J Mater Sci (2007) 42:221–227
DOI 10.1007/s10853-006-1055-y

Preparation of $Pb(Zr,Ti)O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$ piezoelectric ceramics by dry–dry method

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Received: 8 May 2005 / Accepted: 18 January 2006 / Published online: 7 November 2006
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Abstract Ternary perovskite ceramics of $Pb[(Zr_{0.5}Ti_{0.5})_{0.8-x}(Mg_{1/3}Nb_{2/3})_{0.2+x}]_{0.98}Nb_{0.02}O_{3.01}$ (PZTMN, x = –0.075, –0.05, –0.025, 0, 0.025, 0.05, and 0.075), are synthesized via dry–dry method. B-site precursors of PZTMN ($[(Zr_{0.5}Ti_{0.5})_{0.8-x}(Mg_{1/3}Nb_{2/3})_{0.2+x}]_{0.98}Nb_{0.02}O_{2.01}$, ZTMN) can be synthesized via a two-step solid state reaction method. The first calcination temperature is 1,300 °C, and the second is not higher than 1,360 °C. Incorporation of magnesium and niobium ions promotes the formation of the single phase solid solution with $ZrTiO_4$ structure. Single phase perovskite PZTMN is formed at 780 °C, much lower than that in conventional process. Dense ceramics can be sintered at about 1,260 °C with dielectric and piezoelectric properties comparable to that of wet–dry method and higher than that of conventional method. It seems that B-site precursor method is cost effective in preparation of ternary piezoelectric ceramics.

Introduction

It is well known that the perovskite solid solution of $PbZrO_3$–$PbTiO_3$ system (PZT) exhibits many excellent electric properties [1, 2]. This system has high dielectric constants, piezoelectric coefficients and electromechanical coupling factors near the morphotropic phase boundary (MPB) between rhombohedral and tetragonal phases. In the ternary solid solution of $PbZrO_3$–$PbTiO_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$ system (abbreviated as PZTMN hereafter), the MPB extends along a line on the phase diagram [3–5]. Various useful properties can be obtained among the compositions along the MPB line [4, 5]. Doped binary PZT and many ternary systems such as PZTMN have wide applications [6, 7].

Perovskite powder is synthesized from oxides and carbonates via solid state reaction in conventional ceramic procedure which is cost-effective. High temperature calcination is needed, however, and measures should be taken to control PbO evaporation. Ceramics by conventional route often has severe composition fluctuation on B-site [8–10]. Dielectric, pyroelectric and piezoelectric properties of PZT ceramics are strongly sensitive to Zr/Ti ratio. Severe compositional fluctuation means that the sample is composed of regions of quite different Zr/Ti ratio and properties. The excellent properties near MPB cannot be utilized effectively if compositional fluctuation is large. Severe composition fluctuation on B-site is thus detrimental to electrical properties [11, 12].

These shortcomings can be avoided in various wet chemical powder preparation methods [13, 14]. Trade off is the increase in cost because of the use of much more expensive metallorganic compounds as reactants, which are frequently more toxic than corresponding oxides and carbonates.

Swartz et al. proposed a columbite process, a specific B-site precursor method, to suppress pyrochlore formation during synthesis of $Pb(Mg_{1/3}Nb_{2/3})O_3$ [15, 16]. Namchul Kim et al. developed a precursor method to prepare PZT powder [17, 18]. B-site cation oxide, i.e., $ZrTiO_4$, was synthesized via a solid state reaction

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at 1,400 °C. This precursor was then calcined with PbO to form PZT. High energy attrition milling of ten hours is necessary to crush the tough precursor from high temperature calcination. This method can be termed as dry-dry method, since both calcinations involved are solid state reactions. The precursor can also be obtained by wet routes, and this wet–dry method yields compositionally homogeneous PZT and PZTMN ceramics with excellent piezoelectricity [19, 20]. The wet–dry method also employs, however, costly and toxic metallorganic compounds as raw materials.

Applications of piezoelectric ceramics are quite wide and diverse [6, 7]. Excellent property and performance are essential request in some cases. Chemical or wet–dry method is appropriate. Cost and price may be, however, crucial considerations in other applications such as consumer electric products. The aim of this paper is to show that dry–dry method is a possible cost effective procedure for ternary piezoelectric ceramics. PZTMN was investigated intensively in recent years [21, 25]. In present work, PZTMN ceramics has been prepared via dry–dry method. We have shown that precursor of this ternary system, containing dopant, as well as perovskite powder, could be synthesized at a relatively lower temperature using conventional ceramic equipments. X-ray diffraction (XRD) and scanning electron microscope (SEM) are used to evaluate the preparation method. Dielectric and piezoelectric properties were also reported and discussed.

Experimental

Compositions investigated in present work were $Pb[(Zr_{0.5}Ti_{0.5})_{0.8-x}(Mg_{1/3}Nb_{2/3})_{0.2+x}]_{0.98}Nb_{0.02}O_{3.01}$ with x = –0.075, –0.05, –0.025, 0, 0.025, 0.05, and 0.075. Tiny amount of additional niobium was introduced to enlarge the electrical resistivity of the ceramics [26]. Powders of titanium oxide, zirconium oxide, niobium oxide, alkali magnesium carbonate and lead oxide were used as raw materials. Their purities were 99.9% except for Nb_2O_5, whose purity was 99.99%.

Powders were weighted in appropriate proportions to form $[(Zr_{0.5}Ti_{0.5})_{0.8-x}(Mg_{1/3}Nb_{2/3})_{0.2+x}]_{0.98}Nb_{0.02}O_{2.01}$, which is the nominal composition of the precursors (ZTMN). Powders were mixed and milled for 4 h by planetary ball miller using zirconia balls and deionized water. After drying, this mixture was calcinated at 1,300 °C for 6 h, crushed manually, milled again for 4 h and then calcinated at 1,300–1,360 °C for another 6 h. XRD was used to trace the reaction procedure and to make sure that single phase solid solution with $ZrTiO_4$ structure was formed.

The precursor powder was mixed and milled with PbO powder in the stoichiometric ratio for 6 h, and then calcined at 780 °C for 4 h to get PZTMN perovskite phase. The PZTMN powder was grounded by planetary ball miller and pressed into round pellets with the diameter of 22 mm and thickness of about 1.2 mm. The pellets were sintered at 1,220–1,300 °C in a closed double crucible with pellets of $PbZrO_3$ as a source of PbO vapor. Powder of $PbZrO_3$ was prepared via conventional solid reaction of Pb_3O_4 and ZrO_2 at 850 °C. XRD and SEM were used to characterize PZTMN powder and ceramics. Grain sizes were measured using standard intercept count method on polished and then thermally etched samples. Grain sizes were taken as 1.56 times of average chord length.

Silver electrodes were fired onto the pellets. Temperature dependence of the dielectric capacitance and dielectric loss were measured at 1 kHz with a computer-controlled system. Then the samples were poled under 2.5 k voltage/mm. Piezoelectric constant d_{33} was obtained via a piezometer. Planar electromechanical coupling factor kp was measured by the standard resonant–antiresonant method.

Results and discussion

Synthesis of B-site precursor

$ZrTiO_4$ has the orthorhombic structure of α-PbO_2 [27]. There are many variety of $ZrTiO_4$ crystal structure. Order–disorder transition depends strongly on thermal history. $Zr_{0.8}Sn_{0.2}TiO_4$ is also a solid solution with $ZrTiO_4$ structure. Substitutional tin in solid solution stabilizes the high-temperature structure type [28]. Figure 1 shows the XRD spectra of precursors (x = –0.075, x = 0.075) after the second step of calcination. Single phase solid solution of ZTMN with $ZrTiO_4$ structure can be formed at 1,360 °C for the composition of x = –0.075, judged from standard XRD pattern card (JCPDS 81-2214 for $Zr_{0.8}Sn_{0.2}TiO_4$), while ZrO_2 remainder is observed in the sample calcined at 1,340 °C as shown in Fig. 1(a, b). We can get single phase precursor at 1,300 °C for the composition of x = 0.075. This means that the synthesis temperature is appreciably lowered as the nominal composition of magnesium and niobium (MN) increases. The splitting of peaks at about 37° corresponding to (200)/(021) pair is more obvious as the concentration of MN increases. Compared to the standard XRD pattern card JCPDS 84-1018 for $ZrTiO_4$, it is evident that the XRD pattern of the precursor is more $Zr_{0.8}Sn_{0.2}TiO_4$-like when the concentration of MN increases. Yung Park and

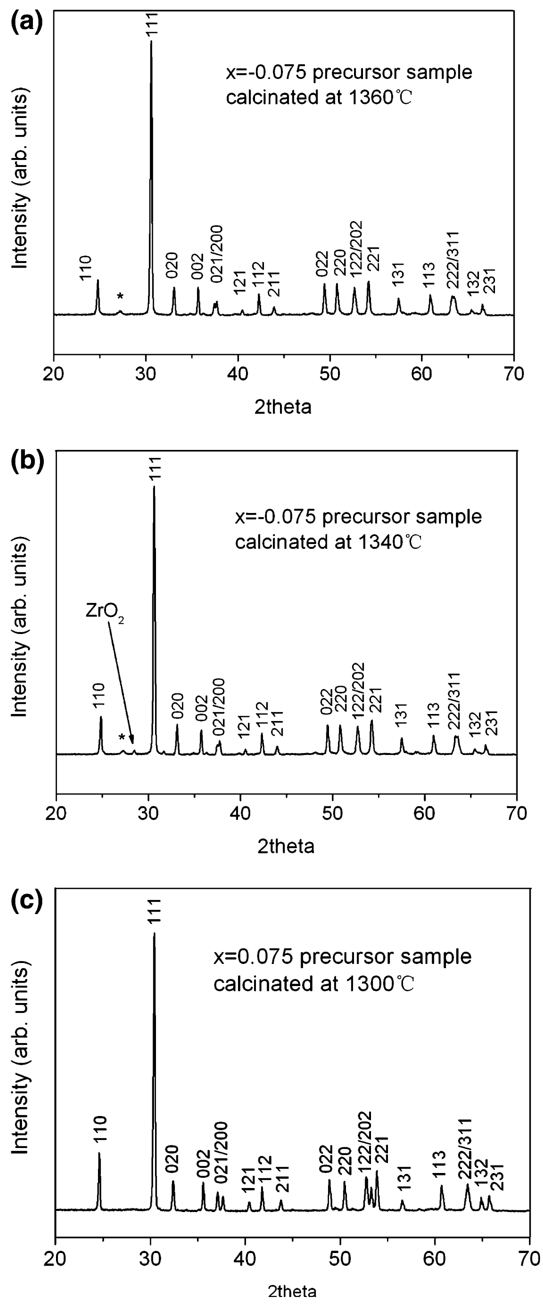

Fig. 1 XRD spectra of the precursor system $[(Zr_{0.5}Ti_{0.5})_{0.8-x}(Mg_{1/3}Nb_{2/3})_{0.2+x}]_{0.98}Nb_{0.02}O_{2.01}$ after the second step of calcinations(**a**: x = –0.075, 1,360 °C; **b**: x = –0.075, 1,340 °C; **c**: x = 0.075, 1,300 °C). Asterisk indicates superlattice reflection due to ordering of Ti and Zr ions

Yoonho Kim [29, 30] reported that order–disorder transition occurred in zirconium titanate when the descent speed of temperature was lower than 100 °C/h. This transition manifested itself in XRD as a peak in the 2θ range of 27–28°. On the spectra a and b, there is a weak peak (signed by *) at $2\theta = 27.2°$, which, we believe, is associated with the ordering of Ti and Zr ions. This superlattice reflection can not be eliminated by calcination at higher temperatures up to 1,380 °C in present work and disappears only when $x > 0.025$.

As stated above, we propose a two-step process to synthesize B-site precursor, and set the first calcination temperature rather lower. This ensures the fragility of the intermediate and final bulks so that possible contamination in milling is greatly reduced and a period of four hours is enough for conventional planetary ball miller to get fine powder. Intermediate milling also kinetically facilitates the formation of single phase solid solution.

In a previous work, we prepared B-site precursor of $x = 0$ with a similar two-step process [31]. The only difference was that both calcinations were carried out at same temperature. Single phase solid solution can be formed at 1,350 °C, higher than present work (i.e., 1,300 °C). The bulk of first calcination was very hard to be crushed. Namchul Kim prepared B-site precursor of PZT with one step calcination at 1,400 °C and attrition mill of 10 h [17–18]. All observations above indicate that addition of Mg^{2+} and Nb^{5+} promotes the formation of solid solution with $ZrTiO_4$ structure and intermediate milling ease the solid state reaction, especially when the first calcining temperature is set lower so that the bulk is soft and milling efficient is relatively higher.

Preparation of ceramics

Single phase perovskite powder can be synthesized at 780 °C (Fig.2), while conventional process without precursor needs a calcining temperature much higher (about 850 °C) [3, 4]. It is worth noting that present calcining temperature is even lower than that of wet–dry method (800 °C) [20].

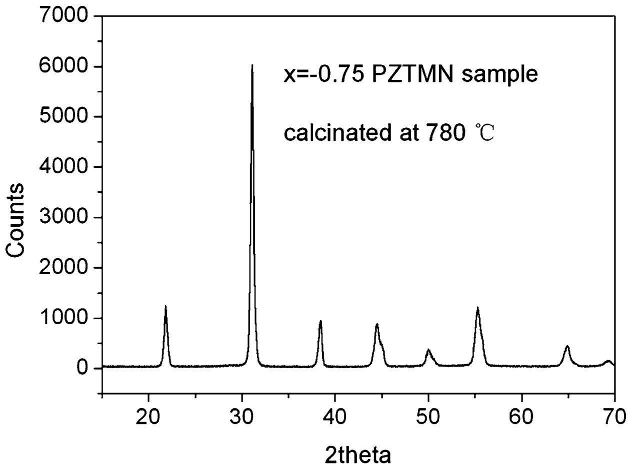

Fig. 2 XRD spectra of $Pb[(Zr_{0.5}Ti_{0.5})_{0.875}(Mg_{1/3}Nb_{2/3})_{0.125}]_{0.98}Nb_{0.02}O_3$ powder calcined at 780 °C

Figure 3 is the SEM micrographs of PZTMN ceramics ($x = 0.075$) sintered at 1,220, 1,260, 1,300 °C, respectively. The porosity reduces remarkably as sintering temperature increases, while the grain size increases slightly. Grain sizes of samples sintered at 1,220, 1,260 and 1,300 °C are 2.3, 2.5 and 2.5 μm, respectively. The temperature dependence of shrink ratio is shown in Fig. 4.

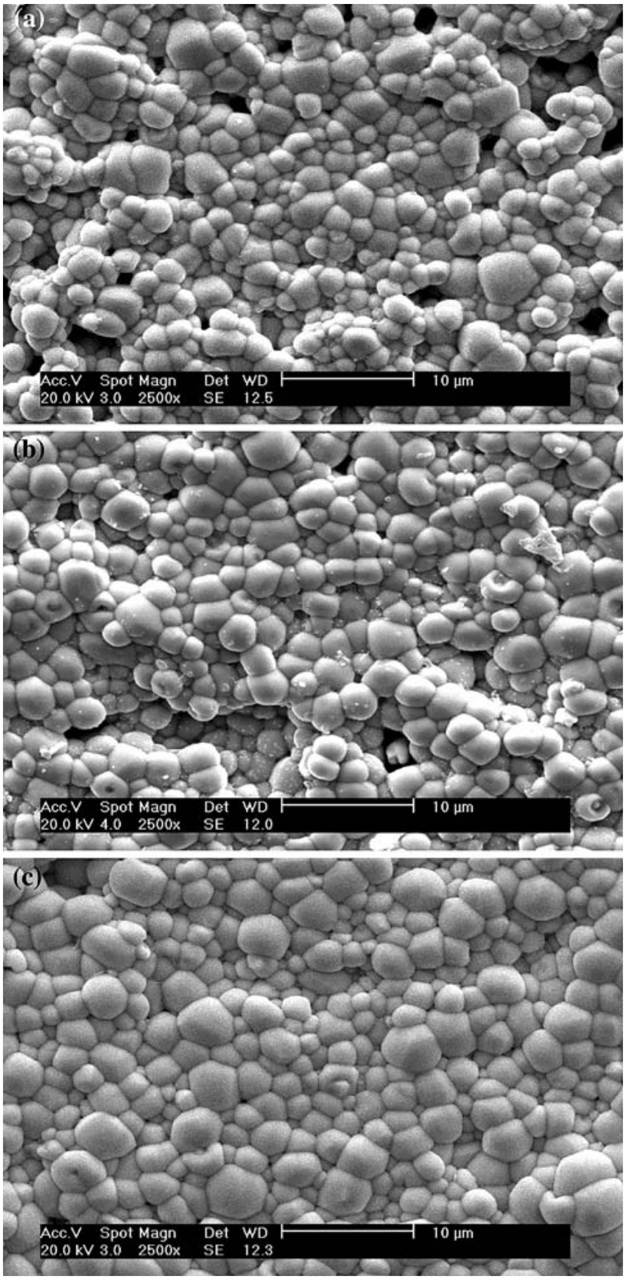

Fig. 3 SEM micrographs of PZTMN samples ($x = 0.075$) sintered at 1,220 °C (**a**), 1260°C (**b**) and 1,300 °C (**c**), respectively

Dielectric and piezoelectric properties

Figure 5 shows the temperature dependence of dielectric constant and dielectric loss (tanδ) of PZTMN samples from different sintering temperatures. These samples have the composition of $x = 0.075$. When the sintering temperature is below 1,280 °C, dielectric constant of the samples increases as the sintering temperature increases. The maximum value of the dielectric constant ε_m of the sample sintered at 1,300 °C is lower than that of the sample sintered at 1,280 °C. For temperatures higher than 267 °C (T_m), the variation of the dielectric constant does not follow the classical Curie–Weiss law. There are two indicators of relaxor behavior. One is the shift of peaks in dielectric constant and dielectric loss curves to higher temperature as frequency increases. The other indicator, which we adopt here, is the deviation from classical Curie–Weiss law. Whatever the sintering temperature, the dielectric constant varies according to the law $(1/\varepsilon) - (1/\varepsilon_m) = K(T - T_m)^\gamma$ with x equals to 1.70, as clearly shown in Fig. 6. This exponent is an intermediate value between that of normal ferroelectrics predicted by Curie–Weiss law (i.e., $\gamma = 1$) and that of relaxor ferroelectrics (i.e., $\gamma = 2$) [32].

As shown in Fig. 7, the piezoelectric coefficient d_{33} and the electromechanical coupling factor kp reach the maximum value at the sintering temperature of 1,260 °C. This reflects the well-known sensitivity of kp on porosity and grain size. Greater grain size may be detrimental to mechanical strength, another critical property for some applications [33, 34]. In view of dielectric and piezoelectric properties, we consider 1,260 °C to be the most proper sintering temperature in present work.

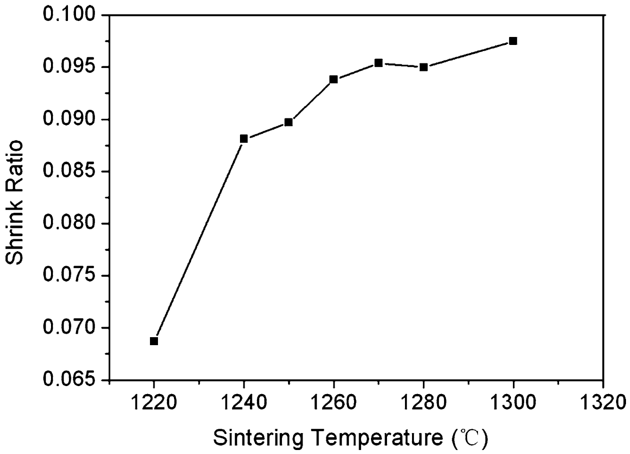

Fig. 4 Shrink ratio as function of sintering temperature

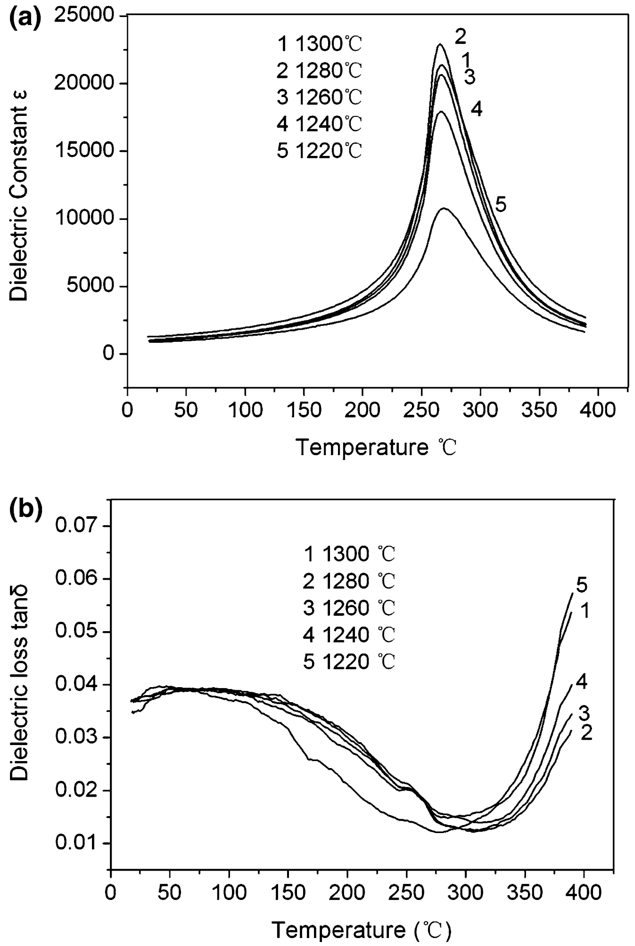

Fig. 5 Temperature dependence of dielectric constant (**a**) and dielectric loss (**b**) for samples (x = 0.075) sintered at different temperatures

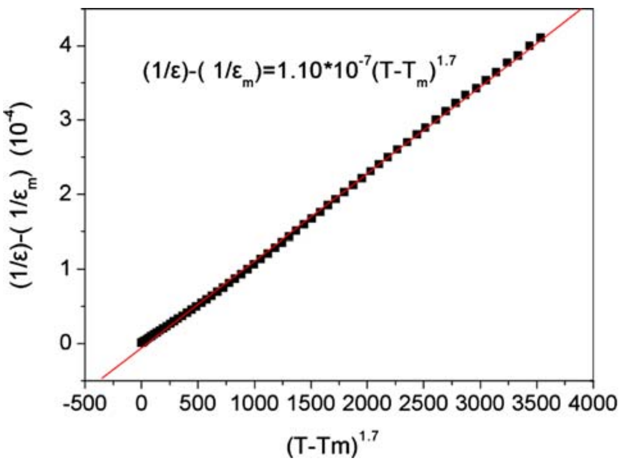

Fig. 6 Reciprocal dielectric constant of PZTMN (x = 0.075) versus T–T_m

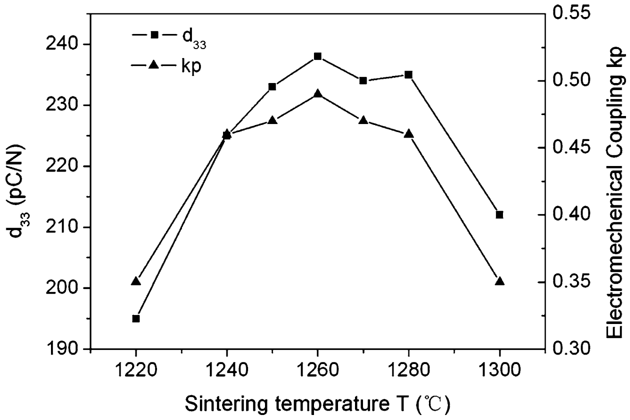

Fig. 7 Piezoelectric coefficient d_{33} and electromechanical coupling factor kp of the PZTMN samples (x = 0.075) as functions of sintering temperature

The compositional dependence of piezoelectric coefficient d_{33} and electromechanical coupling factor kp is shown in Fig. 8. The samples have MN concentrations between 12.5% and 27.5%. Both the piezoelectric coefficient and the electromechanical coupling factor reach the maximum value at 15% nominal concentration of MN (x = –0.05). Figure 9 shows the temperature dependence of dielectric constant for samples (sintered at 1,260 °C) with different MN nominal concentrations. T_m becomes lower as MN% increases. The maximum value of the dielectric constant reaches to 35,000. The maximum dielectric constant of the samples with MN% = 0.2 (x = 0) is 32,000, which is near that of the samples from wet–dry method [19] and much higher than that of the samples from conventional method (about 16,000) [19]. At present, we cannot give exact explanation of differences of dielectric properties from different methods, though it may be related to general advantages of precursor method: depression of compositional fluctuation, depression of loss of PbO during

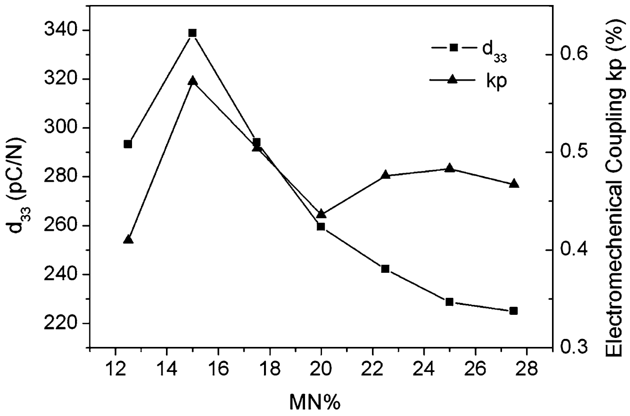

Fig. 8 Piezoelectric coefficient d_{33}, electromechanical coupling factor kp of the PZTMN samples (sintered at 1,260 °C) as functions of MN nominal concentration

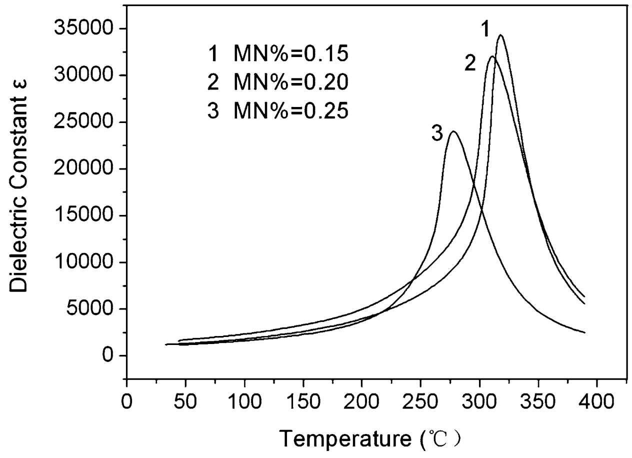

Fig. 9 Temperature dependence of dielectric constant for samples (sintered at 1,260 °C) with different MN nominal concentrations

synthesis of perovskite powder [19, 20], etc. Further research effort is need. In view of piezoelectric and dielectric properties, we suppose that the composition of $Pb[(Zr_{0.5}Ti_{0.5})_{0.85}(Mg_{1/3}Nb_{2/3})_{0.15}]_{0.98}Nb_{0.02}O_3$ lays very close to the MPB line on the phase diagram. Hiromu Ouchi et al. showed that the MPB was near, but not exactly at, $Pb(Zr_{0.44}Ti_{0.435})$ $(Mg_{1/3}Nb_{2/3})_{0.125}$ O_3, if $(Mg_{1/3}Nb_{2/3})$ concentration was fixed as 0.125 [3].When Zr/Ti fixed as (1/2)/(1/2), they prepared samples with concentration Zr = Ti = 0.125,0.25,0.375. Note also that our sample includes Nb as dopant.

Processing technique and property of PZT and PZTMN have been well investigated [3–5, 15–18]. Wet chemical method and wet–dry method can produce excellent dielectric and piezoelectric properties, though expensive and possibly toxic metallorganic compounds have to be employed. Dry–dry method was initially developed to study grain size effect on property of PZT [17–18]. Because of the refractoriness of ZrO_2, high temperature calcining was needed and attrition mill of long time was necessary. Incorporation of Mg^{2+} and Nb^{5+}, fortunately, facilitates the formation of single phase precursor, making dry–dry method much more practicable on ternary PZTMN system. Properties of samples by dry–dry method are comparable to that of wet–dry method. Dry–dry method also partially preserves merits of wet–dry method, such as calcining and sintering temperatures lower than that of conventional method. The additional expense is merely millings and calcinations in precursor preparation by our two-step method. Thus, dry–dry method may be a cost effective method and may be applicable to fabrication of some consumer electric products. Besides, because of the extra step of precursor preparation, optimization of the whole procedure of dry–dry method is needed. Further research should clarify if compositional fluctuation is sensitive to calcinating temperature of B-site precursor and its composition. We show that single perovskite phase powder can be synthesized at temperature as low as 780 °C. It is still an open question whether different condition will facilitate milling of the powder [17, 18]. These investigations are now under way.

Conclusion

B-site precursors of PZTMN ternary system investigated in present work can be synthesized via a two-step solid state reaction. The first calcination temperature is 1,300 °C, and the second is not higher than 1,360 °C. Magnesium and niobium cations promote the formation of single phase solid solution of ZTMN with $ZrTiO_4$ structure. Single phase perovskite powder can form at 780 °C, much lower than that of conventional method. Dense ceramics can be sintered at about 1,260 °C with dielectric and piezoelectric properties comparable to that of wet–dry method and higher than that of conventional method. Dry–dry method preserves virtue of wet–dry method to some extent while avoiding use of expensive metallorganic compounds as raw materials. It seems that B-site precursor method is cost effective in preparation of ternary piezoelectric ceramics and is applicable to the manufacture of consumer electric products.

Acknowledgement The present work was supported by the National Natural Science Foundation of China (contract No. 50472065).

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