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Short communication

Phase development and dielectric responses in PMN–BNT ceramics

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Abstract

$(1-x)\mathrm{Pb}(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$–$x(\mathrm{Bi}_{0.5}\mathrm{Na}_{0.5})\mathrm{TiO}_3$ ceramics were prepared by the conventional mixed-oxide method. All compositions show complete perovskite solid solutions and the structure to change from cubic to rhombohedral at $x = 0.5$. The dielectric constant and dielectric loss tangent were measured as a function of both temperature and frequency. The results indicated a relaxor ferroelectric behavior for all ceramics. The temperature at maximum of the dielectric constant of PMN–BNT ceramics were seen to increase with increasing BNT content. Moreover, the broadest dielectric peak occurs at $x = 0.9$, which leads to a morphotropic phase boundary in this system.

Keywords: C. Dielectric properties; Lead magnesium niobate (PMN); Bismuth sodium titanate (BNT); PMN–BNT

1. Introduction

Perovskite ferroelectric ceramics can be applied to several electronic devices such as transducers, actuators and sensors [1]. Among the many ferroelectric materials, lead magnesium niobate (PMN) and bismuth sodium titanate (BNT) are the most attractive because of their excellent electrical properties [2–7]. The compound $(\mathrm{Bi}_{0.5}\mathrm{Na}_{0.5})\mathrm{TiO}_3$ (BNT) shows the perovskite structure with rhombohedral system at room temperature. Compared with the most widely used ferroelectric ceramics PZT, BNT based ceramics has been reported to possess a high anisotropic electro-mechanical coupling ($K_p \sim 16.5$–25.5%, $K_t \geq 48\%$) and a high frequency constant ($N_t \geq 2550$ Hz m) as demanded for ultrasonic applications [8]. However, the other electronic applications of pure BNT ceramics are limited by some of its shortcomings in electrical properties such as low dielectric constant (ε_r), narrow sintering temperature range and high conductivity at room temperature [2–3,9]. The $\mathrm{Pb}(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$ (PMN) ceramic, a prototype relaxor ferroelectric with perovskite structure, demonstrates a quite high maximum dielectric constant around -10 °C with diffuse phase transition phenomena [5–6,10]. However, pure PMN perovskite is very difficult to obtain by solid-state reaction because of the unwanted pyrochlore phase. Thus, mixing PMN with BNT is expected to enhance the formation a more stabilized perovskite structure, purer perovskite with lower amount of undesirable pyrochlore phases. Moreover, it is expected that the dielectric constant may be enhanced in PMN–BNT ceramics.

Therefore, this study investigated the dielectric properties of $(1-x)$PMN–xBNT compositions prepared by solid-state reaction. The dielectric properties of the PMN–BNT system were determined as a function of temperature and frequency, and the Curie temperature (T_c) was engineered over a wide range of temperature by varying the compositions in the system. The phase development of the PMN–BNT system was investigated by XRD analysis. Finally, the relationships among these experimental results are discussed.

2. Experimental procedure

The following compositions of $(1-x)$PMN–xBNT ($x = 0.0$, 0.1, 0.25, 0.5, 0.75, 0.9 and 1.0) were prepared by a solid-state reaction method. The starting precursors, PMN and BNT, were first formed in order to avoid the unwanted pyrochlore phases. The PMN powder was synthesized through the columbite method, in which magnesium niobate ($\mathrm{MgNb}_2\mathrm{O}_6$) was first prepared and then used as precursor. Pure $\mathrm{MgNb}_2\mathrm{O}_6$ phase powder was formed by calcining $(\mathrm{MgCO}_3)_4\mathrm{Mg}(\mathrm{OH})_2\cdot 5(\mathrm{H}_2\mathrm{O})$ with $\mathrm{Nb}_2\mathrm{O}_5$ at 1150 °C for 2 h. $\mathrm{MgNb}_2\mathrm{O}_6$ powder was then mixed with PbO (99.0%) in ethanol and calcined at 800 °C to produce single phase PMN. For the preparation of BNT powder, $\mathrm{Bi}_2\mathrm{O}_3$,

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Na_2CO_3 and TiO_2 powders were homogeneously mixed via ball-milling for 24 h with zirconia media in ethanol. The well-mixed powder was calcined at 800 °C for 2 h. The $(1-x)$PMN–xBNT compositions were then formulated from PMN and BNT component by employing the similar mixed-oxide procedure and calcined at various temperatures between 1100 and 1250 °C for 2 h in order to obtain single phase $(1-x)$PMN–xBNT powders.

The calcined PMN–BNT powders were then pressed hydraulically to form disc-shaped pellets with a diameter of 15 mm and a thickness of 1.5 mm. The sintering was carried out for 2 h at 1150 °C with heating/cooling rates of 10 °C/min. X-ray diffraction (XRD), using CuK_α radiation, was employed to identify the phase formation. For the electrical measurement, silver paste was painted on both sides of the polished samples as electrodes. The dielectric properties of all sintered samples were measured with a HP4284A LCR meter in connection with a temperature chamber and a sample holder capable of high temperature measurement. The dielectric constant (ε_r) was then calculated using the geometric area and thickness of samples.

3. Results and discussion

The phase composition of the $(1-x)$PMN–xBNT ceramics, where $x = 0.0$, 0.1, 0.25, 0.5, 0.75, 0.9 and 1.0, is shown in Fig. 1. The XRD diffraction patterns of sintered ceramic with $x = 0.0$ match exactly with the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ (JCPDS file no. 81-0861), whereas that with $x = 1.0$ match exactly rhombohedral perovskite $(Bi_{0.5}Na_{0.5})TiO_3$ (JCPDS file no. 36-0340). In the ladder pattern, a series of continuous solid solutions PMN–BNT with perovskite structure normally forms. Previous works [11,12] reported that secondary or pyrochlore phases, such as $Pb_2Nb_2O_7$ and $Pb_3Nb_2O_{13}$, $Pb_3Nb_4O_{13}$ and $Pb_3Nb_2O_8$, always exist prior to perovskite formation in the conventional solid-state reaction as a result of interfacial reaction. However, in the work reported here, it is seen that the PMN–BNT system formed a pure perovskite phase without any trace of unwanted phases. With increasing BNT content, the diffraction peaks shifted towards higher angle. However, it was not possible to determine the correct symmetry for the structure of PMN–BNT ceramics by simply examining the appropriate diffraction patterns. These XRD patterns showed no evidence of any superlattice reflections. However, the strongest reflections were noticeably broader than others when x is increasing. It has been reported earlier that the transition is of the first order with considerable hysteresis [13]. In first-order transition, coexistence of phases of two difficult structures is possible and this has been observed in a number of ABO_3 perovskites [14]. Moreover, it is believed that the broadening of the peaks in the diffraction patterns is due to a combination of effects including strain broadening and possibly a small shift in the position of the sample during processing [15]. This broadening meant that it was not possible to obtain high quality structural refinements in either space group, although reasonable estimates of the lattice parameters were possible. Examination of unit cell parameters and cell volume (shown in Table 1) suggests that the structure is still cubic at $x = 0.1$ and 0.25 and the transition to rhombohedral occurs at $x = 0.5$. The unit cell volume decreases as x increase. Moreover, XRD indicates that the use of high purity PMN and BNT precursors at the optimum firing temperatures can effectively enhance the yield of the perovskite phase.

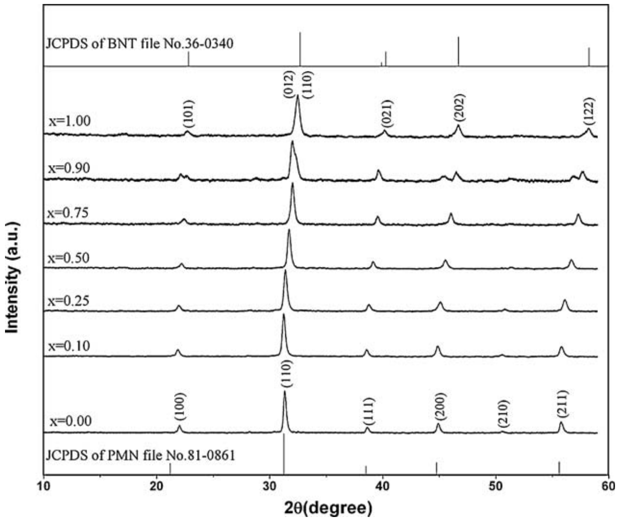

Fig. 1. XRD patterns of $(1-x)$PMN–xBNT ceramics.

The optimized sintering temperature, density and relative density of the sintered $(1-x)$PMN–xBNT ceramics are listed in Table 1. Higher firing temperatures were necessary for compositions containing a large fraction of PMN. The densities of PMN–BNT ceramics were therefore within the range of 5.91–7.94 g/cm^3. It should be noted here that the composition and densification of ceramic can influence the dielectric properties [16], but in the present work the relative density varies between 98.50 and 99.25%, as shown in Table 1, which should not play a significant role in the variation of dielectric properties. The temperature dependence of dielectric constant

Table 1
Characteristics of $(1-x)$PMN–xBNT ceramics with optimized processing condition.

Compositions	Structure	Sintering temperature (°C)	Density (g/cm^3)	Relative density (%)
$x = 0.00$	Cubic	1250	7.94	99.25
$x = 0.10$	Cubic	1200	7.6	97.43
$x = 0.25$	Cubic	1200	7.40	98.66
$x = 0.50$	Rhombohedral	1150	6.94	99.14
$x = 0.75$	Rhombohedral	1150	6.41	98.61
$x = 0.90$	Rhombohedral	1100	6.03	97.25
$x = 1.00$	Rhombohedral	1100	5.91	98.50

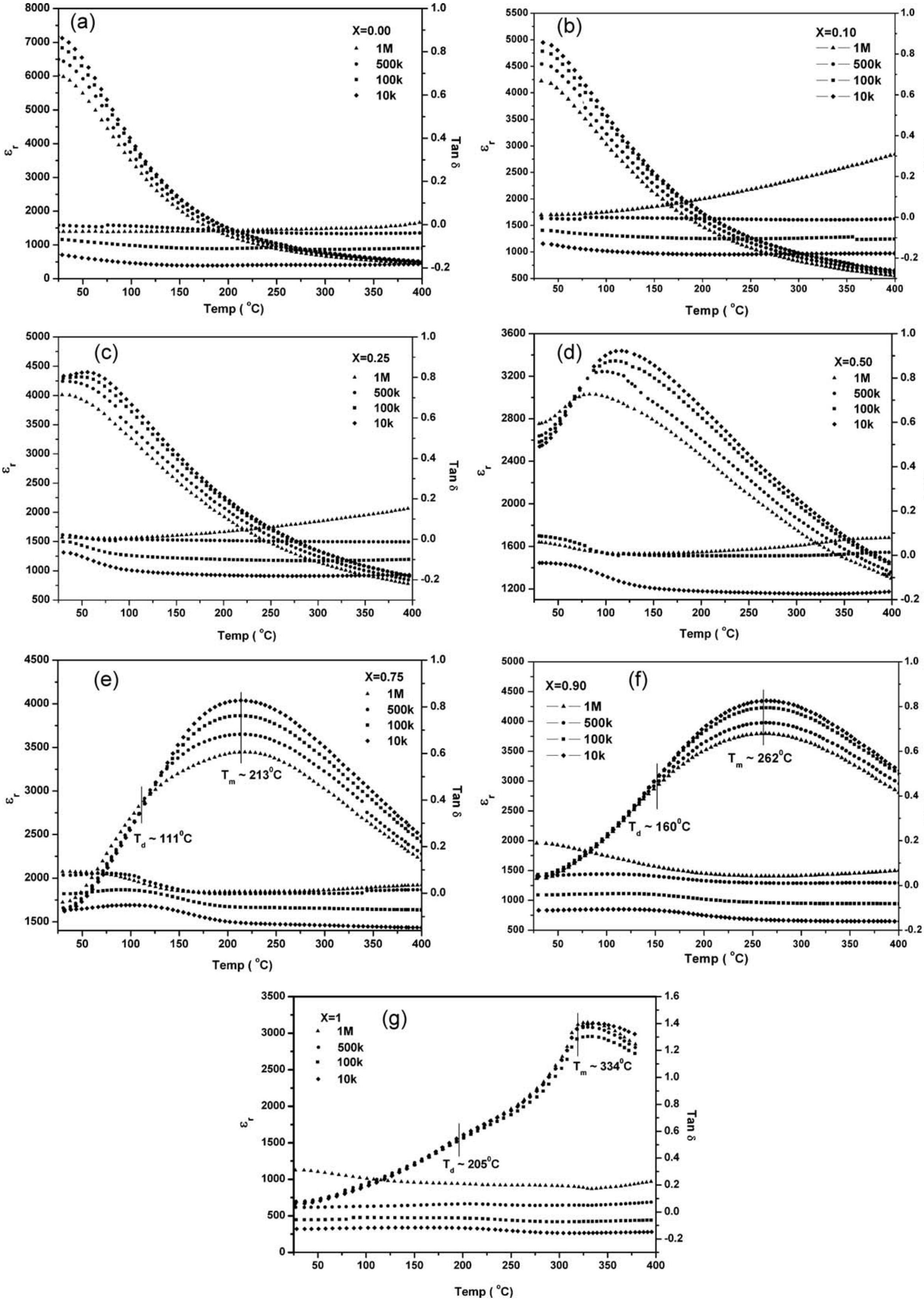

Fig. 2. Temperature dependence of dielectric constant and dielectric loss of $(1-x)$PMN–xBNT ceramics at different frequencies: (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.25$, (d) $x = 0.5$, (e) $x = 0.75$, (f) $x = 0.9$ and (g) $x = 1.0$.

(ε_r) and dielectric loss ($\tan\delta$) at various frequencies for compositions with $x = 0.0$, 0.1, 0.25, 0.5, 0.75, 0.9 and 1.0 is shown in Fig. 2. For pure PMN ($x = 0.0$) (Fig. 2a), the maximum temperatures (T_m) are not completely shown due to the limited range of the measuring set-up, though it is widely known to be close to -10 °C. However, from the dielectric curves it can be seen the typical relaxor behavior with the magnitude of dielectric constant decreases with increasing frequency. Relaxor ferroelectrics are characterized by diffuse phase transition, which has been interpreted as a result of short-range order [17]. For pure BNT ($x = 1.0$) (Fig. 2e), the phase transition temperature can be clearly seen to have a small frequency dependence. It is well known BNT has relaxor properties and has peculiar behavior of the diffused phase transition from the rhombohedral to nonpolar tetragonal phase [18]. Diffuse phase transitions of BNT can be described by a coexistence region between phases. In the present work, three phases of ferroelectric, anti-ferroelectric and paraelectric nature exist in the sample at different temperatures [19]. The depolarization temperature (T_d), referred to the transition temperature between the ferroelectric phase and the anti-ferroelectric phase, was increased to 205 °C and the maximum permittivity temperature (T_m) for this sample is about 334 °C. Two transition points (T_d and T_m at ~110 °C and 213 °C respectively) are still clearly seen in the ε–T plot for 0.25PMN–0.75BNT composition, as shown in Fig. 2e and T_d and T_m at ~160 °C and 264 °C respectively are still clearly seen in the ε–T plot for 0.1PMN–0.9BNT composition, as shown in Fig. 2f that gradually disappear after increasing of PMN amount or when $x \leq 0.50$.

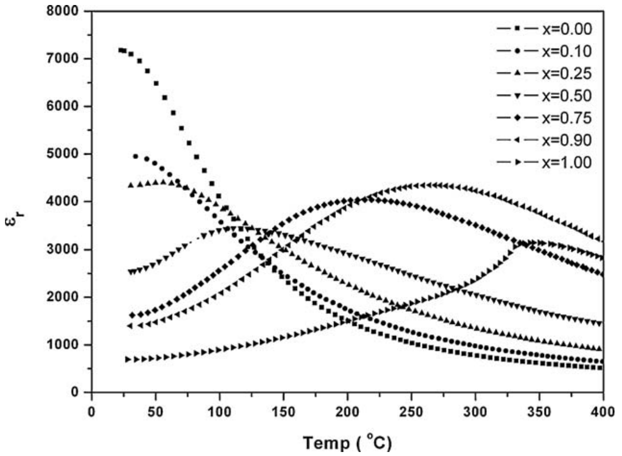

Fig. 3. Temperature dependence of dielectric constant (ε_r) of $(1 - x)$PMN–xBNT ceramics at 10 kHz.

The effect of BNT modification on the dielectric properties of PMN has then been investigated. When BNT is added to form the binary system with PMN, the maximum temperature is shifted towards that of BNT ceramic. The representative temperature dependence of the dielectric constant (ε_r) measured at 10 kHz for $(1 - x)$PMN–xBNT samples with $x = 0.0$, 0.1, 0.25, 0.5, 0.75, 0.9 and 1.0 is shown in Fig. 3. With increasing BNT content, the maximum transition temperature (T_m) shifts monotonously to higher temperatures and the maximum dielectric constant (ε_m) significantly decreases with increasing BNT content up to 50 mol%. The ε_m value rises again after adding more BNT. The broadest dielectric peak is found at the 0.1PMN–0.9BNT composition which indicates diffused phase transition behavior. However, it is well know that PMN and BNT have relaxor characteristics and typical relaxor behavior is characterized by a diffused ferroelectric phase transition. This behavior is explained in terms of a coexistence region between phases [20], and in this case is dominated from one of both polar rhombohedral and nonpolar tetragonal phases of the BNT component [13]. To assess the diffuse phase transition of relaxor ferroelectric, the degree of broadening or diffuseness in the observed dielectric variation could be estimated with the diffusivity (γ) using the $\ln(1/\varepsilon_r - 1/\varepsilon_{\max})$ versus $(T - T_{\max})$. The following equation:

$$\frac{1}{\varepsilon} \approx (T - T_m)^2 \tag{1}$$

has been shown to be valid over a wide temperature range, where T_m is the temperature at which the dielectric constant is maximum [16]. If the local Curie temperature distribution is Gaussian, the reciprocal permittivity can be written in the form:

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m} + \frac{(T - T_m)^\gamma}{2\varepsilon_m \delta^2} \tag{2}$$

where ε_m is maximum dielectric constant, γ is diffusivity, and δ is diffuseness parameter. The γ and δ can be estimated from the slope and intercept of the dielectric data shown in Fig. 4, which should be a linear. The values of γ and δ are both material constants depending on the composition and structure [21]. In a composition with the diffused phase transition such as relaxor ferroelectric, the value of γ is expected to be 2 [20–21]. The plots of $\ln((1/\varepsilon) - (1/\varepsilon_m))$ as a function of $\ln(T - T_m)$ for all compositions are shown in Fig. 4. The value of γ reported in Table 2 varies between 1.77 and 1.99 which confirms relaxor behaviors. The diffusion factor for all composition fluctuates in the same range (1.7–1.9), however the results show the degree

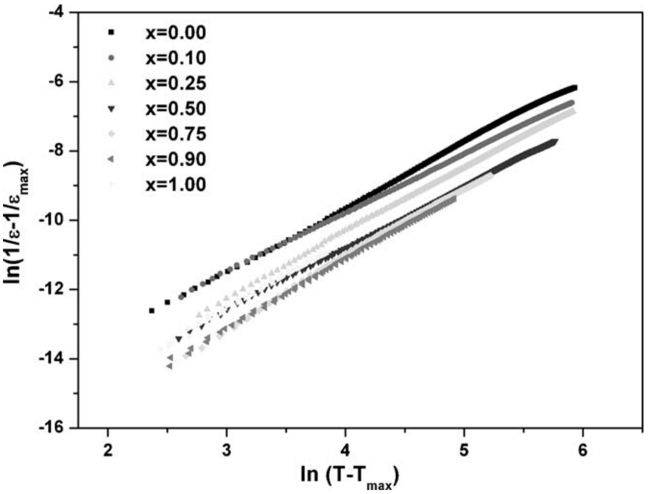

Fig. 4. Plot of $\ln(T - T_{\max})$ versus $\ln((1/\varepsilon_r) - (1/\varepsilon_{\max}))$ for $(1 - x)$PMN–xBNT ceramics.

Table 2
Dielectric properties of $(1-x)$PMN–xBNT ceramics.

Compositions	T_d	T_m	ε_m	γ	δ
$x = 0.00$	–	–	>6030	–	–
$x = 0.10$		33	4948	1.68	−16.54
$x = 0.25$	–	31	4002	1.83	−17.68
$x = 0.50$	–	88	3044	1.77	−17.99
$x = 0.75$	111	213	3473	1.99	−19.03
$x = 0.90$	160	264	4347	1.99	−19.02
$x = 1.00$	205	334	3131	1.98	−18.52

of diffuseness of the phase transition to be highest at the 0.1PMN–0.9BNT composition, which lead to a morphotropic phase boundary (MPB) [22] in this system. In the MPB regions, enhanced dielectric constants are obtained. It was attributed to easily switching of the polarization vector between all allowed polarization orientations [23]. The relationship between phase formation and electrical properties is important and thus helps to improve the understanding on these compositions.

4. Conclusions

Phase formation characteristics of perovskite PMN–BNT ceramics have been investigated with XRD analysis. All compositions show complete solid solutions without any trace of unwanted phases. The crystal structure of PMN–BNT system gradually changes from cubic in PMN ceramic to rhombohedral with increasing BNT content. The dielectric studies indicated that all compositions in the PMN–BNT system exhibit a diffused phase transition and followed the Curie–Weiss law of relaxor ferroelectric behavior.

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