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Low-temperature fabrication of $Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr_{0.3}Ti_{0.7})O_3$ ceramics with $LiBiO_2$ as a sintering aid

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Abstract

Low-temperature sintering of $Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr_{0.3}Ti_{0.7})O_3$ was investigated using $LiBiO_2$ (LBiO) as a sintering aid. LBiO-added PNN–PZT powders could be fully densified to 97% relative density at a temperature as low as 800 °C. An addition of LBiO was effective for improving the sinterability of PNN–PZT powders. However, LBiO was not useful to promote the grain growth. LBiO-added PNN–PZT bodies sintered at 800 and 1100 °C exhibited an electromechanical coupling factor, kp, of approximately 20 and 60%, respectively.

Keywords: Low-temperature sintering; Piezoelectric; PNN–PZT; Sintering aids

1. Introduction

Lead-containing perovskites ceramics are used in various applications such as piezoelectric actuators and piezoelectric transformers. It is well known that the sintering temperature of lead-containing perovskites materials is above 1100 °C. For example, lead zirconate titanate (PZT) bodies are generally sintered around 1200 °C. However, a high-temperature processing of PZT ceramics often involves serious problems such as compositional change and environmental pollution due to the volatility of lead oxide during sintering, and also the Ag–Pd electrode containing a high content of palladium is expensive. The low-temperature fabrication of PZT ceramics using low-melting point additives as sintering aids can solve these problems. Several sintering aids for lead-containing perovskites ceramics have been reported.[1–3] We reported that $LiBiO_2$ (abbreviated as LBiO) was a useful sintering aid for the sintering of PZT(52/48).[4–6] Shiratsuyu et al.[7] reported that PNN–PZT containing excess NiO could be sintered at 800 °C.

In this work, we focused on low-temperature sintering of $0.5Pb(Ni_{1/3}Nb_{2/3})O_3$–$0.5Pb(Zr_{0.3}Ti_{0.7})O_3$ (PNN–PZT) powders using LBiO sintering aid, and investigated sinterability, microstructure and piezoelectric/ferroelectric properties.

2. Experimental

$0.5Pb(Ni_{1/3}Nb_{2/3})O_3$–$0.5Pb(Zr_{0.3}Ti_{0.7})O_3$(PNN–PZT) powder was synthesized by solid state reaction among PbO powder, $NiNb_2O_6$ and $(Zr_{0.3}Ti_{0.7})O_2$ powders prepared by the hydrothermal syntheses method. The mixed oxide powders were calcined at 800 °C for 8 h and after grinding, the calcination was repeated twice and then ball-milled for 48 h. The 0.5 and 1 mass% LBiO powders, as a sintering aid, were added to PNN–PZT powders and were ball-milled in ethanol for 24 h. The mixed powder was pressed into discs and sintered at 750–1100 °C for 2 h. After sintering, the disc samples were polished to an approximately 0.5 mm thickness, and a fired-on silver paste was then applied to both surfaces of the samples as electrodes. The samples were poled at room temperature for 20 min under an electric field of 20 kV/cm in silicone oil. The microstructure of the sintered bodies was observed using a field-emission scanning electron microscope (FE-SEM). The dielectric properties were measured at 1 kHz using an impedance analyzer (HP4192A). Electromechanical coupling factor, kp, was calculated by the resonant–antiresonance

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method. The *P–E* hysteresis loops were carried out at room temperature, and the applied electric field frequency was 50 Hz (Sawyer-Tower circuit).

3. Results and discussion

Fig. 1 shows the relative density of PNN–PZT sintered bodies with LBiO additives as a function of sintering temperature. PNN–PZT powder without LBiO additives was fully densified at 850 °C. On the other hand, the densification of LBiO-added PNN–PZT powder could be achieved at a sintering temperature of 800 °C which is lower by 50 °C than that of PNN–PZT without the additive. This may be attributable to the formation of a liquid phase during sintering.

Fig. 2 shows the grain sizes of PNN–PZT sintered bodies as a function of sintering temperature. The addition of sintering aids did not affect the grain growth. This result was different from that of PZT(52/48) ceramics of which the grain size was promoted by adding LBiO sintering aid. This may be due to little solubility of PNN–PZT toward LBiO liquid phase.

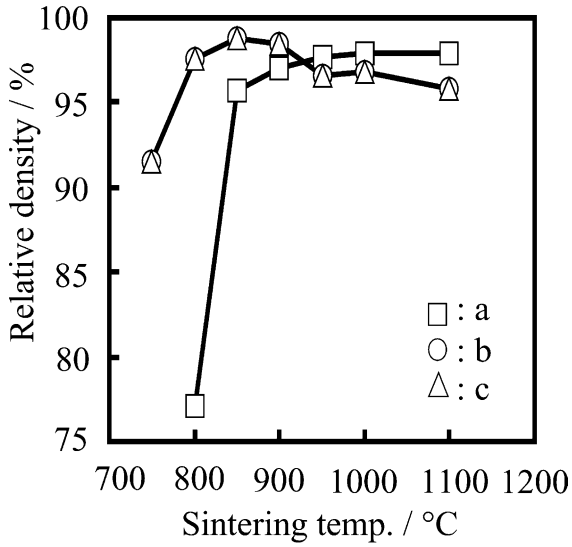

Fig. 1. Relative density of PNN–PZT sintered bodies without and with LBiO additives as a function of sintering temperature. a: without, b: 0.5 mass%, c: 1 mass%.

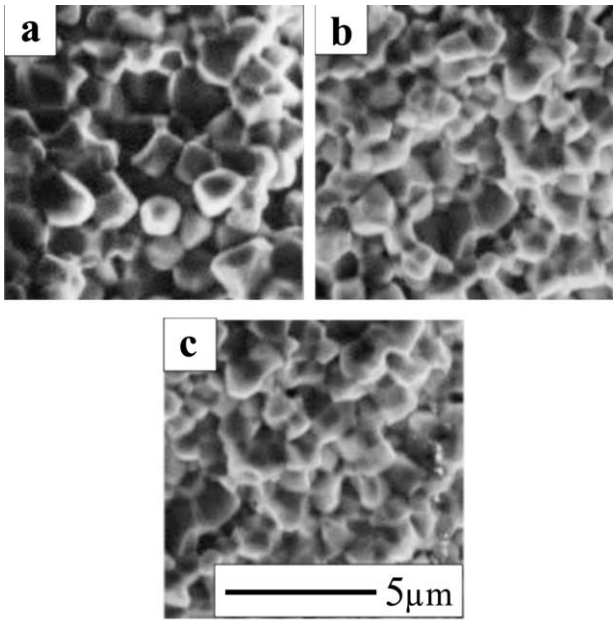

Fig. 3. Microstructure of fracture surface of PNN–PZT bodies sintered at 850 °C without and with LBiO additives. a: without, b: 0.5 mass%, c: 1 mass%.

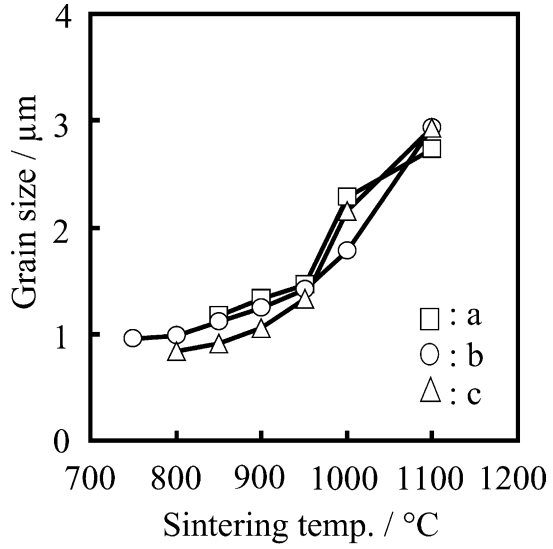

Fig. 2. Grain size of PNN–PZT sintered bodies without and with LBiO additives as a function of sintering temperature. a: without, b: 0.5 mass%, c: 1 mass%.

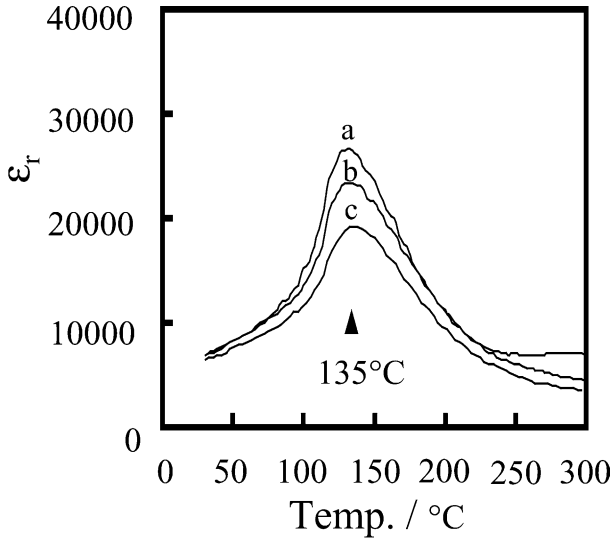

Fig. 4. Temperature dependence of ε_r for PNN–PZT bodies sintered at 1100 °C without and with LBiO additives. a: without, b: 0.5 mass%, c: 1 mass%.

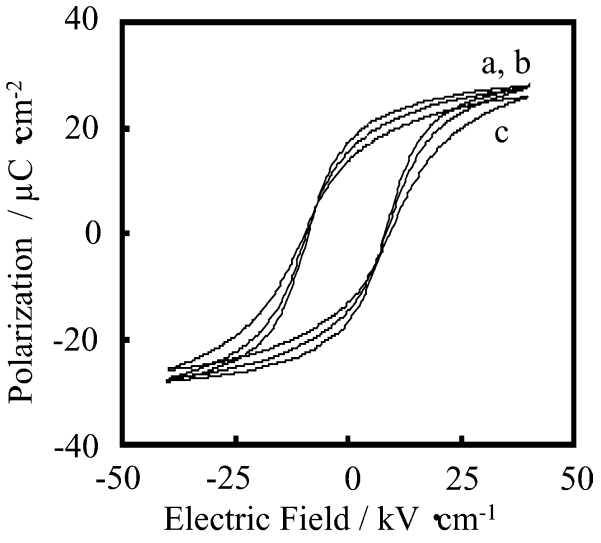

Fig. 5. *P–E* hysteresis loops for PNN–PZT bodies sintered at 850 °C without and with LBiO additives. a: without, b: 0.5 mass%, c: 1 mass%.

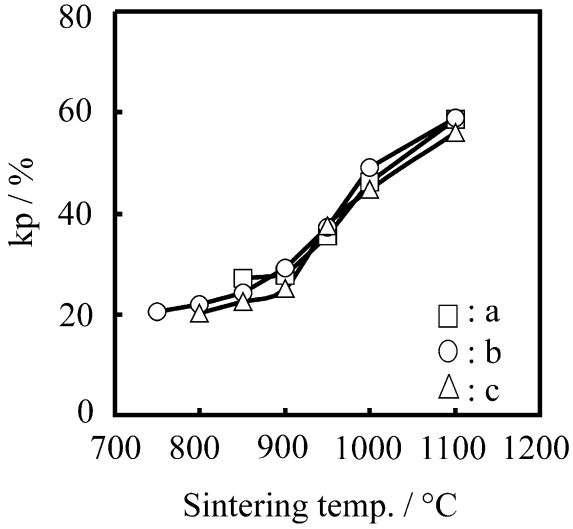

Fig. 6. Electromechanical coupling factor, kp, of PNN–PZT ceramics without and with LBiO additives as a function of sintering temperature. a: without, b: 0.5 mass%, c: 1 mass%.

Fig. 3 shows typical SEM micrographs of PNN–PZT sintered bodies without and with LBiO additives. The grain sizes of PNN–PZT bodies sintered at 850 °C without and with 0.5 mass% LBiO were almost the same as approximately 1.2 μm.

Fig. 4 shows the relative dielectric constants, ε_r, of PNN–PZT bodies sintered at 1100 °C. The dielectric anomalous jump of PNN–PZT sintered body without LBiO was observed around 135 °C. The shift of this temperature corresponding to the Curie point was not observed by an addition of sintering aids.

Fig. 5 shows *P–E* hysteresis loops of PNN–PZT samples sintered at 850 °C. PNN–PZT sintered bodies without and with 0.5 mass% LBiO additive exhibited well-saturated hysteresis curves. The values of remnant polarization, Pr, and coercive field strength, Ec, of PNN–PZT samples without LBiO were 18 μC/cm^2 and 8 kV/cm, respectively. However, 1 mass% LBiO addition deteriorated slightly ferroelectric property of PNN–PZT ceramics.

Fig. 6 shows the electromechanical coupling factor, kp, of PNN–PZT sintered bodies as a function of sintering temperature. The addition of LBiO did not improve kp values of PNN–PZT ceramics. The kp values increased with increasing sintering temperatures. This behavior corresponds well with that of sintering temperature dependence on grain sizes as shown in Fig. 3. The 1100 °C-sintered sample exhibited a kp of approximately 60%.

4. Conclusion

The sinterability, the microstructure, and the piezoelectric/ferroelectric properties of LBiO-added PNN–PZT ceramics were investigated. The addition of LBiO improved the sinterability of PNN–PZT powder to a low temperature of 800 °C. However, LBiO additive did not play an important role for the promotion of grain growth. The addition of small amount of LBiO deteriorated slightly the ferroelectric property, but hardly deteriorated the piezoelectric property of PNN–PZT ceramics.

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