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Effects of Mn Addition or Substitution on High-power Piezoelectric Characteristics for $(Bi_{0.5}Na_{0.5})TiO_3$-based Lead-Free Piezoelectric Ceramics

$(Bi_{0.5}Na_{0.5})TiO_3$ 系非鉛圧電セラミックスのハイパワー特性に及ぼす Mn 添加・置換効果

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1. INTRODUCTION

Recently, many high-power piezoelectric ceramic devices, such as ultrasonic motor and piezoelectric actuators have been developed. Hard $Pb(Zr,Ti)O_3$ [PZT] ceramics or $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ [PMN-PZT] ceramics with high mechanical quality factor, Q_m, are usually used in high-power piezoelectric applications. However, PZT ceramics contain a large amount of Pb, therefore, lead-free piezoelectric materials to replace PZT are recently required from the viewpoint of environmental protection.

Important piezoelectric constants for obtaining high vibration velocity are both piezoelectric strain constant d and mechanical quality factor Q_m. Recently, $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT)-based solid solutions have been attracted attention as lead-free piezoelectric ceramics with high d and Q_m for high-power piezoelectric applications [1]. Especially, $0.88(Bi_{0.5}Na_{0.5})TiO_3$-$0.04(Bi_{0.5}Li_{0.5})TiO_3$ -$0.08(Bi_{0.5}K_{0.5})TiO_3$ [BNLKT4-8] have been characterized with high d and Q_m in BNT-based lead-free piezoelectric ceramics[2]. Also, in general, it is known that a Mn doping to the PZT ceramics is very effective for enhancing the Q_m[3]. In this study, therefore, the effects of Mn addition for Q_m and piezoelectric characteristics were studied on BNLKT4-8 ceramics. In addition, we also investigated the effects of Mn substitution to the B-site and compared these Q_m and piezoelectric properties. Moreover, high-power piezoelectric characteristics of the BNLKT4-8 ceramics with Mn addition and substitution were investigated under continuous driving.

2. EXPERIMENTAL PROCEDURE

BNLKT4-8 ceramics with Mn addtion and substitution are expressed as follows;

Addition: BNLKT4-8+$MnCO_3$ x wt %
(x=0~0.6) [BNLKT4-8-x wt%]

Substitution: BNLKT4-8-$y(Bi_{0.5}Na_{0.5})MnO_3$
(y=0~0.030) [BNLKT4-8-100y]

These ceramics were prepared by a conventional solid-state reaction. The starting raw materials were Bi_2O_3 and Li_2CO_3 of 99.99% of purity, Na_2CO_3 of 99.95% purity, TiO_2 and $MnCO_3$ of 99.9% purity, and $KHCO_3$ of 99.5% purity. They were mixed by ball-milling for 10 h and calcined at 200-600-850ºC for 2-2-2 h. After calcining, the ground and ball-milled powders were pressed into disks 20 mm in diameter. These were processed to cold isostatic press (CIP) of 150 MPa to obtain dense ceramics. After the treatment, these disks were sintered at 1140ºC for 2 h in air. The sintered ceramics were cut and polished into rectangular specimens of 1× 3× 12 mm^3 for (31) mode. Electrodes were made with fired-on Ag paste for electrical measurements such as dielectric, ferroelectric and piezoelectric properties. Piezoelectric properties at small amplitude were measured by the resonance-antiresonance method on the basis of IEEE standards, using an impedance analyzer (HP 4294A). A piezoelectric transducer was driving by a function generator (NF WF1943A) and a power amplifier (NF HAS4052). Vibration velocity $v_{0\text{-}p}$ was measured using a laser Doppler vibrometer (Ono Sokki LV1710) with an oscilloscope (Tektronix TDS3054B). The vibration velocity $v_{0\text{-}p}$ of the short time driving was determined by a frequency sweep measurement around resonant frequency[4]. On contrary, the long time driving was measured under the condition of constant voltage at resonant frequency. In the measurement of sample temperature under the continuous driving, optical thermometer (HIOKI Temperature Hightester 3445) was used.

3. RESULTS AND DISCUSSION

XRD patterns for all ceramics showed single phase perovskite structure with rhombohedral symmetry. The relative densities of sintered ceramics were all higher than 95% measured by Archimedes method. From the piezoelectric measurements, the BNLKT 4-8-2 showed the maximum Q_m value in Mn substitution system and the BNLKT4-8-0.6 wt% showed the maximum Q_m value in Mn addition system. Table I shows

Table I Electrical and piezoelectric properties of small amplitude vibration for BNLKT4-8 ceramics.

	Mn ion	$\varepsilon_{33}^T/\varepsilon_0$	d_{31} (pC/N)	Q_m	d_{31} (pC/N)*Q_m
BNLKT4-8	0	490	24	360	8640
Addition (x wt%)	0.6	348	20	737	14740
Substitution(100y)	2	342	19	791	15029

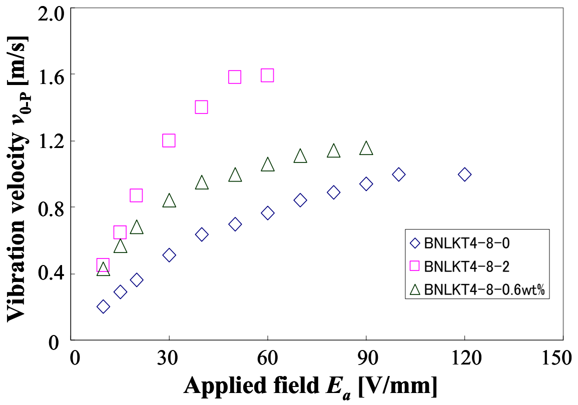

Figure 1 Applied field E_a dependences of vibration velocity v_{0-p} under the continuous driving.

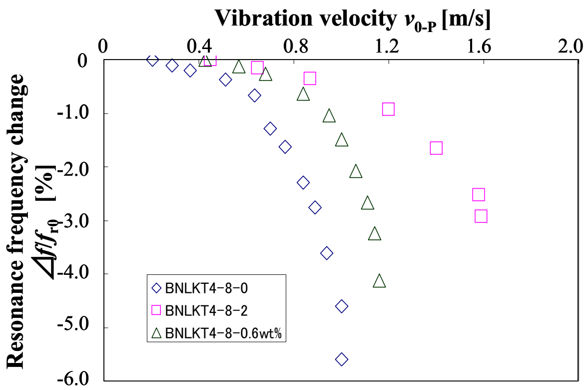

Figure 2 Vibration velocity dependence of resonant frequency change under the continuous driving.

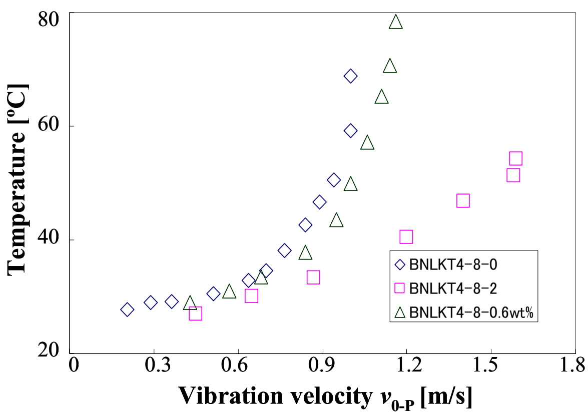

Figure 3 Vibration velocity dependence of temperature change under the continuous driving.

piezoelectric properties of small amplitude vibration for BNLKT4-8-0, BNLKT4-8-2 (Mn substitution) and BNLKT4-8-0.6 wt% (Mn addition) ceramics. The Q_m in (31) mode indicated 791 for the case of Mn substitution of 2 mol% to the B-site of BNLKT4-8. Also, the product of d and Q_m of BNLKT4-8-2 is higher than that of BNLKT4-8-0.6 wt%. Therefore, the BNLKT4-8-2 ceramic is expected to have an excellent high-power piezoelectric property.

Figure 1 shows the applied field E_a dependences of vibration velocity v_{0-p} for BNLKT4-8-0, BNLKT4-8-2 (Mn substitution) and BNLKT4-8-0.6 wt% (Mn addition) ceramics. The maximum v_{0-p} value of BNLKT4-8-2 is 1.6 m/s that is higher than BNLKT4-8-0.6 wt%. The v_{0-p} is proportional to the $d \times Q_m$ product. Figure 2 shows the v_{0-p} dependences of resonant frequency change for BNLKT4-8-0, BNLKT4-8-2 (Mn substitution) and BNLKT4-8-0.6 wt% (Mn addition) ceramics. The resonant frequency change of BNLKT4-8-2 is smaler than that of BNLKT4-8-0.6 wt%. Figure 3 shows the vibration velocity dependence of temperature change for BNLKT4-8-0, BNLKT4-8-2 (Mn substitution) and BNLKT4-8-0.6 wt% (Mn addition) ceramics. Temperature of ceramic samples rises with increasing the v_{0-p}. The temperature change of BNLKT4-8-2 is smaler than that of BNLKT4-8-0.6 wt%. From these results, the BNLKT4-8-2 ceramic indicated stable resonance frequency and temperaute under the large amplitude vibration rather than other compositions. This is probably due to the stability of Q_m under the large amplitude vibration, which relates to a formation of oxygen vacancies by Mn substitution.

4. CONCLUSIONS

High-power piezoelectric characteristics at continuous driving of $0.88(Bi_{0.5}Na_{0.5})TiO_3$-$0.04(Bi_{0.5}Li_{0.5})TiO_3$-$0.08(Bi_{0.5}K_{0.5})TiO_3$ + $MnCO_3$ x wt% and BNLKT4-8-$y(Bi_{0.5}Na_{0.5})MnO_3$ were studied. As result, BNLKT4-8-2 (Mn substitution) with the largest $d \times Q_m$ product is better than other compositions. Therefore, Mn substituted BNLKT4-8 ceramic is a promising candidate material as lead-free high-power piezoelectric devices.

5. REFERENCES

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