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From single crystals to ceramics on $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ composition

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Abstract

Recently, we found a giant electromechanical coupling factor of k_{31} mode over 80% and a piezoelectric d_{31} constant nearly −1700 pC/N in (1 0 0) plane $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ (PZNT91/09) relaxor single crystals in addition to the large k_{33} mode of over 92%. The origin of the giant k_{31} and d_{31} was due to realize the single-domain structure in the direction perpendicular to the poling field as well as in the direction parallel to the poling field. Through our studies, the poling field (E) dependence of ferroelectric properties and their domain structures was investigated. The single-domain structure was achieved at E = 1000–1500 V/mm with decreasing the frequency constant (fc_{31}: half of the bulk wave velocity on k_{31} mode) and the giant k_{31} was obtained at the minimum fc_{31} of 522 Hz m. While the single-domain was divided into two domains over E = 1500 V/mm, the k_{31} decreased and fc_{31} increased. As the formation of a domain wall, which corresponds to a grain boundary in ceramics, caused the increase of the fc_{31} (Young's modulus), the material became mechanically hard. Moreover, we evaluated PZNT91/09 single crystals with (1 0 0), (1 1 0) and (1 1 1) planes for their aging properties. Large aging occurred in the crystals with (1 1 0) plane, on the other hand, little aging in (1 0 0) and (1 1 1) planes. Namely, the ferroelectric and their aging properties depended on the crystal planes. Since ceramics are composed of the small-size single crystals, our results were very helpful to understand the roles of grain boundaries, grain size, domain size and crystal planes in piezoelectric materials. Furthermore, from the relationships between coupling factors of k_{31}, k_{33} and Young's modulus on various kinds of single crystals and ceramics, future research on the piezoelectric materials including lead free materials was proposed.

Keywords: Relaxor single crystals; Perovskites; Grain boundaries; Ferroelectric properties; Piezoelectric properties

1. Introduction

Ferroelectric single crystals made of compounds such as $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ (PZNT91/09) have been attracting considerable attention, because of the large electromechanical coupling factor of the k_{33} mode of over 92%.[1] However, the coupling factors of the k_{31} mode were 49–62%.[1–3] Recently, we found a giant electromechanical coupling factor of k_{31} mode and a piezoelectric d_{31} constant in ferroelectric single crystals composed of (1 0 0) plane PZNT91/09 poled along [0 0 1] of the original cubic direction.[4] The origin of the giant k_{31} and d_{31} was due to realize the single-domain structure in the crystal.[5] In this study, we evaluate the piezoelectricity of the PZNT91/09 single crystals, focusing on particularly the poling field and the crystal plane dependences of the k_{31} mode to compare with the ones of PZT ceramics.

2. Experimental

The PZNT91/09 single crystals evaluated were grown by the solution Bridgman method with a Pt crucible supported at the bottom by a conical insulator stand. The crystals without Pt contamination from the crucible have the dimensions of 50 mm (2 in.) diameter and 35 mm height, and 325 g in weight.[6] As-grown crystals were cut along [0 0 1], [1 1 0] and [1 1 1] of the original cubic direction confirmed by X-ray diffraction (XRD) and from Laue photographs. The single-

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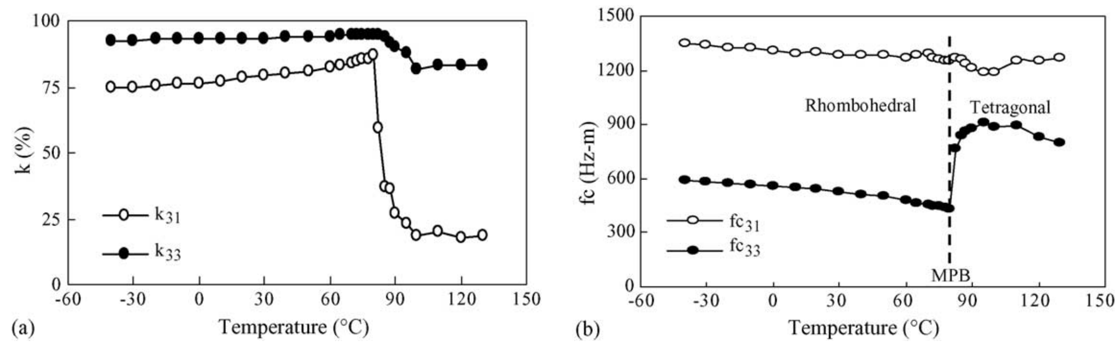

Fig. 1. Temperature dependences of (a) coupling factors (k_{31} and k_{33}) and (b) frequency constants of k_{31} and k_{33} modes (fc_{31} and fc_{33}).

crystal plate samples with dimensions of 4 mm (W) × 13 mm (L) × 0.36 mm (T) were prepared to evaluate the poling field and the crystal plane dependences of the ferroelectric properties such as dielectric constant (ε_r), k_{31} and k_{33}. Gold electrodes for the following dc field applying and electrical measurements were fabricated by conventional sputtering. DC poling was conducted at 40 °C for 10 min by applying 400–2000 V/mm to obtain plate (4 mm (W) × 13 mm (L)) resonators with various crystal planes. After applying the field, the dielectric and piezoelectric properties were mea-

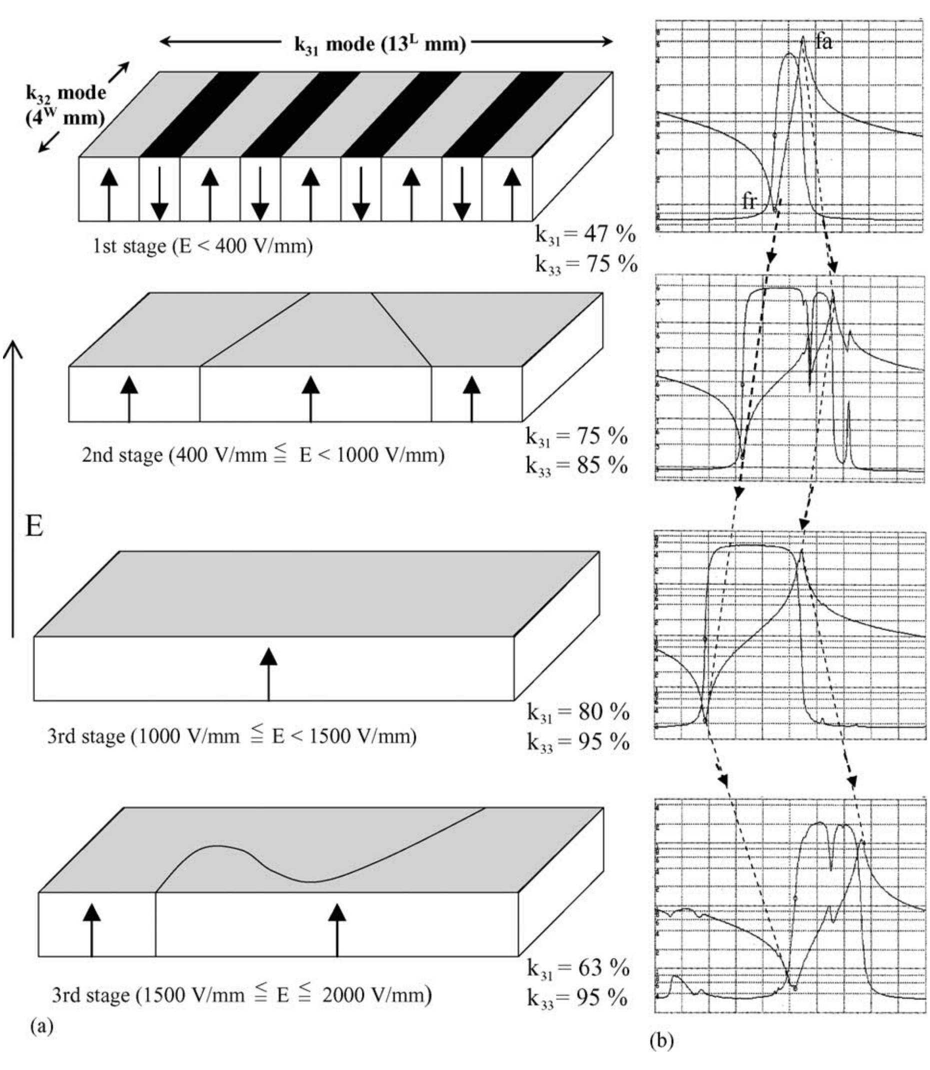

Fig. 2. (a) Schematic picture for domain structures and (b) frequency responses of impedance on k_{31} mode at various dc poling fields (poling temperature: 40 °C, poling time: 10 min).

sured at room temperature using an LCR meter (HP4263A), an impedance/gain-phase analyzer (HP4194A).

3. Results and discussion

3.1. Different roots on piezoelectricity in single crystals and ceramics

High piezoelectricity in ferroelectric materials is realized in the cases of (1 0 0) plane PZNT91/09 single crystals with the giant k_{31} as well as PZT ceramics near the phase boundary between the rhombohedral and tetragonal phases (MPB).[7] Fig. 1(a) and (b) shows the temperature dependences of k_{31}, k_{33} and frequency constant of k_{31} and k_{33} modes (fc_{31} and fc_{33}), which corresponds to the half of the bulk wave velocity, in PZNT91/09 single crystals. While the coupling factors (k), especially k_{31} became relatively high values in the rhombohedral phase in comparison with the ones in tetragonal phase, the fc_{31} showed less than 600 Hz m in the rhombohedral phase. These phenomena were different from PZT ceramics, for example $Pb(Sn_{1/2}Sb_{1/2})O_3$–$PbZrO_3$–$PbTiO_3$ ceramics.[8] In PZT ceramics, the maximum k and minimum fc were obtained concurrently at the MPB. The reason to obtain the high k at the MPB is thought that the number of the polarization axes easy to align in the direction of the dc poling field increase from 8 axes in rhombohedral or 6 axes in tetragonal to 14 (8 + 6) axes near the MPB. However, the giant k_{31} was obtained only in the rhombohedral PZNT91/09, not the existence near the MPB. This means that the origin of high piezoelectricity in PZNT91/09 single crystals is different from the origin in PZT ceramics. It is believed that the giant k_{31} in rhomhedral PZNT91/09 was due to the mechanical softness of the materials with rhombohedral phase easy to symmetrical deform by the poling field.[5,9]

3.2. Roles of grain boundaries

Fig. 2 shows the ferroelectric domain structures and their impedance responses on PZNT91/09 single crystals with (1 0 0) plane under the various dc poling field (E) at the poling temperature of 40 °C and the time of 10 min. Single-domain crystals with giant k_{31} were obtained from the E of 1000 V/mm to 1500 V/mm. On the other hand, the single-domain was divided into two domains while applying the E over 1500 V/mm; as a result, the k_{31} was decreased. The formation of a domain wall or a grain boundary in the PZNT91/09 single crystal caused the rise in resonant frequency (fr) (Fig. 2(b)), namely the fc_{31} (fr × L) and Young's modulus, the material became mechanically hard. Fig. 3 shows the impedance response versus frequency on k_{31} (13 mm (L)) and k_{32} (4 mm (W)) modes. There was the great difference between k_{31} (80%) and k_{32} (58%). Since ceramics are composed of the small-size single crystals, our results were very helpful to understand the roles of grain boundaries, grain size and domain size in piezoelectric materials.

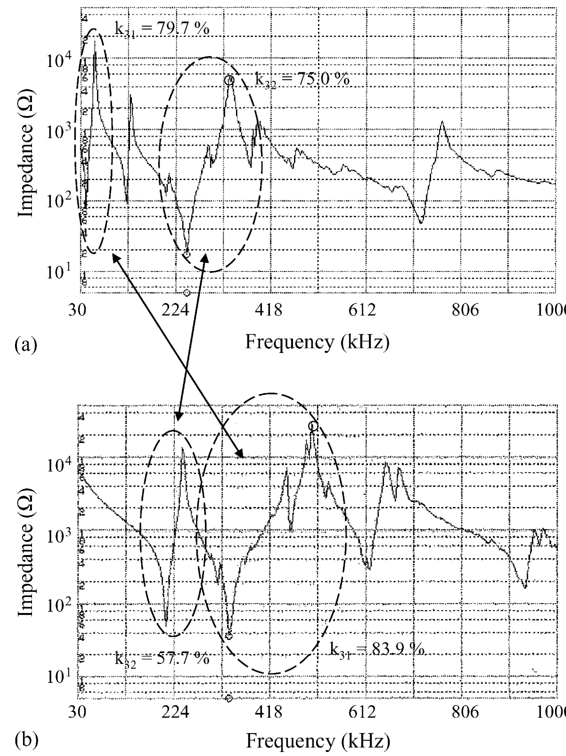

Fig. 3. Frequency responses of impedance on (a) k_{31} (13 mm (L))/k_{32} (4 mm (W)) modes and (b) k_{32} (4 mm (W))/k_{31} (2 mm (L)) modes.

3.3. Aging characteristics

Fig. 4(a)–(c) shows the aging characteristics for dielectric constant (ε_r), k_{31} and fc_{31} versus time at room temperature, respectively. Although the ε_r of (1 0 0) and (1 1 1) planes became constant with time, the ε_r of (1 1 0) crystals increased with time and both the values of the two samples reached to a constant of 6000 in Fig. 4(a). Therefore, it is said that the domain structure of the (1 1 0) plane plate (4 mm (W) × 13 mm (L)) after poling change into a stable domain configuration with time. The same tendencies were observed in the cases of k_{31} versus time (Fig. 4(b)) and fc_{31} versus time (Fig. 4(c)). The giant k_{31} with excellent aging characteristics can be archived in the (1 0 0) crystal plane poled along [0 0 1] of the original cubic direction. In addition, the lowest fc_{31} below 600 Hz m, which is obtained in the (1 0 0) plane (Fig. 4(c)), accompanied giant k_{31} nearly 80%. The aging characteristics and the crystal plane dependences of ε_r, k_{31} and fc_{31} could be explained by the relationships between the directions of the polarization axes in the rhombohedral crystal and the poling field.[9]

3.4. Future research on piezoelectric materials

The Young's modulus (Y^E) of PZNT91/09 single crystals with giant k_{31} ($Y^E = 0.89 \times 10^{10}$ N/m^2) is one order of magnitude smaller than the Y^E (6–9 × 10^{10} N/m^2) of PZT ceramics and, roughly speaking, one order of magnitude larger than

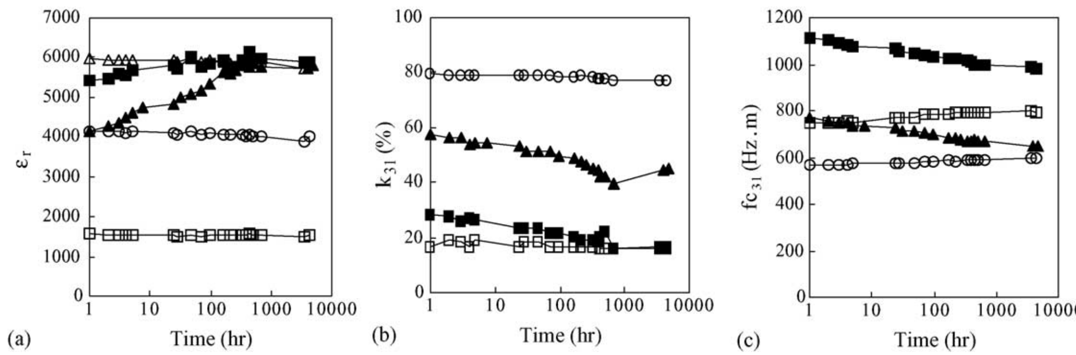

Fig. 4. Aging characteristics for (a) ε_r, (b) k_{31} and (c) fc_{31} vs. time in (1 0 0) plane (No. 1: ◯), (1 1 0) planes (No. 2: ▲, No. 3: ■) and (1 1 1) planes (No. 4: △, No. 5: □).

the Y^E (0.05×10^{10} N/m^2) of rubber.[5] It was thought that the origin of giant k_{31} in PZNT91/09 single crystals was due to the mechanical softness of the materials as mentioned previously. Namely, the most important factor to realize high piezoelectricity is easily symmetrical deformation in ferroelectric rhombohedral phase by the poling field.[9] Fig. 5 shows the relationships with k_{31} and k_{33} versus Y^E on various kinds of single crystals and ceramics reported.[10] There is a linear relationship with k_{31} versus Y^E and k_{33} versus Y^E. Furthermore, there is a blank space between Y^E of PZNT91/09 single crystals and Y^E of ordinary piezoelectric materials. Therefore, new piezoelectric materials including lead free compositions with higher k should be investigated to clarify the blank space, such as the research for elements softened the materials with a rhombohedral perovskite phase.

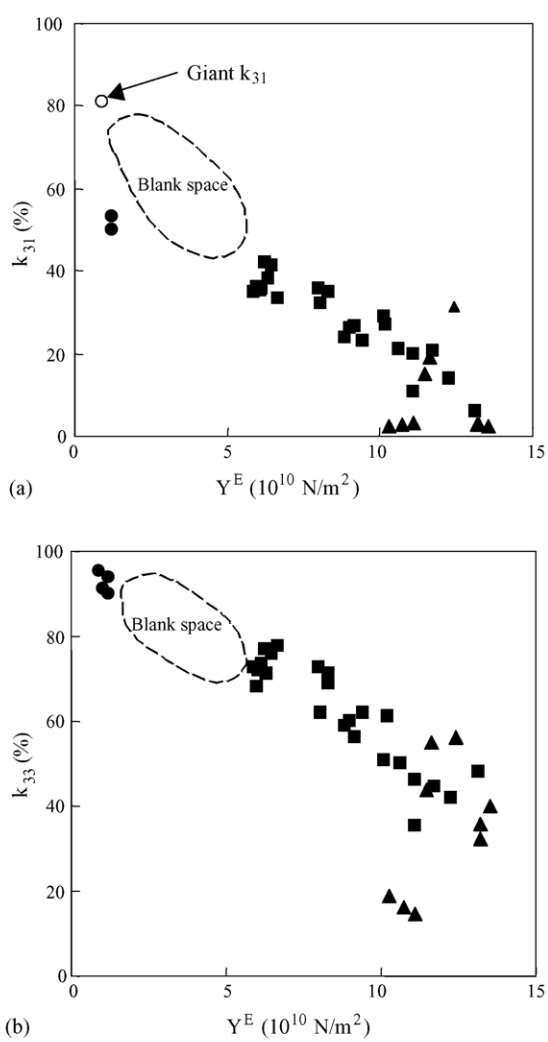

Fig. 5. Relationships with coupling factors of (a) k_{31} and (b) k_{33} vs. Young's modulus (Y^E) in piezoelectric materials.

4. Conclusions

(1 0 0) plane PZNT91/09 single crystals with giant k_{31} and PZNT91/09 single crystals with various kinds of crystal planes such as (1 1 0) and (1 1 1) were evaluated to compare with PZT ceramics. The origin of giant k_{31} was due to the easily symmetrical deformation by poling field, which is the intrinsic property in the rhombohedral (1 0 0) plane PZNT91/09 single crystal because of the materials with the relatively small Young's modulus. In addition, the effect of grain boundaries on the piezoelectric properties and the effect of crystal planes on their aging characteristics were clarified.

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