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$0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ relaxor ferroelectric ceramics produced by a simplified columbite route and a reaction-sintering process

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Abstract

$0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ relaxor ferroelectric ceramics produced by a simplified columbite route (PMNT-SCR) and a reaction-sintering process (PMNT-RS) were studied. The second calcination to react $MgNb_2O_6$, PbO and TiO_2 in the columbite route was omitted to obtain 0.9PMN–0.1PT ceramics in the simplified columbite route. PMNT-SCR ceramic with density higher than 90%of theoretical density was obtained. The dielectric constant of PMNT-SCR at 100 Hz reached 20,000. Without any calcination, the mixture of PbO, $Mg(NO_3)_2$, Nb_2O_5 and TiO_2 was pressed and sintered directly in the reaction-sintering process. Stoichiometric 0.9PMN–0.1PT ceramics of 100% perovskite phase were obtained. PMNT-RS ceramic with density of 8.07 g/cm^3 was obtained after 1230 °C/2 h sintering. Dielectric constant under 1 kHz reaches 26,100 for PMNT-RS ceramics after 1230 °C/2 h sintering.

Keywords: A. Calcination; C. Dielectric properties; D. Perovskites; E. Capacitors

1. Introduction

Lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) has recently attracted considerable attention in the area of electronic ceramics because of its high dielectric constant and high electrostrictive strain coefficient [1–5]. The relaxor ferroelectric PMN was first synthesized in the late 1950s [6]. The main feature of the dielectric properties of PMN is a broad and frequency-dependent dielectric constant peak just below room temperature. The magnitude of this peak decreases and the temperature related to this peak increases as frequency increases. This behavior is typical of relaxor ferroelectrics. The dielectric properties of PMN can be enhanced by the addition of $PbTiO_3$ (PT) [7,8]. The maximum dielectric constant of PMN ($K_{max} = 16{,}000$) increases as PT is added ($K_{max} > 20{,}000$), whereas the temperature related to this maximum shifts upward: for example, at 100 Hz, $T_{max} = -15$ °C for PMN and $T_{max} = 40$ °C for 0.9PMN–0.1PT. PMN and PMN-PT materials are useful in electrostrictive actuator applications because of their large electric-field-induced strains [9,10], and in multilayer capacitor applications because of their high dielectric constants [11]. The processing of PMN and PMN-PT ceramics has been widely studied to improve the reproducibility of the dielectric properties. Excess MgO [4,12] and PbO [12,13] can eliminate the pyrochlore phase and, thus, the dielectric constants are improved. Different calcining and sintering temperatures [3] and times [12] were also studied. Lejeune and Boilot [2] showed that the percentage of PMN phase decreased from 79 to 49% as the heating rate increased from 5 to 170 °C/min. In order to avoid the formation of pyrochlore, Swartz and Shrout [14] proposed a columbite route. It consists of two calcination steps, columbite is formed first and followed by formation of perovskite. However, there are two calcination processes before sintering the PMN ceramics. Liou and Wu [15] proposed an effective and simplified method to produce pyrochlore-free PMN ceramics with dielectric constant >17,000 under 1 kHz. The mixture of $MgNb_2O_6$ and PbO was pressed into pellets and sintered to form PMN ceramics. The second calcination and pulverization stages in the Swartz and Shrout's columbite route were omitted in the simplified columbite route. Han and Kim [16]

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proposed a method to prepare PMN powder with >99% perovskite phase by adding an aqueous $Mg(NO_3)_2$ solution rather than MgO to the alcoholic slurry of PbO and Nb_2O_5, followed by calcination at 950 °C for 2 h. Liou et al. [17] reported a reaction-sintering process to produce PMN ceramics. Without calcination, the mixture of PbO, $Mg(NO_3)_2$ and Nb_2O_5 was pressed and sintered directly. PMN ceramics of 100% perovskite phase are obtained after 1, 2 and 4 h sintering at 1250 and 1270 °C. PMN ceramics with density 8.09 g/cm^3 and dielectric constant of 19,900 under 1 kHz are obtained.

In this study, authors try to use a simplified columbite route and a reaction-sintering process in producing $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ ceramics.

2. Experimental procedure

The composition of the ceramics in this investigation is $Pb((Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1})O_3$ (0.9PMN–0.1PT) and all samples were prepared from reagent-grade oxides: PbO (>99%), MgO (>97%), $Mg(NO_3)_2{\cdot}6H_2O$ (>99%), Nb_2O_5 (99.9%) and TiO_2 (>99%). Under the simplified columbite route (PMNT-SCR), MgO and Nb_2O_5 with 10 mol% excess MgO were calcined at 1100 °C for 3 h, with a heating rate of 10 °C/min to form the columbite precursor, $MgNb_2O_6$. The calcined powder was pulverized and the appropriate amounts of PbO and TiO_2 were then added. The composition was modified with 3 mol% excess PbO to suppress pyrochlore phase formation. After being ball-milled in deionized water with agate media, the slurry was dried. After drying, the pulverized mixture of $MgNb_2O_6$, PbO and TiO_2 was pressed into pellets (12 mm in diameter and 2 mm thick). The pellets were heated to 800 °C for a period $t_{800\,^\circ C}$ 1 and 3 h with a rate 5 °C/min, and then heated to a sintering temperature of 1150–1240 °C with a rate 10 °C/min in air. After sintering, the pellets were cooled with a rate 10 °C/min. The heating profile is illustrated in Fig. 1. In the reaction-sintering process (PMNT-RS), appropriate amounts of PbO, $Mg(NO_3)_2$, TiO_2 and Nb_2O_5 for 0.9PMN–0.1PT were milled in acetone with alumina balls for 22 h. After the slurry was dried and pulverized, the powder was pressed into pellet 12 mm in diameter and 2 mm thick. The pellets were then heated with a rate 10 °C/min and sintered at temperatures ranging from 1150 to 1270 °C for 2 and 4 h in air. The sintered 0.9PMN–0.1PT ceramics were then analyzed by XRD to check the relative amounts of perovskite and pyrochlore phase. The density of sintered pellets was measured by water immersion method. After polishing, the dimension was measured before silver electrodes were formed on the pellets. Dielectric properties were measured with an HP4194A impedance analyzer in a temperature-controlled chamber from 0 to 100 °C. The dielectric constant was measured at various frequencies between 100 Hz and 100k Hz.

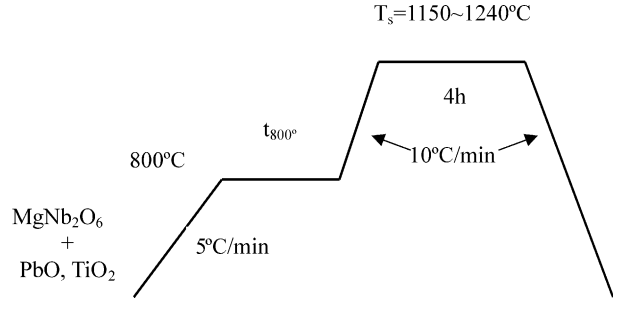

Fig. 1. Heating profile for pellets containing $MgNb_2O_6$, PbO and TiO_2.

3. Results and discussion

3.1. PMNT-SCR

Density of the sintered PMNT-SCR ceramics with $t_{800\,^\circ C}$ = 1 and 3 h are shown in Fig. 2. PMNT-SCR with 800 °C/3 h calcination period before heating up to the sintering temperature were dense and ρ > 7.2 g/cm^3 for T_s = 1150–1240 °C. In PMNT-SCR with 800 °C/1 h calcination, ρ < 6.5 g/cm^3 after 1150 °C/4 h sintering and ρ > 7.1 g/cm^3 after 1180–1240 °C/4 h sintering. The perovskite percentages of PMNT-SCR with $t_{800\,^\circ C}$ = 1 and 3 h were listed in Table 1. The perovskite percentages of PMNT-SCR sintered at 1210 and 1240 °C are higher than

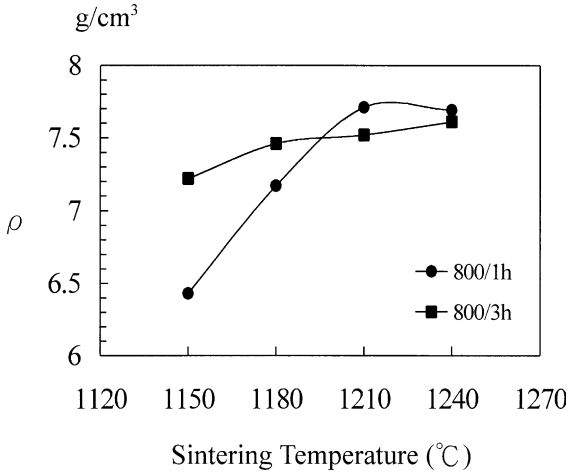

Fig. 2. Density of PMNT-SCR ceramics sintered at various temperature with $t_{800\,^\circ C}$ = 1 and 3 h.

Table 1
Perovskite percentages of PMNT-SCR ceramics sintered at various temperatures with $t_{800\,^\circ C}$ = 1 and 3 h

Sintering temperature (°C)	$t_{800\,^\circ C}$ = 1 h	$t_{800\,^\circ C}$ = 3 h
1150	87%	85%
1180	85%	81%
1210	91%	86%
1240	89%	88%

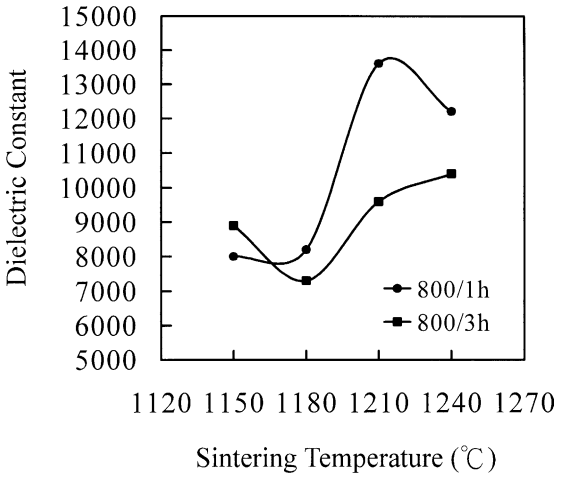

Fig. 3. Dielectric constant at 25 °C under 1 kHz of PMNT-SCR ceramics sintered at various temperature with $t_{800\ ^\circ C} = 1$ and 3 h.

those sintered at 1150 and 1180 °C. The dielectric constant at 25 °C ($K_{25\ ^\circ C}$) under 1 kHz of ceramics sintered at 1150–1240 °C with $t_{800\ ^\circ C} = 1$ and 3 h is illustrated in Fig. 3. $K_{25\ ^\circ C}$ of PMNT-SCR ceramics sintered at 1210 and 1240 °C are higher than those sintered at 1150 and 1180 °C for $t_{800\ ^\circ C} = 1$ and 3 h. This could be resulted from the density and the perovskite percentage of the sample. As in Fig. 2, ρ of 1210 and 1240 °C is larger than that of 1150 and 1180 °C. Comparing samples with $t_{800\ ^\circ C} = 1$ h and 3 h in Fig. 3, $K_{25\ ^\circ C}$ of 1 h calcination period is higher than that of 3 h. This also could be explained by ρ in Fig. 2 and the perovskite percentage in Table 1.

From the results discussed above, dielectric properties of PMNT-SCR ceramics with $t_{800\ ^\circ C} = 1$ h are better than those with $t_{800\ ^\circ C} = 3$ h .Therefore, PMNT-SCR ceramics were then sintered without the calcination period at 800 °C. The SEM photographs of PMNT-SCR ceramics

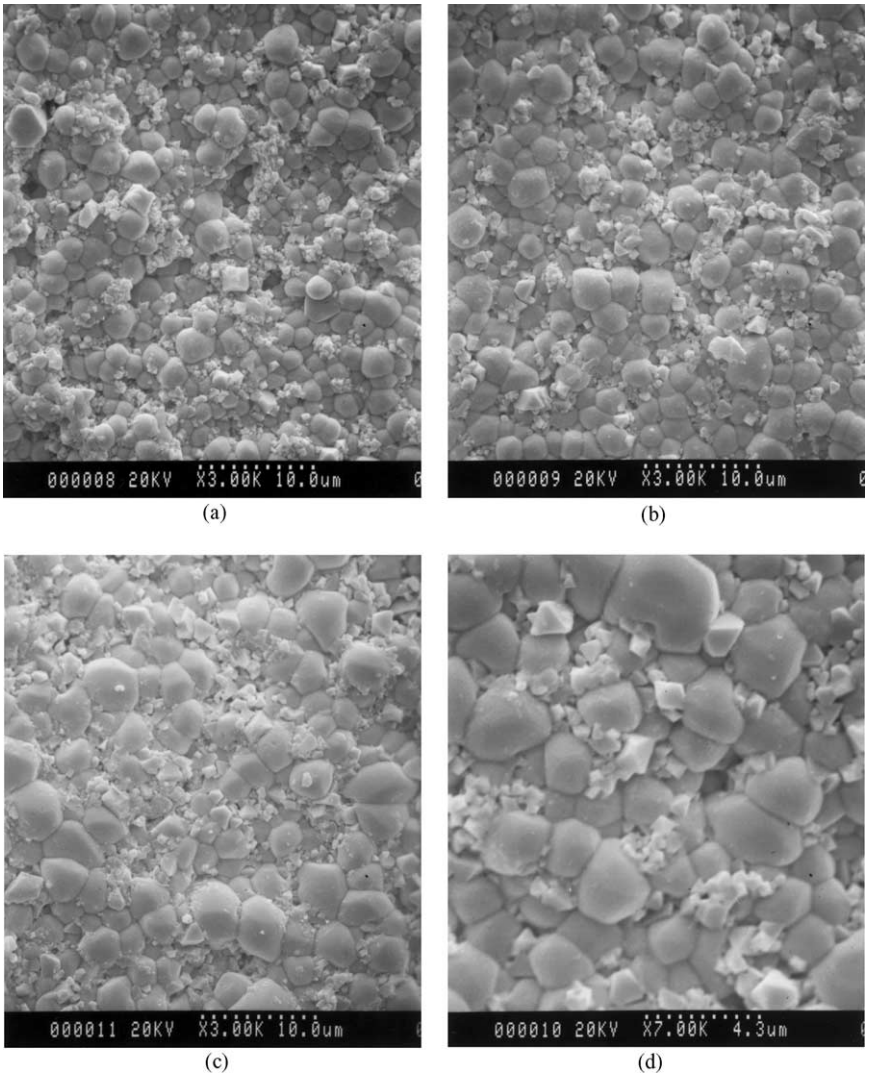

Fig. 4. The SEM photographs of PMNT-SCR ceramics sintered at (A) 1150 °C (B) 1180 °C (C) 1210 °C and (D) 1240 °C for 4 h without the calcination period at 800 °C.

sintered at 1150–1240 °C for 4 h without $t_{800\ °C}$ are illustrated in Fig. 4. There is no large pyrochlore grain in PMNT-SCR ceramics sintered at 1150 and 1180 °C. This means perovskite phase PMNT-SCR grains formed first as the mixture of $MgNb_2O_6$, PbO and TiO_2 was sintered without the calcination period at 800 °C. Fig. 5 shows $K_{25\ °C}$ under 1 kHz of PMNT-SCR ceramics sintered at various temperature for 4 h. $K_{25\ °C}$ increased with sintering temperature, this could be explained by the density and the perovskite percentage in Table 2. From the result in Table 2, dense PMNT-SCR ceramics with theoretical density more than 90% could be produced by sintering the mixture of $MgNb_2O_6$, PbO and TiO_2 directly. The temperature dependence of dielectric constant of PMNT-SCR ceramics sintered at 1270 °C/4 h without 800 °C calcination is shown in Fig. 6. The maximum dielectric constant K_{max} reaches 20,000 at 100 Hz, the temperature for K_{max} is 35 °C.

3.2. PMNT-RS

Density of PMNT-RS ceramics sintered at various temperatures and soak times is shown in Fig. 7. Density of PMNT-RS increases at sintering temperatures and exceeds 8 g/cm^3 at 1230 °C and decreases after 1230 °C. Fig. 8 shows the SEM photographs of as-fired PMNT-RS ceramics sintered at 1150–1250 °C for 2 h. No pyrochlore phase is found in these pellets. Mean grain sizes of PMNT-RS ceramics sintered at various temperatures for 2 and 4 h are listed in Table 3. Grain size increases with sintering temperature and soak time. As compared with 0.9PMN–0.1PT ceramics

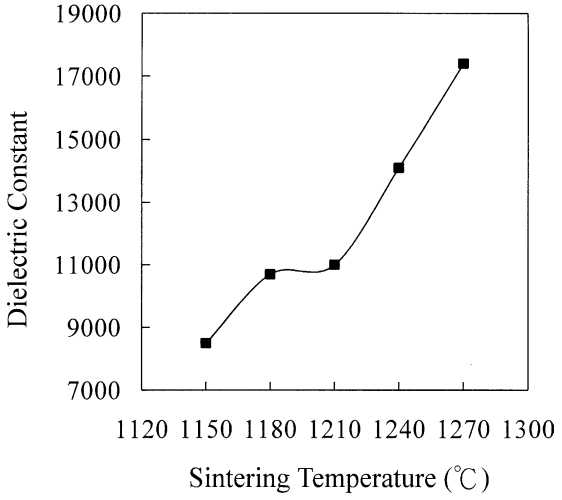

Fig. 5. Dielectric constant at 25 °C under 1 kHz of PMNT-SCR ceramics sintered at various temperature without the calcination period at 800 °C.

Table 2
The density of PMNT-SCR ceramics sintered at various temperatures without the calcination period at 800 °C

Sintering temperature (°C)	ρ (g/cm^3)	Perov. %
1150	7.54	82
1180	7.59	87
1210	7.62	88
1240	7.52	91
1270	7.56	93

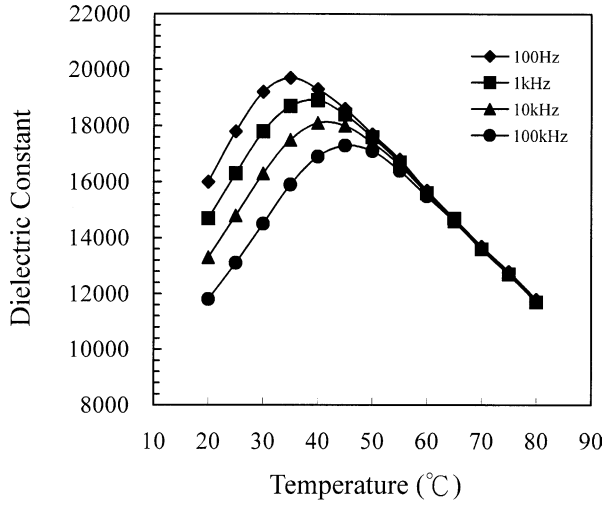

Fig. 6. Temperature dependence of dielectric constant of PMNT-SCR ceramics sintered at 1270 °C/4 h without the calcination period at 800 °C.

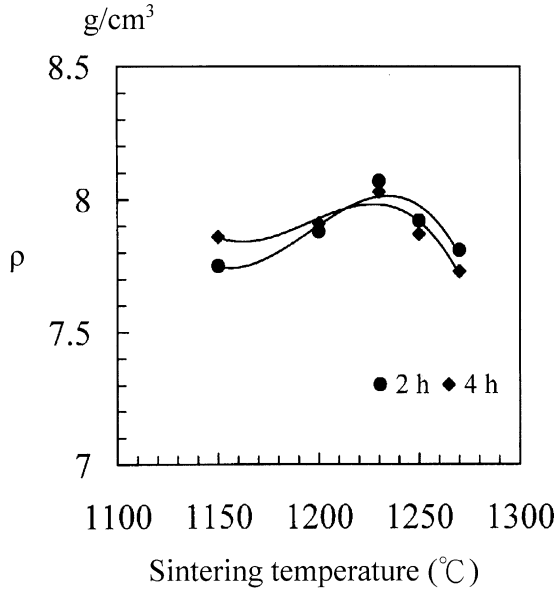

Fig. 7. Density of PMNT-RS ceramics sintered at various temperatures for 2 and 4 h.

Table 3
Mean grain sizes of PMNT-RS ceramics sintered at various temperatures for 2 and 4 h (in μm)

Sintering temperature (°C)	1150	1200	1230	1250	1270
2 h	7.8	8.2	9.1	10.6	11.1
4 h	8.1	8.6	10.8	12.3	12.8

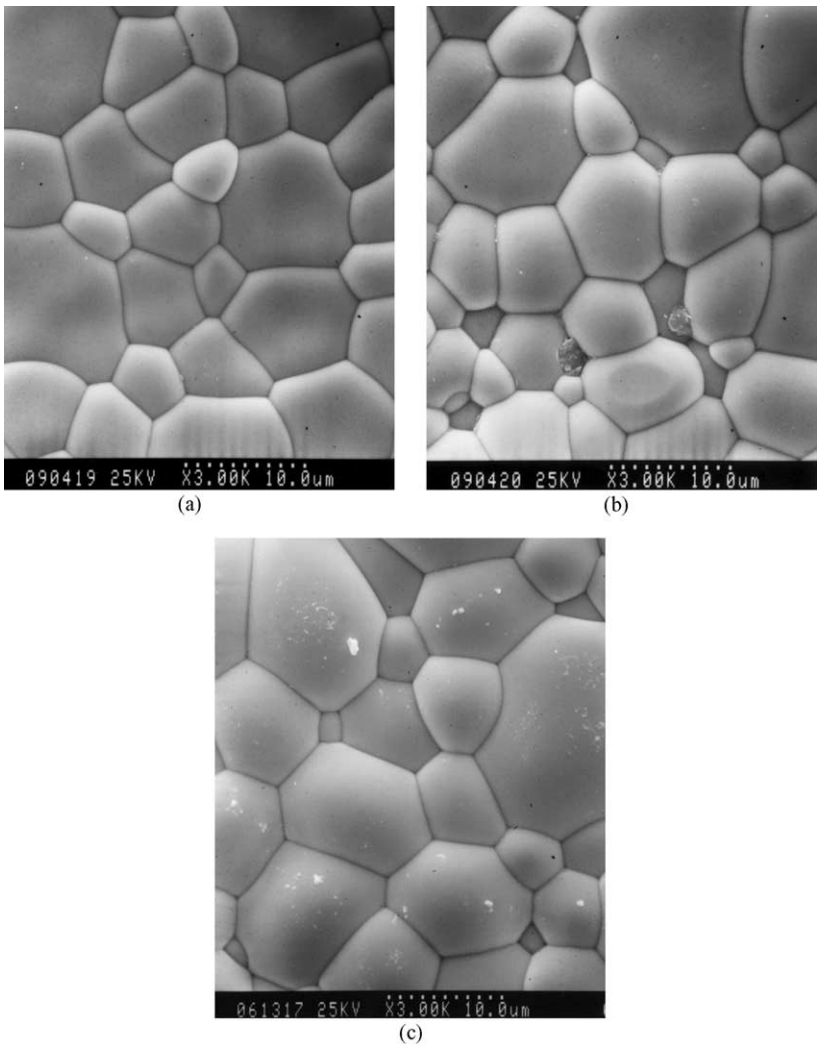

Fig. 8. The SEM photographs of as-fired PMNT-RS ceramics sintered at (A) 1150 °C, (B) 1200 °C, and (C) 1250 °C for 2 h.

produced by columbite route, about 4μm grain size was obtained as sintered at 1260 °C/2 h [5]. Therefore, the temperature for 0.9PMN–0.1PT perovskite grains to grow in reaction-sintering process is much lower than in columbite route. The mixture containing PbO without calcining may be the reason to explain the reduced sintering temperature.

The temperature dependence of dielectric constant of PMNT-RS ceramics sintered at 1230 °C/2 h is shown in Fig. 9. Maximum dielectric constant and related temperature under 1 kHz of PMNT-RS ceramics sintered at various temperatures for 2 and 4 h are listed in Table 4. Dielectric constant increases with sintering temperature and reaches 26,100 and 25,300 for 2 and 4 h sintering at 1230 °C respectively. Since all polished pellets are 100% perovskite phase, density and grain size are the major factors to affect dielectric constant. These are shown in Fig. 7 and Table 3. The temperature related to maximum dielectric constant decreases with increasing sintering temperature obviously. This is different from PMN and PMN-PT ceramics produced by columbite route [3] or simplified columbite route [15]. In those studies, temperature related to maximum dielectric constant did not decrease more than 2 °C as sintering temperature increased 70 °C. The major difference between those routes and reaction-sintering process is

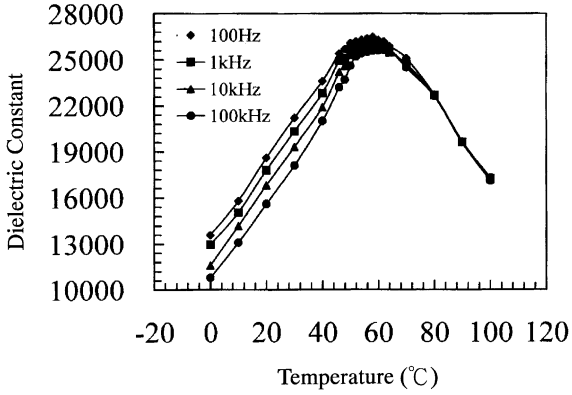

Fig. 9. Temperature dependence of dielectric constant of PMNT-RS ceramics sintered at 1230 °C/2 h.

Table 4
Maximum dielectric constant and related temperature under 1 kHz of PMNT-RS ceramics sintered at various temperatures for 2 and 4 h

Sintering temperature (°C)	1150	1200	1230	1250	1270
2 h	20,900/60 °C	22,600/60 °C	26,100/60 °C	24,300/58 °C	23,100/56 °C
4 h	21,700/60 °C	23,100/60 °C	25,300/58 °C	22,600/56 °C	22,100/54 °C

the precalcining of $MgNb_2O_6$. The mixture of PbO, $Mg(NO_3)_2$, Nb_2O_5 and TiO_2 is mixed, pressed and sintered directly in reaction-sintering process. This maybe result in a different distribution of B-site ions (Mg^{2+}, Nb^{5+} and Ti^{4+}) and Curie point of micro-regions. The temperature related to maximum dielectric constant is at about 60 °C, this is 20 °C higher than those produced by columbite route [5]. The reason is still unknown.

4. Conclusions

Dense 0.9PMN–0.1PT relaxor ceramics with high dielectric constant could be produced by simplified columbite route. Density of PMNT-SCR ceramic higher than 90% of theoretical density was obtained. The dielectric constant of PMNT-SCR at 100 Hz reached 20,000. The second calcination process in columbite route is omitted in this simplified columbite route to simplify the process.

Without any calcination process, a mixture of PbO, $Mg(NO_3)_2$ Nb_2O_5 and TiO_2 was pressed and sintered directly. Pyrochlore-free 0.9PMN–0.1PT perovskite ceramics with density of 8.07 g/cm^3 is obtained after sintered at 1230 °C for 2 h. Maximum dielectric constant under 1 kHz for 0.9PMN–0.1PT ceramics increases with sintering temperature and reaches 26,100 and 25,300 for 2 and 4 h sintering at 1230 °C respectively. The reaction-sintering process is a simple and effective process to produce 0.9PMN–0.1PT ceramics with 100% perovskite phase, high density and high dielectric constant.

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