



PMN-PFN Relaxor Ferroelectric Ceramics by a Reaction-Sintering Process

YI-CHENG LIOU*

Department of Electronic Engineering, Kun-Shan University of Technology, Tainan Hsien, Taiwan, Republic of China

Submitted August 4, 2003; Revised February 15, 2004; Accepted February 26, 2004

Abstract. $\text{Pb}((\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.6}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.4})\text{O}_3$ (PMFN) perovskite relaxor ferroelectric ceramics produced by reaction-sintering process were investigated. Without any calcination, the mixture of PbO , $\text{Mg}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$ and Nb_2O_5 was pressed into pellets and sintered directly. PMFN ceramics of 100% perovskite phase were obtained. Density of 7.84 g/cm^3 (95% of theoretical value) was obtained after sintered at 1250°C for 2 h. Grain sizes of 3–6 μm were formed after 2 h sintering at 1150 – 1250°C . Dielectric constant at room temperature under 10 kHz reaches 22400 after sintered at 1250°C for 2 h.

Keywords: relaxor ferroelectrics, PMN-PFN, reaction-sintering process

1. Introduction

Lead based perovskite ceramics have been widely investigated for capacitor application [1–4]. Both $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) and $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN) have excellent dielectric properties [5, 6]. However, stable cubic pyrochlore phase always existed in these perovskite ceramics as produced by the conventional mixed oxide method. Therefore, methods to obtain pyrochlore-free ceramics have been widely studied. Swartz and Shroud proposed a columbite/wolframite route. Two calcination stages were involved, MgNb_2O_6 (FeNbO_4) columbite (wolframite) formed first and followed by formation of perovskite [7, 8]. Liou and Wu proposed a simplified columbite route to produce pyrochlore-free PMN ceramics with dielectric constant >17000 under 1 kHz [9]. The mixture of MgNb_2O_6 and PbO was pressed and sintered into PMN ceramics. Liou et al. proposed a simplified wolframite route to produce pyrochlore-free PFN ceramics [3]. The mixture of FeNbO_4 and PbO was pressed and sintered into PFN ceramics. The second calcination and pulverization stages in the columbite and wolframite routes were bypassed in the simplified routes. Liou et al. proposed a reaction-

sintering process to prepare PMN and PFN ceramics [10, 11]. 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. These are the first successful synthesis of perovskite relaxor ferroelectric ceramics without having to go through the calcination step.

In this study, the reaction-sintering process were used to prepare pyrochlore-free $\text{Pb}((\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.6}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.4})\text{O}_3$ (PMFN) perovskite ceramics.

2. Experimental Procedure

All samples in this study were prepared from reagent-grade oxides: PbO (99.9%, J.T. Baker, USA), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($>99\%$, E. Merck, Darmstadt, Germany), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($>99\%$, E. Merck, Darmstadt, Germany) and Nb_2O_5 (99.8%, High purity chemicals, Japan). Appropriate amounts of PbO , $\text{Mg}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$ and Nb_2O_5 for stoichiometric PMFN 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 $10^\circ\text{C}/\text{min}$ and sintered in covered alumina crucible at temperatures ranging from 1150°C to 1250°C for 2 h in air.

*To whom all correspondence should be addressed.

The sintered PMFN ceramics were analyzed by X-ray diffraction (XRD). Microstructures were analyzed by scanning electron microscopy (SEM). The average grain size was determined by the line interception method. All grains intercepted by 8 different lines on the SEM photographs were counted and the average grain size was then calculated according to the scale. The density of sintered PMFN pellets was measured by water immersion method. After polishing, the dimensions were measured before silver electrodes were deposited on the pellets. Dielectric properties were measured with an HP4194A impedance analyzer.

3. Results and Discussion

The XRD pattern of PMFN ceramics sintered at 1250°C for 2 h is shown in Fig. 1. The major peak (2 2 2) of $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ pyrochlore phase at $2\theta = 29.2^\circ$ is not found in the pattern. PMFN ceramics of 100% perovskite phase could be obtained by reaction-sintering process. PMFN ceramics sintered at 1150–1230°C for 2 h are also 100% perovskite phase as shown in Fig. 2. These results indicate that reaction-sintering process is simple and effective not only in producing pyrochlore-free PMN and PFN but also in PMFN ceramics. Density of PMFN ceramics sintered at various temperatures is listed in Table 1. Density increased with sintering tem-

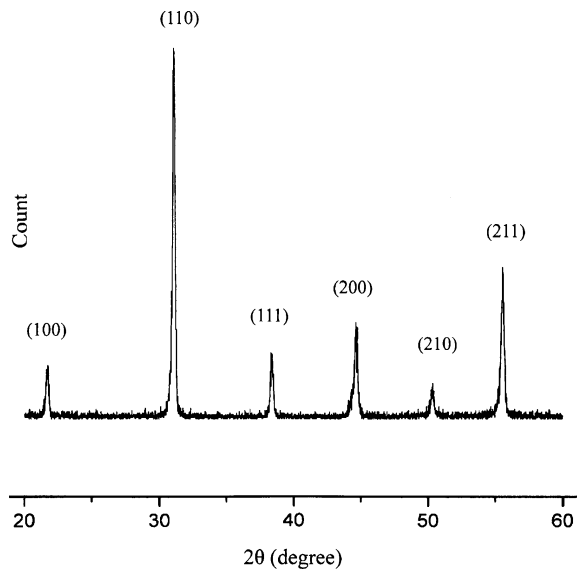


Fig. 1. XRD profile of PMFN ceramic sintered at 1250°C/2 h.

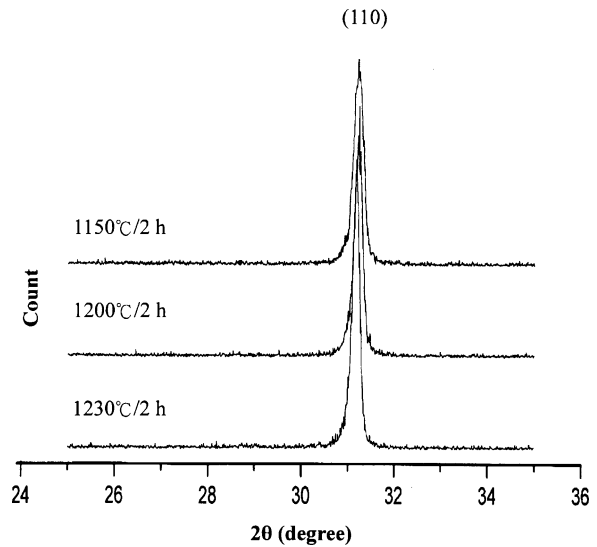


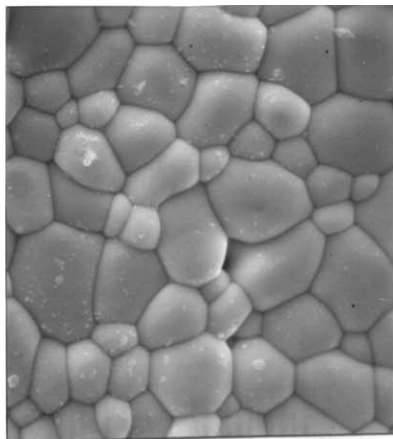
Fig. 2. XRD profiles of PMFN ceramics sintered at 1150–1230°C for 2 h.

perature and reached a value of 7.84 g/cm^3 (95% of theoretical value) at 1250°C. 96% of theoretical value was obtained after 1250°C/2 h sintering in PMN ceramics prepared by reaction-sintering process [10]. While in PFN ceramics, 97% of theoretical value was obtained after 1180°C/2 h sintering [11]. This means that sintering temperature for dense pellets was not lowered as PMN is modified by 40% of PFN. This is different from $\text{Pb}((\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.7}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.3})\text{O}_3$ in our another investigation [12]. The sintering temperature for dense pellets was lowered to 1200°C as PMN is modified by 30% of PZN.

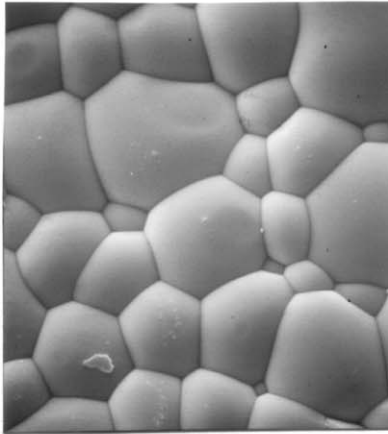
The SEM photographs of as-fired PMFN ceramics sintered at 1150°C to 1250°C for 2 h are illustrated in Fig. 3. No pyrochlore phase is found in these pellets. Dense pellets without pores were obtained at 1230 and 1250°C. At 1230 and 1250°C, uniform grain-size

Table 1. Density, mean grain size and dielectric constant at room temperature of PMFN ceramics sintered at various temperatures for 2 h.

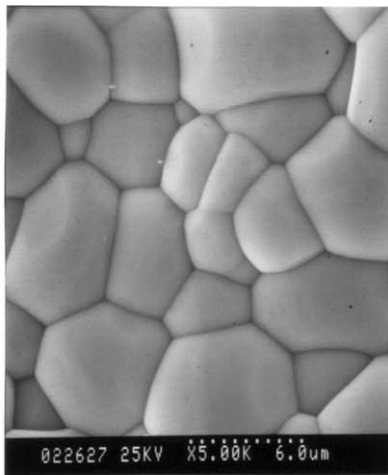
Sintering temperature (°C)	1150	1200	1230	1250
Density (g/cm^3)	7.12	7.55	7.76	7.84
Grain size (μm)	2.9	3.8	4.7	5.8
Dielectric constant at 10 kHz	9800	14900	18500	22400



(A)



(B)



(C)

Fig. 3. SEM photographs of as-fired PMFN ceramics sintered at (A) 1150°C, (B) 1230°C and (C) 1250°C for 2 h.

growth was observed. While at 1150°C, the grain-size growth was not so uniform. The calcination reaction during the heating-up period was not completed. Some regions were completely calcined at the forefront of 1150°C sintering period. This made the periods for grain growth in various regions to be different and the grain-size growth was not so uniform. As the sintering temperature increased, the calcination reaction during the heating-up period was completed. Most of the grains began to grow at the same time and uniform grain-size growth was observed. Mean grain sizes of PMFN ceramics sintered at various temperatures are also listed in Table 1. The grain size increased apparently with sintering temperature. 3–6 μm grain size was obtained in PMFN ceramics sintered at 1150–1250°C for 2 h by reaction-sintering process. As compared with PMN ceramics prepared by reaction-sintering process, grain size of 4.46 μm was obtained after 1250°C/2 h sintering [10]. While in PFN ceramics prepared by reaction-sintering process, grain size of 3.6 μm and 4.6 μm were obtained after 1150°C/2 h and 1210°C/2 h sintering [11]. Grain growth increased at same sintering temperature after modified 40% of PFN in PMN ceramics.

The dielectric constants of PMFN ceramics at room temperature under 10 kHz are listed in Table 1. It increases with sintering temperature and reaches 22400 at 1250°C. As all of the samples are pyrochlore-free, this was resulted from the increased density value and grain size. More pores formed in the PMFN pellets with lower density. These pores with low dielectric constant resulted in pellets with low dielectric constant. Larger grains resulted in fewer grain boundaries in PMFN pellets. These boundaries with low dielectric constant also resulted in a pellet with low dielectric constant. The dielectric constant values in Table 1 are close to those reported by Jun et al. [13]. Dielectric constant at room temperature under 10 kHz was found in the range between 18000 and 20000 for $\text{Pb}((\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.6}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.4})\text{O}_3$ perovskite ceramics synthesized by B-site precursor method. The variation of dielectric constant with temperature (K-T curves) under 10 kHz and 100 kHz for PMFN ceramic sintered at 1250°C/2 h is illustrated in Fig. 4. For a comparison of PMFN with PMN and PFN ceramics produced by reaction-sintering process, the K-T curves are illustrated in Fig. 5. The dielectric constant increased and the temperature related to the maximum dielectric constant shifted to higher temperature as PMN is modified by 40% of PFN.

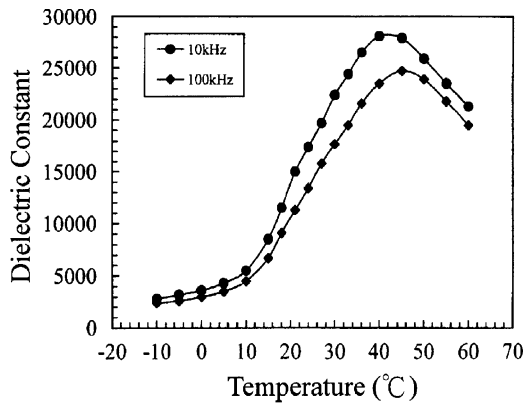


Fig. 4. Variation of dielectric constant with temperature under 10 kHz and 100 kHz for PMFN ceramic sintered at 1250°C/2 h.

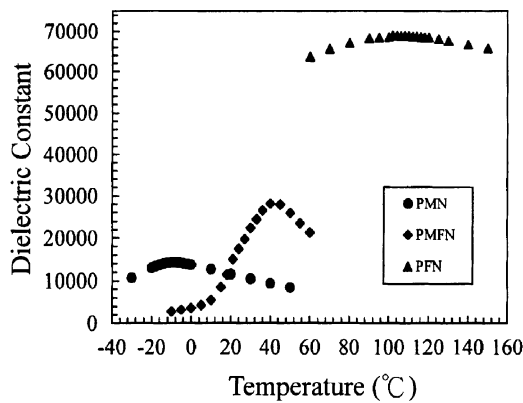


Fig. 5. Variation of dielectric constant with temperature under 10 kHz for PMFN (1250°C/2 h), PMN (1250°C/2 h) and PFN (1210°C/2 h).

4. Conclusion

Pyrochlore-free $\text{Pb}((\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.6}(\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.4})\text{O}_3$ perovskite ceramics have been successfully produced by a simple and effective reaction-sintering process.

Without any calcination process, the mixture of PbO , $\text{Mg}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$ and Nb_2O_5 was pressed and sintered directly. Density of 7.84 g/cm^3 (95% of theoretical value) was obtained after sintered at 1250°C for 2 h. 3–6 μm grain size was obtained in PMFN ceramics sintered at 1150–1250°C for 2 h by reaction-sintering process. The dielectric constant of PMFN at room temperature under 10 kHz increases with sintering temperature and reaches 22400 at 1250°C.

Acknowledgments

The author is grateful to Miss Shi-Yuea Hsu for her help in obtaining the SEM photos. This study was supported by the National Science Council of the Republic of China under contract NSC 91-2216-E-168-006.

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