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Low-firing PZN–PFN–PFW relaxor ferroelectric ceramics produced by a reaction-sintering process

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Abstract

$Pb((Zn_{1/3}Nb_{2/3})_{0.16}(Fe_{1/2}Nb_{1/2})_{0.48}(Fe_{2/3}W_{1/3})_{0.36})O_3$ (PZFNW) relaxor ferroelectric ceramics produced by a reaction-sintering process of low sintering temperatures were investigated. Without any calcination, the mixture of PbO, $Zn(NO_3)_2$, $Fe(NO_3)_3$, Nb_2O_5 and WO_3 was pressed and sintered directly. PZFNW ceramics of 100% perovskite phase were obtained after sintering at 830–950 °C. A density of 8.66 g cm^{-3} (98.6% of theoretical value) was obtained after sintering at 930 °C for 2 h. Grain sizes of 2–7 and 3–12 μm were formed after sintering at 830–950 °C for 2 and 4 h, respectively. The dielectric constant for 1 kHz at room temperature increases with sintering temperature and reaches the value of 17,400 at 930 °C due to the increased density and grain size.

Keywords: Ceramics; Sintering; Microstructure; Ferroelectric ceramics

1. Introduction

Because of their high dielectric constants, $Pb(Zn_{1/3}Nb_{2/3})O_3$, $Pb(Fe_{1/2}Nb_{1/2})O_3$ and $Pb(Fe_{2/3}W_{1/3})O_3$ have been widely investigated for capacitor application [1–4]. In producing these perovskite ceramics, the stable cubic pyrochlore phase could not be eliminated by the conventional mixed-oxide method. Therefore, methods to obtain pyrochlore-free perovskite relaxor ferroelectric ceramics have been widely studied. In the proposed columbite and wolframite routes [5,6], two calcination stages were involved. $MgNb_2O_6$ columbite and $FeNbO_4$ wolframite were formed first and followed by formation of perovskite. An effective and simplified method to produce pyrochlore-free $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics was proposed by Liou et al. [7]. A $MgNb_2O_6$ and PbO mixture was pressed and sintered into $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics. A simplified wolframite route to produce pyrochlore-free $Pb(Fe_{1/2}Nb_{1/2})O_3$ ceramics was reported by Liou et al. [8]: a mixture of $FeNbO_4$ and PbO was pressed and sintered. The second calcination and pulverization stages in the columbite or wolframite route were bypassed in these simplified routes.

A novel mechanochemical processing route has been used to produce $Pb(Zr,Ti)O_3$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$ [9,10]. In this mechanical technique, the powders of the reactants are homogenized and activated in a high-energy vibromill. Several materials such as $BaTiO_3$ and $PbTiO_3$ were prepared by using this process [11–13]. The reaction-sintering process is a simple and effective route to synthesize ceramics. The calcination step is bypassed and the mixture of the raw materials is sintered directly. Kong and Ma [14] proposed $Pb(Zr,Ti)O_3$ ceramics prepared by sintering the oxide mixture directly. Almost at the same time, Liou et al. [15–19] proposed a reaction-sintering process in preparing $Pb(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ and $Pb(Fe_{1/2}Nb_{1/2})O_3$ ceramics. These are the first successful syntheses of perovskite relaxor ferroelectric ceramics without having to go through the calcination step or the high-energy milling. $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics with a density of 8.09 g cm^{-3} and a dielectric constant of 19,900 (1 kHz) were obtained. This reaction-sintering process had also been used to produce other complex perovskite relaxor ceramics [20–25]. In the latest studies, we also prepared dense and pure-phased columbite $ZnNb_2O_6$

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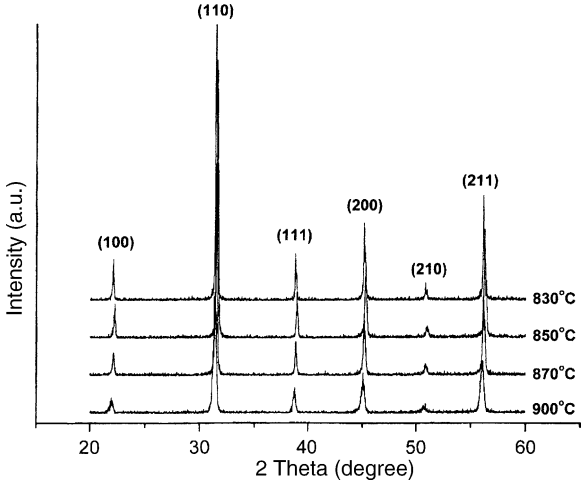

Fig. 1. XRD profiles of PZFNW ceramics sintered at 830–900 °C for 2 h.

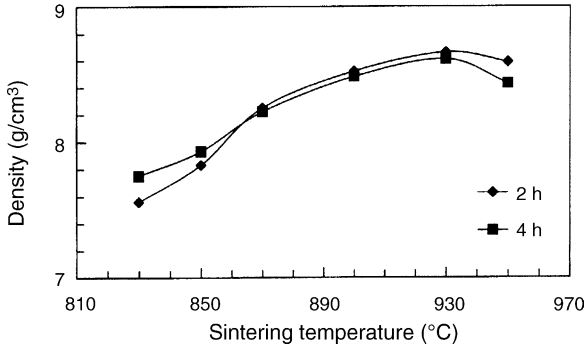

Fig. 2. Variation of the density with sintering temperature of PZFNW ceramics.

and $NiNb_2O_6$ microwave ceramics by this process successfully [26,27].

In this study, $Pb((Zn_{1/3}Nb_{2/3})_{0.16}(Fe_{1/2}Nb_{1/2})_{0.48}(Fe_{2/3}W_{1/3})_{0.36})O_3$ (PZFNW) perovskite ceramics prepared by the reaction-sintering process of low sintering temperatures were investigated.

2. Experimental procedure

$Pb((Zn_{1/3}Nb_{2/3})_{0.16}(Fe_{1/2}Nb_{1/2})_{0.48}(Fe_{2/3}W_{1/3})_{0.36})O_3$ (PZFNW) is the composition investigated in this study. All

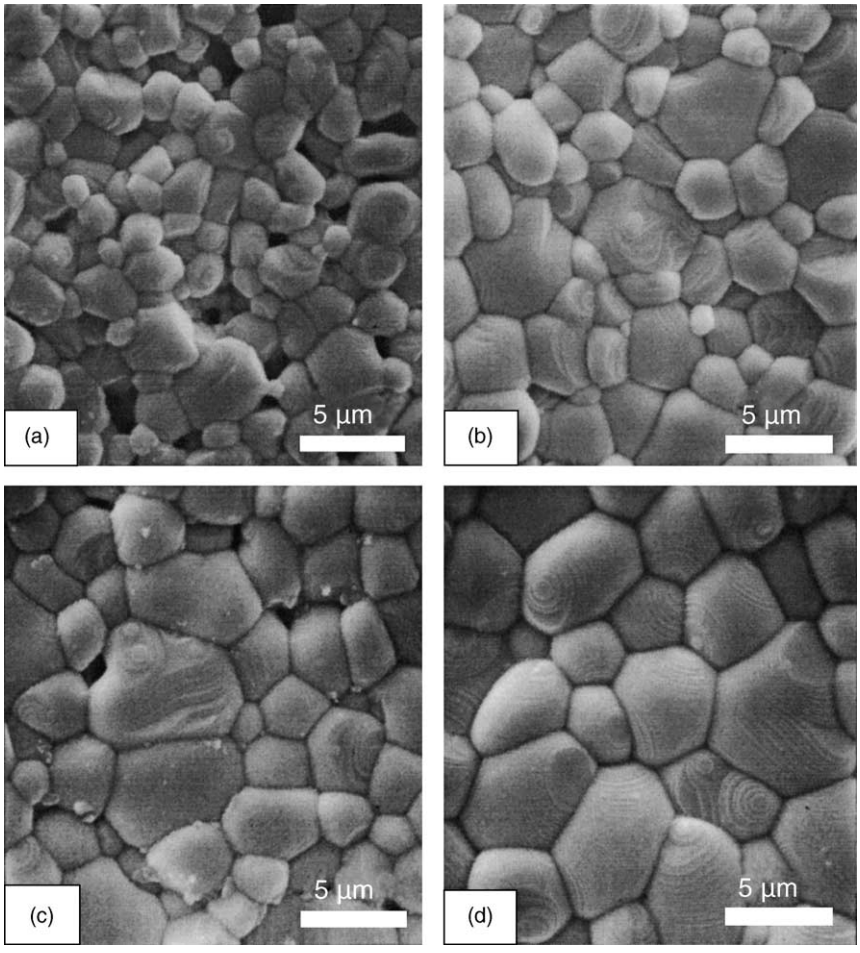

Fig. 3. SEM images of as-fired PZFNW ceramics sintered for 2 h at (a) 830 °C, (b) 850 °C, (c) 870 °C and (d) 900 °C.