

Synthesis of $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})_{0.72}\text{Ti}_{0.28}\text{O}_3$ perovskite ceramics by a reaction-sintering process

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Abstract $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})_{0.72}\text{Ti}_{0.28}\text{O}_3$ (PNNT) perovskite ceramics produced by a reaction-sintering process were investigated. Without any calcination, the mixture of PbO , $\text{Ni}(\text{NO}_3)_2$, Nb_2O_5 and TiO_2 was pressed and sintered directly into PNNT ceramics. PNNT ceramics of 100% perovskite phase were obtained. For PNNT sintered for 2 h in PbO compensated atmosphere, maximum density reaches a value 8.49 g/cm^3 (99.8% of the theoretical value) at 1250°C . A maximum dielectric constant 20600 occurred around 37°C at 1 kHz in PNNT sintered at 1250°C for 2 h.

Keywords PNN-PT · Dielectric · Reaction-sintering process

1. Introduction

$\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PNN) is a lead-based complex perovskite ceramics. It is a relaxor ferroelectric material and exhibits a broad maximum in the dielectric constant. PNN single-crystals showed typical relaxor ferroelectric behavior with dielectric constant ~ 2500 at room temperature and ~ 4000 at -120°C under 1 kHz [1]. Curie temperature shifts to a higher temperature as lead titanate (PbTiO_3 or PT) is added to form the solid solution PNN-PT. This also increases the maximum dielectric constant to values of 10000–20000 [2, 3]. Single phased perovskite PNN is very difficult to obtain via the conventional mixed-oxide method [4]. Veitch reported pure phase perovskite PNN ceramic could be produced by the columbite precursor method [5]. Swartz and

Shrout first proposed this method to prepare single-phase perovskite $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) [6]. Two calcination stages were involved, columbite MgNb_2O_6 formed first and then reacted with PbO to form PMN perovskite powder. A simplified columbite route to produce single-phase PMN ceramics was proposed by Liou and Wu [7]. The second calcination and pulverization steps in the columbite routes were bypassed. The mixture of MgNb_2O_6 and PbO was pressed into pellets and sintered directly. Kwon et al. prepared 0.65PMN-0.35PT ceramics via a low-temperature reactive sintering from $(\text{PbCO}_3)_2\text{Pb}(\text{OH})_2$, MgNb_2O_6 and TiO_2 at 1000°C [8, 9]. A novel mechanical activation process has been employed to produce PMN, PT and $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ [10–12]. In this mechanical technique, the powder of reactants are homogenized and activated in a high-energy vibromill. Liou and co-workers further developed a reaction-sintering process to produce pyrochlore-free PMN and $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN) ceramics [13, 14]. The mixture of PbO , $\text{Mg}(\text{NO}_3)_2$ (or $\text{Fe}(\text{NO}_3)_3$) and Nb_2O_5 was pressed and sintered directly into PMN and PFN ceramics without any calcination stage involved.

In this study, the authors try to produce $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})_{0.72}\text{Ti}_{0.28}\text{O}_3$ (PNNT) perovskite ceramics by the reaction-sintering process.

2. Experimental procedure

All samples in this study were prepared from reagent-grade oxides: PbO (99.9%, J. T. Baker, USA), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($>98\%$, Showa, Japan), Nb_2O_5 (99.8%, High purity chemicals, Japan) and TiO_2 (99.8%, Showa, Japan). Appropriate amounts of PbO , $\text{Ni}(\text{NO}_3)_2$, Nb_2O_5 and TiO_2 for stoichiometric $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})_{0.72}\text{Ti}_{0.28}\text{O}_3$ were milled in acetone with zirconia balls for 12 h. After the slurry was dried and

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pulverized, the powder was then pressed into pellets 12 mm in diameter and 1–2 mm thick. The pellets were then heated at a rate 10°C/min and sintered in covered alumina crucible at temperatures ranging from 1200°C to 1270°C for 2 h and 4 h in air or in 3 wt% PbO compensated atmosphere.

The density of sintered pellets was measured by water immersion method. Microstructures were analyzed on the fracture surface of the pellets by a scanning electron microscopy (SEM). The sintered PNNT ceramics were analyzed by X-ray diffraction (XRD) to calculate the content of pyrochlore phase. The relative amounts of perovskite and pyrochlore phases were determined from XRD patterns of the samples by measuring the major peak intensities for the perovskite (110) and pyrochlore (222) phases. The following qualitative equation was used.

$$\% \text{ of perovskite} = 100 \times I_{\text{perov.}} / (I_{\text{perov.}} + I_{\text{pyro.}})$$

After polishing, the dimensions were measured before silver electrodes were formed on the pellets. Dielectric properties at various frequencies between 100 Hz to 100 kHz were measured with an HP4194A impedance analyzer in a temperature-controlled chamber from –5°C to 60°C.

3. Results and discussion

Weak reflections of $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ pyrochlore phase (222) peak were detected in the XRD patterns of PNNT ceramics sintered at 1230–1270°C for 2 h as shown in Fig. 1. The content

of pyrochlore phase is 1–3% at 1230°C and 1250°C. 7.88% of pyrochlore phase existed in PNNT sintered at 1270°C due to the increased PbO evaporation. For 4 h sintering, the intensity of (222) peak increases in Fig. 2. This means ceramics with perovskite phase as main phase could be obtained even with the calcination stage bypassed. From the formation mechanisms of perovskite $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PNN) in the reaction-sintering process, pyrochlore phase $\text{Pb}_2\text{Nb}_2\text{O}_7$ (P_2N_2) was found in pellets heated to 500°C and cooled immediately without any soaking period. Cubic $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ (P_3N_4) pyrochlore phase formed and became the main phase in pellets heated to 600°C. After being heated to 800°C, $\text{Pb}_3\text{Nb}_2\text{O}_8$ (P_3N_2) pyrochlore phase formed. As the pellets were heated to 900°C, NiNb_2O_6 columbite phase appeared. At 950°C, PNN perovskite phase began to form. This means the perovskite phase formed at a temperature between 900°C and 950°C. As the pellets were heated to 1000°C, a large amount of PNN was formed and became dominant. After heated to 1250°C, the P_3N_4 content decreased significantly [15]. Therefore, perovskite phase could be formed during the heating up period to the sintering temperature. 4.8 ~ 6.5% content of pyrochlore phase are detected in PNN pellets sintered at 1150–1230°C for 2 h in our other investigation [16]. This implies that the formation of pyrochlore decreased as PNN was modified by 28% PT.

Density of PNNT ceramics sintered at various temperatures for 2 h and 4 h are listed in Table 1. For 2 h sintering, it increases with sintering temperature and reaches a maximum value 8.41 g/cm³ at 1250°C. As the soak time increased, maximum density value 8.37 g/cm³ occurred at 1230°C and

Fig. 1 XRD patterns of PNNT ceramics sintered at 1230–1270°C for 2 h

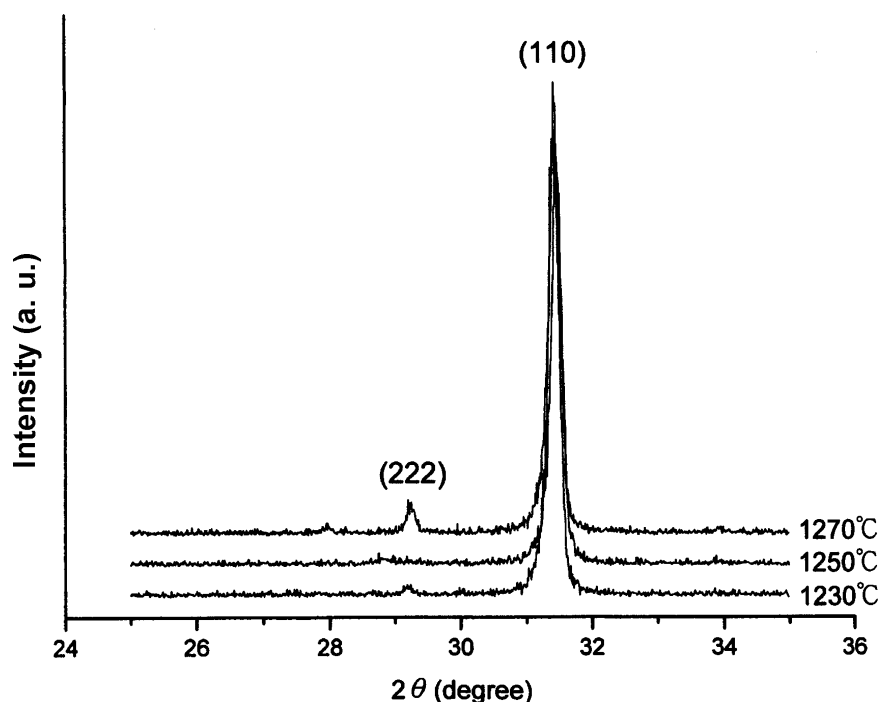
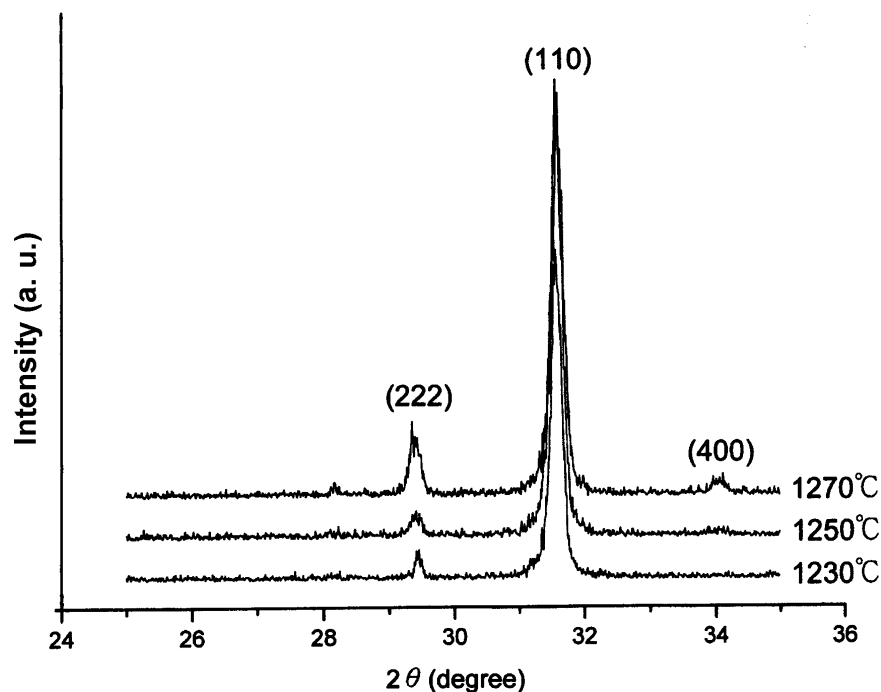


Fig. 2 XRD patterns of PNNT ceramics sintered at 1230–1270°C for 4 h**Table 1** Density and mean grain size of PNNT ceramics sintered at various temperatures for 2 h and 4 h

Sintering Temperature (°C)	Density (g/cm ³)	Grain Size (μm)
2 h		
1200	7.14	2.7
1230	8.32	3.2
1250	8.41	4.1
1270	8.26	4.9
4 h		
1200	7.63	3.1
1230	8.37	4.0
1250	8.28	5.3
1270	8.13	7.0

decreased at 1250°C and 1270°C due to the increased evaporation of PbO. In our study of PNN ceramics prepared by the reaction-sintering process, 98.5% of theoretical value was obtained at 1230°C/2 h sintering [16]. The sintering temperature for dense PNN ceramic pellets is lower than PNNT with a soak time of 2 h. The maximum density of PNNT ceramic is higher than those obtained by a columbite route. In the study of Takahashi et al., the maximum relative densities of the (1-x)PNN-xPT ceramics with $x = 0.2$ and 0.4 were 97.0 and 97.8% upon sintering at 1050°C and 1150°C by the columbite route. The sintering temperature indicating the maximum relative density tended to increase with an increase of the composition x [2].

The SEM photographs of the fracture surfaces from PNNT ceramics are illustrated in Fig. 3 and Fig. 4. There is no pyrochlore grain found in these sintered pellets. Therefore, the pyrochlore phase detected by XRD in Fig. 1 and 2 was formed on the surface. Grains of typical perovskite ceramics such as regular, multifaceted and equiaxed morphology were formed. Grains of same morphology were observed in PNN ceramics by the columbite precursor process reported by Alberta and Bhalla [17]. Grain sizes are found increased with sintering temperature and almost no pore is observed. Mean grain size of PNNT ceramics sintered at various conditions are listed in Table 1. The grain size increases with sintering temperature and soak time. This is consistent with results in Fig. 3 and Fig. 4. About 3–7 μm grain size was obtained in PNNT ceramics sintered at 1200–1270°C for 2 h and 4 h by reaction-sintering process. In the study of Alberta and Bhalla, grain of 3.7 μm was reported in PNN ceramics after 1200°C/2 h sintering [17]. In our study of PNN ceramics prepared by reaction-sintering process, 4.1 μm and 5.2 μm grains were obtained after 1230°C/2 h and 1250°C/2 h sintering [16]. All these results indicate that higher temperature is needed for grain growth in PNNT ceramics than in PNN ceramics.

The PNNT ceramics are about of 92–99% perovskite phase at 1230–1270°C sintering in air. Sintering in PbO compensated atmosphere was used to eliminate the pyrochlore phase. In the study of PNN ceramics prepared by reaction-sintering process, 5 wt% PbO powder was added beside the

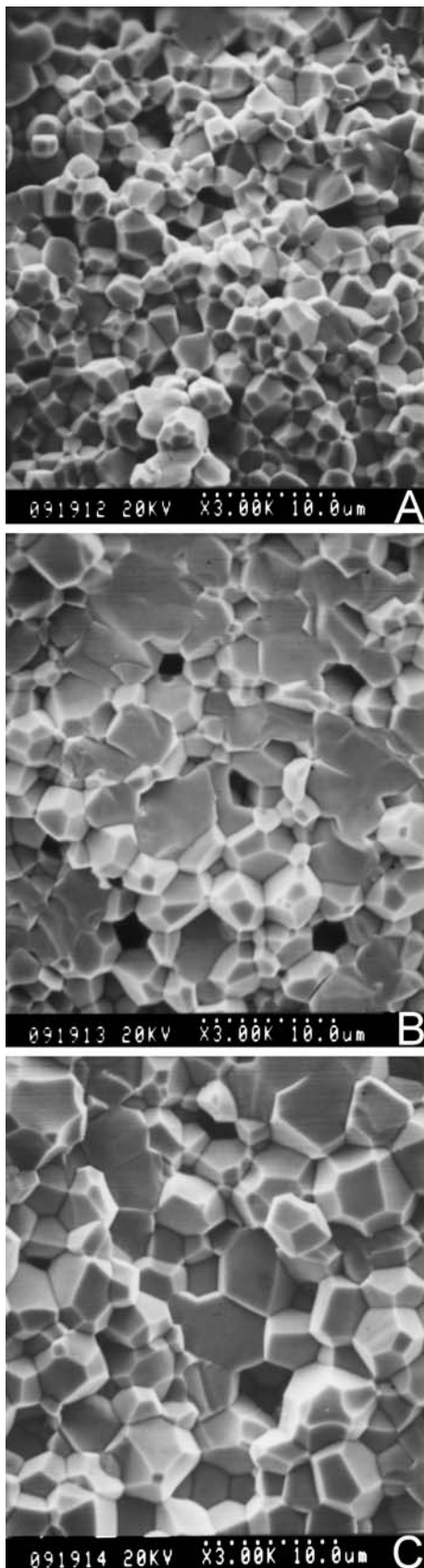


Fig. 3 SEM photographs of as-fired surfaces of PNNT ceramics sintered at (A) 1230°C, (B) 1250°C and (C) 1270°C for 2 h

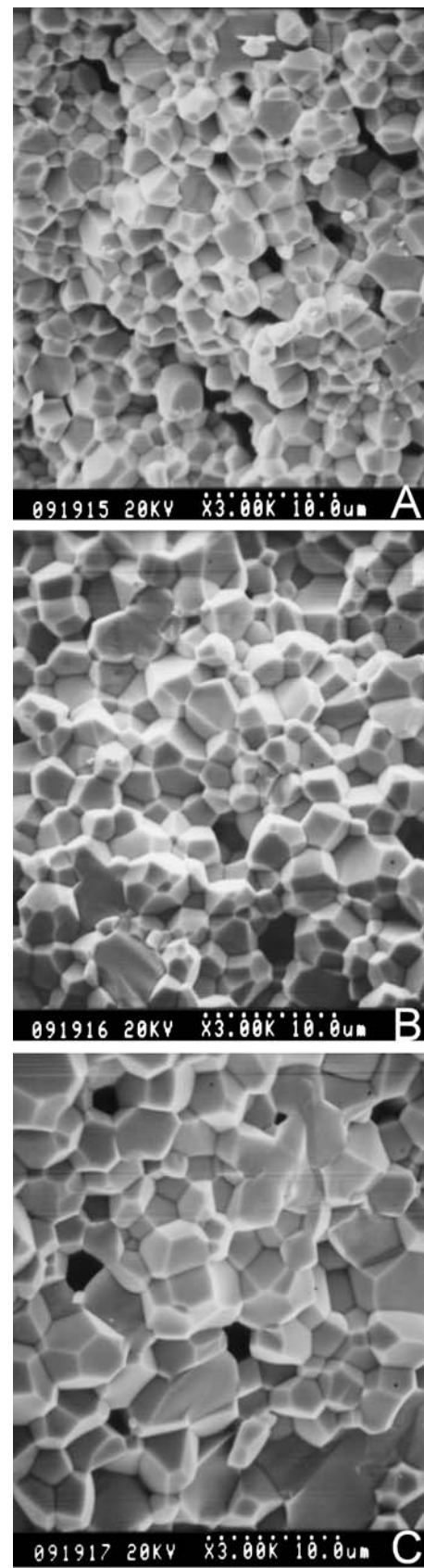
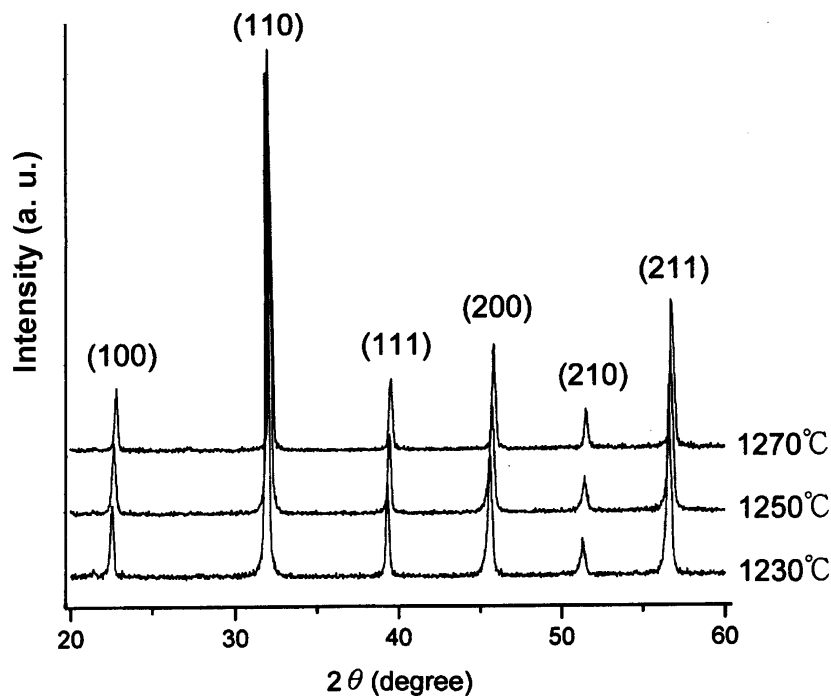


Fig. 4 SEM photographs of as-fired surfaces of PNNT ceramics sintered at (A) 1200°C, (B) 1230°C and (C) 1250°C for 4 h

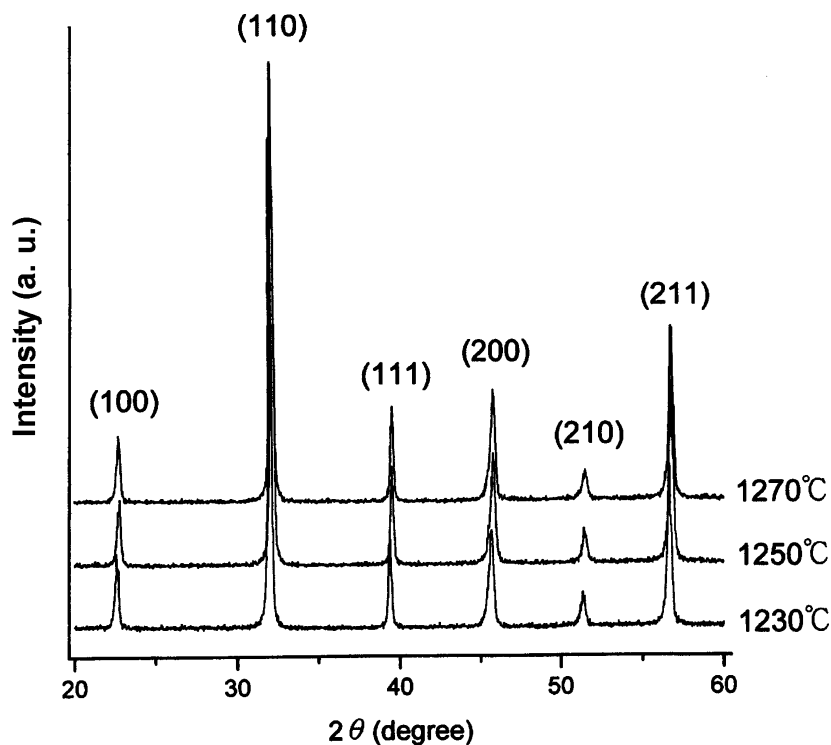
Fig. 5 XRD patterns of PNNT ceramics sintered at 1230–1270°C for 2 h in PbO compensated atmosphere



stacked pellets in the covered alumina crucible. This resulted in pyrochlore-free PNN ceramics [16]. As higher perovskite contents were obtained in PNNT ceramics than in PNN ceramics sintered in air, a lower amount PbO powder of 3 wt% was added in PNNT. XRD patterns of PNNT ceramics

sintered in PbO compensated atmosphere (PNNT3P) at 1230–1270°C for 2 h and 4 h are shown in Fig. 5 and Fig. 6, respectively. No reflection of pyrochlore phase appears in these patterns. From the results discussed, PNNT perovskite phase seems more difficult to form as compared with PMN,

Fig. 6 XRD patterns of PNNT ceramics sintered at 1230–1270°C for 4 h in PbO compensated atmosphere



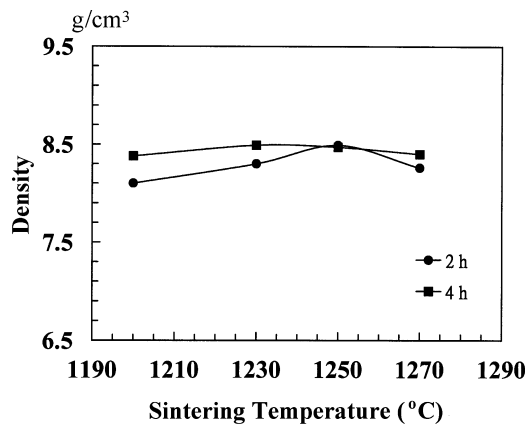


Fig. 7 Variation of density with sintering temperature for PNNT ceramics in PbO compensated atmosphere

PFN, PMN-PFN and PMN-PZN perovskite ceramics by a reaction-sintering process. Pure perovskite phase could be obtained in these materials without any PbO compensation (mixed into the pellets or added beside the pellets) [13–14, 18–19]. The results in Fig. 5 and Fig. 6 prove that monophasic PNNT ceramics could be prepared successfully by the reaction-sintering process. Although monophasic PNNT ceramics could be prepared via columbite precursor method, there are two calcining and pulverizing steps [3]. These steps were bypassed in reaction-sintering process and the mixture of raw materials was sintered directly into perovskite ceramics. Therefore, the reaction-sintering process is a simple and effective process.

Density values higher than 95% of the theoretical value are observed in PNNT3P pellets sintered at 1200–1270°C for 2 h as shown in Fig. 7. It reaches a value 8.49 g/cm³ (99.8% of the theoretical value) after 1250°C sintering. This is higher than the maximum value obtained in PNNT without PbO compensation as discussed previously. Therefore, PbO compensation has positive effect on the perovskite yield and densification improvement. For a longer sintering of 4 h, maximum density value 8.49 g/cm³ occurred at 1230°C. The SEM photographs of PNNT3P ceramics sintered at 1200°C to 1250°C for 2 h are illustrated in Fig. 8. Pyrochlore phase is not found in these photographs. The grain size increased apparently with sintering temperature. Pores are observed in pellets sintered at 1200°C and decreased drastically at higher sintering temperatures. As compared with 2 h sintered pellets, grain size increases obviously in pellets sintered for 4 h as shown in Fig. 9. Mean grain sizes of PNNT3P ceramics sintered at various temperatures are listed in Table 2. 2.8–7.9 μm grain size was obtained in PNNT3P ceramics sintered at 1200–1270°C for 2 h and 4 h by reaction-sintering process. As compared with grain sizes of PNNT sintered in air, larger grains are observed in PNNT3P for same sintering condition.

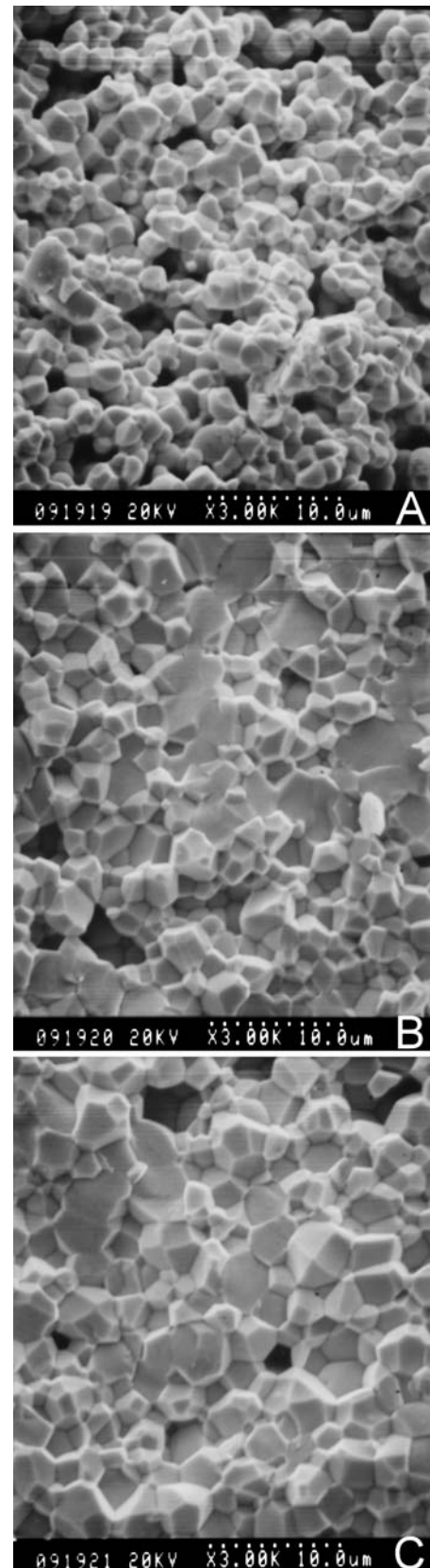


Fig. 8 SEM photographs of as-fired surfaces of PNNT ceramics sintered at (A) 1200°C, (B) 1230°C and (C) 1250°C for 2 h in PbO compensated atmosphere

Table 2 Mean grain size of PNNT ceramics sintered at various temperatures for 2 h and 4 h in PbO compensated atmosphere. (in μm)

Sintering Temperature ($^{\circ}\text{C}$)	2 h	4 h
1200	2.8	3.2
1230	3.4	4.4
1250	4.3	5.6
1270	5.8	7.9

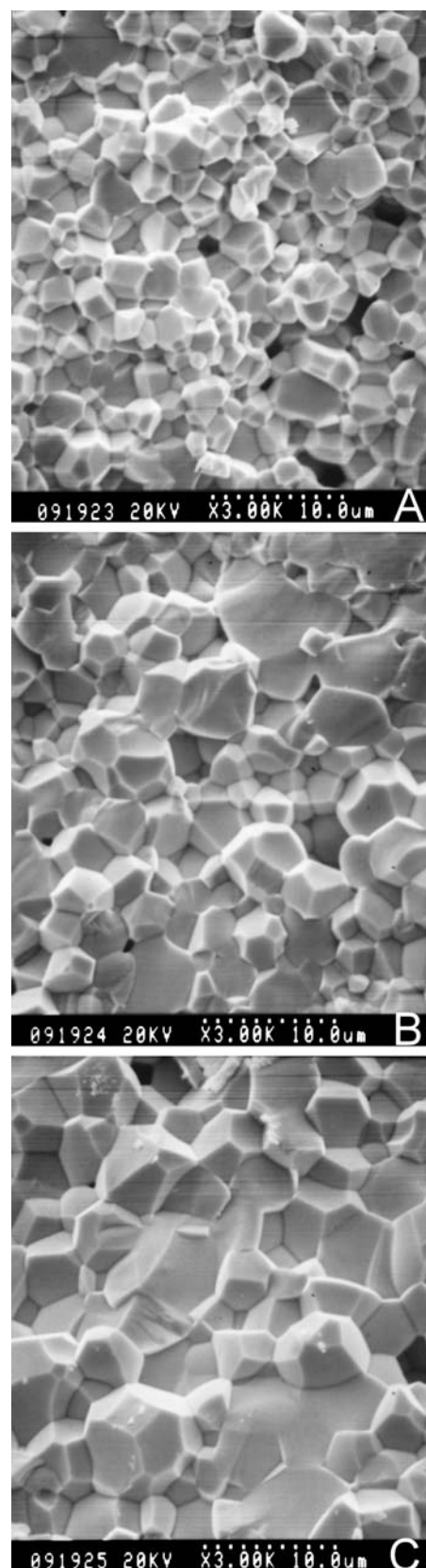
Table 3 Dielectric constants (K_{RT}) and loss tangent at room temperature and 1 kHz for PNNT ceramics sintered at various temperatures for 2 h in PbO compensated atmosphere

Sintering Temperature ($^{\circ}\text{C}$)	K_{RT}	Loss Tangent
1200	11500	0.049
1230	16300	0.061
1250	17900	0.066
1270	15200	0.063

The dielectric constant (K_{RT}) and loss tangent at room temperature and 1 kHz for PNNT3P ceramics sintered at various temperatures for 2 h are listed in Table 3. K_{RT} increased with sintering temperature and reached a maximum value 17900 at 1250°C . As all pellets are 100% of perovskite phase, this was resulted from the increased density and grain size. Figure 10 shows the variation of dielectric constant and loss with temperature for PNNT3P sintered at 1250°C for 2 h. These curves are similar to those of PNN and PNNT ceramics reported by other researchers [3, 17]. A maximum dielectric constant 20600 occurred around 37°C at 1 kHz. Lei et al. reported maximum dielectric constant 17002 at 1 kHz was found at 33°C in PNNT ceramic prepared by columbite route. There was still some pyrochlore phase in their pellets and resulted in a lower dielectric constant [3]. Therefore, pyrochlore-free and highly dense PNNT ceramics with good dielectric property could be prepared by a simple and effective reaction-sintering process.

4. Conclusion

Pyrochlore-free $0.72\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.28\text{PbTiO}_3$ (PNNT) perovskite ceramics have been successfully produced by a simple and effective reaction-sintering process. The PNNT ceramics are about of 92–99% perovskite phase at $1230\text{--}1270^{\circ}\text{C}$ sintering in air. Pyrochlore-free PNNT ceramics were obtained as sintered in 3 wt% PbO compensated atmosphere. For PNNT sintered for 2 h in PbO compensated atmosphere, maximum density reaches a value 8.49 g/cm^3 (99.8% of the theoretical value) at 1250°C . A maximum dielectric constant 20600 occurred around 37°C at 1 kHz in PNNT sintered at 1250°C for 2 h.

**Fig. 9** SEM photographs of as-fired surfaces of PNNT ceramics sintered at (A) 1200°C , (B) 1230°C and (C) 1250°C for 4 h in PbO compensated atmosphere

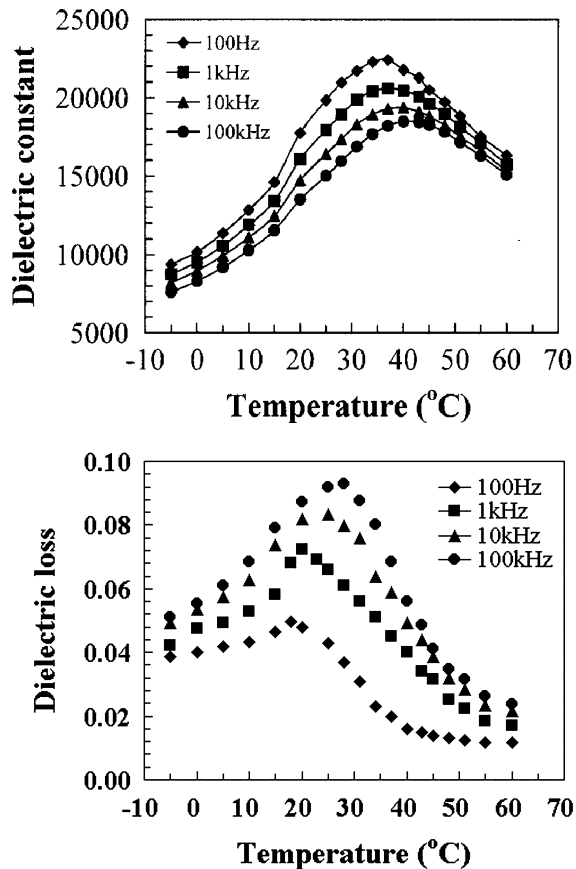


Fig. 10 Variation of dielectric constant with temperatures for PNNT ceramics sintered at 1250°C for 2 h in PbO compensated atmosphere

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