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Preparation and phase formation of perovskite $Pb(Ni_{1/3}Nb_{2/3})O_3$ by a reaction-sintering process

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Abstract Pyrochlore-free $Pb(Ni_{1/3}Nb_{2/3})O_3$ perovskite ceramics produced by a simple and effective reaction-sintering process were investigated. Without any calcination, the mixture of PbO, $Ni(NO_3)_2$ and Nb_2O_5 was pressed and sintered directly into PNN ceramics. Density of 98.5% of theoretical value was obtained after sintered at 1230 °C for 2 h in air. 99.3% of theoretical density was obtained after sintered at 1,200 °C for 2 h in PbO compensated atmosphere. PNN ceramic with dielectric constant 1,680 at 25 °C and 1 kHz has been obtained.

Introduction

Ferroelectric relaxor lead nickel niobate ($Pb(Ni_{1/3}Nb_{2/3})O_3$ or PNN) is a member of lead-based complex perovskite ceramics. It exhibits a broad maximum in the dielectric constant. PNN single-crystals showed typical relaxor ferroelectric behavior with dielectric constant ~2,500 at room temperature and ~4,000 at –120 °C under 1 kHz [1]. As lead titanate ($PbTiO_3$ or PT) is added, the Curie temperature of the solid solution PNN-PT shifts to a higher temperature. The maximum dielectric constant also increases to values of 10,000–20,000 [2]. Monophasic perovskite PNN is very difficult to produce by the conventional mixed-oxide method [3]. Veitch reported pure phase perovskite PNN ceramic could be prepared via the columbite precursor method [4]. This method was first proposed by Swartz and Shrout to prepare single-phase perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) [5]. There were two calcination stages involved, $MgNb_2O_6$ columbite formed first and followed by formation of PMN perovskite. Liou and Wu proposed a simplified columbite route to produce single-phase perovskite PMN ceramics [6]. The mixture of $MgNb_2O_6$ and PbO was pressed into pellets and sintered directly. The second calcination and pulverization steps in the columbite route were bypassed. Liou and co-workers further proposed a reaction-sintering process to prepare pyrochlore-free PMN and $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) ceramics [7, 8]. Without any calcination stage involved, the mixture of PbO, $Mg(NO_3)_2$ (or $Fe(NO_3)_3$) and Nb_2O_5 was pressed and sintered directly into PMN and PFN ceramics. In this study, $Pb(Ni_{1/3}Nb_{2/3})O_3$ (PNN) perovskite ceramics were prepared by a reaction-sintering process.

Experimental procedure

All samples in this study were prepared from reagent-grade oxides: PbO (99.9%, J. T. Baker, USA), $Ni(NO_3)_2{\cdot}6H_2O$ (>98%, Showa, Japan) and Nb_2O_5 (99.8%, High purity chemicals, Japan). Appropriate amounts of PbO, $Ni(NO_3)_2$ and Nb_2O_5 for stoichiometric PNN were milled in acetone with zirconia balls for 12 h. After the slurry was dried and pulverized, the powder was pressed into pellets 12 mm in diameter and 1–2 mm thick. The pellets were then heated with a rate 10 °C/min and sintered in a covered alumina

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crucible at temperatures ranging from 1,150 °C to 1,250 °C.

The sintered PNN ceramics were analyzed by X-ray diffraction (XRD) to calculate the content of pyrochlore phase. Microstructures were analyzed by scanning electron microscopy (SEM). The density of sintered pellets was measured by the Archimedes's method. The dielectric constant was measured by an impedance analyzer (Agilent 4294A).

Results and discussion

XRD patterns of PNN ceramics sintered at 1,150–1,250 °C for 2 h are shown in Fig. 1. The (222) and (400) peaks of $Pb_3Nb_4O_{13}$ pyrochlore phase are found in pellets sintered at 1,150–1,230 °C. The content of pyrochlore phase is calculated to be 4.8–6.5%. These pyrochlore peaks disappear after 1,250 °C sintering. XRD patterns of PNN ceramics sintered at 1,150–1,250 °C for 4 h are similar to patterns in Fig. 1. The (222) and (400) peaks of $Pb_3Nb_4O_{13}$ pyrochlore phase are also observed in pellets sintered at 1,150–1,230 °C. These pyrochlore peaks disappear again after 1,250 °C sintering. This proves that monophasic PNN ceramics are possible to be prepared by the reaction-sintering process. In the study of Lu and Hwang, PNN of 97.5% perovskite phase was obtained via the columbite precursor process. As 1 wt% excess NiO and 5 wt% excess PbO were added, phase-pure PNN ceramics could be obtained [9]. Two calcining and pulverizing steps were involved in the columbite precursor process. While in our reaction-sintering process, these steps were bypassed and the mixture of raw materials was sintered directly. Therefore, the reaction-sintering process is a simple and effective process. In order to understand the formation of the pyrochlore phase, the reaction mechanism was investigated. The mixture of the starting materials was heated to various temperatures then cooled immediately. The XRD results are illustrated in Fig. 2. At 800 °C, PbO was detected in the pellets. Two kinds of pyrochlore phases were formed in the pellets. These are $Pb_3Nb_4O_{13}$ and $Pb_3Nb_2O_8$ pyrochlore phases. The intensity of $Pb_3Nb_4O_{13}$ is higher than that of $Pb_3Nb_2O_8$. It indicates $Pb_3Nb_4O_{13}$ pyrochlore phase was first formed during the heating-up period to 800 °C. In the study of Chen et al., cubic $Pb_3Nb_4O_{13}$ pyrochlore phase was first formed in the 3PbO–$2Nb_2O_5$ mixture around 580 °C and remained stable up to the temperature 800 °C. While in the 3PbO–Nb_2O_5 mixture, $Pb_3Nb_4O_{13}$ was the first formed pyrochlore phase and further transformed into $Pb_2Nb_2O_7$ by reacting with PbO at 700 °C. $Pb_3Nb_2O_8$ began to appear at 700 °C and became dominant at temperature of 800 °C. This change from $Pb_3Nb_4O_{13}$ to $Pb_2Nb_2O_7$ and finally to $Pb_3Nb_2O_8$ is strongly dependent on PbO amount and phase stability [10]. The peaks of $Pb_3Nb_2O_8$ were enhanced and PbO was still detected in the pellets heated to 900 °C. A weak reflection of $NiNb_2O_6$ was

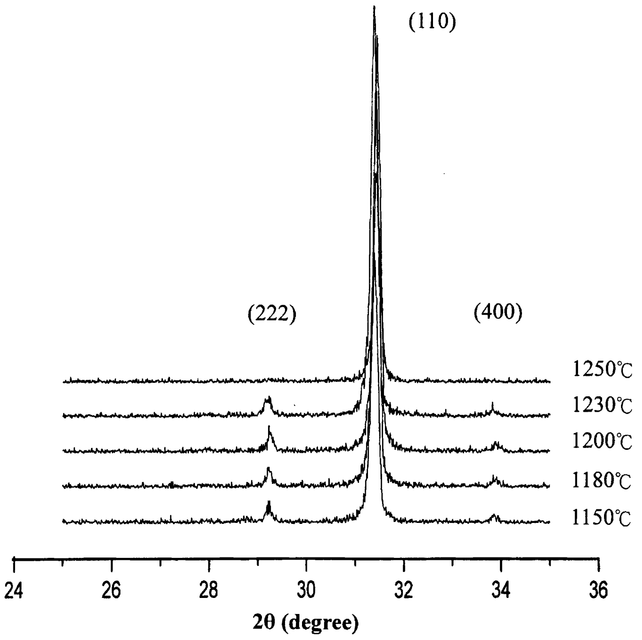

Fig. 1 XRD patterns of PNN ceramics sintered at 1,150–1,250 °C for 2 h

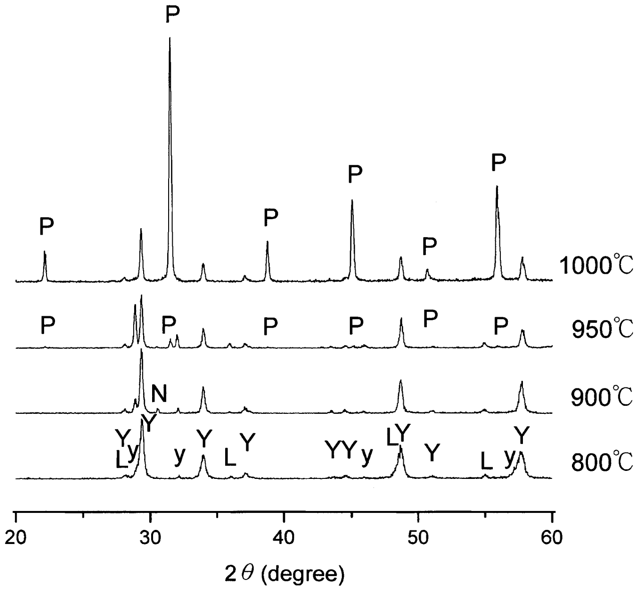

Fig. 2 XRD patterns of PNN pellets heated to 800–1,000 °C then cooled immediately. P: PNN, Y: $Pb_3Nb_4O_{13}$, y: $Pb_3Nb_2O_8$, L: PbO, N: $NiNb_2O_6$

also detected in these pellets as shown in Fig. 2. In the study of Lu and Hwang, a large amount of $NiNb_2O_6$ was formed at 800°C in the calcined mixture of NiO and Nb_2O_5 [9]. In PNN-PT powder synthesized by only one-calcination step using a coating method, Xiang et al. reported $2.31PbO{\cdot}Nb_2O_5$ formed at 400–600 °C/2 h calcining and $3PbO{\cdot}2Nb_2O_5$ ($Pb_3Nb_4O_{13}$) formed at 500–800 °C/2 h calcining [11]. There is no $NiNb_2O_6$ phase observed in their study. While in the reaction-sintering process, although Nb_2O_5 is easy to react with PbO to form pyrochlore phases, some Nb_2O_5 still remained at a temperature near 900 °C due to the fast heating rate 10 °C/min and a short period (30 min from 600 °C to 900 °C) for reaction. These remained Nb_2O_5 reacted with NiO and minor $NiNb_2O_6$ phase formed. For pellets heated to 950 °C and cooled immediately, the peaks of PNN perovskite phase appeared. This means the perovskite phase formed at a temperature between 900 °C and 950 °C. There were two possible formation paths for perovskite PNN: the reaction of pyrochlore with NiO (the same as the conventional mixed oxide method) or the reaction of $NiNb_2O_6$ with PbO (the same as the columbite route). As the pellets were heated to 1,000 °C, large amount of PNN was formed and became dominant. The PbO, $NiNb_2O_6$ and $Pb_3Nb_2O_8$ phases disappeared. It indicates that the perovskite PNN phase was almost formed during the heating-up period to a temperature between 950 °C and 1,000 °C. This proves the calcination stages in the conventional mixed oxide method or the columbite route could be bypassed.

Density values of PNN ceramics sintered at various temperatures are listed in Table 1. Density increased

Table 1 Density and mean grain size of PNN and PNN5P ceramics sintered at various temperatures

Sintering Temperature (°C)		1,150	1,180	1,200	1,230	1,250
Density (g/cm^3)	PNN 2 h	8.21	8.26	8.34	8.44	8.29
	PNN5P 2 h	8.39	8.44	8.51	8.33	8.18
	PNN5P 4 h	8.32	8.39	8.46	8.25	8.07
Grain size (μm)	PNN 2 h	2.9	3.5	3.8	4.1	5.2
	PNN5P 2 h	2.4	3.1	4.0	5.3	6.5
	PNN5P 4 h	2.8	3.4	5.4	6.3	7.5

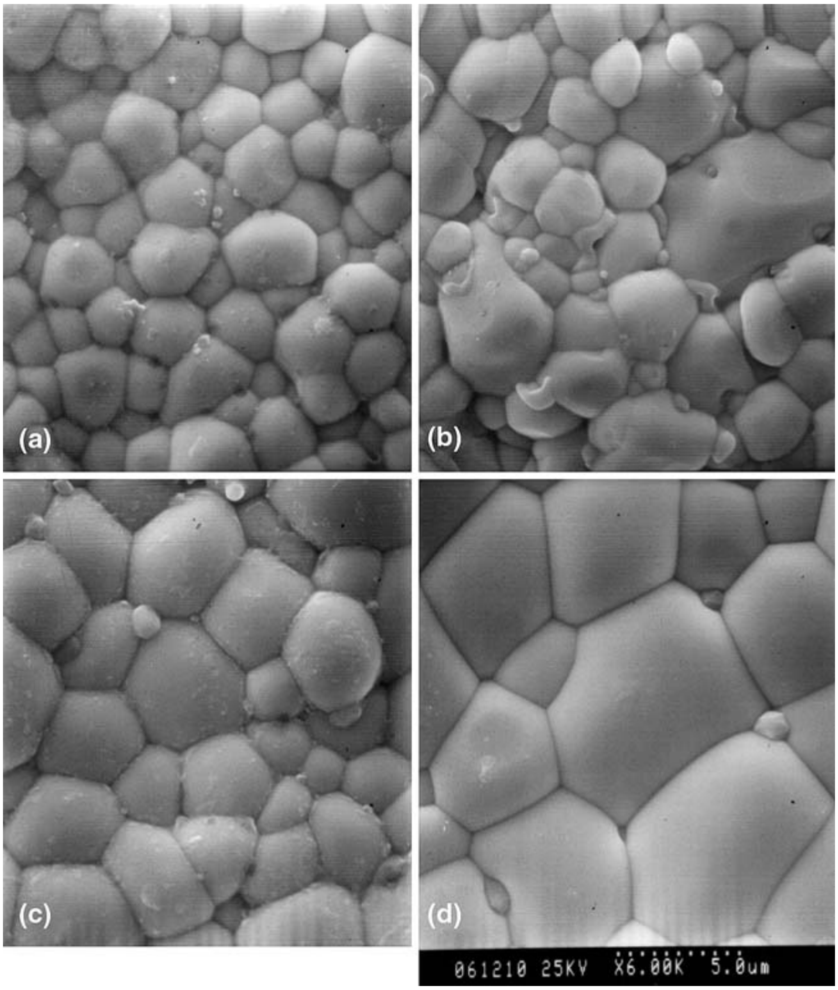

Fig. 3 SEM photographs of as-fired PNN ceramics sintered at (**a**) 1,150 °C, (**b**) 1,180 °C, (**c**) 1,230°C and (**d**) 1,250 °C for 2 h

with the sintering temperature and reached a value 8.44 g/cm^3 (98.5% of the theoretical value) at 1,230 °C. In PNN prepared by a columbite precursor process, the maximum density of 8.04 g/cm^3 was obtained after 1,200 °C/2 h sintering [12]. Therefore, the reaction-sintering process is more effective than the columbite precursor process to obtain dense PNN ceramics. The SEM photographs of as-fired PNN ceramics sintered at 1,150–1,250 °C for 2 h are illustrated in Fig. 3. Dense pellets without pores were observed. Grains of typical perovskite ceramics such as regular, multifaceted and equiaxed morphology were formed. Grains of same morphology were observed in the study of Alberta and Bhalla by the columbite precursor process [12]. In the studies of Lu and Hwang, quite different results were reported. Grains of cube-like morphology formed in PNN ceramics prepared by the columbite precursor and the hydrothermal processes [9, 13]. The reason for the formation of different morphology is still unknown. Mean grain sizes of PNN ceramics sintered at various temperatures are also listed in Table 1. The grain size increased apparently with sintering temperature. About 2.9–5.2 μm grain size was obtained in PNN ceramics sintered at 1,150–1,250 °C for 2 h by the reaction-sintering process. In the study of Alberta and Bhalla, grain size of 3.7 μm was reported in PNN ceramics after 1,200 °C/2 h sintering [12].

The PNN ceramics are of 100% perovskite phase only at 1,250 °C sintering in air. At temperatures below 1,250 °C, 4.8–6.5% pyrochlore phase existed in the sintered pellets. Sintering in PbO compensated atmosphere was used to eliminate the pyrochlore phase. 5 wt% PbO powder was added beside the stacked green pellets in a covered alumina crucible. XRD patterns of PNN ceramics sintered in PbO compensated atmosphere (PNN5P) at 1,150–1,230°C for 2 h and 4 h are shown in Fig. 4. Very weak peak of pyrochlore phase appears only in pellets sintered at 1,150 °C. The reflection of the remained and non-reacted Nb_2O_5 was also detected. Pyrochlore-free PNN5P ceramics were obtained at 1,180–1,230°C. The weak peaks of pyrochlore and non-reacted Nb_2O_5 disappeared in pellets sintered for 4 h at 1,150 °C. It indicates that 2 h is not enough for a complete formation of perovskite phase. From the results discussed, PNN perovskite phase seems more difficult to form as compared with PMN or PFN by a reaction-sintering process. Pure perovskite phase could be obtained in PMN and PFN without any PbO compensation (mixed into the pellets or added beside the green pellets) [7, 8]. Density values higher than 97% of the theoretical value are observed in PNN5P pellets sintered at 1,150–1,230 °C for 2 h as listed in Table 1. It reaches a value 8.51 g/cm^3 (99.3% of the theoretical value) at 1,200 °C. This is higher than the maximum value obtained in PNN 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, density decreases slightly due to increased PbO evaporation and reduced liquid-phase sintering. The SEM photographs of as-fired PNN5P ceramics sintered at 1,180–1,250 °C for 2 h and 4 h are illustrated in Figs. 5 and 6. Pores are not found in these photographs. This is consistent with the results of density values in Table 1. The grain size increased apparently with sintering temperature. Mean grain sizes of PNN5P ceramics sintered at various temperatures are also listed in Table 1. About 2.4–7.5 μm grain size was obtained in PNN5P ceramics sintered at 1,150–1,250 °C for 2 h and 4 h by the reaction-sintering process.

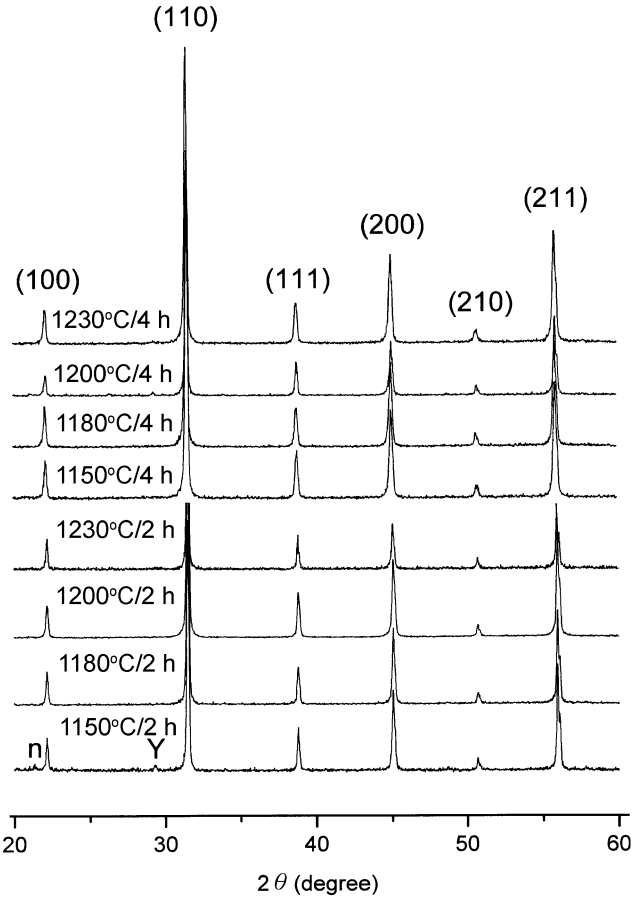

Fig. 4 XRD patterns of PNN ceramics sintered at 1,150–1,230 °C for 2 and 4 h in PbO compensated atmosphere. Y: $Pb_3Nb_4O_{13}$, n: Nb_2O_5

Properties of PNN ceramics produced by various methods are compared in Table 2. Highly dense PNN

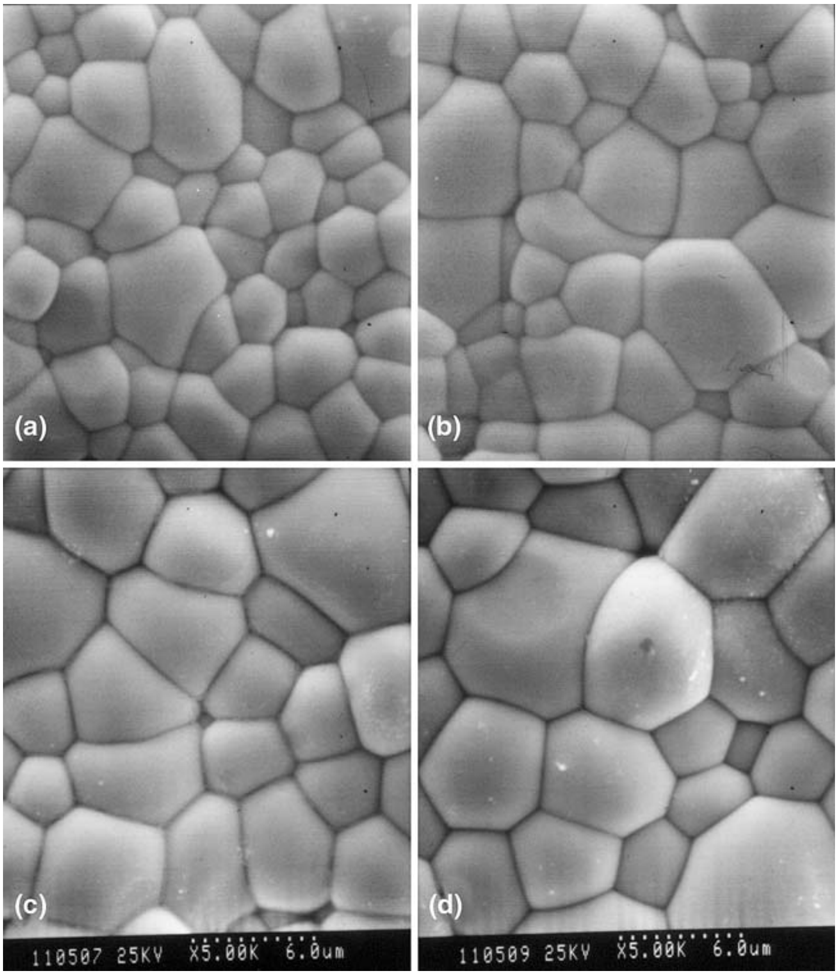

Fig. 5 SEM photographs of as-fired PNN ceramics sintered at (**a**) 1,180 °C, (**b**) 1,200 °C, (**c**) 1,230 °C and (**d**) 1,250 °C for 2 h in PbO compensated atmosphere

Table 2 Properties of PNN ceramics produced by various methods

Sample from	Lu et al. [13]	Alberta et al. [12]	This work
Processing	Hydrothermal process (250 °C)	Columbite route	Mixed oxide with $Ni(NO_3)_2$
Calcination temp./time	600–900 °C/2 h	1,000 °C/4 h& 950°C/4 h	No calcining
Sintering temp./time	1,200 °C/2 h	1,200 °C/2 h	1,200 °C/2 h in PbO atmosphere
Relative density	n.a.	93.8%	99.3%
Dielectric constant 25 °C, 1 kHz	~1,400	1,550	1,680
Grain size (μm)	n.a.	3.7	4.0

n.a.: not available

ceramic with higher dielectric constant 1,680 at 25 °C and 1 kHz has been obtained by the reaction-sintering process. It is simple and effective as compared with the columbite route or the hydrothermal process.

Conclusion

Pyrochlore-free $Pb(Ni_{1/3}Nb_{2/3})O_3$ perovskite ceramics have been successfully produced by a simple and effective reaction-sintering process. Pyrochlore phase formed in the PNN pellets sintered in air. Pure perovskite phase was obtained in PNN pellets sintered in PbO compensated atmosphere. Density values higher than 97% of the theoretical value are observed. It reached a value 8.51 g/cm^3 (99.3% of the theoretical value) at 1,200 °C. PNN ceramic with dielectric constant 1,680 at 25 °C and 1 kHz has been obtained.

$Pb_3Nb_4O_{13}$ and $Pb_3Nb_2O_8$ pyrochlore phases were formed in the pellets heated to 800 °C. In pellets heated to 950 °C, the peaks of PNN perovskite phase

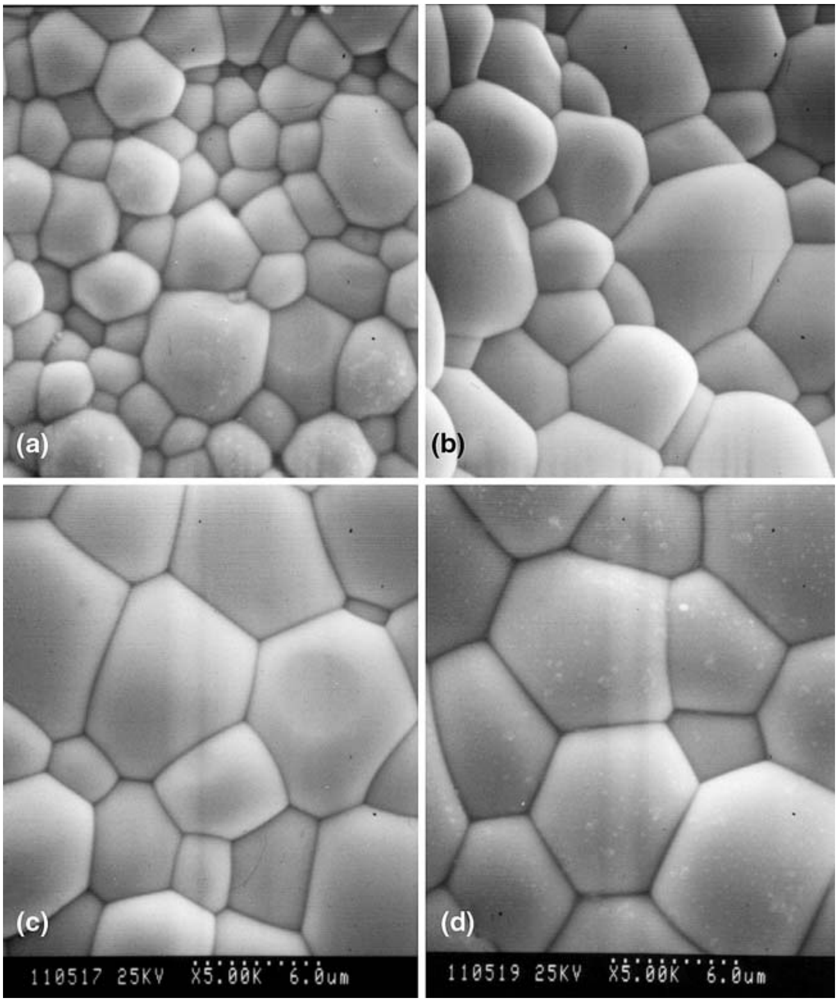

Fig. 6 SEM photographs of as-fired PNN ceramics sintered at (**a**) 1,180 °C, (**b**) 1,200 °C, (**c**) 1,230° C and (**d**) 1,250° C for 4 h in PbO compensated atmosphere

appeared. As the pellets were heated to 1,000 °C, large amount of PNN was formed and became dominant.

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