



# PZN-PFW and PFN-PFW Relaxor Ferroelectric Ceramics by a Reaction-Sintering Process

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**Abstract.**  $\text{Pb}((\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.6}(\text{Fe}_{2/3}\text{W}_{1/3})_{0.4})\text{O}_3$  and  $\text{Pb}((\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.7}(\text{Fe}_{2/3}\text{W}_{1/3})_{0.3})\text{O}_3$  (PZNFW and PFNW) perovskite ceramics prepared by a reaction-sintering process were investigated. Without any calcination, the mixture of  $\text{PbO}$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{WO}_3$  for stoichiometric PZNFW and PFNW was pressed and sintered directly. Pyrochlore phase more than 25% were formed in PZNFW ceramics after 2 h sintering at 930–980°C. PFNW ceramics of 100% perovskite phase were obtained after 4 h sintering at 930–1080°C. A density of 8.13 g/cm<sup>3</sup> (93.4% of theoretical value) was obtained after sintered at 1080°C for 4 h. Dielectric constant at room temperature under 1 kHz reaches 32000 after sintered at 1080°C for 4 h.

**Keywords:** relaxor ferroelectrics, PZN-PFW, PFN-PFW, reaction-sintering process

## 1. Introduction

$\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PZN),  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PFN) and  $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$  (PFW) are members of the relaxor ferroelectric family. Owing to their high dielectric constants, they have been widely investigated for capacitor application [1–4]. The main problem in producing these perovskite ceramics by the conventional mixed oxide method is the formation of stable cubic pyrochlore phase. Therefore, methods have been widely studied to obtain pyrochlore-free perovskite ceramics. Swartz and Shrout proposed a columbite/wolframite route. Two calcination stages were involved,  $\text{MgNb}_2\text{O}_6$  columbite ( $\text{FeNbO}_4$  wolframite) formed first and followed by formation of perovskite [5, 6]. Liou and Wu proposed an effective and simplified method to produce pyrochlore-free  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN) ceramics [7]. The mixture of  $\text{MgNb}_2\text{O}_6$  and  $\text{PbO}$  was pressed and sintered into PMN ceramics. Liou et al. also proposed a simplified wolframite route to produce pyrochlore-free PFN ceramics [1]. The mixture of  $\text{FeNbO}_4$  and  $\text{PbO}$  was pressed and sintered into PFN ceramics. In these simplified routes, the second calcination and pul-

verization stages in the columbite or wolframite route were bypassed. Liou et al. proposed a reaction-sintering process to prepare PMN and PFN ceramics [2, 8]. The mixture of  $\text{PbO}$ ,  $\text{Mg}(\text{NO}_3)_2$  ( $\text{Fe}(\text{NO}_3)_3$  for PFN) and  $\text{Nb}_2\text{O}_5$  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,  $\text{Pb}((\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.6}(\text{Fe}_{2/3}\text{W}_{1/3})_{0.4})\text{O}_3$  (PZNFW) and  $\text{Pb}((\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.7}(\text{Fe}_{2/3}\text{W}_{1/3})_{0.3})\text{O}_3$  (PFNW) perovskite ceramics prepared by the reaction-sintering process were investigated.

## 2. Experimental Procedure

$\text{Pb}((\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.6}(\text{Fe}_{2/3}\text{W}_{1/3})_{0.4})\text{O}_3$  and  $\text{Pb}((\text{Fe}_{1/2}\text{Nb}_{1/2})_{0.7}(\text{Fe}_{2/3}\text{W}_{1/3})_{0.3})\text{O}_3$  (PZNFW and PFNW) are the compositions investigated in this study. All samples were prepared from reagent-grade oxides:  $\text{PbO}$  (99.9%, J. T. Baker, USA),  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (99%, Kanto chemical, Japan),  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (>99%, E. Merck, Darmstadt, Germany),  $\text{Nb}_2\text{O}_5$  (99.8%, High purity chemicals, Japan) and  $\text{WO}_3$  (99.9%, E. Merck, Darmstadt, Germany). Appropriate amounts of  $\text{PbO}$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{WO}_3$  for

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stoichiometric PZNFW and PFNW 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 at temperatures ranging from 900°C to 980°C for 2 h (PZNFW) or 930°C to 1080°C for 4 h (PFNW) in air.

The sintered pellets were analyzed by X-ray diffraction (XRD). Microstructures were analyzed by scanning electron microscopy (SEM). The density of sintered pellet 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

#### 3.1. $Pb((Zn_{1/3}Nb_{2/3})_{0.6}(Fe_{2/3}W_{1/3})_{0.4})O_3$

The XRD profiles of PZNFW ceramics sintered at 930–980°C for 2 h is shown in Fig. 1. The peaks of pyrochlore phase appear in the patterns. The amount of pyrochlore phase is more than 25% after calculated. In the study of Khim et al., the amount of perovskite phase decreased with a increasing PZN content in  $(1-x)PFW + xPZN$ . With 0.4 mole PZN in PFW

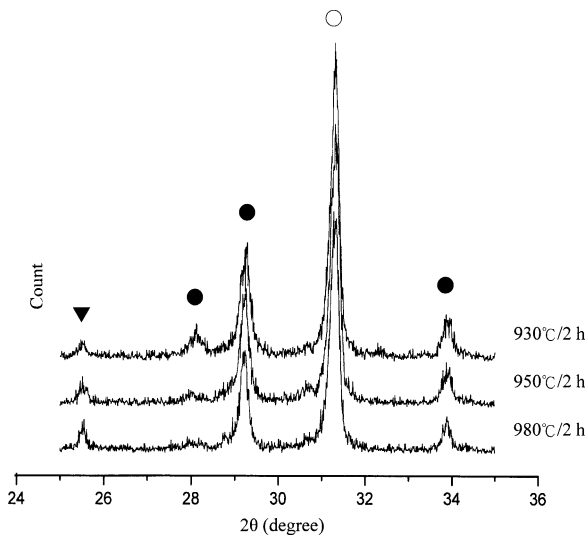


Fig. 1. XRD profiles of PZNFW ceramics sintered at 930–980°C for 2 h. (○, perovskite; ●, pyrochlore; ▼,  $Pb_2WO_5$ )

the amount of perovskite phase is less than 70% after 900°C sintering [3]. They thought this is due to the thermal instability of PZN at temperatures above 600°C [9]. A peak of  $Pb_2WO_5$  is also found in these profiles. Lu et al. reported that  $Pb(Li_{1/4}Fe_{1/4}W_{1/2})O_3$  coexisted with a small amount of  $Pb_2WO_5$  in the sample quenched at 780°C and the amount of  $Pb_2WO_5$  was increased as quenched at 800°C [10]. In  $0.16Pb(Zn_{1/3}Nb_{2/3})O_3-0.48Pb(Fe_{1/2}Nb_{1/2})O_3-0.36Pb(Fe_{2/3}W_{1/3})O_3$  ceramics,  $Pb_2WO_5$  formed after sintered at 870°C for 2 h by traditional mixed oxide process [4].

The SEM photographs of as-fired PZNFW ceramics sintered at 900°C to 950°C for 2 h are illustrated in Fig. 2. Size of perovskite grains increase apparently with sintering temperature. In the study of Khim et al., numerous small pyrochlore grains of 0.5–0.8  $\mu m$  occurred at the grain boundaries and grain junctions of large perovskite grains as 0.2 mole PZN was doped. When doped with 0.4 mole PZN, the fracture surface is dominated by the clusters of fine pyrochlore particles in  $(1-x)PFW + xPZN$  after 850°C sintering [3].

#### 3.2. $Pb((Fe_{1/2}Nb_{1/2})_{0.7}(Fe_{2/3}W_{1/3})_{0.3})O_3$

The XRD patterns of PFNW ceramics sintered at 950–1050°C for 4 h are shown in Fig. 3. The major peak (2 2 2) of  $Pb_3Nb_4O_{13}$  pyrochlore phase at  $2\theta = 29.2^\circ$  is not found in the patterns. PFNW ceramics of 100% perovskite phase were prepared successfully by reaction-sintering process. This result indicates that reaction-sintering process is simple and effective not only in producing pyrochlore-free PMN [7] and PFN [2] but also in PFNW ceramics. Density of PFNW ceramics sintered at various temperatures is listed in Table 1. The density value increased with sintering temperature and reached a value of 8.13  $g/cm^3$  (93.4% of theoretical value) at 1080°C. In PFN ceramics prepared by reaction-sintering process, 94.3% of theoretical value was obtained after 1180°C/4 h sintering [2]. This means

Table 1. Density, mean grain size and dielectric constant at room temperature of PFNW ceramics sintered at various temperatures for 4 h.

Sintering Temperature (°C)	950	980	1000	1050	1080
Density ( $g/cm^3$ )	7.27	7.32	7.61	8.07	8.13
Grain size ( $\mu m$ )	7.6	7.1	8.3	26.2	35.1
Dielectric constant at 1 kHz	22300	27100	28400	30800	32000

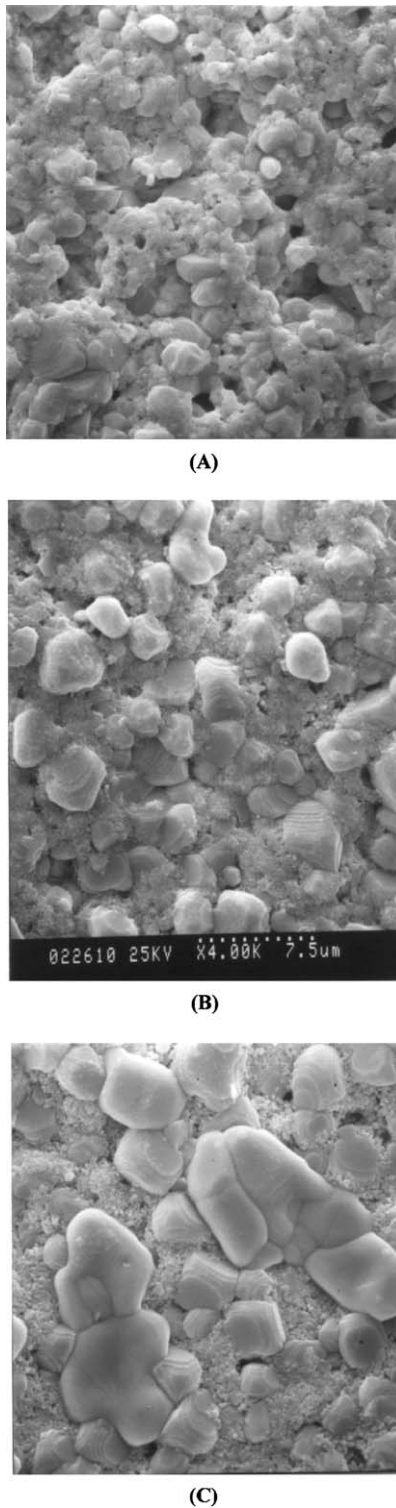


Fig. 2. SEM photographs of as-fired PZFNW ceramics sintered at (A) 900°C, (B) 930°C and (C) 950°C for 2 h.

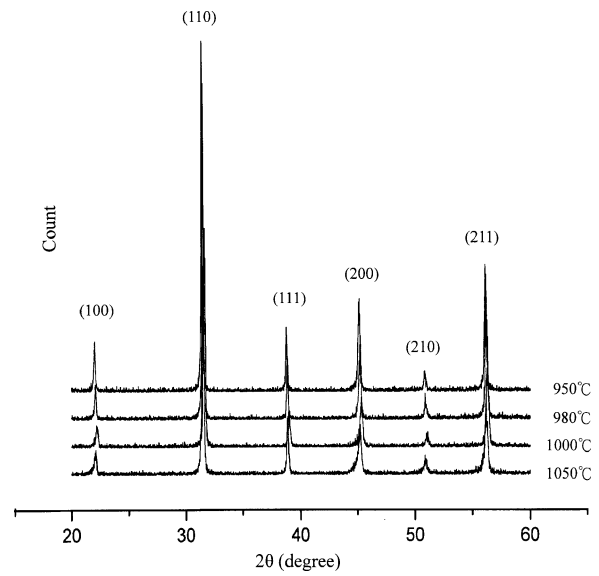


Fig. 3. XRD profiles of PFNW ceramics sintered at 950–1050°C for 4 h.

that the sintering temperature for pellets of similar theoretical value was lowered as PFN is modified by 30% of PFW.

The SEM photographs of as-fired PFNW ceramics sintered at 930°C to 1000°C for 4 h are illustrated in Fig. 4. No pyrochlore phase is found in these pellets. Pores are found in PFNW sintered at 930°C and disappear at temperatures above 950°C. Mean grain sizes of PFNW ceramics sintered at various temperatures are listed in Table 1. The grain size of 7–8 μm were obtained after 950–1000°C sintering and increased apparently at 1000–1080°C. As compared with PFN ceramics, grain size of 4.4 and 7.3 μm were obtained after sintered at 1180°C and 1210°C for four hours [2]. Grain growth seems to be easier in PFNW than in PFN ceramics produced by reaction-sintering process. The dielectric constant of PFNW ceramics at room temperature under 1 kHz are also listed in Table 1. It increases with sintering temperature and reaches 32000 at 1080°C. As all of the samples are pyrochlore-free, this is resulted from the density value and the grain size as listed in Table 1.

#### 4. Conclusion

The amount of pyrochlore phase in PZFNW ceramics is more than 25% after sintered at 930–980°C for

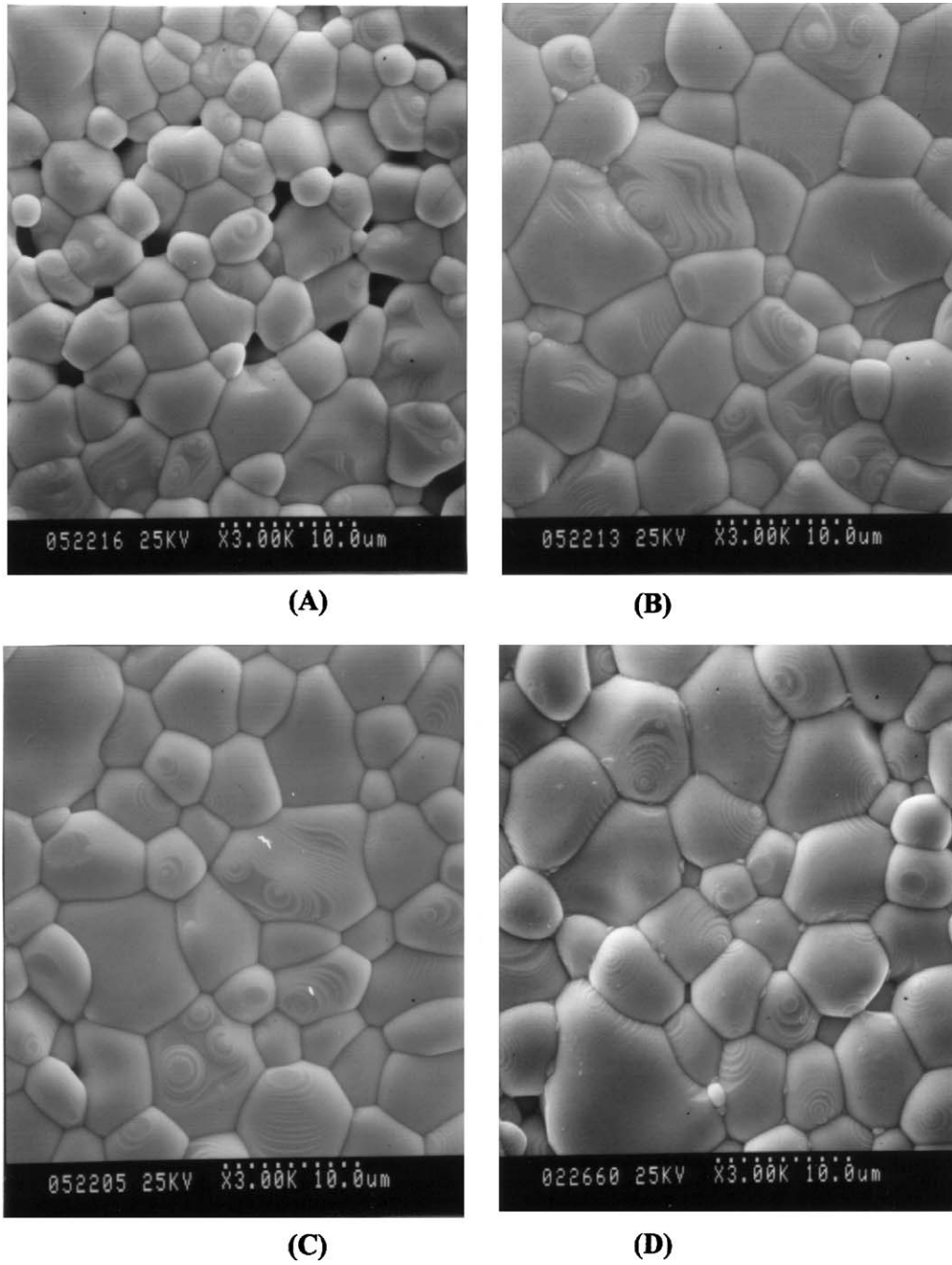


Fig. 4. SEM photographs of as-fired PFNW ceramics sintered at (A) 930°C, (B) 950°C, (C) 980°C and (D) 1000°C for 4 h.

2 h. This is due to the thermal instability of PZN. A small amount of  $Pb_2WO_5$  is found in PZNFW ceramics. The clusters of fine pyrochlore particles formed in sintered PZNFW ceramics. Therefore, pyrochlore-free

$Pb((Zn_{1/3}Nb_{2/3})_{0.6}(Fe_{2/3}W_{1/3})_{0.4})O_3$  perovskite ceramics could not be produced by reaction-sintering process. While in  $Pb((Fe_{1/2}Nb_{1/2})_{0.7}(Fe_{2/3}W_{1/3})_{0.3})O_3$ , 100% perovskite ceramics were produced by a simple

and effective reaction-sintering process successfully. Density of  $8.13 \text{ g/cm}^3$  (93.4% of theoretical value) was obtained after sintered at  $1080^\circ\text{C}$  for 4 h.  $7\text{--}8 \mu\text{m}$  grains were obtained after  $950\text{--}1000^\circ\text{C}$  sintering and increased apparently at  $1000\text{--}1080^\circ\text{C}$ . The dielectric constant of PFNW ceramics at room temperature under 1 kHz increases with sintering temperature and reaches 32000 at  $1080^\circ\text{C}$  due to the increased density value and grain size.

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