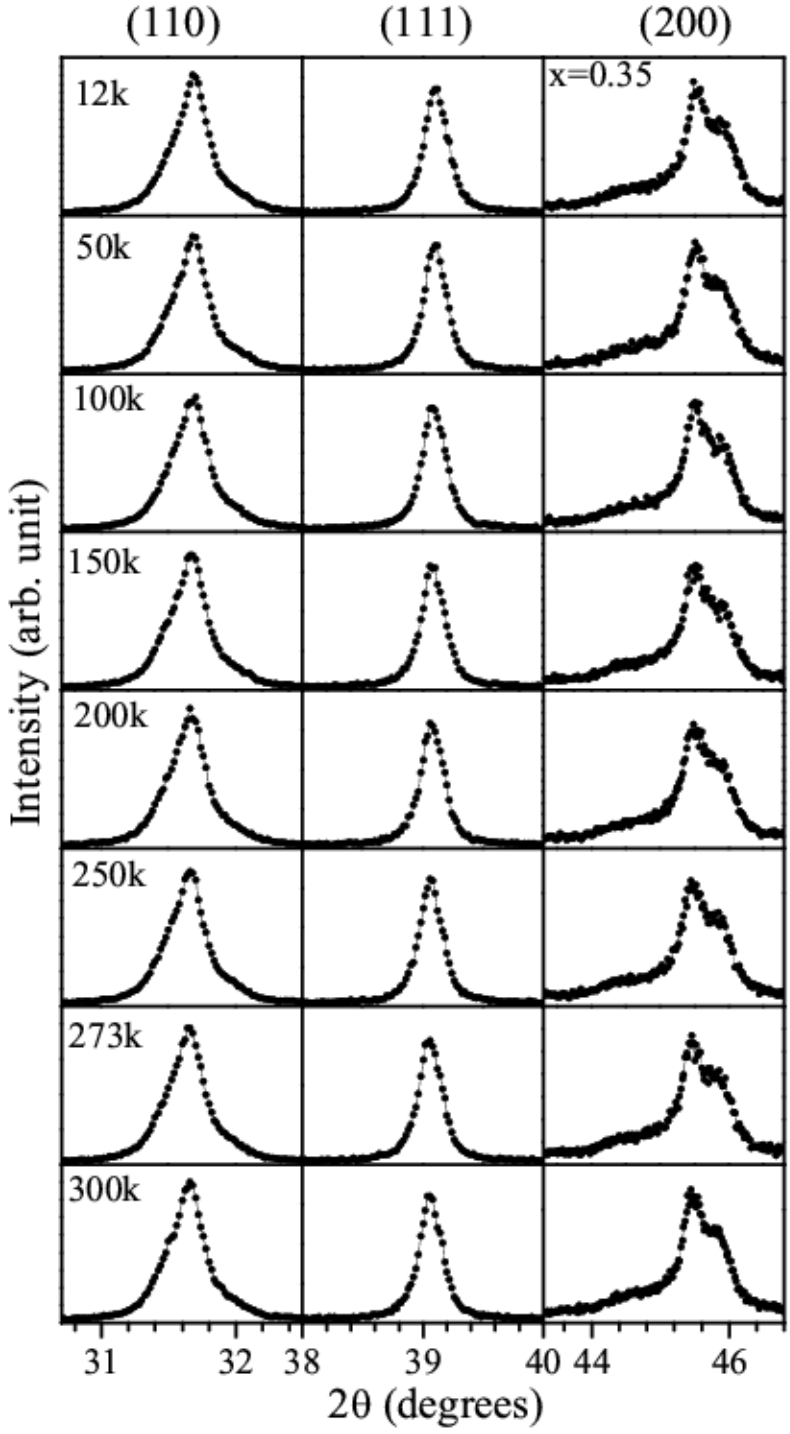

Fig.5.4 Evolution of pseudocubic (110), (111) and (200) XRD profiles for 0.65BMT-0.35PT with temperature.

Thus this composition of BMT-PT also exhibit negligible thermal contraction in the temperature range 300K to 12K. Hu et al. (2009) have reported zero thermal expansion at higher temperature in BMT-PT.

5.3.3 Low temperature dielectric studies in BMT-PT

To further verify the absence of any low temperature phase transition we have carried out the dielectric measurements at various frequencies on unpoled BMT-PT piezoceramics for the compositions with x=0.32, 0.37, and 0.40. Fig.5.5 depicts the temperature variation of real part of dielectric constant and loss tangent (tanδ) in the temperature range 5K to 300K, measured at various frequencies from 5Hz to $7x10^5$Hz for the compositions with x=0.32, 0.37, and 0.40. As can be seen from Fig. 5.5, the real part of dielectric constant does not show any clear anomaly on lowering the temperature from 300K to 5K, but the frequency dispersion at higher temperature is clearly seen for all the compositions. However, an anomaly is observed on lowering the temperature from room temperature to 5K with significant frequency dispersion in loss tangent (tanδ). The maxima of peak corresponding to the loss tangent (tanδ) shifts towards the higher temperature side with increasing measuring frequency from 5Hz to $7x10^5$Hz. This may happens due to relaxational freezing of the dipolar cluster [Cross (1987); (1994), Pandey (1995)]. For a given frequency, the maxima of peaks for loss tangent (tanδ) are shifting towards the lower temperature side on increasing the PT concentration in BMT-PT piezoceramics for the composition range x=0.32-0.40. These features suggest the relaxor nature in the BMT-PT for these compositions below room temperature.

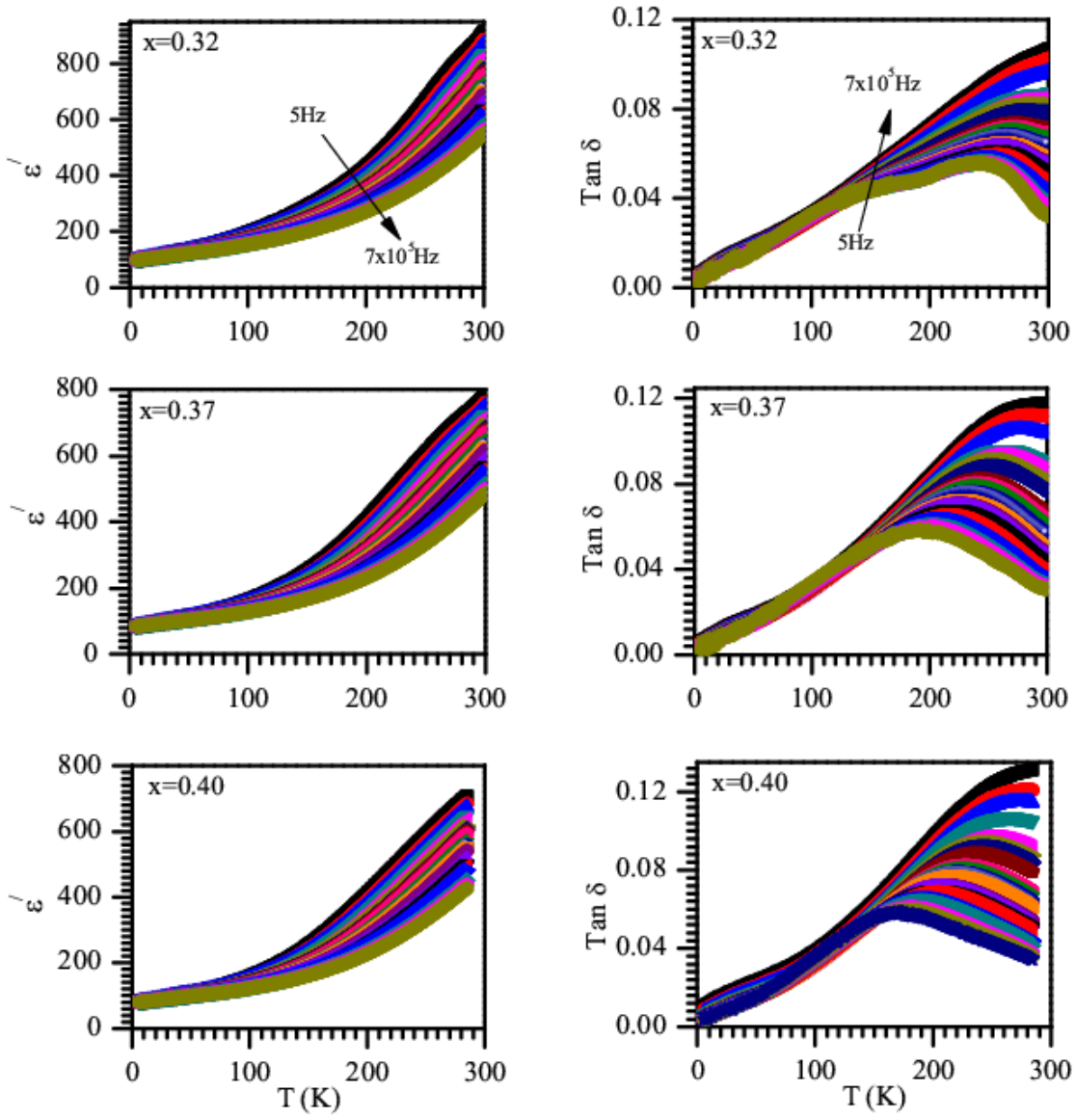

Fig.5.5 Temperature dependence of real parts (ε') of dielectric permittivity and loss tangent (tanδ) in the temperature range 5K to 300K, measured at various frequencies from 5Hz to $7x10^5$Hz for BMT-PT piezoceramics for the compositions with x=0.32, 0.37, and 0.40.

The relaxational peak in loss tangent observed below room temperature were modeled by Arrhenius and Vogel-Fulcher type fits which reveals Arrhenius type dielectric relaxation for all the compositions. The Arrhenius type behaviour for the relaxation time (τ), as obtained from the loss tangent ($\tan\delta$) data is shown in Fig. 5.6 for the compositions with x=0.32, 0.37 and 0.40. The relation between temperature and relaxation time (τ) for Arrhenius type [Bokov et al. (2006)] and Vogel-Fulcher type [Vogel (1921); Fulcher (1925)] are given in the equations (5.1) and (5.2), respectively.

$$\ln(\tau) = \ln(\tau_o) + \frac{Ea}{kT} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5.1)$$

$$\ln(\tau) = \ln(\tau_o) + \frac{Ea}{k(T-Tvf)} \quad \ldots\ldots\ldots\ldots \quad (5.2)$$

Where, E_a correspond to the activation energy, T_{vf} is the Vogal-Fulcher freezing temperature, τ is relaxation time and k is the Boltzmann constant. The linear curve for $\ln(\tau)$ vs $(1/T)$ shown in the Fig. 5.6 indicates the Arrhenius type behaviour. As can be seen from Fig. 5.5 the dielectric relaxation is prominent from just below the room temperature for all the composition of BMT-PT piezoceramics.

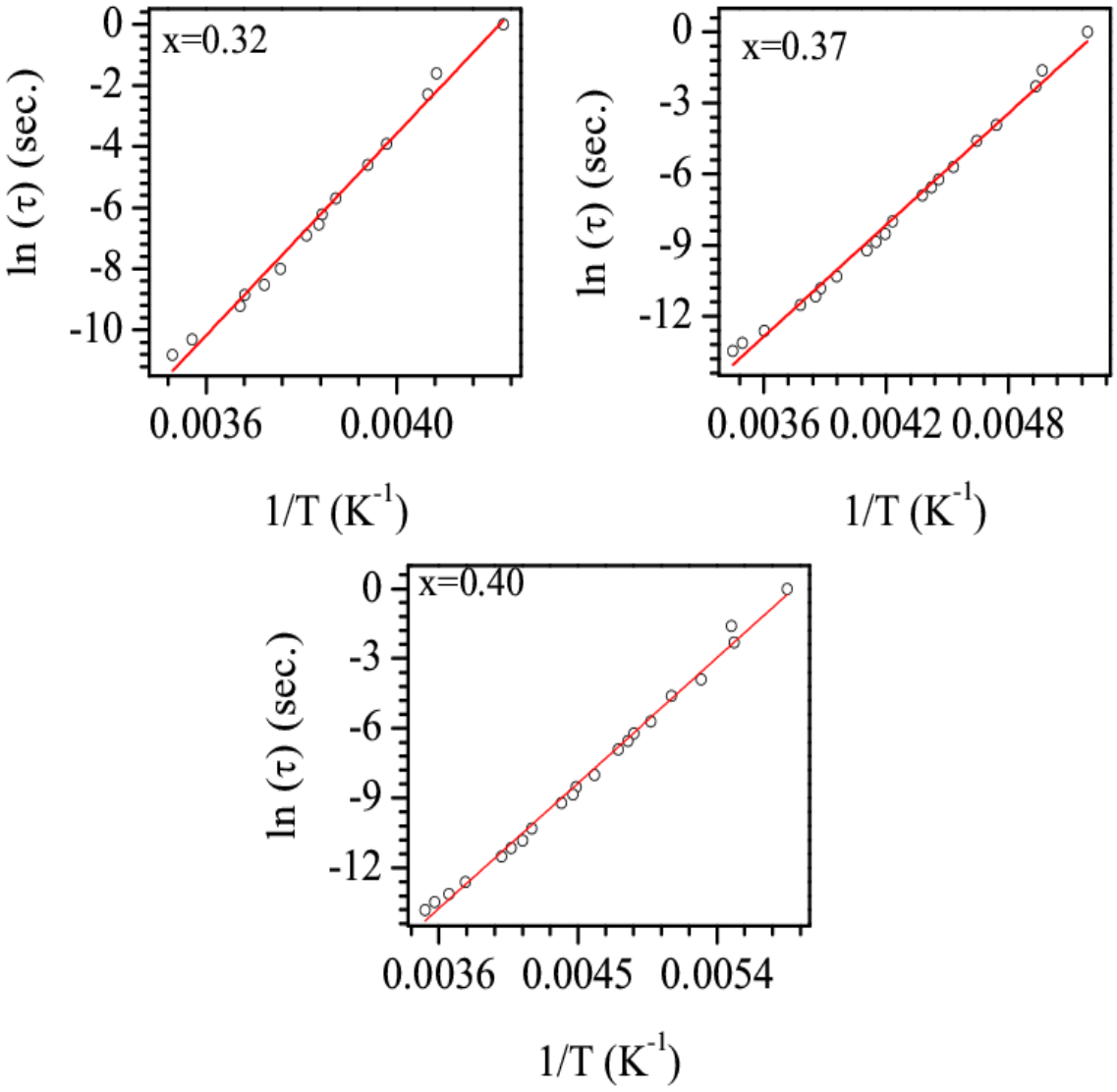

Fig.5.6 Arrhenius fits for the relaxation time, as obtained from anomaly in the loss tangent (tanδ) data in BMT-PT for the compositions with x=0.32, 0.37 and 0.40 BMT-PT.

5.3.4 Low temperature dielectric studies in BMZ-PT

Fig.5.7 depicts the temperature variation of real part of dielectric permittivity and loss tangent (tanδ) in the temperature range 5K to 300K measured at various frequencies from 5Hz to $7x10^5$Hz for the compositions with x=0.55, 0.58, and 0.60. As can be seen from Fig. 5.7, the real part of dielectric constant does not show very clear anomaly on lowering the temperature from 300K to 5K, but significant frequency dispersion at higher temperatures is clearly seen for all the compositions similar to BMT-PT piezoceramics. In contrast clear anomaly is observed below room temperature in loss tangent (tanδ) with significant frequency dispersion. Similar to BMT-PT piezoceramics the maxima of peak corresponding to the loss tangent (tanδ) for BMZ-PT piezoceramics also shifts towards the higher temperature side with increasing the frequency. This may also happens due to relaxational freezing of the dipolar cluster [Cross (1987), Pandey (1995)]. These features suggest relaxor nature in the BMZ-PT piezoceramics for all these compositions below room temperature. The Arrhenius type behaviour for the relaxation time (τ), as obtained from the anomaly in loss tangent (tanδ) data is shown in Fig. 5.8 for the compositions with x=0.58, and 0.60. The linear curve shown in the Fig. 5.8 indicates the Arrhenius type behaviour for the compositions with x=0.58, and 0.60.

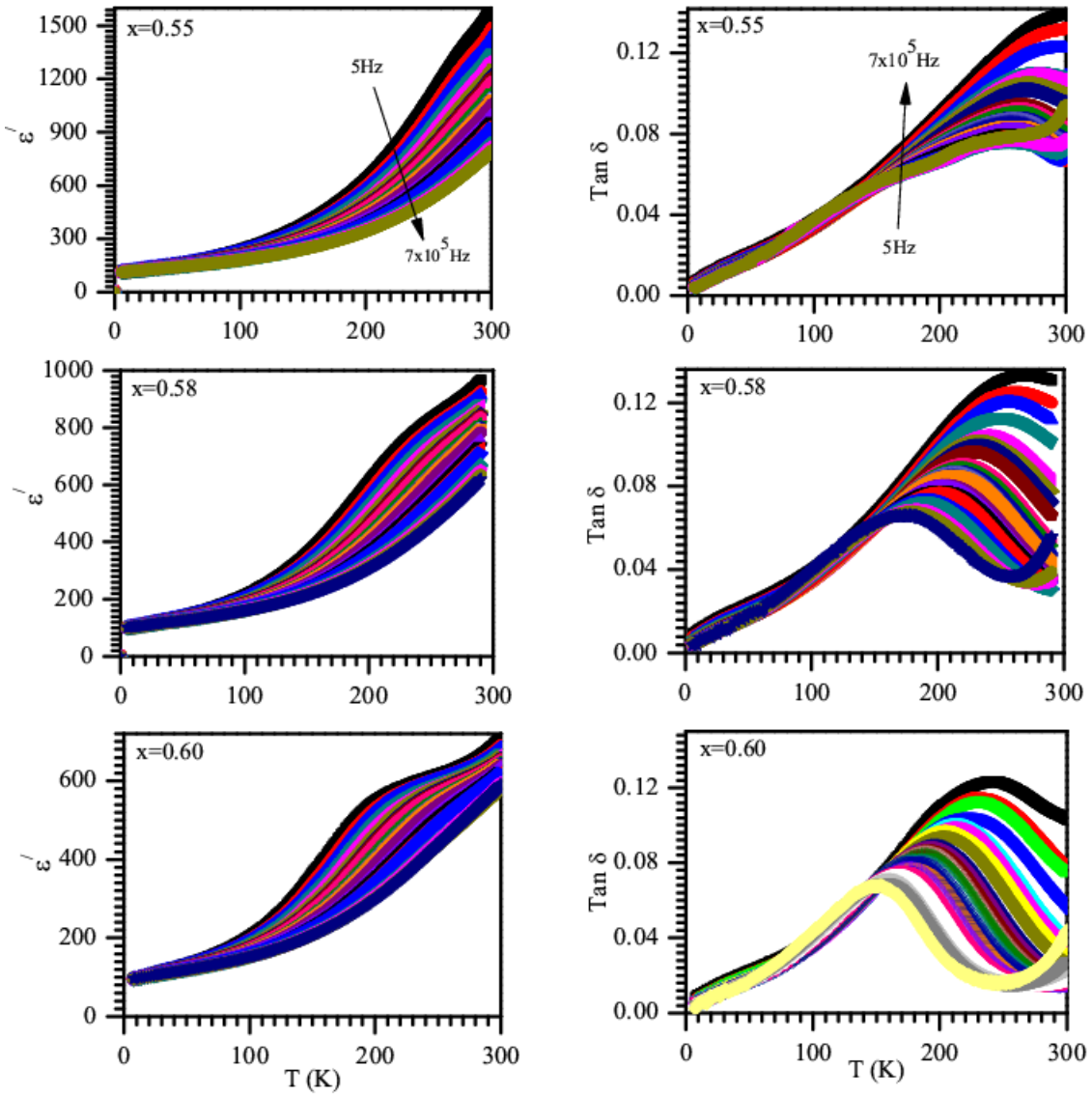

Fig.5.7 Temperature dependence of real parts (ε/), of dielectric permittivity and loss tangent (tanδ) in the temperature range 5K to 300K measured at various frequencies from 5Hz to $7x10^5$Hz in BMZ-PT piezoceramics for the compositions with x=0.55, 0.58, and 0.60.

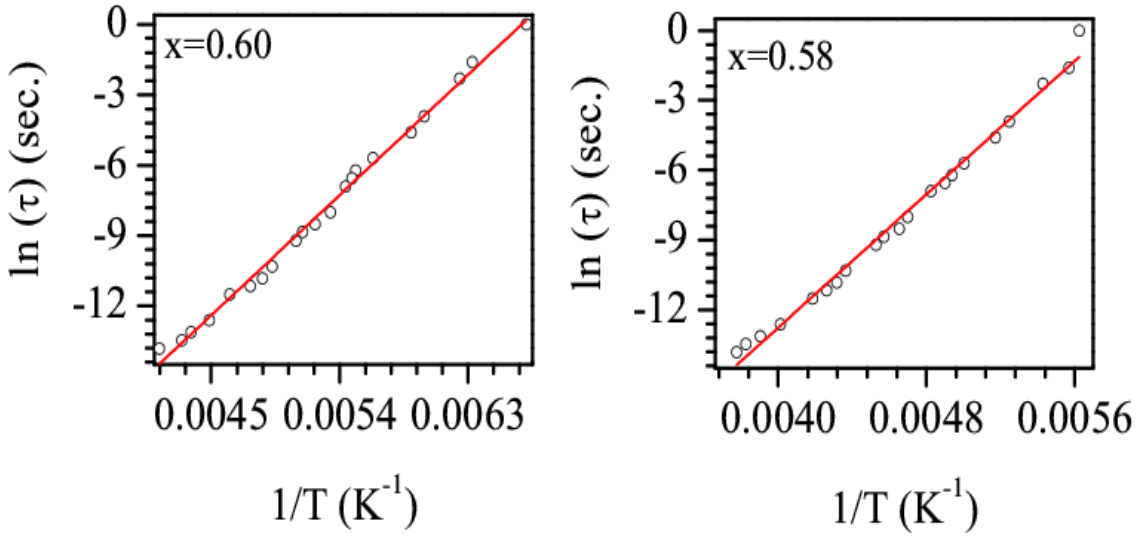

Fig.5.8 Arrhenius fits for the relaxation time, as obtained from anomaly in loss tangent (tanδ) data in BMZ-PT for the compositions with x=0.58, and 0.60.

5.4 Discussions

PZT and PMN-PT piezoceramics undergo the structural phase transformation below room temperature. The room temperature tetragonal (space group P4mm) phase of PZT piezoceramics transform to monoclinic (space group Cm) phase at cryogenic temperatures [Noheda et al. (1999)], while the tetragonal phase of PMN-PT transform to monoclinic (space group Pm) phase on lowering the temperature [Singh et al. (2006)]. Unlike PZT and PMN-PT, the BMT-PT and BMZ-PT piezoceramics do not undergo any structural phase transformation below room temperature. Chen et al. (2009) and Leist et al. (2012) have observed the structural phase transformation in the BMT-PT piezoceramics above room temperature (T_C) where ferroelectric phase transforms to paraelectric phase. The dielectric relaxation at higher temperatures is also observed in case of BMT-PT and BMZ-PT piezoceramics around the T_C. The low temperature dielectric relaxation in BMT-PT and BMZ-PT is investigated by us for the first time. The anomalies are observed in loss tangent of BMT-PT piezoceramics, but we did not observe any structural phase transformation below room temperature in BMT-PT. Up to now there is no clear explanation about the origin of the dielectric relaxation below room temperature. In present work we have not observed any structural phase transformation but we have observed the dielectric anomalies in loss tangent for all the composition viz tetragonal, monoclinic, and MPB phase. The possible reason and mechanism for the dielectric anomalies below room temperature needs to be investigated in future.

5.5 Conclusions

Different compositions of BMT-PT and BMZ-PT across MPB were characterized for low temperature dielectric behaviour. Anomaly in loss tangent (tanδ) at cryogenic temperatures is observed in all the compositions of BMT-PT and BMZ-PT irrespective of their crystal structure at room temperature. Dielectric relaxation below room temperature obeys Arrhenius type behaviour for all the composition of BMT-PT and BMZ-PT piezoceramics. The powder x-ray diffraction studies of BMT-PT below room temperature shows that there is no structural phase transformation for the composition with x=0.32, and 0.35 at cryogenic temperatures.