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$Pb((Mg_{0.7}Zn_{0.3})_{1/3}Nb_{2/3})O_3$ Relaxor Ferroelectric Ceramics by a Reaction-Sintering Process

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Abstract. $Pb((Mg_{1/3}Nb_{2/3})_{0.7}(Zn_{1/3}Nb_{2/3})_{0.3})O_3$ (PMZN) relaxor ferroelectric ceramics produced by a reaction-sintering process were investigated. Without any calcination, the mixture of PbO, $Mg(NO_3)_2$, $Zn(NO_3)_2$ and Nb_2O_5 was pressed into pellets and sintered directly. PMZN ceramics of 100% perovskite phase were obtained. Density of 8.11 g/cm^3 (>98% of theoretical value) was obtained after sintered at 1200°C for 2 h. 3–9 μm grain size was obtained in PMZN ceramics sintered at 1180°C–1250°C for two hours by reaction-sintering process. Dielectric constant at room temperature under 1 kHz reaches 18200 after sintered at 1200°C for 2 h.

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

1. Introduction

Lead based relaxor ferroelectric ceramics have been widely investigated for capacitor application [1–4]. Both $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) have high dielectric constant (~20,000 for PMN and ~30,000 for PZN single crystals) [5]. However, stable cubic pyrochlore phase always existed in these perovskite ceramics as produced by the conventional mixed oxide method. Therefore, methods to obtain relaxor ferroelectric ceramics of pure perovskite phase have been widely studied. Swartz and Shrout proposed a columbite route. Two calcination steps were involved, $MgNb_2O_6$ columbite formed first and followed by the formation of perovskite [6]. Liou and Wu proposed an effective and simplified method to produce pyrochlore-free PMN ceramics with dielectric constant >17000 under 1 kHz [7]. The mixture of $MgNb_2O_6$ and PbO was pressed and sintered into PMN ceramics. The second calcination and pulverization stages in the columbite route were bypassed in the simplified columbite route. In the study of Han and Kim, PMN powder with >99% perovskite phase was prepared 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 [8]. Liou et al. proposed a reaction-sintering process to prepare PMN and $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) ceramics [9, 10]. The mixture of PbO, $Mg(NO_3)_2$ ($Fe(NO_3)_3$ for PFN), 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 $Pb((Mg_{1/3}Nb_{2/3})_{0.7}$-$(Zn_{1/3}Nb_{2/3})_{0.3})O_3$ perovskite ceramics.

2. Experimental Procedure

$Pb((Mg_{1/3}Nb_{2/3})_{0.7}(Zn_{1/3}Nb_{2/3})_{0.3})O_3$ (PMZN) is the composition investigated in this study. All samples were prepared from reagent-grade oxides: PbO (99.9%, J. T. Baker, USA), $Mg(NO_3)_2{\cdot}6H_2O$ (>99%, E. Merck, Darmstadt, Germany), $Zn(NO_3)_2{\cdot}6H_2O$ (99%, Kanto chemical, Japan), Nb_2O_5 (99.8%, High purity chemicals, Japan). Appropriate amounts of PbO, $Mg(NO_3)_2$, $Zn(NO_3)_2$ and Nb_2O_5 for stoichiometric PMZN 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

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and sintered in covered alumina crucible at temperatures ranging from 1180°C to 1250°C for 2 h in air.

The sintered PMZN ceramics were analyzed by X-ray diffraction (XRD) (D-max, Rigaku) on the polished surfaces. Microstructures were analyzed by scanning electron microscopy (SEM). The density of sintered PMZN 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 (Hewlett Packard) impedance analyzer.

3. Results and Discussion

Density of PMZN ceramics sintered at various temperatures is listed in Table 1. Density increased with sintering temperature and reached a value of 8.11 g/cm^3 (>98% of theoretical value) at 1200°C. Above 1200°C, density decreased with sintering temperature. In PMN ceramics prepared by reaction-sintering process, 1250°C/2 h sintering was needed to obtain 96% of theoretical value [9]. This means that sintering temperature for dense pellets was lowered as PMN is modified by 30% of PZN. The XRD profile of PMZN ceramic sintered at 1180°C for 2 h 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 pattern. PMZN ceramics of 100% perovskite phase could be obtained by

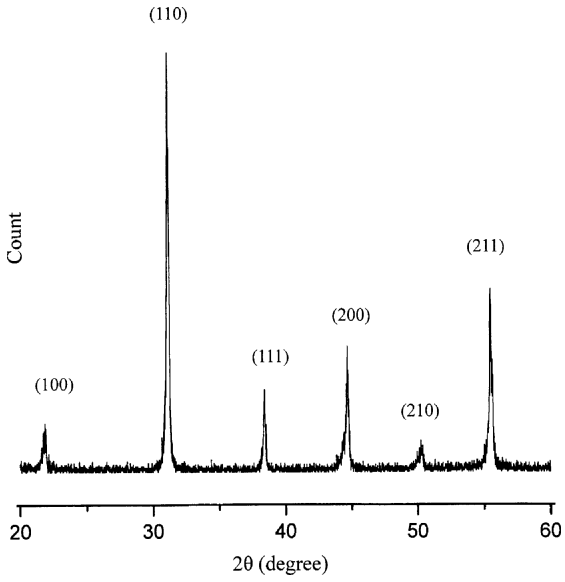

Fig. 1. XRD profile of PMZN ceramic sintered at 1180°C/2 h.

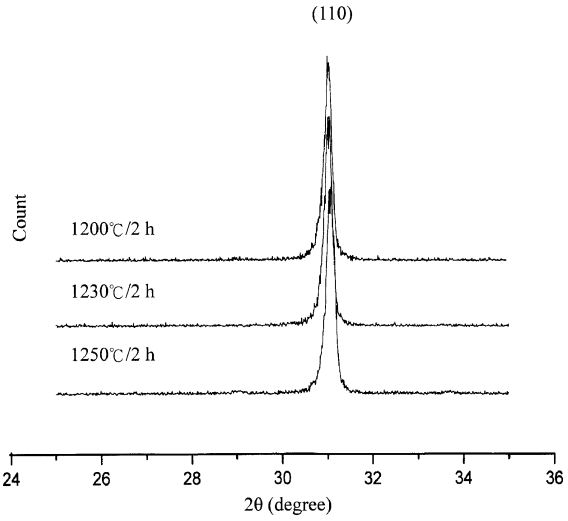

Fig. 2. XRD profiles of PMZN ceramics sintered at 1200°C–1250°C for 2 h.

reaction-sintering process. PMZN ceramics sintered at 1200°C–1250°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 in producing pyrochlore-free PMZN ceramics.

The SEM photographs of as-fired PMZN ceramics sintered at 1180°C to 1250°C are illustrated in Fig. 3. No pyrochlore phase and pore is found in these PMZN pellets. Grain size increases apparently with sintering temperature. Mean grain sizes of PMZN ceramics sintered at various temperatures are also listed in Table 1. 3–9 μm grain size was obtained in PMZN ceramics sintered at 1180°C–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 [9]. Grain growth in PMN ceramics increased at same sintering temperature after modified by 30% of PZN. The dielectric constant of PMZN ceramics at room temperature under 1 kHz are listed in Table 1. It reached 18200 at 1200°C/2 h sintering and decreased at other temperatures. As all of

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

Sintering Temperature (°C)	1180	1200	1230	1250
Density (g/cm^3)	8.02	8.11	7.98	7.87
Grain size (μm)	3.1	4.7	6.7	9.3
Dielectric constant at 1 kHz	17100	18200	17500	16600

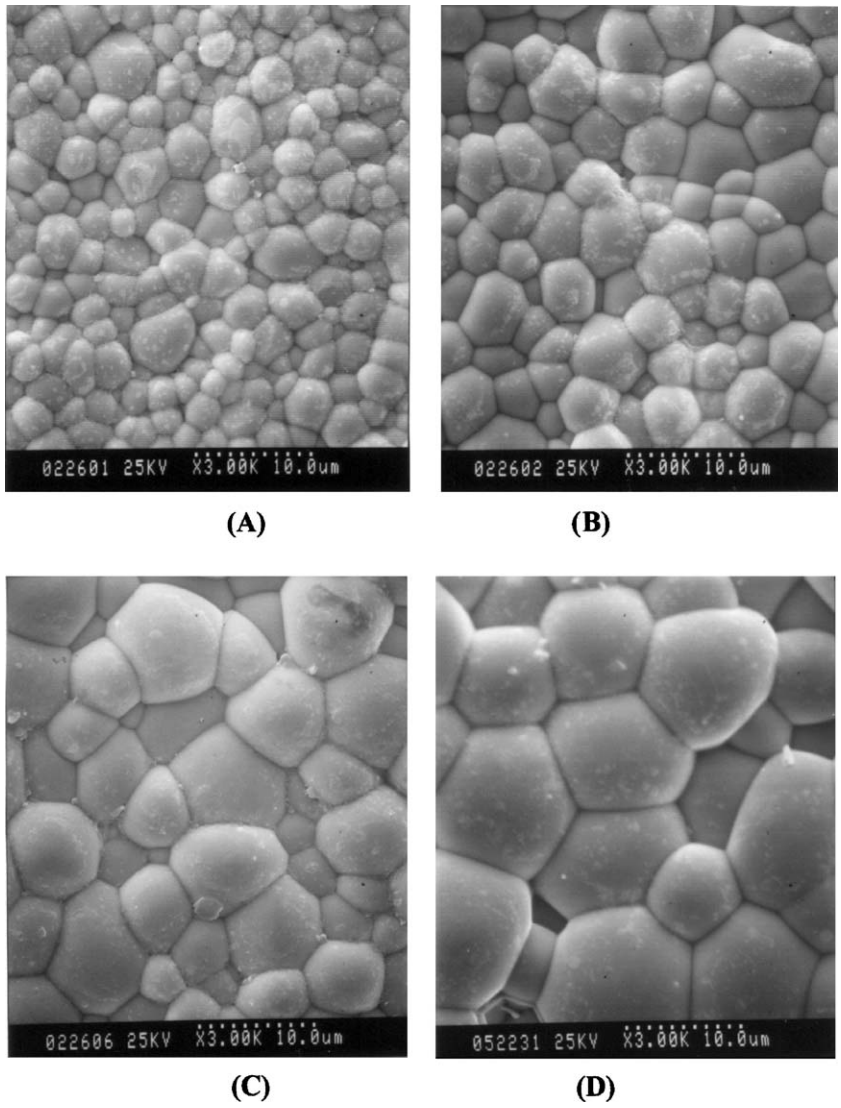

Fig. 3. SEM photographs of as-fired PMZN ceramics sintered at (A) 1180°C, (B) 1200°C, (C) 1230°C and (D) 1250°C for 2 h.

the samples are pyrochlore-free, the deceased dielectric constant was mainly resulted from the decreased density value. More pores formed in the PMZN pellets with lower density. These pores with low dielectric constant resulted in pellets with low dielectric constant.

4. Conclusion

Pyrochlore-free PMN-PZN perovskite ceramics were produced by a simple and effective reaction-sintering process successfully. Without any calcination process, the mixture of PbO, $Mg(NO_3)_2$, $Zn(NO_3)_2$, and Nb_2O_5 was pressed and sintered directly. Density of 8.11g/cm^3 (>98% of theoretical value) was obtained after sintered at 1200°C for 2 h. 3–9 μm grain size was obtained in PMZN ceramics sintered at 1180°C–1250°C for 2 h by reaction-sintering process. The dielectric constant of PMZN ceramics at room temperature under 1 kHz reaches 18200 at 1200°C sintering.

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