

Effect of lead zinc niobate addition on sintering behavior and piezoelectric properties of lead zirconate titanate ceramic

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We investigated the effect of lead zinc niobate (PZN) on the sintering behavior and piezoelectric properties of lead zirconate titanate (PZT) ceramics. The addition of PZN improved the sinterability of PZT ceramic so remarkably, that at additions of more than 10%, the specimens were fully dense at a temperature as low as 900 °C. The phase of the PZT-PZN ceramics was affected by PZN content and the Zr/Ti ratio in the PZT. With increasing PZN content, a lower Zr/Ti ratio was required for the morphotropic phase boundary (MPB). Specimens with the MPB composition showed the highest piezoelectric properties; $d_{33} = 500$ pC/N, $k_p = 0.68$, and $S_{33} = 0.38\%$ at 2 kV/mm.

Pb(Zr,Ti)O₃ (PZT) ceramic has been widely used for various actuator applications because of its excellent piezoelectric properties.¹ Many efforts have been made to improve its electrical, mechanical, and physical properties. In addition, there have been many attempts to lower the sintering temperature of PZT. The low-temperature fabrication of lead-based ceramics enables such ceramics to be co-fired with less expensive metals, such as Ag, for multilayer devices.² Furthermore, through low-temperature sintering, one may minimize the problems associated with the vaporization of PbO during sintering.

Many researchers have reported different techniques to decrease the sintering temperature of Pb-based ceramics. However, most procedures have both disadvantages and advantages. Solid-state substitution of Bi and Nb ions in the ceramics did not lower the sintering temperature significantly.³ A fine-powder approach, through chemical procedures such as the sol-gel process, is quite complex and difficult to control.⁴ Densification by hot-pressing is an effective process, but not efficient.⁵ The addition of low-temperature melting additives generally decreases the piezoelectric properties.⁶⁻⁸

Relaxor-type perovskites, such as Pb(Zn_{1/3}Nb_{2/3})O₃ and Pb(Mg_{1/3}Nb_{2/3})O₃, exhibit excellent piezoelectric as well as dielectric properties.^{9,10} The sintering temperature of relaxors is much lower than that of PZT.¹¹ However, those relaxors are difficult to sinter in the perovskite structure due to the easy formation of pyrochlore phases. Hence, other perovskite materials (such as

BaTiO₃, PbTiO₃, or Pb(ZrTiO₃) need to be incorporated for the structure stabilization.¹²⁻¹⁴ Conversely speaking, the addition of such relaxor materials to PZT might be beneficial for lowering the sintering temperature.¹⁵

The purpose of this study was to investigate the effect of lead zinc niobate (PZN) content on the sintering behavior and piezoelectric properties of PZT ceramics. The effect of Zr/Ti ratio in the PZT was also observed and correlated to the phase evolution, as well as to the electromechanical properties of the specimens.

The general formula of the materials studied was Pb(Zn_{1/3}Nb_{2/3})_x(Zr_yTi_{1-y})_{1-x}O₃, where $x = 0.05 \sim 0.4$, $y = 0.45 \sim 0.53$. Excess PbO was not added. The samples were prepared by mixing appropriate amounts of commercially available oxide powders. Pure PbO, ZnO, Nb₂O₅, ZrO₂, and TiO₂ powders (all 99.9% purity, Aldrich, Milwaukee, WI) were weighed and mixed by ball-milling with zirconia balls as media in alcohol.

After mixing and drying, the mixture was calcined in a covered alumina crucible at 850 °C for 4 h. The calcined powders were ball-milled again for 48 h to reduce the particle size of the powder. The powders were cold isostatically pressed to a disk shape at 150 MPa. The specimens were sintered at 900 °C for 4 h in a sealed alumina crucible with a PbZrO₃ atmosphere powder.

The specimen phase was examined using x-ray diffractometry (XRD: MXP18A-HF, MAC Science, Tokyo, Japan) with a 2θ range from 20° to 60°. A step scan with a step size of 0.02° was used with a counting time of 1 s/step. Microstructural evolution was observed using a field-emission scanning electron microscope (FE-SEM, JEOL Technics, Tokyo, Japan). The specimen density was measured by the Archimedes method and the mean grain size was calculated by the line intercept method. For the piezoelectric property measurements, the sintered

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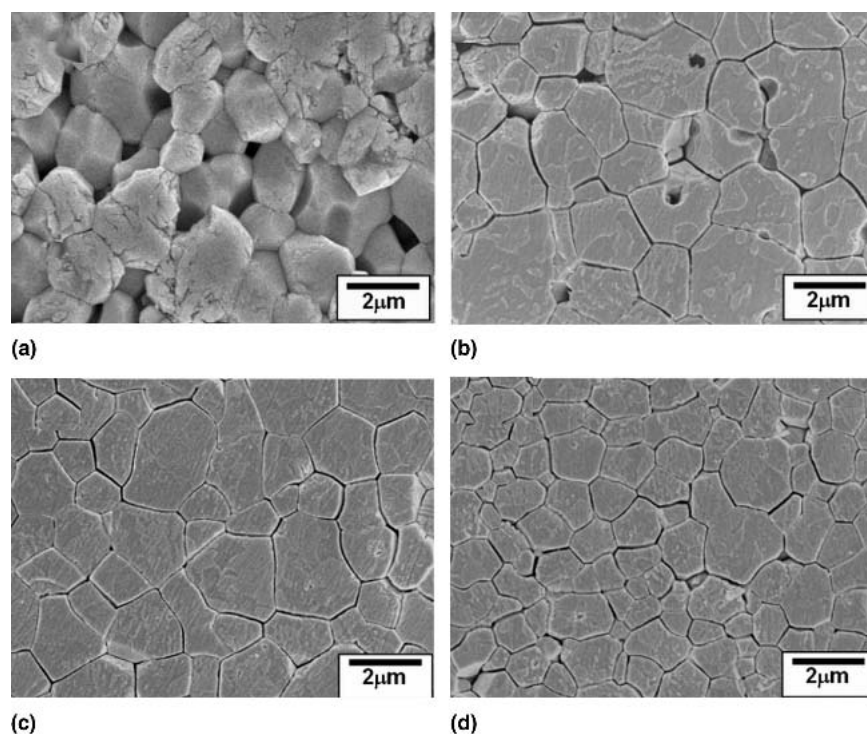


FIG. 1. SEM microstructures of the polished surfaces of the specimens: (a) pure PZT, (b) with 5% PZN, (c) with 10% PZN, and (d) with 20% PZN.

disks were lapped and electroded with a silver paste. The specimens were poled in a silicone oil bath at 200 °C by applying an electric field of 2 kV/mm for 20 min. The specimens were aged for 24 h prior to testing. The piezoelectric coefficient (d_{33}) was measured using a quasi-static piezoelectric d_{33} meter (Model ZJ-3D, Institute of Acoustics Academic Sinica, Beijing, China). The electromechanical coupling coefficient (k_p) was determined by the resonance and antiresonance technique, using an impedance analyzer (Model SI1260 Impedance/Gain-Phase Analyzer, Solartron, Slough, Berkshire, UK). The field-induced strain of the poled specimens was monitored by using a displacement sensor (DT/2/S, Solartron, Bognor Regis, West Sussex, UK).

The sintering behavior of calcined PZT–PZN powder was strongly influenced by the composition of the powder. The effect of PZN content on the microstructure of the specimens sintered at 900 °C for 4 h is clearly seen in the SEM micrographs shown in Fig. 1. Pure PZT ($Zr/Ti = 52/48$) was barely sintered at 900 °C, as shown in Fig. 1(a). This result is not surprising, because the sintering temperature of pure PZT for full densification is around 1200 °C.¹⁶ When 5 mol% of PZN was added to PZT and sintered at the same temperature, the density of the specimen was enhanced markedly as shown in Fig. 1(b). However, there are still some pores inside the grains as well as at the grain boundaries. On the other hand, when 10% PZN was added to PZT and processed under the same conditions, the specimen became almost

fully dense, as shown in Fig. 1(c). With further additions of PZN ($\geq 20\%$), the high specimen density was maintained, as typically shown in Fig. 1(d).

Along with the density, the specimen grain size was changed by the addition of PZN. With increasing PZN content in the specimen, the grain size apparently decreased. The density and the average grain size of the specimen (as a function of PZN content) are shown in Fig. 2. With increasing PZN content, the density increased first rapidly and then slowly up to 40% PZN, while the average grain size decreased steadily. The effect of PZN on the densification behavior of the PZT specimen is well illustrated in this graph.

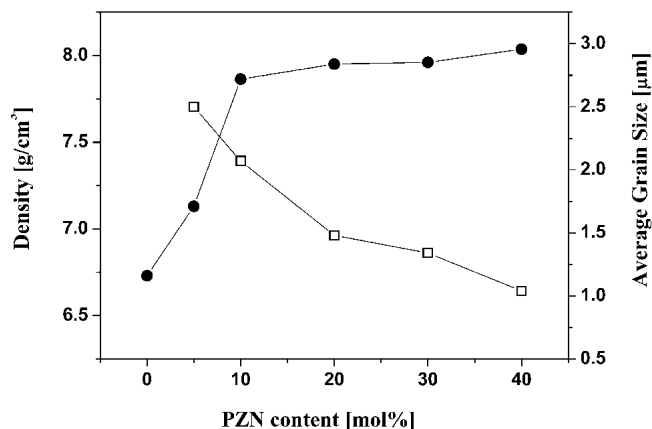


FIG. 2. Density and average grain size of the specimens as a function of PZN content.

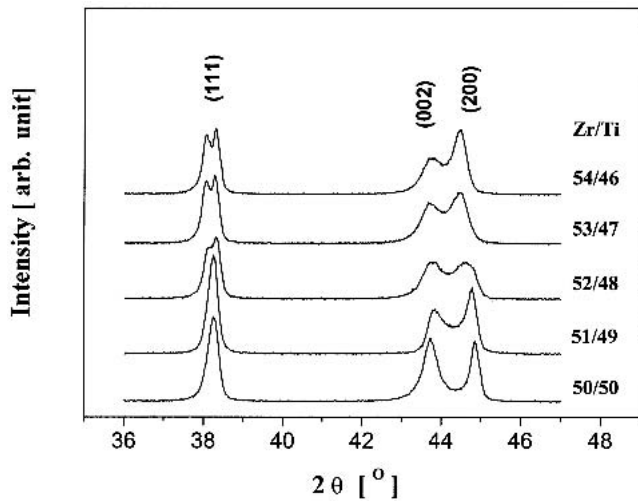


FIG. 3. X-ray diffraction patterns of 0.9 PZT-0.1 PZN specimens with different Zr/Ti ratios in the PZT.

Even though the PZT-PZN specimens sintered at 900 °C were fully dense without pyrochlore phases, there is another variable to be considered: the Zr/Ti ratio in the PZT. The phase of specimen was strongly dependent on the Zr/Ti ratio. As an example, the phase change of the 90% PZT-10% PZN specimens (monitored by using the XRD patterns) is shown in Fig. 3. When Zr/Ti = 50/50, the tetragonal phase was formed, as manifested by the two distinct (002) and (200) peaks. With increasing Zr content, the structure gradually changed to a rhombohedral phase. Based on these XRD patterns, even though

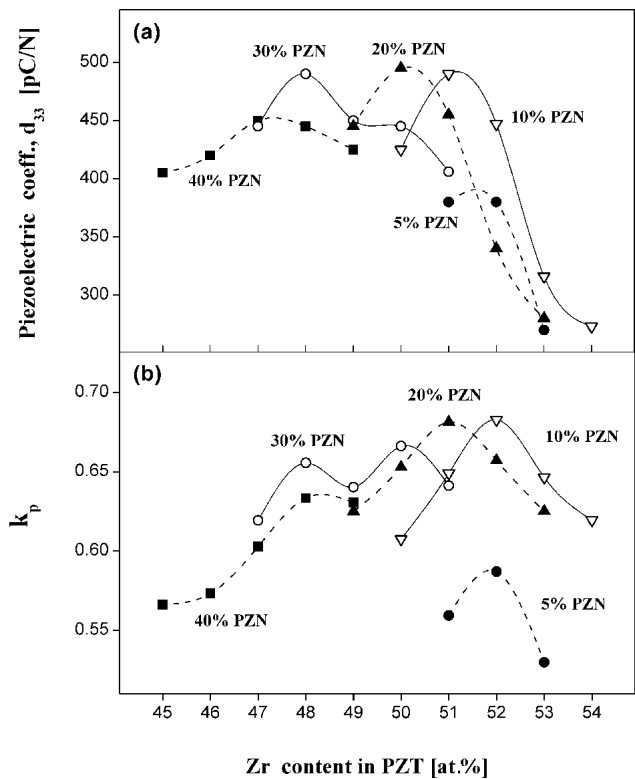


FIG. 4. Piezoelectric coefficients and electromechanical-coupling factors of the PZT-PZN specimens as a function of Zr/Ti ratio: (a) piezoelectric coefficients and (b) electromechanical-coupling factors.

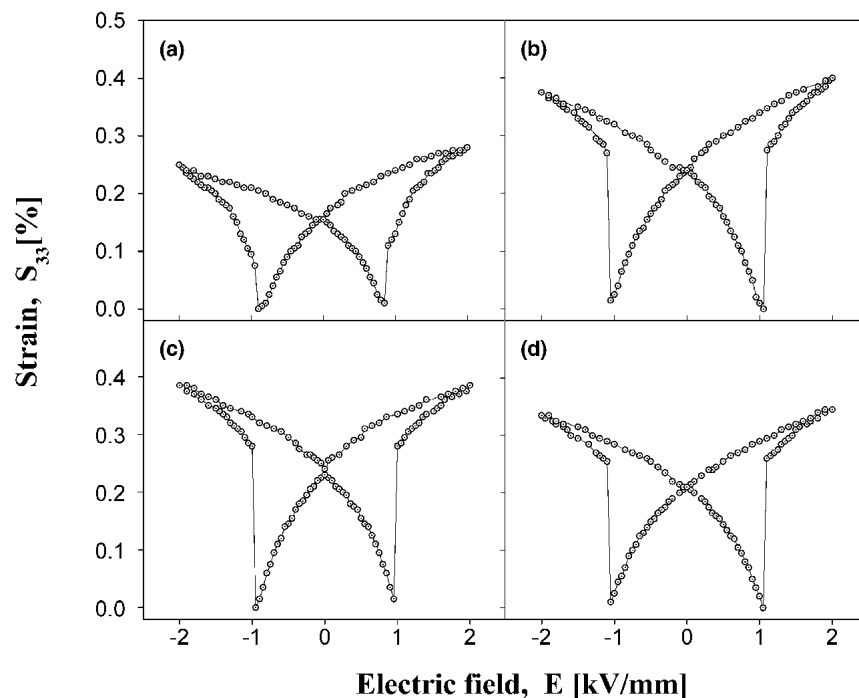


FIG. 5. Strain of the PZT-PZN specimens as a function of the electric field: (a) with 5% PZN, Zr/Ti = 52/48; (b) with 10% PZN, Zr/Ti = 51/49; (c) with 20% PZN, Zr/Ti = 50/50; and (d) with 30% PZN, Zr/Ti = 48/52.

not analyzed quantitatively, the morphotropic phase boundary (MPB) composition of the present system is $Zr/Ti = 51/49 \sim 52/48$. The phase of the perovskite material is expected to influence the electrical properties of the specimens.

The piezoelectric properties of PZT–PZN ceramics at various PZN contents and Zr/Ti ratios are shown in Fig. 4. The sinterability of PZT–PZN ceramics was affected mostly by PZN content; however, the electrical properties of these ceramics were also strongly influenced by the Zr/Ti ratio, as shown in Fig. 4. Figure 4(a) shows the piezoelectric coefficients (d_{33}) of each composition. Depending on the PZN content in the specimen, maximum d_{33} values were observed at different Zr/Ti ratios. For example, the maximum d_{33} of PZT–10% PZN specimen was observed at a Zr/Ti ratio of 51/49. However, the specimens containing 20% PZN showed the maximum d_{33} when the Zr/Ti ratio was 50/50. As the PZN content was increased, the maximum d_{33} was observed at lower Zr content. The compositions showing the maximum d_{33} are deemed to be the MPB compositions of the system. Interestingly, the maximum d_{33} values for specimens with different PZN content and Zr/Ti ratio were almost identical. The electromechanical coupling factor (k_p) exhibited a similar trend to that of the maximum d_{33} ; however, the Zr/Ti ratio at which maximum k_p was observed was slightly different from the case of d_{33} , as shown in Fig. 4(b).

The longitudinal strains (S_{33}) of the specimens as a function of the electric field are presented in Fig. 5. As in the case of d_{33} or k_p , the strain was strongly dependent on the PZN content and Zr/Ti. When 5% PZN was added, the highest strain (0.26% at 2 kV/mm) was observed when the Zr/Ti ratio was 52/48, as shown in Fig. 5(a). As PZN content increased to 10% (Zr/Ti ratio = 51/49) and 20% (Zr/Ti = 50/50), the strains were enhanced markedly [as shown in Figs. 5(b) and 5(c), respectively]. With further addition of PZN to 30% (Zr/Ti = 48/52), the strain was decreased slightly, as shown in Fig. 5(d). This trend matched well with the electromechanical coupling factor [Fig. 4(b)]. The coercive field of these specimens was changed only slightly, because all the specimens were in MPB compositions.

In summary, the sinterability, microstructure, and piezoelectric properties of the PZT-added PZN ceramics were investigated. The addition of PZN improved the sinterability of PZT, so that with the addition of more than 10% PZN, the specimen was almost fully densified at a

temperature as low as 900 °C. The phase evolution of the specimens was affected by the PZN content and the Zr/Ti ratio in the PZT. With an increase in the PZN content, a lower Zr/Ti ratio was required for MPB composition. The highest piezoelectric coefficient and electromechanical coupling factor were 500 pC/N and 0.68, respectively.

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