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Effects of DC bias fields on dielectric properties and phase transition behaviour of the $(1-x)[(\text{Pb}_{0.7}\text{Ba}_{0.3})(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]-x\text{PbTiO}_3$ system of morphotropic phase boundary compositions

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Abstract. The effect of DC bias on the dielectric properties and the phase transition behaviour of the $(1-x)[(\text{Pb}_{0.7}\text{Ba}_{0.3})(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]-x\text{PbTiO}_3$ ceramic system near the morphotropic phase boundary ($0.35 \leq x \leq 0.5$) have been investigated. The phase transition goes through a series of character changes from being a diffuse phase transition at $x = 0.35$ to being a more or less normal phase transition at $x = 0.5$. Between the extreme compositions, the system has shown a rather anomalous phase transition behaviour due to the existence of the morphotropic phase boundary centred around $x = 0.44$. On subjection to a series of external biases, the averaged dielectric constant maximum temperatures of the specimens of intermediate compositions tend to oscillate with respect to the bias field. Such anomalous dielectric behaviour is ascribed to the coexistence of multiple phases in a narrow composition band whose centre of gravity may be assigned as the morphotropic phase boundary.

1. Introduction

The compositions near the morphotropic phase boundary (hereafter referred to as MPB) of the $\text{Pb}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ (PZT) ceramic system have attracted wide ranging attention because their piezoelectric and dielectric properties are very useful in electronic device applications [1]. In the PZT ceramics, the tetragonal and rhombohedral phases coexist in a range of compositions across the MPB which is shown to be altered by applied stresses and DC bias fields [2, 3]. In the solid solutions of other diffuse phase transition (DPT) materials doped with PbTiO_3 (PT), the existence of MPB between the rhombohedral and tetragonal structures has also been reported [4, 5]. Like the dielectric behaviour of the PZT ceramic system, these ceramics with chemical compositions near the MPB possess anomalously high dielectric and piezoelectric constants.

Recently, anomalous behaviour of the dielectric constant K has been reported by Choi *et al* [6] and ShROUT *et al* [7] in MPB compositions of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -PT ceramics and single crystals. The poled ceramic specimens presented two different anomalies in the dielectric constant against temperature curve from the rhombohedral to the tetragonal ferroelectric phase and from the normal ferroelectric to paraelectric phase transition respectively. The effects of external fields on the dielectric responses in the temperature ranges around phase transitions were previously investigated in DPT

materials with MPB, e.g. in $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ [8] and $(\text{Pb},\text{Ba})(\text{Zr},\text{Ti})\text{O}_3$ [9]. In these DPT materials, the gradient of the dielectric constant against temperature curve on the low temperature side of the transition increased in magnitude after poling the specimens near the MPB. These changes in the K against temperature curves by poling seem to occur owing to the coexistence of multiple phases in the MPB compositions. However, more evidence is needed to prove the coexistence of multiple phases and to elucidate their effect on the dielectric responses and the DPT behaviour under direct DC bias fields.

In a separate study [10], we have determined the phase diagram of the ternary $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 ceramic system by x-ray powder diffraction and dielectric measurements. It has revealed that an MPB between the rhombohedral phase and the tetragonal phase exists in this system and the two phases coexist in a limited range of composition. Part of the evidence for the multiple phase coexistence will be presented in this study. Based on the work, we have chosen the composition range $0.35 \leq x \leq 0.5$ of $(1-x)[(\text{Pb}_{0.7}\text{Ba}_{0.3})(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]-x\text{PbTiO}_3$ (hereafter referred to as $(1-x)\text{PBMN}-x\text{PT}$). In particular, we have carried out a series of dielectric constant and dielectric loss tangent measurements under DC bias. We have focused our attention on the effects of DC bias fields on the phase transition behaviours of the specimens near the MPB.

2. Experimental procedure

Ceramic specimens of the $(1-x)\text{PBMN}-x\text{PT}$ series ($0.35 \leq x \leq 0.5$) were prepared from chemical reagent grade PbO , BaCO_3 , MgO , Nb_2O_5 , and TiO_2 . Mixtures of the raw material powders of given compositions were wet ball-milled in acetone, then dried and finally calcined at 900°C for 2 h. The calcined powders were reground, and pressed into discs of 12 mm diameter and 2–3 mm thickness. The green discs were sintered at 1250°C for 1 h under a PbO atmosphere in order to prevent loss of PbO . The apparent densities of sintered specimens were above 96% of the theoretical densities. No second phase has been observed by x-ray diffraction. For the dielectric measurements, sintered pellets were cut with a diamond wafering saw and polished to the final thickness of about 0.1 mm. Then electrodes were formed on the specimens with silver paste (Dupont No. 7075) by firing at 590°C for 5 min. The capacitance and the dielectric loss tangent were measured at several frequencies between 1 kHz and 1 MHz on a Hewlett-Packard 4194A Impedance/Gain Phase Analyzer interfaced with an IBM PC/AT while the DC bias field was varied up to 3.5 kV cm^{-1} . The specimen under investigation was housed in a thermostat, and the specimen temperature was varied from -150°C to 300°C . During dielectric measurements, the test specimens were initially heated to temperatures far above their mean Curie points to eliminate the DC bias histories and then cooled rapidly to below -150°C with liquid nitrogen. The specimen was heated at a constant rate of 2°C min^{-1} and its temperature was monitored, by a Fluke 2190A Digital Thermometer coupled to a copper-constantan thermocouple, to an accuracy of $\pm 0.5^\circ\text{C}$. Measured capacitance and specimen dimensions were used to calculate the relative dielectric constant K .

3. Experimental results and discussion

Figure 1 shows a plot of the dielectric constant and $\tan \delta$ of $0.65\text{PBMN}-0.35\text{PT}$ as a function of temperature with the frequency as a parameter. The frequency dependence of the dielectric response shows a typical characteristic of DPT material or relaxor.

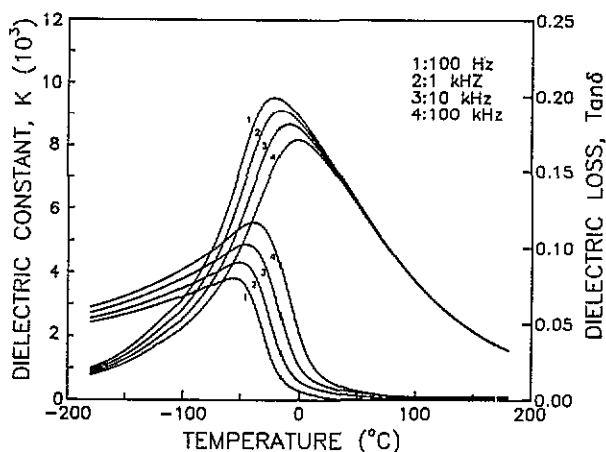


Figure 1. Temperature dependence of the dielectric constant K and the dielectric loss $\tan \delta$ at different frequencies for $0.65[(\text{Pb}_{0.7}\text{Ba}_{0.3})(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]-0.35\text{PbTiO}_3$ ceramics.

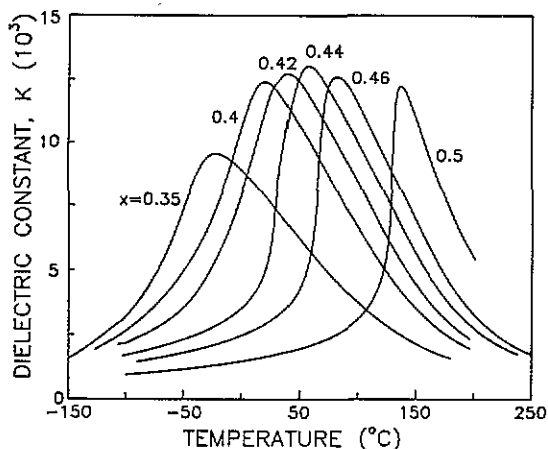


Figure 2. Dielectric constants of $(1-x)[(\text{Pb}_{0.7}\text{Ba}_{0.3})(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]-x\text{PbTiO}_3$ ceramics as a function of temperature measured at 1 kHz.

The dielectric constant against temperature behaviour at 1 kHz is shown in figure 2 for a series of $(1-x)\text{PBMN}-x\text{PT}$ solid solutions. The K maximum increases with increasing x until $x = 0.44$ is reached. However, in the range of $x > 0.44$, the K maximum decreases with increasing x . The temperature T_a at which the dielectric constant maximum is located increases as the PT content increases.

Figure 3 shows the x-ray diffraction results for the $(1-x)\text{PBMN}-x\text{PT}$ series at room temperature. For $x = 0.35$ and 0.4 , the diffraction line corresponds to $\{200\}$ of the cubic phase since the transition temperature is below room temperature. It has been confirmed by x-ray diffraction at liquid nitrogen temperature that the structure of the low temperature ferroelectric phase of these compositions has a rhombohedral symmetry. In the case of the compositions for which transition temperatures are higher than room temperature, the x-ray diffraction profiles correspond to a ferroelectric phase that

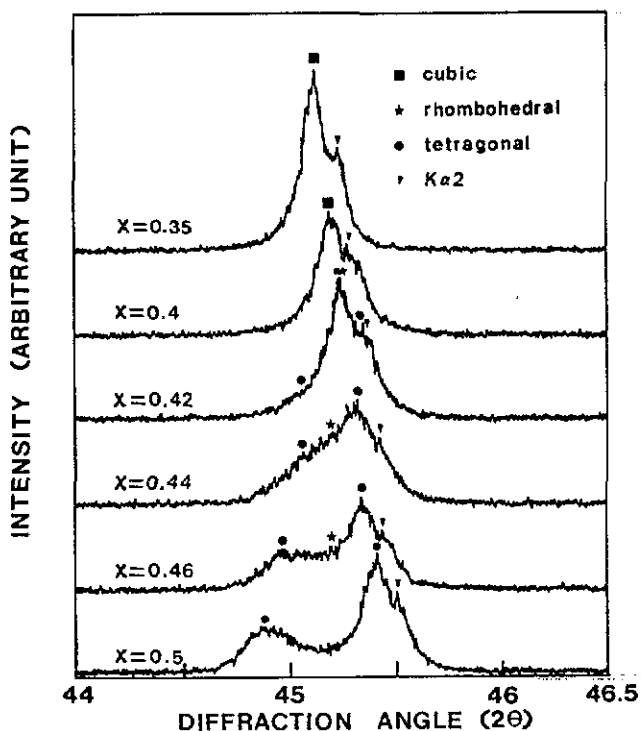


Figure 3. Variation of x-ray diffraction profile with compositional change in $(1-x)\{(Pb_{0.7}Ba_{0.3})(Mg_{1/3}Nb_{2/3})O_3\}-xPbTiO_3$ for $0.35 \leq x \leq 0.5$.

deviates from cubic symmetry. However, when the transition temperature is just above room temperature, $x = 0.42$, it is difficult to determine the symmetry of the ferroelectric phase at room temperature by x-ray diffraction since x-ray peak splitting has not been observed. Therefore, this specimen is a mixture of cubic paraelectric and ferroelectric phases around the transition temperature. In the composition range $0.42 \leq x \leq 0.46$, the diffraction line corresponding to $\{200\}$ of the low temperature rhombohedral phase is located between the $(200)/(020)$ and (002) lines of the tetragonal phase. In particular, in the case of $x = 0.44$, the high angle $(200)/(020)$ line and the low angle (002) line of the tetragonal phase nearly overlap with that of the rhombohedral phase. The complete separation of the tetragonal $(200)/(020)$ and (002) lines are apparent at $x = 0.5$. The line intensity of $x = 0.5$ that corresponds to the $(200)/(020)$ line couple is nearly twice that of the (002) line. The latter fact confirms the tetragonality of the low temperature phase at $x = 0.5$. In view of the variations in the dielectric constant behaviour and the x-ray diffraction profiles, we can infer the existence of an MPB which separates the rhombohedral and the tetragonal phases. The MPB is located near $x = 0.44$, at which the dielectric constant maximum takes the highest value.

The DPT or the relaxor behaviour of $Pb(Mg_{1/3}Nb_{2/3})O_3$ (hereafter referred to as PMN) is already well established [11, 12]. For that matter, PBMN is a no less DPT ferroelectric itself (figure 1). Granting that the existence of an MPB is established, a question arises as to how the DPT behaviour is changed across the MPB. The DPT behaviour is still retained to a certain degree in the entire compositional range under consideration. One measure

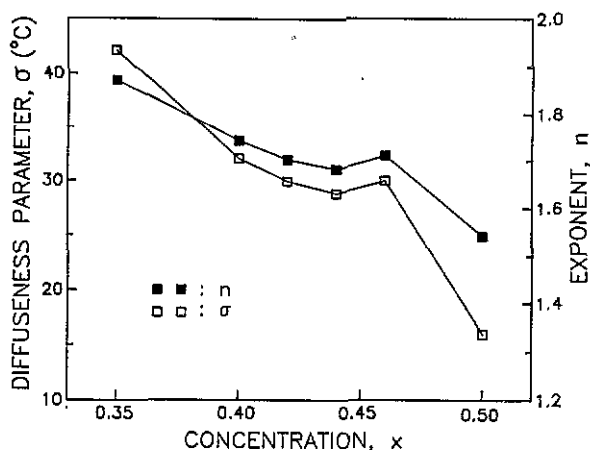


Figure 4. Variation of exponent n and diffuseness parameter σ as a function of composition x for the $(1-x)[(Pb_{0.7}Ba_{0.3})(Mg_{1/3}Nb_{2/3})O_3]-xPbTiO_3$ system.

of the extent of the DPT is given by the broadness of the dielectric constant against temperature curve. The best fit to the curve for the DPT dielectric constant near the transition has been presented in the form [13, 14, 15]

$$(K_m - K)/K = (T_a/\sigma)^n (T/T_a - 1)^n \quad (1)$$

where K_m is the maximum value of the dielectric constant at the apparent transition T_a , σ is a measure of the extent of thermal diffuseness, and n is an exponent also of another measure of the DPT. In the extreme case of $n = 1$, σ is simply a Curie-Weiss constant, while σ^2 approximates a degree of the temperature fluctuation of the polarization distribution in a Gaussian approximation for $n = 2$ [13]. The exponent n can be determined from the slope of the log-log plot of equation (1), while σ can be determined from the y-axis intercept of the same plot. Both n and σ can together indicate the extent of the DPT.

In figure 4, n and σ are shown as a function of the PT concentration x . Both n and σ vary similarly with x . Although an ideal DPT is presumed at $n = 2$, n can only reach its highest value of 1.87 at the lowest concentration $x = 0.35$. The latter value is still larger than that of the reported value for PMN of 1.64 [13]. Instinctively the DPT behaviour will decrease with each increasing PT content, the n value decreasing to 1.54 at $x = 0.5$. However, the diffuseness of the transition is not diminished until after the PT content passes by the MPB. One distinct feature that ought to be pointed out at this juncture is the fact that both n and σ remain virtually unchanged in the compositional range between $x = 0.42$ and 0.46 . The cause of the anomalous dielectric behaviour may be assigned to the multiphase coexistence in the compositions near the MPB.

Figure 5 shows the temperature dependence of the dielectric constant K of the off-MPB specimens $x = 0.35$, 5(a), and $x = 0.5$, 5(b), at 100 kHz under various DC bias fields up to 3.5 kV cm^{-1} . The system 0.65PBMN-0.35PT exhibits a typical relaxor behaviour. A considerable curve shift is seen in the vicinity of the transition temperature T_a . As the bias E_d increases, the dielectric constant maximum K_m is lowered, the K versus temperature curve becomes more rounded and T_a moves toward a higher temperature. This latter phenomenon is quite consistent with a manifestation of the first-order phase transition [16]. Such a DC field effect on the dielectric constant has been already observed

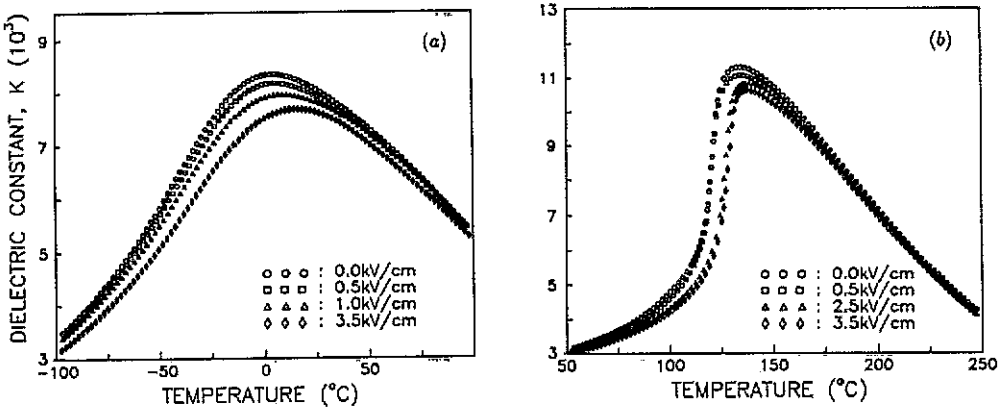


Figure 5. Temperature dependence of the dielectric constant K at 100 kHz for different DC bias field E_d at atmospheric pressure for (a) $x = 0.35$ and (b) $x = 0.5$.

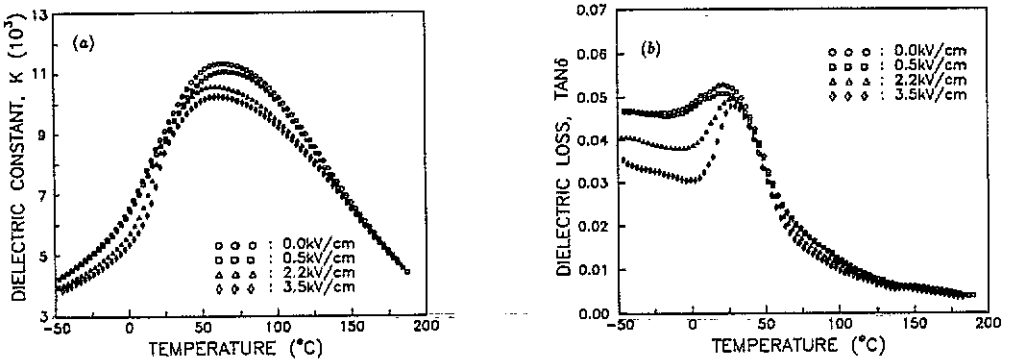


Figure 6. The temperature dependence of (a) the dielectric constant K and (b) the dielectric loss $\tan \delta$ for $x = 0.42$ at 100 kHz for different DC bias fields E_d .

in DFT ferroelectrics $\text{Sr}_{0.67}\text{Ba}_{0.33}\text{Nb}_2\text{O}_6$ (SBN) [17] and $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ (PFN) [18]. The measured rate of the T_a shift with increasing bias E_d for 0.65PBMN–0.35PT is $3.3^\circ\text{C kV}^{-1}\text{ cm}$ which is comparable with $3.5^\circ\text{C kV}^{-1}\text{ cm}$ for pure PMN [11] and $3.9^\circ\text{C kV}^{-1}\text{ cm}$ for SBN [17]. The decrease of the dielectric constant $K(E_d)$ under bias E_d over unbiased $K(0)$ shows a similar rate of decrease of those of PMN and SBN.

The system 0.5PBMN–0.5PT, which is primarily tetragonal, exhibits an inclination toward the normal ferroelectric phase transition. For instance, T_a increases on increasing bias E_d and the K against temperature curve narrows near the transition. The rate of the T_a shift with DC bias is only smaller than that of 0.65PBMN–0.35PT. The rate $K_{\max}(E_d)/K_{\max}(0)$ is likewise smaller.

In figures 6(a) and (b), the bias effect on the dielectric constant and $\tan \delta$ of the MPB specimen of 0.58PBMN–0.42PT is shown. Two considerable featural differences from the dielectric behaviours of both the off-MPB specimens of $x = 0.35$ and $x = 0.5$ are clearly seen. A complex behavioural tendency under DC bias is displayed near T_a . The first is that the rising part of the K against temperature curve below the apparent transition T_a becomes steeper contrary to the expectation that the phase transition ought to broaden

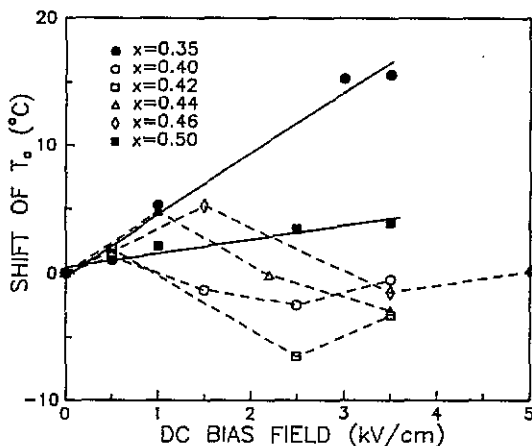


Figure 7. Shift in the temperature T_a with increasing DC bias field E_d for $(1-x)[(Pb_{0.7}Ba_{0.3})(Mg_{1/3}Nb_{2/3})O_3]-xPbTiO_3$ for $0.35 \leq x \leq 0.5$.

with increasing DC bias [16]. The value of the dielectric constant maximum decreases with increasing bias. The second is the shift of the K maximum temperature to a lower temperature under moderate field biasing ($E_d \geq 0.5 \text{ kV cm}^{-1}$). The second change may be directly linked to the cause of the first change. As shown in figure 6(b), $\tan \delta$ has decreased on DC biasing in the whole range of measured temperatures. The temperature of the $\tan \delta$ maximum slightly increases with the bias. Such bias effects on the dielectric properties are also observed in all of the other specimens of MPB compositions.

The shifts in temperature T_a ($\Delta T_a = T_a(E_d) - T_a(0)$) under bias E_d for the specimens of $x = 0.35$ to $x = 0.5$ are together shown in figure 7. As already stated above, T_a s of the off-MPB specimens tend to increase with increasing bias. T_a s of the MPB specimens on the other hand seem to fluctuate. In particular, the variation with T_a for 0.58PBMN-0.42PT may be stated as follows. When the bias is smaller than a certain critical value, the rate of change of the dielectric constant with change in the bias field becomes similar to that of DPT specimens. When the DC bias is further increased, T_a decreases in parallel with the steepening of the low temperature portion of the K against temperature curve. As the bias is further increased, T_a is again shifted to a higher temperature. If we consider that these specimens are a mixture of retained cubic paraelectric, rhombohedral and tetragonal ferroelectric phases in the vicinity of the phase transition, as can be deduced from figure 3, we can see the observed results more clearly. In the mixture, the phase fraction changes as a function of PT concentration under zero bias. Additionally, we can assume that each phase has its own distribution of Curie temperature T_c and thus conjecture that the physical properties of the mixture are critically dependent on the fraction of the tetragonal and rhombohedral phases in the MPB region. Hence, the fraction of the coexisting phases will also determine the shape of the K against T curve. As can be seen in figure 2, it is thus quite natural to expect that the low temperature portion will be reduced with decrease in the rhombohedral phase which contributes preferentially the low temperature portion of the K against T curve. The effect of bias is not only to shift T_a in accordance with Landau and Devonshire's free energy function [16] but also to induce a structural transition from one ferroelectric phase to the other. According to Stotz [2] and Amin *et al* [3], the MPB of the PZT system is shifted to the high

Zr concentration direction under bias. This is equivalent to stating that in a mixture of rhombohedral and tetragonal phases the tetragonal phase becomes more stable, and so the bias field induces a structural transition from the rhombohedral phase to the tetragonal phase. As inferred from the MPB behaviour in PZT ceramics, this pattern of change may be explained in terms of the relative stability of rhombohedral and tetragonal phases under biasing. A high DC field preferentially stabilizes the tetragonal phase. As a consequence, the contribution to permittivity of the tetragonal phase becomes larger. Hence, the high temperature segment of the dielectric constant curve is weighted more heavily after high field biasing. However, because of the low K value of the tetragonal phase, the higher temperature segment of the K against temperature curve near the transition can be diminished. We once again emphasize that this interpretation is only made possible by the stipulation that the rhombohedral phase has an overall lower transition temperature than the tetragonal phase.

The falling $\tan \delta$ below the transition on increasing temperature, as shown in figure 6(b), clearly indicates that the dielectric loss in 0.58PBMN–0.42PT originates from a source other than a DC charge conduction process. The dielectric loss due to the electrical conduction process may be traced either to the bulk heterogeneities or to the slow charge relaxation of the localized space charge accumulated at the interfaces (mainly domain walls and grain boundaries). Ruling out the charge carrier contribution to the dielectric loss near the transition, the other likely possible loss mechanism is attributed to the polarization displacement. The response of the dielectric loss to the external field is rather sensitive in the ferroelectric phase. At the same time the shape of the $\tan \delta$ against temperature curve sharpens near the transition temperature with the increasing external field. The $\tan \delta$ reduction below the transition may also be ascribed to the reduced contribution from the rhombohedral phase as a consequence of the field-induced structural transition from the coexisting rhombohedral to tetragonal phase with a smaller $\tan \delta$.

In figure 8, the loss, $\tan \delta$, against temperature curve with the PT content as a parameter is shown. In the immediate vicinity of MPB composition $x = 0.42$, the $\tan \delta$ response to the additional PT content is strikingly similar in pattern to that of the bias-induced effect. The extent of T_a change and the sharpening of the $K(T)$ curve is even more prominent in the latter case. It is thus apparent that the volume fraction of the tetragonal phase increases with the increasing PT content in the mixture. For this reason, the averaged transition temperature is likely to increase with the increasing PT content. As the tetragonal phase has a peaked $\tan \delta$ curve, the $\tan \delta$ of the multiple phase mixture will sharpen up corresponding to the increasing PT content. This is exactly the same reasoning we used to explain the DC bias effect on the loss, $\tan \delta$, behaviour of the MPB specimens.

4. Summary

The experimental behaviour of the dielectric constant for the compositions in the MPB region of the $(1 - x)[(\text{Pb}_{0.7}\text{Ba}_{0.3})(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3] - x\text{PbTiO}_3$ ceramic system imply that the phase transition of the system is diffuse overall. In the specimens of $x = 0.35$ and $x = 0.5$ that exhibit typical DPT and more or less normal ferroelectric phase transition behaviours respectively, the maximum K -values are lowered and the temperatures of the dielectric constant maximum are shifted to higher values with $dT_a/dE_a = 3.3^\circ\text{C kV}^{-1}\text{ cm}$ and $1.18^\circ\text{C kV}^{-1}\text{ cm}$ as the applied DC bias field E_a increases. Anom-

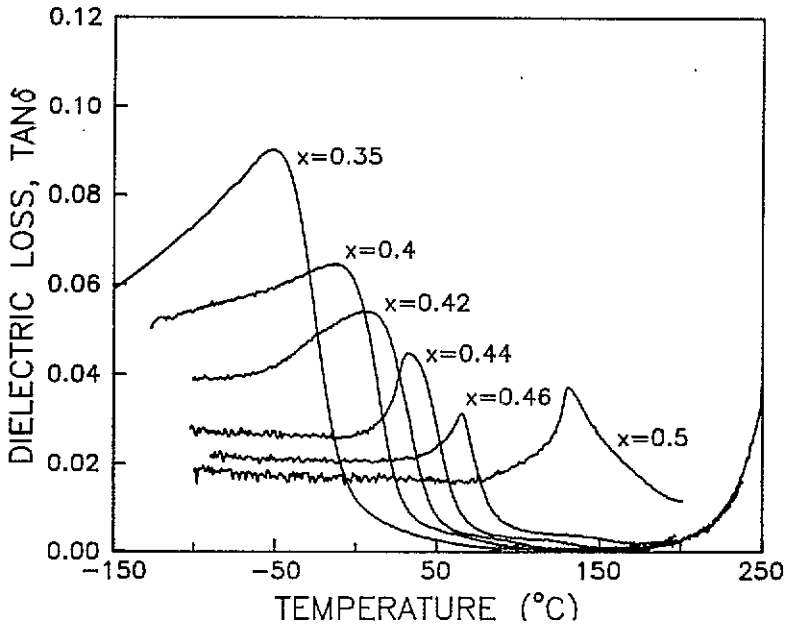


Figure 8. The temperature dependence of the loss $\tan \delta$ in $(1-x)[(\text{Pb}_{0.7}\text{Ba}_{0.3})(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]-x\text{PbTiO}_3$ near the transition temperature measured at 1 kHz. Near the MPB composition ($x = 0.42$), $\tan \delta$ shifts toward higher temperatures and at the same time its curve shape sharpens up with increasing PT concentration, x .

alous behaviour under the DC bias field in the specimens lying near the MPB compositions is ascribed to the coexistence of a paraelectric and two ferroelectric phases in the vicinity of the phase transition. In a certain range of electric field intensity, phase transition from rhombohedral to tetragonal phase is induced by the applied DC bias field. Consequently, the shape and thus symmetry of the K against T curves is changed due to the variation of the distribution of the constituent phases in the MPB ceramic specimens.

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