

# Study of the structure and electrical properties of PMN-PNN-PT ceramics near the morphotropic phase boundary

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**Abstract** A series of  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{PbTiO}_3$  (PMN-PNN-PT) ceramics with compositions of  $(1-x)(0.67\text{PMN}-0.33\text{PT})-x(0.64\text{PNN}-0.36\text{PT})$  ( $x = 0.1-0.9$ ) were synthesized using the columbite precursor method. The phase structures, as well as the dielectric and piezoelectric properties of the ceramics were investigated in detail. X-ray diffraction results demonstrate that all the samples possess a pure perovskite structure. It is found that the morphotropic phase boundary (MPB) region of the PMN-PNN-PT ternary system is located near the line connecting the MPBs of the PMN-PT and PNN-PT binary systems. A high value of the maximum dielectric constant ( $\epsilon_m = 45540$ , at 1 kHz), together with a high value of the piezoelectric coefficient ( $d_{33} = 780$  pC/N), were obtained for the composition  $x = 0.2$ . The results show that a partial substitution of PNN-PT for PMN-PT can lead to improved electrical properties in this ternary system.

**Keywords** Relaxor ferroelectrics · Morphotropic phase boundary · PMN-PNN-PT · Dielectric properties · Ferroelectric properties · Piezoelectric properties

## 1. Introduction

$\text{Pb}(\text{B}'_{1/3}\text{B}''_{2/3})\text{O}_3$ -type complex perovskites, such as  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN),  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PZN) and

$\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PNN), are important relaxor ferroelectrics [1, 2]. In recent years, binary solid solutions of these perovskites with normal ferroelectrics  $\text{PbTiO}_3$  (PT) with compositions near the morphotropic phase boundary (MPB) have attracted particular attention, owing to the excellent electrical properties of these systems, which make them promising candidate materials for a large number of applications in both electronics and microelectronics [3, 4]. For instance, it has been reported that the piezoelectric coefficient ( $d_{33}$ ) of PZN-PT single crystals with a composition near the morphotropic phase boundary can reach 2500 pC/N [3], much higher than that of the widely used  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  (PZT) ceramics [5]. To understand the origin of the anomalous electrical properties of such systems, the phase structures of MPB compositions have been thoroughly investigated. It was originally thought that MPB compositions were characterized by the coexistence of tetragonal and rhombohedral phases. It is now accepted that the very high electromechanical response of these materials is directly related to the existence of low symmetry monoclinic phases [6, 7].

Compared with the binary systems described above, there are considerably fewer reports on the phase structures and electrical properties of MPB compositions in relaxor-PT ternary systems. Several  $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{PbTiO}_3$  (PSN-PMN-PT) and  $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{PbTiO}_3$  (PSN-PNN-PT) systems with compositions on the MPB lines between the MPBs of the corresponding binary systems [8, 9] have been investigated by Yamashita et al. A value of  $d_{33} = 640$  pC/N was obtained in the former system. Pan et al., in their investigation of PZN-PNN-PT systems, demonstrated the use of linear combinations of MPB compositions of two binary systems as an effective way to search for the approximate MPB regions in corresponding ternary systems [10].

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Recently Kim et al. reported that the peak dielectric constant in the  $\text{Pb}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PT}$  ceramic system was as high as 37900 at 1 kHz [11]. All these results indicate that the solid solutions of relaxor-PT ternary systems are worthy of further investigation.

To our knowledge, there have been few published studies on the PMN-PNN-PT ternary system. In this paper, the phase structures and electrical properties of near MPB compositions in the PMN-PNN-PT ternary system were investigated.

## 2. Experimental procedure

As the MPB in the PMN-PT system exists at a composition of 33 mol% PT [12, 13], while the MPB in the PNN-PT system occurs at 36 mol% PT [14], we therefore select compositions of  $(1-x)(0.67\text{PMN}-0.33\text{PT})-x(0.64\text{PNN}-0.36\text{PT})$  for this study. The possible MPB region of the PMN-PNN-PT (hereafter denoted as PMNNT) system is illustrated in Fig. 1 by black dots, which show the compositions used in this investigation.

The columbite precursor method [15] was used to prepare the PMNNT powders. Firstly, reagent-grade  $\text{Nb}_2\text{O}_5$  and  $\text{Ni}(\text{Ac})_2 \cdot 6\text{H}_2\text{O}$  were mixed. The mixture was then ball-milled in acetone, and then calcined at  $1000^\circ\text{C}$  for 6 h to form  $\text{NiNb}_2\text{O}_6$ . A similar procedure was used for  $\text{Mg}(\text{OH})_2 \cdot 4\text{MgCO}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Nb}_2\text{O}_5$  to produce  $\text{MgNb}_2\text{O}_6$ . The  $\text{NiNb}_2\text{O}_6$ ,  $\text{MgNb}_2\text{O}_6$ ,  $\text{PbO}$  and  $\text{TiO}_2$  powders were then mixed to give the PMNNT compositions 1~9 listed in Table 1. Almost 3 mol% excess  $\text{PbO}$  was added in each case in order to compensate for lead loss during sintering. After further ball-milling and drying, the PMNNT powders were obtained by heating at  $900^\circ\text{C}$  for 4 h. The powders of

**Table 1** Compositions of the different ceramics according to  $(1-x)(0.67\text{PMN}-0.33\text{PT})-x(0.64\text{PNN}-0.36\text{PT})$

Sample	X	PMN	PNN	PT
PMNNT1	0.1	0.603	0.064	0.333
PMNNT2	0.2	0.536	0.128	0.336
PMNNT3	0.3	0.469	0.192	0.339
PMNNT4	0.4	0.402	0.256	0.342
PMNNT5	0.5	0.335	0.320	0.345
PMNNT6	0.6	0.268	0.384	0.348
PMNNT7	0.7	0.201	0.448	0.351
PMNNT8	0.8	0.134	0.512	0.354
PMNNT9	0.9	0.067	0.576	0.357

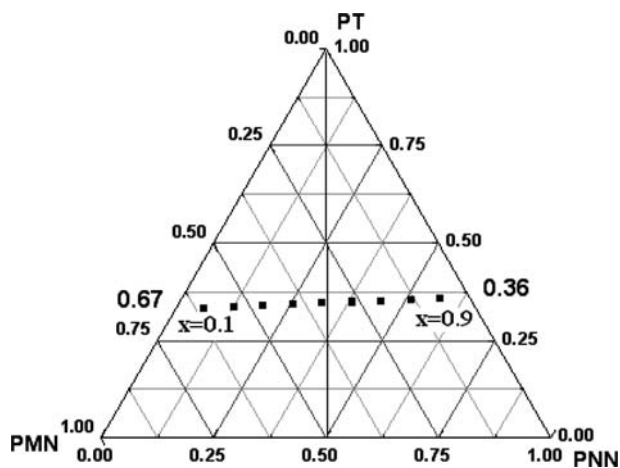
various compositions were then pressed into disks of 10 mm diameter and 1.5 mm thickness. The disks were then covered with  $\text{PbZrO}_3$  powder to minimize the lead loss during final sintering at  $1200^\circ\text{C}$  for 2 h in a sealed alumina crucible.

After milling and polishing, both sides of the sintered pellets were painted with silver paste, and the pellets were fired to form electrodes. Dielectric measurements were obtained in an automated system, which was composed of a HP4192A Precision LCR meter, a Delta2300-automated temperature-controller box and a computer-automated control program. The frequencies used were 0.1, 1, 10, 100 kHz. The temperature range investigated was varied from  $40\sim 180^\circ\text{C}$ , with a heating rate of  $2^\circ\text{C}/\text{min}$ . Piezoelectric data were measured using the ZJ-3A static  $d_{33}$  measurement method. Before measurement the samples were poled under the E-fields of 20 kV/cm at room temperature for 20 min. Phase structures were investigated using an X-ray diffractometer (Rigaku, D/max3B).

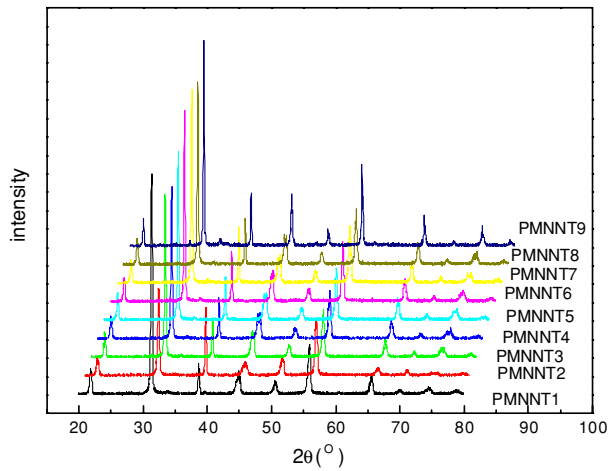
## 3. Results and discussion

### 3.1. Phase structure of the PMNNT samples

Figure 2 shows the XRD profiles of PMNNT1~PMNNT9. The results show the presence of the perovskite phase for each sample. The reflection lines were indexed assuming a pseudocubic structure. It was found that the (111) and (200) reflection lines became broader or even split, for increasing values of  $x$ . The (200) reflection lines of all samples were measured by slow scanning; some typical profiles are shown in Fig. 3. Two separated peaks emerge with increasing  $x$ , but the intensity ratio of the two peaks are not equal to 1:2 as should be the case for the single tetragonal phase. In addition the full width-half maximum (FWHM) of the first peak seems larger than the second, indicating the co-existence of the tetragonal phase with other phases in these samples. None of the samples were in a single phase, which proves that all samples are in the MPB region undergoing a phase transition.



**Fig. 1** Compositions of the different samples in the PMN-PNN-PT ternary system



**Fig. 2** X-ray diffraction patterns of the PMNNT ceramics

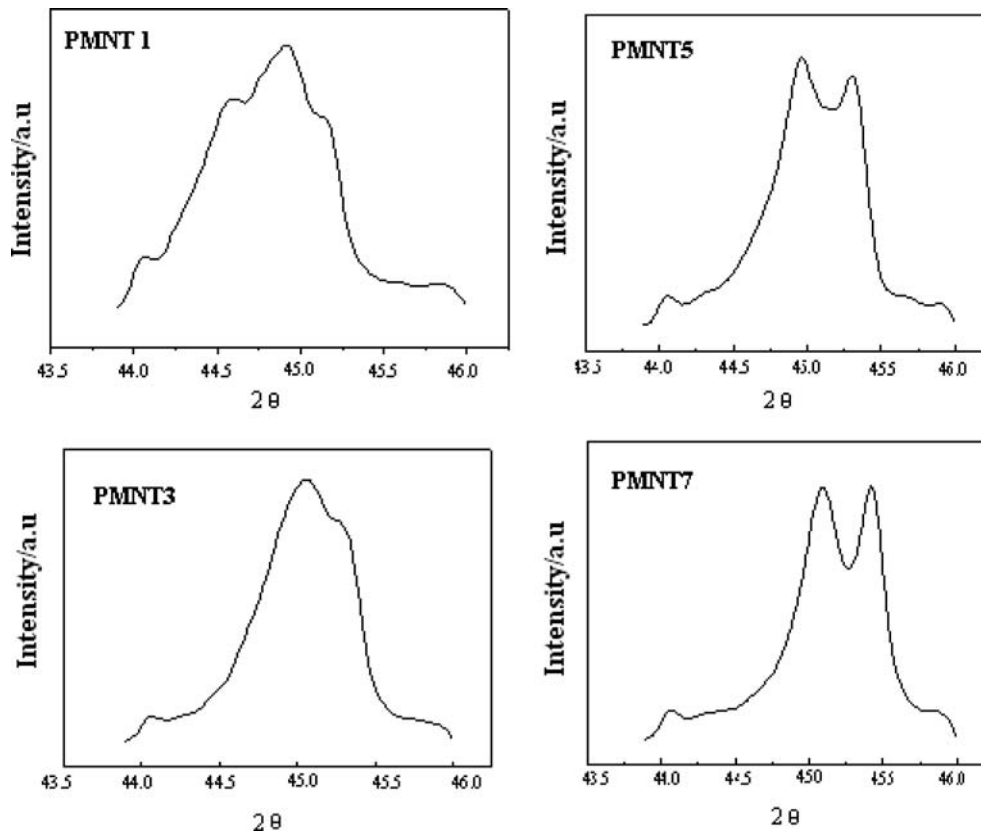
We can therefore confirm that the line linking the MPB compositions of two binary systems will be in the MPB region of the corresponding ternary system.

### 3.2. Dielectric behavior of the PMNNT system

The temperature dependency of the dielectric constant at different frequencies (0.1, 1, 10, 100 kHz) for some PMNNT

samples is illustrated in Fig. 4. It is found there are weak frequency dispersion and DPT (diffusion phase transition) behavior, which implies that these samples are in a transition state from relaxor to normal ferroelectrics. These results are consistent with the results for PMN-PT and PNN-PT binary systems [13, 14]. The relation between the dielectric constant and temperature can be expressed as  $(\frac{1}{\epsilon'} - \frac{1}{\epsilon'_m})^{1/n} = \frac{T-T_m}{C}$  ( $T > T_m$ ), where  $n$  is considered as a parameter representing the degree of the relaxor behavior for a ferroelectric material. In this study,  $\log(1/\epsilon' - 1/\epsilon'_m)$  is linear with  $\log(T-T_m)$  for all samples, where  $T_m$  is the characteristic temperature (the value when  $\epsilon$  reaches the maximum value). The profile of PMNNT2 is shown in Fig. 5. For all the PMNNT samples the values of the parameter  $n$  are in the range of 1.3~1.8.

The values of the peak dielectric constant ( $\epsilon_m$ ) and the corresponding dissipation factor ( $tg\delta$ ) at different frequencies as well as  $\Delta T_0 = T_{m,0.1\text{ kHz}} - T_{m,100\text{ kHz}}$  for all samples are shown in Table 2. The temperature dependence of the dielectric constant for all samples at 1 kHz is shown in Fig. 6. The peak dielectric constants of all samples are very high. It is worth noting that  $\epsilon_m$  of PMNNT2 reaches a value of 45540. Such a high value of  $\epsilon_m$ , even superior to that of the PZT-PMN-PT system in a recent report [11], is exceptional



**Fig. 3** XRD diffraction patterns for selected PMNNT ceramic samples around  $2\theta = 45^\circ$

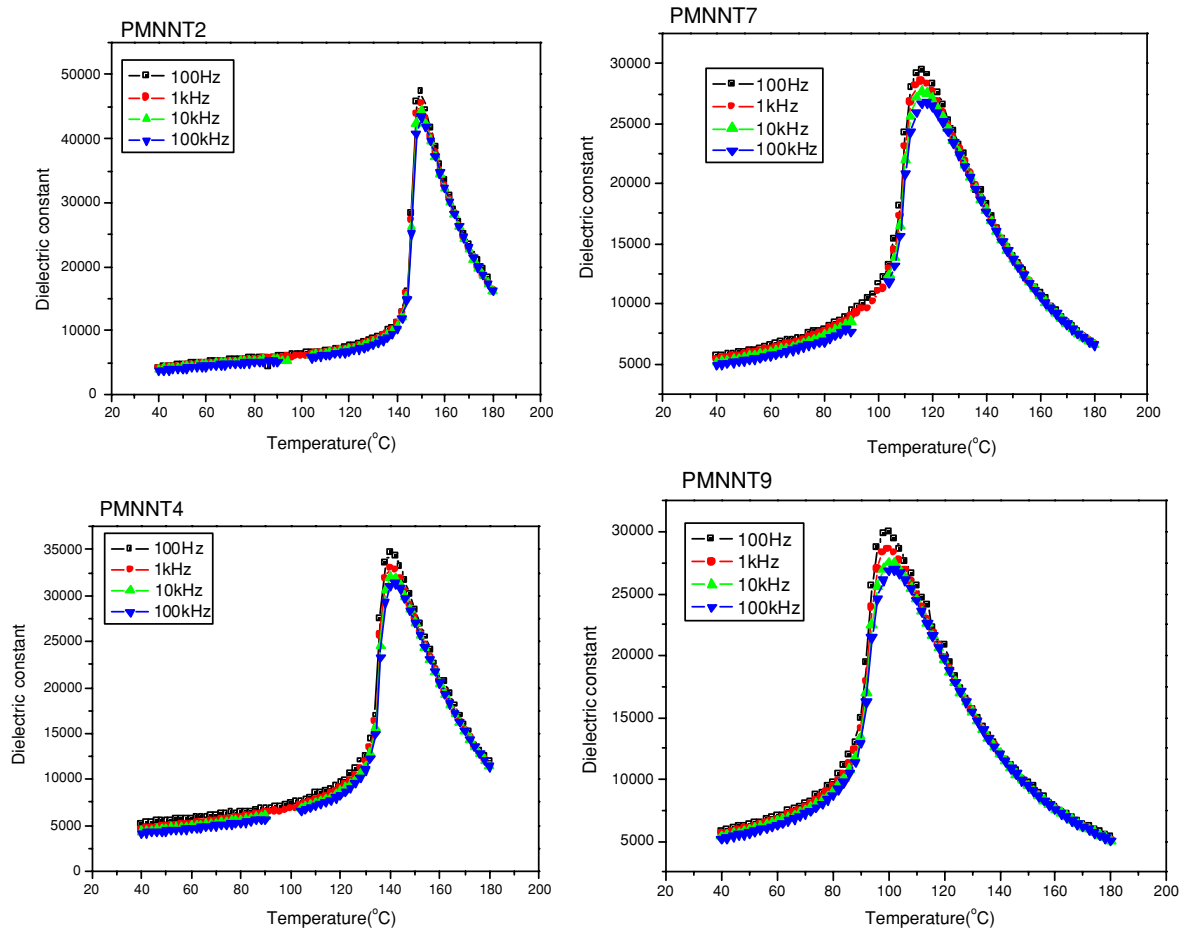


Fig. 4 Temperature and frequency dependence of the dielectric constant for the PMNNT ceramics

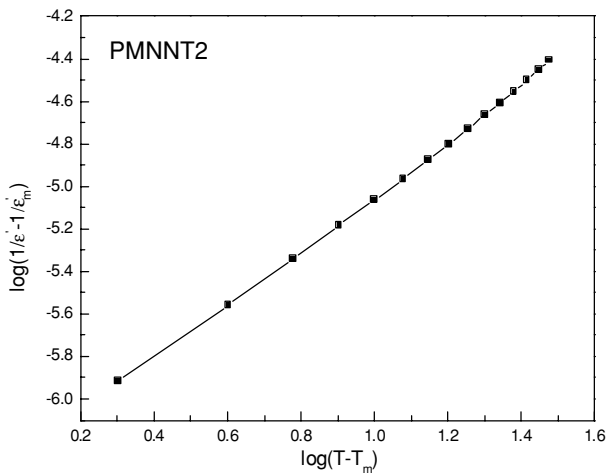


Fig. 5 Dependence of  $(1/\epsilon' - 1/\epsilon'_m)$  on  $(T - T_m)$  for PMNNT2 ceramic samples

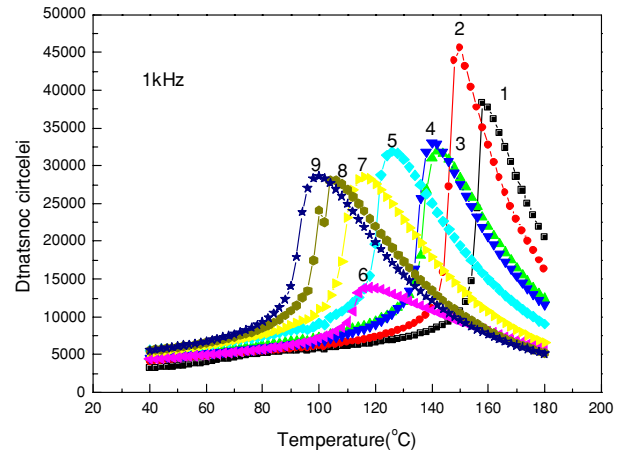


Fig. 6 Temperature dependence of the dielectric constant for the PMNNT ceramics at 1 kHz

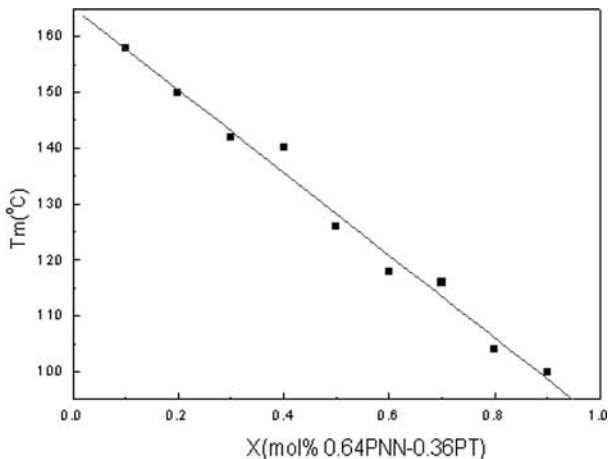
even for Pb-based relaxor compositions. The dependence of  $T_m$  on  $x$  for the various PMNNT ceramics is described in Fig. 7. It is found that  $T_m$  decreases linearly with increasing  $x$ , implying that this system forms to a perfect solid solution.

### 3.3. Piezoelectric behavior of PMNNT2

PMNNT2 ( $x = 0.2$ ) shows not only the highest peak dielectric constant, but also the best piezoelectric properties among all samples. The  $d_{33}$  value of PMNNT2 is 780 pC/N, which

**Table 2** Dielectric properties of the PMNNT ceramics

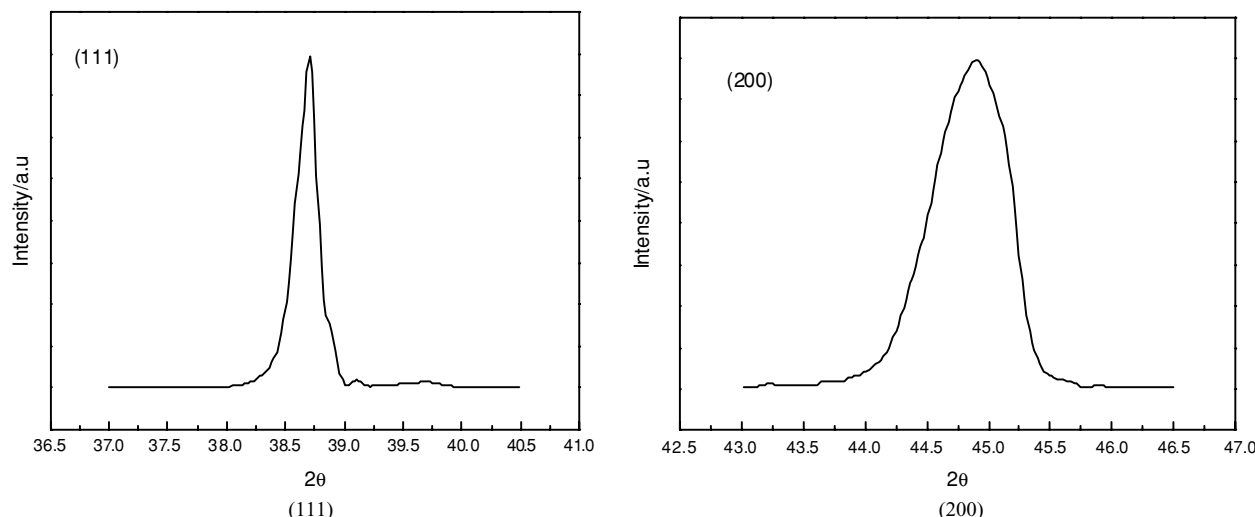
Sample	Frequency (kHz)	$T_m(^{\circ})$	$\epsilon_m$	$\text{tg}\delta(\%)$	$\Delta T_0(^{\circ})$ (0.1~100 kHz)
PMNNT1	0.1	158	43,930	9.434	0
	1	158	38,320	8.336	
	10	158	34,870	6.346	
	100	158	33,090	12.8	
PMNNT2	0.1	150	47,410	2.946	0
	1	150	45,540	2.230	
	10	150	44,380	3.196	
PMNNT3	0.1	142	33,940	4.689	2
	1	142	31,970	3.447	
	10	142	30,690	3.722	
PMNNT4	0.1	140	34,720	3.601	2
	1	140	33,060	2.822	
	10	140	31,990	3.262	
	100	142	31,360	11.47	
PMNNT5	0.1	126	37,070	13.74	2
	1	126	31,890	7.747	
	10	126	29,790	4.806	
	100	128	28,760	11.55	
PMNNT6	0.1	118	14,340	0	2
	1	118	13,860	1.143	
	10	118	13,620	1.598	
	100	120	13,420	2.553	
PMNNT7	0.1	116	29,450	2.823	2
	1	116	28,510	2.166	
	10	116	27,660	3.249	
	100	118	26,780	10.83	
PMNNT8	0.1	104	29,020	2.51	2
	1	104	28,030	2.338	
	10	106	27,260	3.067	
	100	106	26,380	11.72	
PMNNT9	0.1	100	29,970	4.119	2
	1	100	28,630	2.925	
	10	100	27,500	2.897	
	100	102	26,980	4.052	



**Fig. 7** Dependence of  $T_m$  on  $x$  for compositions given by  $(1 - x)$   $(0.67\text{PMN}-0.33\text{PT})-x(0.64\text{PNN}-0.36\text{PT})$  ceramics

is superior to that of most reported relaxor-PT ceramics. It can be noted that all results (including  $d_{33}$  and  $\epsilon_m$ ) reported in this study have been measured repeatedly to avoid measurement errors. The results indicate that for certain compositions given by a linear combination of the MPBs of two binary systems, the resulting ternary can have significantly improved properties. Similar results have been found for the PZN-PNN-PT system [10].

Theoretically a material will show good piezoelectric properties if the energy difference between the rhombohedral (R) and tetragonal (T) phases is small. In this case the material can easily respond to an applied field through a polarization rotation from [111] to [100]. In addition it was recently found that the presence of a lower symmetry phase in the MPB region of the PMN-PT system



**Fig. 8** XRD diffraction patterns of the PMNNT2 ceramic samples around  $2\theta = 38.5^\circ$  and  $45^\circ$

results in a special anisotropic XRD peak broadening. The reason for this broadening is still unclear [18]. As shown in Fig. 8, for the PMNNT2 sample we also find that the (200) reflection line is much broader than the (111) line. This observation does not of course prove the existence of a lower symmetry phase, but it may indicate the existence of a special phase structure and associated microstructure at the PMNNT2 composition. More work is required to confirm the identity of the phase components in the MPB region. Although this will require a complicated characterization [18], the results of the present study suggest that further investigation of the PMNNT2 ceramic will be worthwhile.

#### 4. Conclusions

A series of PMN-PNN-PT ternary ceramics with the compositions of  $(1-x)(0.67\text{PMN}-0.33\text{PT})-x(0.64\text{PNN}-0.36\text{PT})$  ( $x = 0.1-0.9$ ) have been investigated in this study, where 0.67PMN-0.33PT and 0.64PNN-0.36PT are the compositions near the MPBs of the respective binary systems. X-ray diffraction results demonstrate that all samples show a pure pseudocubic form. No obvious frequency dispersion was seen, but a small amount of DPT behavior was observed for all samples, typical of the transition from a relaxor ferroelectric to a normal ferroelectric state. The MPB region of the PMN-PNN-PT ternary system was found to be located on a line given by linear combinations of the MPBs of PMN-PT and PNN-PT. A piezoelectric coefficient  $d_{33}$  of up to 780 pC/N, and a maximum dielectric constant of  $\epsilon_m = 45540$  (at 1 kHz), were observed for the PMNNT2 sample ( $x = 0.2$ ). The results show therefore that a partial substitution of PNN-PT for PMN-PT can lead to an obvious improvement in electrical properties. The piezoelectric coefficient and dielectric constant show a non-linear relation

over the range investigated, although the Curie point,  $T_m$ , obeys a linear relation in this range. The very high dielectric and piezoelectric response for the PMNNT2 composition may be attributed to the existence of a special phase structure and microstructure. A further detailed study is therefore suggested for this composition.

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