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Effect of heating rate on properties of $Pb(Fe_{1/2}Nb_{1/2})O_3$ ceramics produced by simplified wolframite route

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Abstract

Effect of heating rate on properties of $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) perovskite ceramics produced by a simplified wolframite route are investigated. Without calcining, the mixture of $FeNbO_4$ and PbO was pressed and heated to 1050 °C directly at various rates. PFN ceramics of 100% perovskite phase were obtained at 5, 10, 15, and 20 °C/min heating rates. Density increases as heating rate increased from 5 to 10 °C/min and reaches a maximum of 8.29 g/cm^3 at 10 °C/min. As the heating rate increased from 5 to 10 °C/min, K_{max} increases and reaches a maximum of approximately 21,000 at 10 °C/min.

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

1. Introduction

$Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) has been reported difficult to produce as single-phase ceramics due to the appearance of stable pyrochlore phases on calcination. In the study of Lejeune and Boilot [1], pure PFN powder is obtained after firing of a mixture of 4PbO, Fe_2O_3, and Nb_2O_5 at 850 °C for 16 h. Shrout et al. [2] prepared PFN powders by first mixing and reacting Fe_2O_3 and Nb_2O_5 at 1000 °C for 4 h to form $FeNbO_4$ (wolframite precursor). The obtained material was subsequently reactively sintered together with PbO at temperatures ranging from 750 to 800 °C for 4 h. Chiu et al. reported that single-phase stoichiometric PFN powders were formed by molten salt synthesis using mixtures of NaCl and KCl salts at 800 °C for 1.5 h [3]. Liou et al. [4] proposed a simplified wolframite route to produce pyrochlore-free PFN ceramics. The mixture of $FeNbO_4$ and PbO was pressed to pellets and sintered to PFN ceramics. The second calcination and pulverization stages in Shrout and Swartz's wolframite route were omitted. In their other study, a simple and effective reaction-sintering process was used to produce pyrochlore-free PFN ceramics. Without calcination, a mixture of PbO, Nb_2O_5 and $Fe(NO_3)_3$ was pressed and sintered directly into stoichiometric PFN ceramics after 2 and 4 h sintering at 1120–1210 °C [5].

Lejeune and Boilot [1] showed that the percentage of $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) phase decreased from 79 to 49% as the heating rate increased from 5 to 170 °C/min. Liou and Wu [6] reported an increasing heating rate to result in high perovskite content and dense $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ (0.9PMN–0.1PT) ceramics. The maximum dielectric constant was optimized with a heating rate of 10 °C/min.

In this investigation, the effect of heating rate on the properties of $Pb(Fe_{1/2}Nb_{1/2})O_3$ perovskite ceramics produced by the simplified wolframite route are studied.

2. Experimental procedure

$Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) ceramics were prepared from reagent-grade oxides: PbO (>99%), Fe_2O_3 (>97%), Nb_2O_5 (99.9%). First, Fe_2O_3 and Nb_2O_5 with 10 mol% excess Fe_2O_3 were ball-milled in distilled water with alumina media for 24 h. The slurry was dried and calcined at 1000 °C for 3 h with a heating rate 10 °C/min to form the wolframite precursor, $FeNbO_4$. The calcined powder was pulverized, and the appropriate amounts of PbO with 3 mol% excess were then added. After ball-milling and drying, the mixture of $FeNbO_4$ and PbO was pressed to pellets (12 mm in

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diameter and 2 mm thick). The pellets were heated at variable rates of 5, 10, 15, and 20 °C/min to 1050 °C before sintering in air for 4 h. The density of sintered PFN pellets was measured by the water immersion method. Microstructures were analyzed by scanning electron microscopy (SEM). Sintered PFN ceramics were analyzed by X-ray diffraction (XRD) to check the relative amounts of perovskite and pyrochlore phases. The ratio of the major X-ray peak intensity of the perovskite (I_{perov}) and the pyrochlore phases (I_{pyro}) is used to determine the volume percent of the perovskite phase as follows:

$$\text{Perovskite (\%)} = 100\left(\frac{I_{perov}}{I_{perov} + I_{pyro}}\right)$$

After polishing, the dimensions were measured before silver electrodes were deposited onto the pellets. Dielectric properties were measured with an HP4194A impedance analyzer in a temperature-controlled chamber from 60 to 150 °C.

3. Results and discussion

The variation of density with the heating rate for PFN ceramics produced by the simplified wolframite route were listed in Table 1. The density increases as the heating rate is increased from 5 to 10 °C/min and reaches a maximum of 8.29 g/cm^3 at 10 °C/min. It decreases at heating rates of 15 and 20 °C/min. This behavior is different from 0.9PMN–0.1PT ceramics proposed by the columbite route [6]. In 0.9PMN–0.1PT ceramics, the density increases with increased heating rate due to the decreased evaporation of PbO. In the simplified wolframite route, pellets of a mixture of $FeNbO_4$ and PbO powders were sintered directly without any calcining. At rates of 5 and 10 °C/min, the mixture was calcined completely during the heating-up period, and densification was also completed in that process. In contrary, at rates of 15 and 20 °C/min, the mixture was not calcined completely during the heating-up period. This resulted in calcination at early sintering period. Therefore, densification was not completed after sintering at 1050 °C for 4 h. Compared with PFN produced by the molten salt synthesis reported by Chiu et al. [3], the density of PFN sintered with our simplified wolframite route reaches 97% of the theoretical density, whereas in their study, it was found to be about 90% of the theoretical density. The XRD profile of PFN ceramic sintered with a heating rate 10 °C/min is shown in Fig. 1. The major peak (2 2 2) of $Pb_3Nb_4O_{13}$ pyrochlore phase at $2\theta = 29.2°$ is not found in the profile. For other heating rates, 100% perovskite phase were also obtained in PFN ceramics as illustrated in Fig. 2.

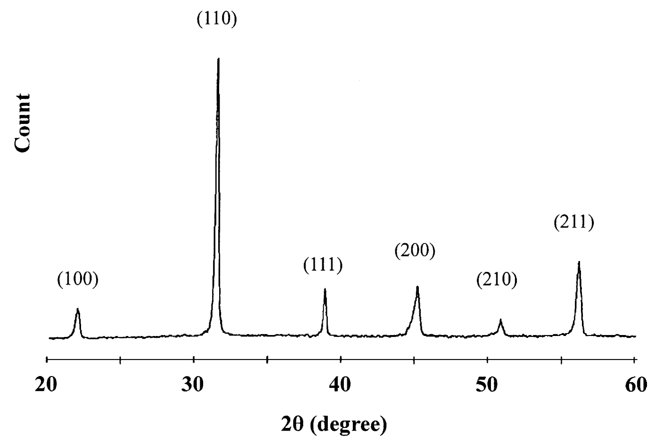

Fig. 1. XRD profile of the as-fired PFN ceramic after 1050 °C/4 h sintering at 10 °C/min.

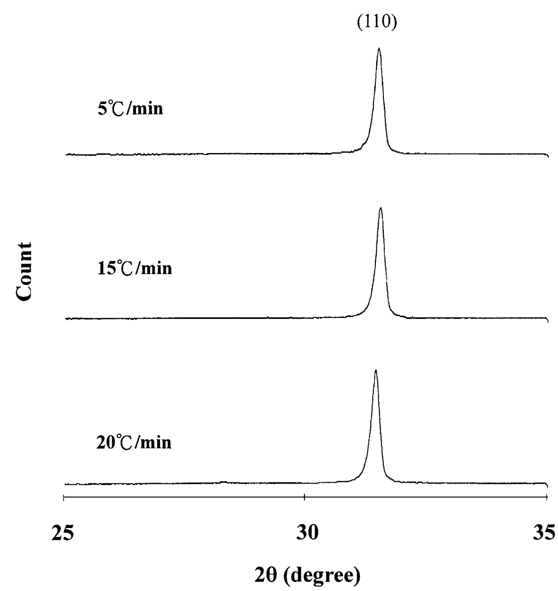

Fig. 2. XRD profiles of the as-fired PFN ceramics after 1050 °C/4 h sintering at 5, 15, and 20 °C/min.

SEM photographs of the as-fired PFN ceramics after sintering at various heating rates are illustrated in Fig. 3. No pyrochlore phase is found. Obviously, the grain size does not seem to be influenced by the heating rate. This may be

Table 1
The density, average grain sizes, maximum dielectric constant (K_{max}), and tan δ under 10 kHz of PFN ceramics sintered at 1050 °C/4 h at various heating rates

	Heating rate (°C/min)			
	5	10	15	20
Density (g/cm^3)	8.13	8.29	8.22	8.16
Grain size (μm)	2.3	3.3	2.7	2.6
K_{max}	18100 (102 °C)	21000 (100 °C)	14500 (102 °C)	13300 (102 °C)
tan δ	0.21	0.24	0.19	0.15

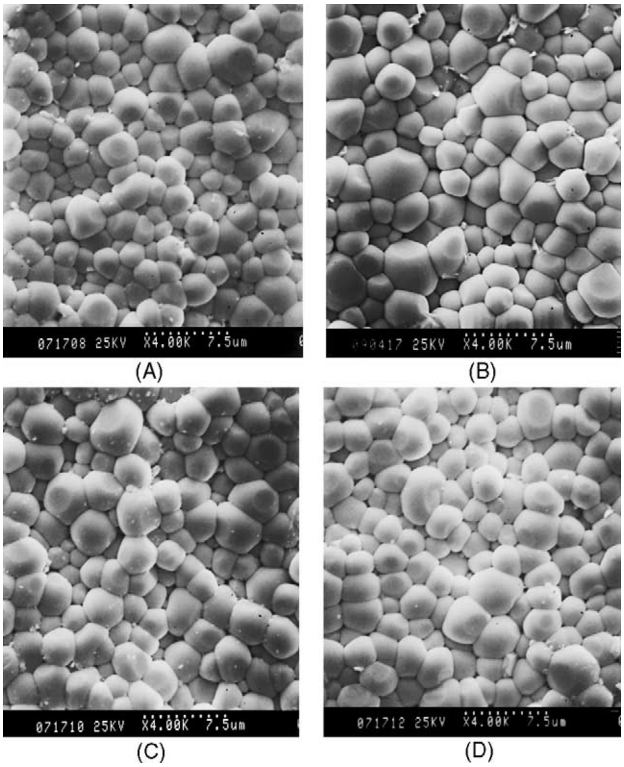

Fig. 3. SEM photographs of the as-fired PFN ceramics after 1050 °C/4 h sintering at (A) 5 °C/min, (B) 10 °C/min, (C) 15 °C/min, and (D) 20 °C/min.

because of the long sintering period of 4 h, resulting in grain growth. It is much longer than the heating up period, which makes the influence of the heating rate on the grain size unobservable. The average grain size of PFN ceramics after sintering at various heating rates is listed in Table 1. The grain size was found to be in the range of 2.3–3.3 μm for all heating rates.

Maximum dielectric constant (K_{max}) and tan δ values under 10 kHz of PFN ceramics are listed for various heating rates in Table 1. K_{max} increases as the heating rate increased from 5 to 10 °C/min and reaches a maximum of approximately 21,000 at 10 °C/min. It decreases at heating rates of 15 °C/min and 20 °C/min. The amount of the perovskite phase and the grain size did not change much for various heating rates. This is resulted from density of PFN pellet listed in Table 1. As the heating rate increases from 5 to 20 °C/min, tan δ varies between 0.15 and 0.24.

4. Conclusion

PFN ceramics produced by the simplified wolframite route and sintered at a temperature 1050 °C for 4 h are all pyrochlore-free for heating rates of 5–20 °C/min. The density reaches a maximum of 8.29 g/cm^3 at 10 °C/min. The grain size did not change much for various heating rates, grains of 2.3–3.3 μm are obtained at heating rates from 5 to 20 °C/min. K_{max} under 10 kHz of PFN ceramics reaches a maximum of approximately 21,000 at 10 °C/min.

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