

# Piezoelectric properties of low-temperature sintered $\text{Pb}_{0.95}\text{Ba}_{0.05}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.125}\text{Zr}_{0.445}\text{Ti}_{0.43}]\text{O}_3$ ceramics with chemically-added $\text{LiBiO}_2$ sintering aid

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Available online 22 April 2005

## Abstract

Low-temperature fabrication of  $\text{Pb}_{0.95}\text{Ba}_{0.05}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.125}\text{Zr}_{0.445}\text{Ti}_{0.43}]\text{O}_3$  (PBMNZT) ceramics was investigated, and their microstructure, ferroelectric and piezoelectric properties were examined. In order to improve the sinterability and piezoelectric properties,  $\text{LiBiO}_2$  sintering aid was uniformly added to PBMNZT powders with surface chemical modification using hydrolysis of alkoxides. PBMNZT powders without  $\text{LiBiO}_2$  could not be fully densified at sintering temperatures lower than  $1100^\circ\text{C}$ . However, an addition of  $\text{LiBiO}_2$  considerably improved the sinterability of PBMNZT powders, and sintering temperature consequently decreased from  $1100$  to  $850^\circ\text{C}$ . This may be attributable to the promotion of liquid-phase sintering. And also,  $0.7$  wt.%  $\text{LiBiO}_2$ -added PBMNZT ceramics could be fabricated without deteriorating the piezoelectric properties in the sintering temperatures below  $1000^\circ\text{C}$ . A high electromechanical coupling factor ( $k_p$ ) of  $61.7\%$ , as well as a large field-induced strain of  $\sim 0.17\%$  ( $40$  kV/cm) was obtained for  $950^\circ\text{C}$ -sintered specimens with  $0.7$  wt.%  $\text{LiBiO}_2$  additive.

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**Keywords:**  $\text{Pb}_{0.95}\text{Ba}_{0.05}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.125}\text{Zr}_{0.445}\text{Ti}_{0.43}]\text{O}_3$  ceramics; Actuators; Piezoelectric properties; Preparation; Dielectric properties

## 1. Introduction

$\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  (PZT)-based piezoelectric ceramics have received great attention for their utilization in advanced electronic components such as ultrasonic mortars, actuators and transformers. Recently, it has strongly been required for fabrication of multilayer piezoelectric devices to use Ag–Pd internal electrode with a lower Pd content or other electrodes such as Ag and Cu. However, because PZT-based ceramics must undergo high-temperature processing ( $\geq 1100^\circ\text{C}$ ) to obtain practical piezoelectric properties, these electrodes can not be used. Therefore, low-temperature processing is one of the most important techniques for fabrication of multilayer piezoelectric devices. In addition, decreasing sintering temperature can also afford the advantages of suppressing the compositional change, reducing the energy consumption and decreasing the environmental pollution.

As one of low-temperature sintering techniques, an addition of low-melting-point materials such as glasses and metal oxides can easily be adopted for the conventional ceramic processing.<sup>1–7</sup> However, some research results have indicated that piezoelectric properties are often deteriorated by low-temperature sintering with addition of sintering aid. Therefore, it is very important to select a suitable sintering aid and to disperse homogeneously a small amount of sintering aid in the matrix powders in order to improve the piezoelectric properties and reliability.

$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – $\text{PbZrO}_3$ – $\text{PbTiO}_3$  (PMN–PZ–PT) ternary ceramics were known to have excellent piezoelectric properties. Ouchi et al. systematically investigated<sup>8</sup> the PMN–PZ–PT ternary system with various compositions and reported the change in piezoelectric properties with the compositions. Moreover, they also studied<sup>9</sup> the effects of Ba and Sr substitution on electrical properties and phase relations of PMN–PZ–PT ternary system and reported that  $\text{Pb}_{0.95}\text{Ba}_{0.05}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.125}\text{Zr}_{0.445}\text{Ti}_{0.43}]\text{O}_3$  (PBMNZT) ceramics exhibited the electromechanical

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coupling factor ( $k_p$ ) as high as 66%. We have already investigated<sup>10</sup> the low-temperature sintering of  $\text{Pb}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.375}\text{Zr}_{0.25}\text{Ti}_{0.375}]\text{O}_3$  (PMNZT) powders uniformly coated with  $\text{LiBiO}_2$  sintering aid by surface modification method using alkoxide hydrolysis and reported that low-temperature fabricated PMNZT ceramics with enhanced piezoelectric properties was successfully developed.

In this work,  $\text{LiBiO}_2$  was selected as a sintering aid and surface chemical modification process were applied for low-temperature fabrication of PBMNZT ceramics, and their microstructures, crystalline phase, ferroelectric and piezoelectric properties were investigated.

## 2. Experimental procedure

Reagent grade oxide powders of  $\text{PbO}$ ,  $\text{BaCO}_3$ ,  $\text{MgO}$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2$  were used as raw materials. In order to suppress the formation of pyrochlore phase, the specimen with chemical composition of  $\text{Pb}_{0.95}\text{Ba}_{0.05}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.125}\text{Zr}_{0.445}\text{Ti}_{0.43}]\text{O}_3$  was synthesized by solid-state reaction through the columbite precursor method.<sup>11</sup> First,  $\text{MgO}$  and  $\text{Nb}_2\text{O}_5$  powders were mixed in ethanol and ball-milled for 24 h using zirconia grinding media and was then calcined at  $1000^\circ\text{C}$  for 2 h. The phase of calcined powders was determined by X-ray diffraction to be a single phase of  $\text{MgNb}_2\text{O}_6$ . Next,  $\text{PbO}$ ,  $\text{BaCO}_3$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2$  powders were mixed with synthesized  $\text{MgNb}_2\text{O}_6$  powders by ball milling in ethanol for 24 h. The mixed powders were dried and calcined at  $850^\circ\text{C}$  for 8 h, and then the calcined powders were ground by ball milling in ethanol for 60 h.

The addition of  $\text{LiBiO}_2$  sintering aid to PBMNZT calcined powders was carried out by surface modification method using chemical solution process, and the addition amount used was 0.7 wt.%. Lithium ethoxide and bismuth tri-*t*-amiloxyde were mixed together in 2-methoxyethanol and heated at  $80^\circ\text{C}$  for 1 h, and then the resulting  $\text{LiBiO}_2$  precursor solution was added to the suspension of  $\text{H}_2\text{O}$ -absorbed PBMNZT powders in toluene, followed by mixing to induce the hydrolysis reaction at room temperature for 12 h in  $\text{N}_2$  atmosphere. And then,  $\text{LiBiO}_2$ -coated powders were obtained by evaporating the solvent. The more detailed addition process of sintering aid using chemical process is described elsewhere.<sup>10,12</sup>

These powders with  $\text{LiBiO}_2$  sintering aid were cold-isostatically pressed into discs, and sintered at temperatures from  $750$  to  $1250^\circ\text{C}$  for 4 h in air. The PBMNZT specimens were poled at  $120^\circ\text{C}$  for 20 min under an electric field of  $20\text{ kV/cm}$  in silicon oil.

The crystalline phase was analyzed using an X-ray diffractometer (XRD). The microstructures of the sintered bodies and their average grain sizes were examined using a field-emission scanning electron microscope (FE-SEM). The dielectric permittivity was calculated from the electrostatic capacity measured using an impedance analyzer (YHP-4192A) at 1 kHz. The electromechanical coupling factor ( $k_p$ ) was calculated by a resonant-antiresonant frequency

method. The polarization–electric field ( $P$ – $E$ ) hysteresis loops were measured by a charge-amplifier circuit at 0.1 Hz, and the field-induced longitudinal strain was determined using contact-type displacement sensor (Model JP005-SE) at 0.1 Hz.

## 3. Results and discussion

### 3.1. Physical properties and microstructures

Fig. 1 shows the bulk density of PBMNZT ceramics with 0.7 wt.%  $\text{LiBiO}_2$  additive as a function of sintering temperature. PBMNZT powders without  $\text{LiBiO}_2$  could not be fully densified at sintering temperature lower than  $1100^\circ\text{C}$ . However, saturated densities of approximately  $7.7\text{ g/cm}^3$  were obtained by an addition of  $\text{LiBiO}_2$  sintering aid in the temperatures above  $850^\circ\text{C}$ . Thus, the addition of  $\text{LiBiO}_2$  sintering aid markedly improved the sinterability of PBMNZT powders, resulting in reduction in sintering temperature by approximately  $250^\circ\text{C}$ .

Fig. 2 shows the fracture surfaces morphologies of PBMNZT ceramics fabricated at different sintering temperatures. For PBMNZT ceramics with a  $\text{LiBiO}_2$  additive, the increase of average grain sizes with an increase in sintering temperature was confirmed, and their fractured surfaces suggest that the fracturing mode is owing to an intergranular fracture, as shown in Fig. 2a–c. And also, the addition of  $\text{LiBiO}_2$  to PBMNZT powders considerably promoted the grain growth, and their sintered specimens exhibited pore-free and dense microstructure in spite of the low sintering temperatures below  $1000^\circ\text{C}$ . The average grain size of 0.7 wt.%  $\text{LiBiO}_2$ -added specimens sintered at  $950^\circ\text{C}$  was  $2.2\text{ }\mu\text{m}$ , which corresponds to that of  $1100^\circ\text{C}$ -sintered

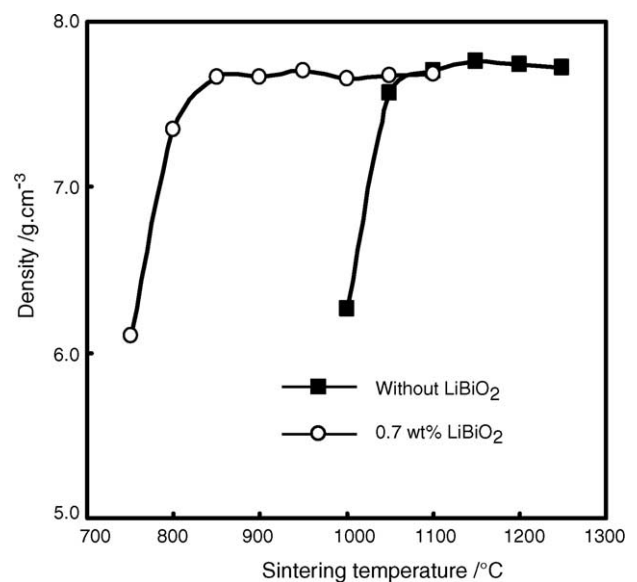


Fig. 1. Bulk density of PBMNZT ceramics with 0.7 wt.%  $\text{LiBiO}_2$  additive as a function of sintering temperature.

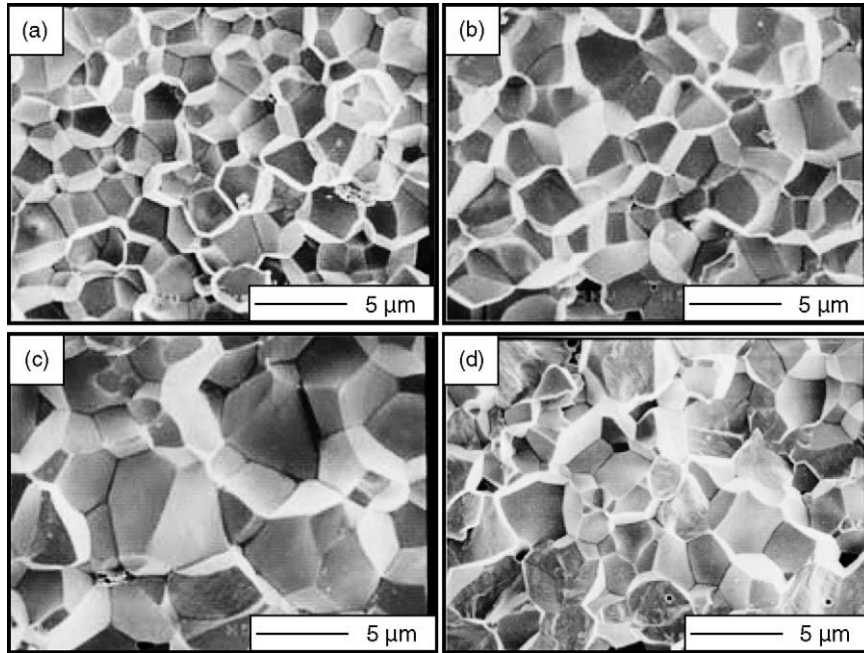


Fig. 2. FE-SEM micrographs of fracture surfaces of PBMNZT ceramics with LiBiO<sub>2</sub> fabricated at (a) 900, (b) 950 and (c) 1000 °C, and without LiBiO<sub>2</sub> fabricated at (d) 1100 °C.

bodies without LiBiO<sub>2</sub>. The above results were similar with those of our previous work.<sup>10</sup> Therefore, it was considered that PBMNZT powders were fully densified by liquid phase sintering at low temperatures.

### 3.2. Dielectric properties

Fig. 3 shows the temperature dependence of dielectric permittivity for 0.7 wt.% LiBiO<sub>2</sub>-added PBMNZT ce-

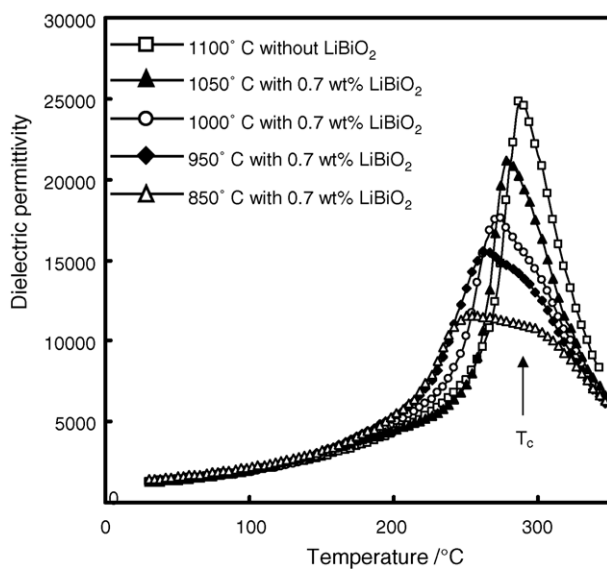


Fig. 3. Temperature dependence of dielectric permittivity for 0.7 wt.% LiBiO<sub>2</sub>-added PBMNZT ceramics fabricated at various sintering temperatures.

ramics fabricated at various sintering temperatures. The Curie point ( $T_c$ ) of the specimens without LiBiO<sub>2</sub> was observed at 290 °C. However, new dielectric anomaly peaks appeared at approximately 250 °C lower temperatures than the  $T_c$  for LiBiO<sub>2</sub>-added specimen fabricated at 850 °C. The dielectric anomaly peaks shifted to higher temperature with an increase in sintering temperature, which could not be clearly confirmed for 1050 °C-sintered specimens with LiBiO<sub>2</sub>. If the solid solution between LiBiO<sub>2</sub> additive and PBMNZT matrix was formed, the  $T_c$  would be considered to shift slightly to lower temperature.<sup>10</sup> Therefore, the behaviors of temperature dependence of dielectric permittivity for specimens with LiBiO<sub>2</sub> fabricated below 1000 °C can not be explained only with the influence of LiBiO<sub>2</sub> additive.

### 3.3. Ferroelectric and piezoelectric properties

Fig. 4 shows the electromechanical coupling factor ( $k_p$ ) of 0.7 wt.% LiBiO<sub>2</sub>-added PBMNZT ceramics as a function of sintering temperature. The  $k_p$  values of LiBiO<sub>2</sub>-added specimens reached approximately 61% in sintering temperatures from 900 to 1000 °C, which were nearly the same as that of 1250 °C-sintered bodies without LiBiO<sub>2</sub>. And also, the  $k_p$  values of specimens with LiBiO<sub>2</sub> tended to decrease gradually with an increase in sintering temperature above 1000 °C. This may be related to the formation of a solid solution between the PBMNZT matrix and LiBiO<sub>2</sub> additive.

Fig. 5 shows the  $P$ - $E$  hysteresis loops of 0.7 wt.% LiBiO<sub>2</sub>-added PBMNZT ceramics fabricated at 900, 1000 and 1100 °C. The well-saturated hysteresis loops were observed

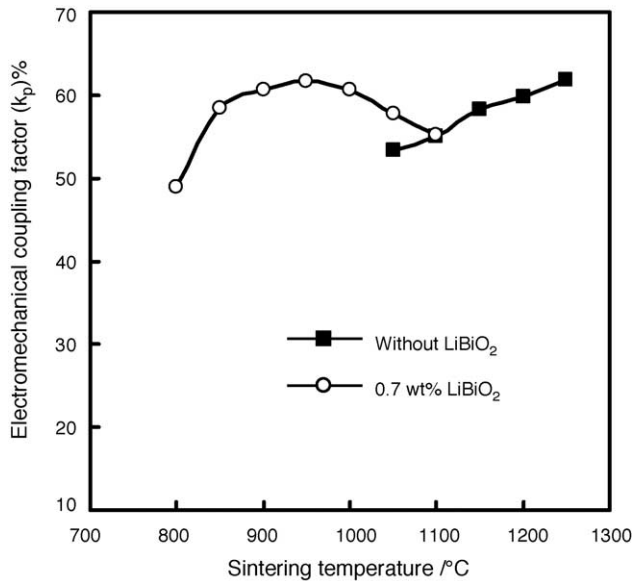


Fig. 4. Electromechanical coupling factor ( $k_p$ ) of 0.7 wt.%  $\text{LiBiO}_2$ -added PBMNZT ceramics as a function of sintering temperature.

for all the specimens. The remanent polarization ( $P_r$ ) and coercive field ( $E_c$ ) decreased with an increase in sintering temperatures. The highest  $P_r$  value of  $40.3 \mu\text{C}/\text{cm}^2$  was obtained for  $\text{LiBiO}_2$ -added specimen fabricated at  $900^\circ\text{C}$ , which was much larger than the value of  $33.6 \mu\text{C}/\text{cm}^2$  of  $1250^\circ\text{C}$ -sintered specimens without  $\text{LiBiO}_2$ . The reason for this is not clear, but, may be related to the phase transition from tetragonal to rhombohedral structure with an increase in sintering temperature.

Fig. 6 shows a unipolar field-induced strain behavior for 0.7 wt.%  $\text{LiBiO}_2$ -added PBMNZT ceramics fabricated at  $950^\circ\text{C}$ . The strain of  $\sim 0.17\%$  was observed under the applied

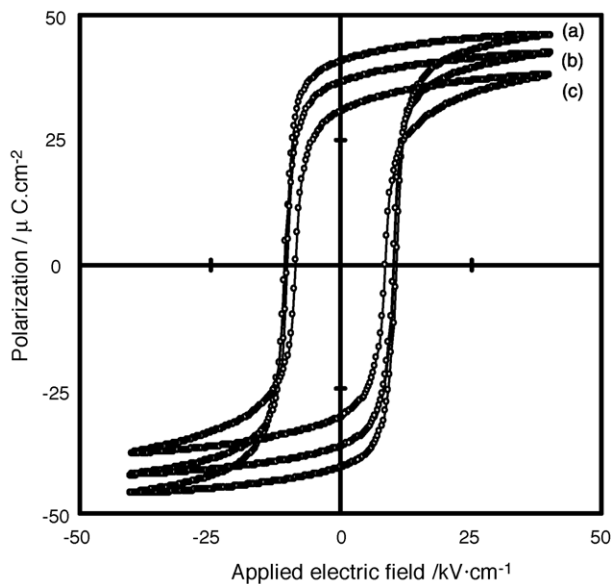


Fig. 5.  $P$ - $E$  hysteresis loops of 0.7 wt.%  $\text{LiBiO}_2$ -added PBMNZT ceramics fabricated at (a)  $900^\circ\text{C}$ , (b)  $1000^\circ\text{C}$  and (c)  $1100^\circ\text{C}$ .

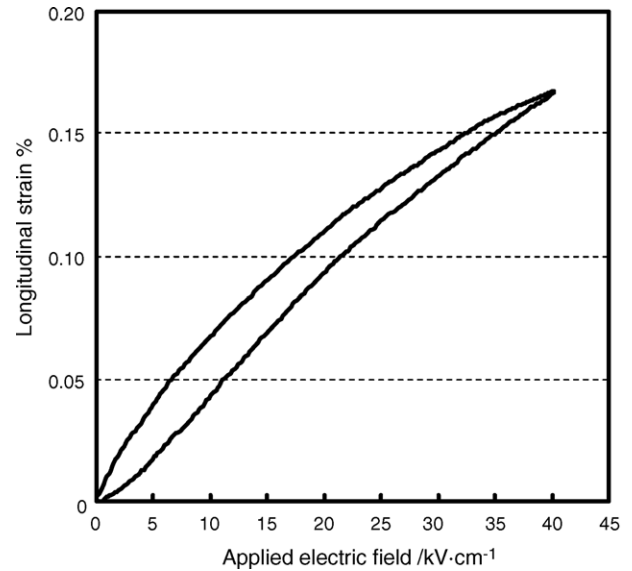


Fig. 6. Unipolar field-induced strain behavior for 0.7 wt.%  $\text{LiBiO}_2$ -added PBMNZT ceramics fabricated at  $950^\circ\text{C}$ .

electric field at  $40 \text{ kV}/\text{cm}$ , and piezoelectric coefficient ( $d_{33}$ ), which was calculated from slope of strain under unipolar driving field of  $20 \text{ kV}/\text{cm}$ , was approximately  $467 \text{ pm}/\text{V}$ . The PBMNZT ceramics without  $\text{LiBiO}_2$  fabricated at  $1250^\circ\text{C}$  exhibited similar strain behavior. Thus, these values are sufficient for piezoelectric actuator device application.

#### 4. Conclusions

Low-temperature sintering of PBMNZT powders with  $\text{LiBiO}_2$  added by surface chemical modification method was investigated, and their microstructure and electrical properties were examined. The results are summarized as follows:

- (1) The addition of  $\text{LiBiO}_2$  sintering aid to PBMNZT powders using surface chemical modification method through the hydrolysis of alkoxides was very useful to improve the sinterability and thereby,  $\text{LiBiO}_2$ -added PBMNZT ceramics with pore-free and dense microstructures could be developed.
- (2) Crystalline phase of 0.7 wt.%  $\text{LiBiO}_2$ -added PBMNZT ceramics was transformed from tetragonal to rhombohedral structure with an increase in sintering temperature from  $900$  to  $1000^\circ\text{C}$ .
- (3) Excellent piezoelectric properties were attained at low temperatures of  $950^\circ\text{C}$  for 0.7 wt.%  $\text{LiBiO}_2$ -added PBMNZT ceramics, and the  $k_p$  and  $d_{33}$  values of the specimens were  $61.7\%$  and  $467 \text{ pm}/\text{V}$ , respectively.

The low-temperature fabrication ( $\leq 1000^\circ\text{C}$ ) without deteriorating piezoelectric properties was achieved for PBMNZT ceramics to which  $\text{LiBiO}_2$  was added by surface chemical modification method.

## Acknowledgment

This work was supported by a Grant-in-Aid for Scientific Research (B), No. 14350357, from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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