High-temperature and high-power piezoelectric characteristics of (Bi0.5Na0.5)TiO3-Based lead-free piezoelectric ceramics

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The high-power piezoelectric characteristics of (Bi0.5Na0.5)TiO3 (BNT)-based solid solutions at a high temperature (~130°C) were studied, by comparing them with those of hard Pb(Zr,Ti)O3 (PZT) ceramics. The vibration velocity $v_{0-p}$ of the BNT-based ceramics was stable as the temperature increased to 130°C, whereas that of the PZT-based ceramics markedly decreased with increasing temperature. It is generally known that the stability of $v_{0-p}$ under high-amplitude vibration is related to mechanical losses caused by domain wall motion. Therefore, the temperature dependence of the mechanical quality factor $Q_m$ of these ceramics was measured by electric transient response measurement. The measured $Q_m$ values of the BNT-based ceramics were nearly constant or slightly decreased with increasing temperature, whereas $Q_m$ for the PZT ceramic markedly decreased with increasing temperature.

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Key-words: Lead-free piezoelectric ceramics, Perovskite, Piezoelectric property, High-power, High-temperature

1. Introduction

Recently, many high-power piezoelectric ceramic devices, such as ultrasonic motors and piezoelectric actuators, have been developed.1-3 Hard Pb(Zr,Ti)O3 (PZT) ceramics or Pb(Mn1/3Nb2/3)O3-Pb(Zr,Ti)O3 (PMN-PZT) ceramics with a high mechanical quality factor ($Q_m$) are commonly used in high-power piezoelectric applications. However, PZT ceramics have certain problems in high-power applications, namely the vibration velocity is unstable, the mechanical quality factor $Q_m$ decreases with increasing $v_{0-p}$ and temperature, and the resonance frequency $f_r$ decreases with increasing $v_{0-P}$. Because of these problems, hard PZT is usually used below $v_{0-P} = 1$ m/s. Moreover PZT contains a large amount of PbO; therefore, lead-free piezoelectric materials to replace PZT are required from the viewpoint of environmental protection.

As materials for lead-free high-power applications, SrBi2-Nb2O9 and (Sr,Ca)2NaNb5O15 ceramics and LiNbO3 single crystals have been reported.4-5 Furthermore, there have been some studies on the high-power piezoelectric characteristics of lead-free piezoelectric ceramics with a perovskite structure.6-13 Candidate materials for perovskite-type lead-free piezoelectric ceramics are BaTiO3 (BTO), (Bi1/2Na1/2)TiO3 (BNT) and KNbO3 (KN) among others.6-13 Important piezoelectric constants for obtaining a high vibration velocity are the piezoelectric strain constant $d$ and mechanical quality factor $Q_m$. BNT-based solid solutions have attracted attention as lead-free piezoelectric ceramics with relatively high $d$ and $Q_m$ for high-power piezoelectric applications.4,14 Recently, we have clarified6-14 that $Q_m$ for rhombohedral compositions is higher than those of tetragonal and MPB compositions for BNT-based ternary systems, such as (Bi1/2Na1/2)TiO3-(Bi1/2Li1/2)TiO3-(Bi2/3K1/3)TiO3 (BNLKT)6,14 and (Bi1/2Na1/2)TiO3-(Bi1/2Li1/2)TiO3-BaTiO3 (BNLBT).15 Moreover, the high-power piezoelectric properties of BNT-based ceramics with the above-mentioned compositions have been examined and relatively good properties were observed.10,13 However it is known that the temperature usually increases owing to heat generation under continuous driving. Additionally, the high-power piezoelectric characteristics of BNT-based ceramics at a high temperature have not sufficiently clarified been cleared enough.16 In this study, therefore, the high-power piezoelectric characteristics at a high temperature (~130°C) were studied to clarify the temperature stability of high-power piezoelectric properties of BNT-based ceramics such as BNLK and BNLBT ceramics. Moreover, we compared the temperature dependences of high-power piezoelectric properties with those of hard PZT ceramic [NEC Tokin: PZT-N82].

2. Experimental procedure

In this experiment, we selected the following compositions as BNT-based ceramics such as BNLKT and BNLBT ceramics.

- Non-doped (Bi1/2Na1/2)TiO3 (BNT)
- (1-x-y-z)(Bi1/2Na1/2)TiO3-x(Bi1/2Li1/2)TiO3-y(Bi1/2K1/2)TiO3-z(Bi1/2Na1/2)MnO3 (BNLKT 100x-100y-100z, x = 0.04, y = 0.08, z = 0.02; BNLKT4-8-2)12)
- (1-x-y-z)(Bi1/2Na1/2)TiO3-x(Bi1/2Li1/2)TiO3-yBaTiO3-z(Bi1/2Na1/2)MnO3 (BNLBT 100x-100y-100z, x = 0.04, y = 0.04, z = 0.25; BNLBT4-4-2.5)13)

These ceramics were prepared by a conventional solid-state reaction. The starting raw materials were Bi2O3 and Li2O of 99.99% purity, Na2CO3 of 99.95% purity, and TiO2, K2CO3, BaCO3, and MnCO3 of 99.9% purity. They were mixed by ball-milling for 10 h and calcined at 200°C for 2 h, 600°C for 2 h, and 850°C for 2 h. After calcining, the resulting ground and ball-milled powders were pressed into disks 20 mm in diameter. These disks were processed by cold isostatic pressing (CIP) at 150 MPa to obtain dense ceramics. After the processing, these disks were sintered at 1140°C for 2 h in air. The crystal structures and lattice

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Footnotes:

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2) Preface for this article: DOI http://dx.doi.org/10.2109/jcersj2.122.P6-1

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constants of the sintered ceramics were determined using an X-ray diffractometer (Rigaku; RINT2000). The sintered ceramics were cut and polished into rectangular specimens of $1 \times 3 \times 12$ mm$^3$ in the (31) mode. Electrodes were prepared using fired-on Ag paste for electrical measurements such as their dielectric, ferroelectric, and piezoelectric properties. Samples were then poled in a silicone oil bath at RT. A DC electric field of 5–8 kV/mm was applied to the samples for 5 min during poling. Piezoelectric properties at low amplitude were measured by the resonance-antiresonance method on the basis of IEEE standards using an impedance analyzer (HP 4294A). The temperature dependences of the electromechanical coupling factor $k_{31}$ and mechanical quality factor $Q_m$ were measured using the same impedance analyzer with the same set up from RT to about 200°C. The vibration velocity $v_{0-p}$ was measured using a laser Doppler vibrometer (Ono Sokki LV1710) equipped with an oscilloscope (Tektronix TDS3054B). The value of $v_{0-p}$ for short-time driving was determined by frequency sweep measurement at approximately the resonant frequency. The value of $Q_m$ under high-amplitude vibration was determined by electric transient response measurement. In addition, a PZT ceramic (NEC-Tokin N82) was also studied for comparison. The temperature dependences of $v_{0-p}$ and $Q_m$ under high-amplitude vibration were measured using the same impedance analyzer for high-power measurement attached to a thermostatic oven for heat treatment. The sample temperature was directly monitored using thermocouples.

3. Results and discussion

Figure 1 shows X-ray diffraction patterns of the BNT-based ceramics, which revealed a single-phase perovskite structure. The relative density ratios of the sintered ceramics were all higher than 95%, as measured by the Archimedes method. Table 1 shows the electrical and piezoelectric properties of the BNT, BNLBT4-4-2.5, BNLKT4-8-2, and PZT ceramics under low-amplitude vibration. The piezoelectric strain constants ($d_{31}$) of both BNT-based solid solutions were approximately 20 pC/N. The mechanical quality factors $Q_m$ of BNLBT4-4-2.5 and BNLKT4-8-2 were 496 and 784, respectively. These values are consistent with those reported previously. In contrast, the PZT ceramic exhibited a large $d_{31}$ of approximately 100 pC/N and a high $Q_m$ of 1300 at RT, which are much larger than those of the BNT-based ceramics.

Table 1. Electrical and piezoelectric properties of BNT, BNLBT4-4-2.5, BNLKT4-8-2, and PZT ceramics under low-amplitude vibration

|      | $k_{31}$ | $d_{31}$(pC/N) | $Q_m$ | $\varepsilon_{31}/\varepsilon_0$ | $s_{31}$(pm/N) | $\tan \delta$ | $\rho$ (Ω·cm) |
|------|----------|----------------|-------|----------------------------------|----------------|--------------|--------------|
| BNT  | 0.10     | 15.1           | 366   | 345                              | 7.2            | 0.02         | 1.98 $\times 10^{11}$ |
| BNLBT4-4-2.5 | 0.13     | 21.4           | 496   | 351                              | 8.4            | 0.19         | 1.76 $\times 10^{11}$ |
| BNLKT4-8-2 | 0.13     | 21.6           | 784   | 380                              | 7.7            | 0.12         | 2.45 $\times 10^{11}$ |
| PZT  | 0.30     | 97.9           | 1340  | 802                              | 1.5            | 0.09         | 4.05 $\times 10^{13}$ |

Figure 2 shows the temperature dependence of the electromechanical coupling factor $k_{31}$ of the BNT, BNLBT4-4-2.5, BNLKT4-8-2, and PZT ceramics under the small-amplitude vibration. The $k_{31}$ values of the BNT, BNLBT4-4-2.5, BNLKT4-8-2, and PZT ceramics markedly dropped at approximately 170, 130, and 280°C, respectively, indicating that these ceramics were depolarized at these temperatures. Considering this finding, the maximum temperature for piezoelectric measurement was determined to be 130°C in this study for the comparison of high-power characteristics of these compositions. Figure 3 shows the temperature dependence of $Q_m$ of the BNT, BNLBT4-4-2.5, BNLKT4-8-2, and PZT ceramics under the small-amplitude vibration in the temperature range from RT to 130°C. $Q_m$ for the PZT ceramic continuously decreased with increasing temperature.
Table 1. On the other hand, the PZT ceramic under the low-amplitude vibration as shown in the BNLKT and BNLBT ceramics were smaller than that of applied fields up to 2.0 m/s. This corresponds to the stability of domain walls under the high-amplitude vibration, which was considered that the domain walls in the PZT ceramic dynamically vibrated even during the low-amplitude measurement. On the other hand, the BNT-based ceramics basically have a smaller $d_{31}$ and $Q_m$ values and a larger coercive field $E_c$ than the PZT ceramic. This is why the BNT-based ceramics showed more stable $Q_m$ values the increasing temperature than the PZT ceramic. Among the BNT-based ceramics, the BNLKT ceramic showed the strongest temperature dependence of $Q_m$. Presently, it is difficult for us to determine the exact reason for this dependence. However, it is reasonable to assume the lowest depolarization temperature $T_0$ of the BNLKT ceramic to be 130°C.

Figure 4 shows the vibration velocity $v_{0-p}$ as a function of the applied field $E_a$ for the BNT, BNLBT4-4-2.5, BNLKT4-8-2, and PZT ceramics. The $v_{0-p}$ values were obtained by frequency sweep measurement at approximately the resonant frequency. In the case of the BNT-based ceramics, the $E_a$ dependence of $v_{0-p}$ in BNLKT and BNLBT ceramics was larger than that in the BNT ceramic. The $v_{0-p}$ values of both BNLKT and BNLBT were larger than 3 m/s under the short driving. On the other hand, $v_{0-p}$ for the hard PZT ceramic increased to 2.5 m/s. Moreover, the hard PZT ceramic has larger $v_{0-p}$ values at small $E_a$ than the BNT-based ceramics. This is because the hard PZT ceramic has larger $d_{31}$ and higher $Q_m$ values. In terms of the linearity of $v_{0-p}$ vs $E_a$, the hard PZT ceramic exhibited nonlinearity at approximately 1.0 m/s under the short time driving. In contrast, the BNLKT and BNLBT ceramics exhibited better linearity than the PZT and BNT ceramics up to 2.0 m/s. This linearity is considered to be associated with the stability of domain walls under the high-amplitude vibration, which corresponds to the stability of $Q_m$. Figure 5 shows $Q_m$ as a function of the vibration velocity $v_{0-p}$ for the BNT, BNLBT4-4-2.5, BNLKT4-8-2, and PZT ceramics. The PZT ceramic showed a significant drop in $Q_m$ with increasing $v_{0-p}$. The $Q_m$ values of the BNLKT and BNLBT ceramics were smaller than that of the PZT ceramic under the low-amplitude vibration as shown in Table 1. On the other hand, the $Q_m$ values of the BNLKT and BNLBT ceramics in the region of $v_{0-p}$ > 1.0 m/s were similar to or higher than that of the PZT ceramic. Therefore, BNT-based ceramics possess superior mechanical stability. This is a very good sign for high-power applicability.

Figure 6 shows the temperature dependence of the vibration velocity $v_{0-p}$ under frequency sweeping for the BNT, BNLBT4-4-2.5, BNLKT4-8-2, and PZT ceramics. First, it is considered that the temperature dependence of $v_{0-p}$ should differ among the samples with different $v_{0-p}$ values owing to the variation of vibration stress. We considered it necessary to normalize $v_{0-p}$ by its value at RT. We found that $v_{0-p}$ was about 1.4 m/s at RT in this study. To obtain at value of 1.4 m/s at RT, the electric fields required for driving are different for BNT-based and PZT ceramics, as shown in Fig. 4. The applied fields for these ceramics are shown in the inset of Fig. 6. Again, Fig. 6 shows the temperature dependences of the vibration velocity $v_{0-p}$ under frequency sweeping at a constant electric field for the BNT, BNLBT4-4-2.5, BNLKT4-8-2, and PZT ceramics. $v_{0-p}$ of the PZT ceramic markedly decreased with increasing temperature. On the other hand, the $v_{0-p}$ values of the BNT-based ceramics were nearly constant with increasing temperature. To understand the reason for the difference in the trend of $v_{0-p}$ in relation to temperature, the temperature dependence of $Q_m$ was examined. Figure 7 shows the temperature dependences of the $Q_m$ at a constant electric field for the BNT, BNLBT4-4-2.5, BNLKT4-8-2, and PZT ceramics. $Q_m$ for the PZT ceramic markedly decreased with increasing temperature. This trend is similar to that of the temperature dependence of $Q_m$ under the low-amplitude vibration, as shown in Fig. 5. $Q_m$ for the BNT-
based ceramic slightly decreased with increasing temperature. Comparing the $Q_m$ reduction of BNLKT between low- and high-amplitude vibrations shown in Figs. 3 and 7, $Q_m$ under the small amplitude is almost constant whereas that under the large amplitude slightly decreases with increasing temperature. It is generally considered that the mechanical loss is mainly due to the domain wall motion under high-amplitude vibration. Therefore, it is supposed that domain wall motion is activated with increasing temperature under high-amplitude vibration even in the BNLKT ceramic. Taken together, $v_{0-p}$ for the PZT ceramic decreased owing to the decrease in $Q_m$ as a function of temperature.

4. Summary

High-power piezoelectric characteristics at a high temperature ($\sim 130^\circ$C) were compared between BNT-based ceramics and PZT ceramic. The mechanical quality factor $Q_m$ and vibration velocity $v_{0-p}$ of the PZT ceramic markedly decreased with increasing temperature. On the other hand, $Q_m$ and $v_{0-p}$ for the BNT-based ceramics were nearly constant or slightly decreased with increasing temperature. The decrease in piezoelectric characteristics with increasing temperature was due to the mechanical and elastic losses resulting from the vibration of the domain walls at a high power. From these results, the high-power piezoelectric characteristics of BNT-based ceramics at a high temperature were more stable than those of the PZT ceramic. Therefore, BNT-based ceramics promising candidate materials for lead-free high-power piezoelectric devices.

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