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Piezoelectric Properties of (Li,Mn)-doped $Ba(Zr,Ti)O_3$-$(Ba,Ca)TiO_3$ Lead-free Piezoelectric Ceramics

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Abstract

Li_2CO_3 and $MnCO_3$ co-doped $(1\text{-}x)Ba(Zr_{0.2}Ti_{0.8})O_3$ $\text{-}x(Ba_{0.7}Ca_{0.3})TiO_3$ [BZT-xBCT] ceramics were prepared by conventional solid-state reaction method and their piezoelectric properties were examined in detail. The product of piezoelectric constant d and mechanical quality factor Q_m ($d \times Q_m$) at $MnCO_3$ 0.6 wt% and Li_2CO_3 1 wt% doped BZT-0.6BCT ceramics was approximately 4 times larger than that of non-doped BZT-BCT ceramics. In addition, BZT-BCT+0.6Mn+1.0Li showed relatively higher vibration velocity $v_{0\text{-}p}$ at small applied electric field ($E_{0\text{-}p}$ = 15 V/mm), which is related to the small signal $d_{31} \times Q_m$.

1. Introduction

High-power piezoelectric ceramic devices such as ultrasonic vibrator for ultrasonic cleaner, has been widely used[1)]. For high-power piezoelectric applications, vibration velocity $v_{0\text{-}p}$ is one of the important parameters, which is generally known as proportional to a product of piezoelectric constant d and mechanical quality factor Q_m ($d \times Q_m$). Then, both larger d and Q_m values are required for the practical applications of high-power piezoelectric devices. At practical devices, hard-type $Pb(Zr,Ti)O_3$ [PZT] based ceramics are mainly used because of high $d \times Q_m$ value. However, the $v_{0\text{-}p}$ of PZT shows non-linearity at large amplitude vibration, moreover, PZT contains harmful element PbO[2)]. Therefore, development of lead-free piezoelectric materials is required for even high-power piezoelectric devices.

$(1\text{-}x)Ba(Zr_{0.2}Ti_{0.8})O_3\text{-}x(Ba_{0.7}Ca_{0.3})TiO_3$ [BZT-xBCT] has been reported to have a relatively high piezoelectric constant d, making it a potential candidate for lead-free piezoelectric ceramics[3~8)]. This is because BZT-xBCT has a morphotropic phase boundary (MPB) starting from a tricritical triple point in which it has large piezoelectric constant d_{33} about 620 pC/N[9)]. In this study, we selected the composition of $x = 0.6$ where T_C is at around 100°C and the piezoelectric characteristics are relatively stable for temperature[10)]. However, the d of this composition is relatively low as compared with that of MPB composition and the Q_m is not large enough for practical high-power piezoelectric application. To solve these problems, we focused on the doping effect of Mn ions as hard dopant and Li ions for liquid-phase sintering. Therefore, doping effect of Li and Mn ions for BZT-0.6BCT ceramics was examined in detail to improve piezoelectric properties such as $v_{0\text{-}p}$ and $d \times Q_m$.

2. Experimental procedure

BZT-0.6BCT + Li_2CO_3 y wt% [BZT-0.6BCT+Liy] and BZT-0.6BCT + $MnCO_3$ 0.6 wt% + Li_2O_3 y wt% [BZT-0.6BCT+0.6Mn+Liy] (y = 0, 0.4, 1.0, 1.5) ceramics were prepared by conventional solid-state reaction method. Carbonate and oxide powders, i.e., $BaCO_3$, TiO_2, ZrO_2, $CaCO_3$, Li_2CO_3, and $MnCO_3$. (≥ 99.9%), were used as starting materials. These starting raw materials without Li_2CO_3 were weighed in accordance with the chemical formula $0.4Ba(Zr_{0.2}Ti_{0.8})O_3\text{-}0.6(Ba_{0.7}Ca_{0.3})TiO_3$ and then ball -milled with zirconia balls in ethanol for 5 h. The mixture was dried and uniaxially pressed into pellets, then calcined at 1000°C for 4 h. The calcined pellets were ground and ball-milled for 15 h with Li_2CO_3 addition. After drying, the mixed powders were press into pellets and subjected to a cold isostatic pressing (CIP) treatment at 150 MPa, then sintered at 1300°C and 1400°C for 2 h.

The phases of the sintered samples were identified by X-ray diffraction. Scanning electron microscopy (SEM) was used to observe the microstructure. For the measurement of the piezoelectric properties, the samples were cut into appropriated shapes of the (31) mode (12×3×1 mm^3) and silver-electrode on both surfaces, then poled in a silicone oil bath by applying dc electric fields of 3.5 kV/mm for 20 min at room temperature. The piezoelectric properties were investigated by a resonance–antiresonance method using an impedance analyzer (HP4294A) and the vibration velocity $v_{0\text{-}p}$ was measured using a laser doppler vibrometer (ONOSOKKI LV1710).

3. Results and discussion

All (Li, Mn)-doped BZT-BCT ceramics showed high relative density ratio over 94% of the theorical density and a single-phase perovskite structure was observed in each sample from XRD patterns. **Fig. 1(a)** and **Fig. 1(b)** show small signal d_{31} and Q_m as a function of Li_2CO_3 content of BZT-BCT+Liy and BZT-BCT+0.6Mn+Liy ceramics. The d_{31} values were improved by Li_2CO_3 doping and the maximum obtained at y = 1 wt% under all experimental conditions. Among them, d_{31} value on BZT-BCT+1.0Li showed largest about 160 pC/N. This is because Li_2CO_3 doping improved dielectric constant ε_r which is responsible for the increase of d_{31}. Also, the Q_m values were enhanced by $MnCO_3$ doping. As shown in **Fig. 1(b),** the Q_m value was approximately 2 times larger than that of non-Mn doped ceramics at $y = 1$ wt%. This is because Mn ions work as accepter that increase oxygen vacancies. Therefore, the Q_m increased and piezoelectric characteristics became harder due to the domain pinning effect.

Fig. 2 shows $d_{31} \times Q_m$ as a function of Li_2CO_3 content of BZT-BCT+Li*y* and BZT-BCT+0.6Mn +Li*y* ceramics. The value of $d_{31} \times Q_m$ is the highest at BZT-BCT+0.6Mn+1.0Li ceramic. This is because the Q_m has large enhancement due to the co-doping effect of Li_2CO_3 and $MnCO_3$, as compared with the small deterioration of d_{31} value. As a result, the $d_{31} \times Q_m$ value was approximately 4 times larger than that of non-doped BZT-0.6BCT ceramics. Also, BZT-BCT+0.6Mn+1.0Li showed the highest $v_{0\text{-}p}$ at small applied electric field ($E_{0\text{-}p}$ = 15 V/mm), which is related to the small signal $d_{31} \times Q_m$. From these results, (Li, Mn)-doped BZT-0.6BCT has excellent piezoelectric properties, which could be one of the potential candidates for lead-free materials on high-power piezoelectric applications.

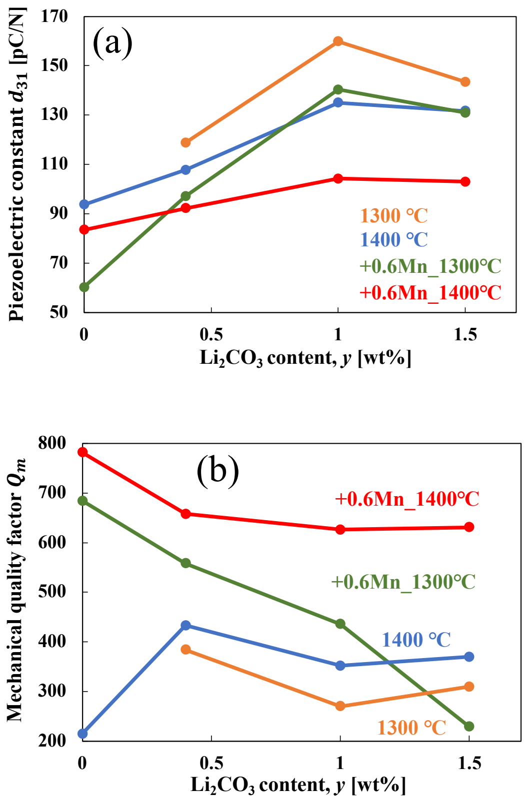

Fig. 1 (a) d_{31} and (b) Q_m as a function of Li_2CO_3 content of BZT-BCT+Li*y* and BZT-BCT+0.6Mn +Li*y* ceramics.

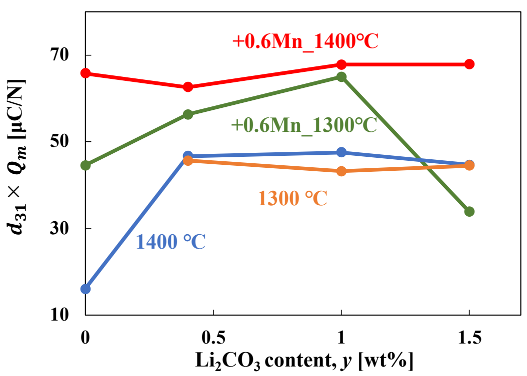

Fig. 2 $d_{31} \times Q_m$ as a function of Li_2CO_3 content of BZT-BCT+Li*y* and BZT-BCT+0.6Mn+Li*y* ceramics.

4. Conclusion

In this work, Li_2CO_3 and $MnCO_3$ co-doped BZT-0.6BCT ceramics were prepared by conventional solid-state reaction method. The piezoelectric properties have been investigated, and as a result, the $d_{31} \times Q_m$ value was approximately 4 times larger than that of non-doped BZT-BCT ceramics. In addition, BZT-BCT+0.6Mn+1.0Li showed relatively higher $v_{0\text{-}p}$ at small applied electric field ($E_{0\text{-}p}$ = 15 V/mm), which is related to the small signal $d_{31} \times Q_m$. From these results, (Li, Mn)-doped BZT-0.6BCT has excellent piezoelectric properties which could be one of the potential candidates for lead-free ceramics on high-power piezoelectric applications.

5. References

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