

Current Status and Prospects of Lead-free Piezoelectric Ceramics

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Abstract:

Dielectric, ferroelectric and piezoelectric properties of perovskite ferroelectric and bismuth layered-structured ferroelectric (BLSF) ceramics are described as superior candidates for lead-free piezoelectric materials to reduce environmental damages. Perovskite type ceramics seem to be suitable for actuator and high power applications that are required a large piezoelectric constant, d_{33} (>300 pC/N) and a high Curie temperature, T_c (>200 °C). For BaTiO₃-based solid solutions, that is, $(1-x)\text{BaTiO}_3-x(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ [BTBK-100x] ceramics, the T_c increases with increasing the amount of x . BTBK-20+MnCO₃ 0.1wt% ceramic shows the high T_c than 200 °C and the electromechanical coupling factor, $k_{33} = 0.35$. In the case of $a(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3 - b\text{BaTiO}_3 - c(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ [BNBK (100a/100b/100c)] solid solution ceramics, the d_{33} and T_c are 191 pC/N and 301 °C for the BNBK (85.2/2.8/12), respectively. On the other hand, BLSF ceramics seem to be excellent candidates as piezoelectric sensors for high temperatures and ceramic resonators with high mechanical quality factor, Q_m , and low temperature coefficient of resonance frequency, $\text{TC-}f_r$. Donor-doped Bi₄Ti₃O₁₂ ceramics such as Bi₄Ti_{3-x}Nb_xO₁₂ [BITN- x] and Bi₄Ti_{3-x}V_xO₁₂ [BITV- x] show high T_c than 650 °C. The k_{33} value of the grain-oriented (HF) BITN-0.08 ceramic is 0.39 and is able to keep the same value up to 350 °C. Bi₃TiTaO₉ (BTT)-based solid solution system, $\text{Sr}_{x-1}\text{Bi}_{4-x}\text{Ti}_{2-x}\text{Ta}_x\text{O}_9$ [SBTT2(x)] ($1 \leq x \leq 2$), displays the high Q_m value (=13500) in (p)-mode at the $x=1.25$ composition.

Keywords:

Ferroelectric properties, Piezoelectric properties, Perovskites, Bismuth layer-structured ferroelectrics, Lead-free piezoelectric ceramics

1. INTRODUCTION

The piezoelectric properties play an important role for electronics and mechatronics materials. The most widely used piezoelectric materials are $\text{PbTiO}_3\text{-PbZrO}_3$ (PZT)-based three component system [1-2]. However, it is recently desired to use lead-free materials for environmental protection. For example, the legislation will be enforced in the EU as the draft Directives on Waste from Electrical and Electronic Equipment (WEEE), Restriction of Hazardous Substances (RoHS) and End-of Life Vehicles (ELV). Therefore, lead-free piezoelectric materials have been widely attracting attention as new materials in place of PZT ceramics.

Lead-free piezoelectric materials, such as piezoelectric single crystals, *e. g.* langasite [3], and ferroelectric ceramics with perovskite structure [4-22], tungsten bronze structure and bismuth layer-structured ferroelectrics (BLSF) [23-41], have been reported. However, no materials display more excellent piezoelectric properties than PZT systems. To replace PZT systems, it is necessary that required piezoelectric properties for various applications were divided and were developed the corresponding each application. For example, the perovskite type ceramics seem to be a suitable for actuator and high power applications. On the other hand, bismuth layered-structured ferroelectric (BLSF) ceramics seem to be candidate materials for ceramic filter and resonator applications.

In this paper, dielectric ferroelectric and piezoelectric properties of perovskite ferroelectric and BLSF ceramics are described as superior candidates for lead-free piezoelectric materials to reduce environmental damages.

2. EXPERIMENTAL

Ceramic samples were prepared by a conventional sintering technique (ordinarily fired, OF samples). Reagent-grade powders of oxides or carbonates with 99+% purity were used as the starting materials. These materials were mixed by ball-milling and calcined at 600 - 850 °C for 1 - 2 h. After calcining, the ground and ball-milled powders were pressed into disks 20 mm in diameter and about 10 mm in thickness. These disks were sintered at 900 - 1350 °C for 2 - 4 h in air. Grain-oriented samples were prepared by the hot-forging (HF) method [29, 34]. The grain orientation factor, F , was calculated using the Lotgering method [38].

The crystal structure was confirmed by X-ray diffraction analysis using $\text{CuK}\alpha$ radiation at a scanning speed of 1 deg/min. Samples for observations of the microstructure were polished and thermally etched. Finally, the microstructures were observed by scanning electron microscopy (SEM, HITACH S-2400). The weight loss during the sintering process was analyzed by TG-DTA spectrometer (Rigaku, Thermo Plus 2).

Electrodes made of fired-on Ag-Pd pastes were formed for electrical measurements, such as dielectric, ferroelectric and piezoelectric properties. The temperature dependence of dielectric constant, ϵ_r , and dielectric loss tangent, $\tan\delta$, were measured at 1 MHz using an automatic dielectric measurement system with a multi-frequency LCR meter (YHP 4275A) in the temperature range from RT to 900 °C. The D-E hysteresis loop was observed at RT using a standard Sawyer-Tower circuit at 50 Hz. The temperature dependence of resistivity, ρ , was measured using a high-resistance meter (YHP 4329A and 4339B).

Specimens for piezoelectric measurements were poled in stirred silicone oil under applied fields of $E_p=7\text{-}12$ kV/mm at temperatures of $T_p=\text{RT-}300$ °C for times of $t_p=7\text{-}10$ min. Piezoelectric properties were measured by a resonance-antiresonance method on the basis of EMAS standards, using an impedance analyzer (YHP 4192A and 4194A). A longitudinal vibration of the (33)-mode was measured using a rectangular specimen of $4\times 2\times 2$ mm³. The electromechanical coupling factor, k_{33} , was calculated from the resonance and antiresonance frequencies. The free permittivity, ϵ_{11}^T , was determined from the capacitance at

1 kHz of the poled specimen. The elastic constants, s_{ij}^E , was calculated from the frequency constant, N_{ij} , and the measured density, ρ_0 . Finally, the piezoelectric constants, d_{ij} , was calculated from the k_{ij} , ϵ_{ii}^T and s_{ij}^E by the relation of $d_{ij} = k_{ij} \rho (\epsilon_{ii}^T s_{ij}^E)$.

3. RESULTS and DISCUSSION

3.1 Perovskite-structured ferroelectrics

The perovskite-type ferroelectrics such as BaTiO₃, (Bi_{1/2}Na_{1/2})TiO₃ and KNbO₃ are well known lead-free piezoelectric materials. These ceramics show the relative large piezoelectric constant, d , among lead-free piezoelectrics, and are expected for actuator and high power applications. However, there are some problems such as low Curie temperatures, T_c , difficulties in poling treatments and/or low relative densities and so on.

(1) BaTiO₃-based ceramics

Barium titanate, BaTiO₃ (BT), is the first ferroelectric oxide with perovskite structure. This ceramic has a relatively high electromechanical coupling factor, k_{33} , and has been partially used for piezoelectric applications such as sonar. However, BT has a low Curie temperature, T_c (=135 °C) [4-6]. Thus, the working temperature range of this ceramic is narrow for actual piezoelectric applications. To expand of the working temperature range, that is, to elevate the T_c of BaTiO₃-based ceramics, dielectric and piezoelectric properties of (1-x)BaTiO₃-x(Bi_{0.5}K_{0.5})TiO₃ solid solution (BTBK-100x) system were investigated because the T_c of (Bi_{0.5}K_{0.5})TiO₃ (BKT) was reported to be about 380 °C.

X-ray diffraction patterns of BTBK ceramics with $0 \leq x \leq 1$ show the single phase of perovskite structure. **Figure 1** shows the temperature dependence of dielectric constant, ϵ_r and loss tangent, $\tan\delta$ for the BTBK-100x ceramics. The T_c increased lineally with increasing x in BTBK-100x, as shown in **Fig. 2**. The T_c of BTBK-20 shows higher than 200 °C. However, both the ϵ_r at RT and at T_c decrease with increasing x in BTBK-100x.

Figure 3 shows the resistivity, ρ , of BTBK ceramics as a function of the doped Mn content. The ρ reaches maximum at $x=0.1$. **Figure 4** shows the frequency dependence of impedance, Z (magnitude $|Z|$, and phase θ , of the (33)-mode for the BTBK20+Mn (0.1 wt%).

Table 1 summarizes the Curie temperature, T_c , and piezoelectric properties of BTBK ceramics. Electromechanical coupling factor, k_{33} and piezoelectric constant, d_{33} of BTBK20+MnCO₃ (0.1wt%) (T_c =223 °C) were 0.35 and 59 pC/N, respectively. On the other hand, the d_{33} of BTBK5+MnCO₃ (0.1wt%) (T_c =174 °C) was 117 pC/N.

(2) (Bi_{1/2}Na_{1/2})TiO₃-based ceramics

Bismuth sodium titanate, (Bi_{1/2}Na_{1/2})TiO₃ (BNT) [7-8], shows strong ferroelectric properties of a large remanent polarization, P_r =38 μ C/cm², and has a Curie temperature, T_c =320 °C. However, data on piezoelectric properties of the BNT ceramic are scarce in still works, because of difficulties in poling treatments to pole this ceramic. On the other hand, the BNT ceramic need to a high sintering temperature more than 1200 °C to obtain the dense body. It is thought that a vaporization of Bi ions was occurred during the sintering process higher than 1200 °C, resulting in the poor poling treatments because of the low resistivities. From the thermograph (TG, weight loss) measurement, the weight loss caused by the Bi vaporization was carried out at over 1130 °C. So, the BNT ceramic was sintered at 1100 °C. The high density-ratio of 95 % was obtained for this ceramic by keeping the long soaking time of 100 h at 1100 °C. The k_{33} and d_{33} of this ceramic displayed for 0.47 and 91 pC/N, respectively, and these values were almost the same to above results. In view of these facts, the large piezo-electricity, k_{33} and d_{33} , of the BNT ceramic

as lead-free piezoelectric materials could be clear for the first time.

Furthermore, BNT-based solid solutions that can be poled easily were recently studied [9-12]. Especially, the large piezoelectricity is expected on the BNT-based solid solutions with a morphotropic phase boundary (MPB). BaTiO₃ (BT) and bismuth potassium titanate, (Bi_{1/2}K_{1/2})TiO₃ (BKT), are well known lead-free piezoelectric materials with the tetragonal symmetry. Two solid solution systems, that is, (1-x)(Bi_{1/2}Na_{1/2})TiO₃–xBaTiO₃ (BNBT-100x) and (1-y)(Bi_{1/2}Na_{1/2})TiO₃–y(Bi_{1/2}K_{1/2})TiO₃ (BNKT-100y) had been already reported by Takenaka *et al.*[13] and Sasaki *et al.*[14], respectively. It is reported that MPB compositions existed on $x = 0.06-0.07$ for BNBT-100x and $y = 0.16-0.20$ for BNKT-100y, respectively. Then, dielectric and piezoelectric properties of the three-component system, (Bi_{1/2}Na_{1/2})TiO₃–BaTiO₃–(Bi_{1/2}K_{1/2})TiO₃ (BNBK), were investigated, focusing on the MPB compositions.

Figure 5 shows the phase relation of the BNBK system around the MPB area. The MPBs of both BNBT-6 and BNKT-16 exist on the rhombohedral side, and the MPBs of both BNBT-7 and BNKT-20 exist on the tetragonal side around the MPB region, respectively. Prepared compositions in this experiment are expressed as follows:

$$a(\text{BNBT6})-(1-a)(\text{BNKT16}) \text{ (BNBK1-}a\text{)}$$

$$a(\text{BNBT7})-(1-a)(\text{BNKT20}) \text{ (BNBK2-}a\text{)},$$

where, $a = 0, 0.2, 0.4, 0.6, 0.8$, and 1 , for each system.

It was found by X-ray diffraction that the MPB between the rhombohedral and tetragonal phases exists between the two systems of BNBK1 and BNBK2. Curie temperature, T_c , of BNBK1 and BNBK2 are almost constant at about 300 °C.

Figure 6 shows compositional dependence of the piezoelectric constant, d_{33} , for BNBK1 and BNBK2 ceramics. All of d_{33} values of the BNBK2 are larger than those of the BNBK1. The d_{33} value showed the maximum, $d_{33}=191$ pC/N, at the BNBK2-0.4. The maximum value of d_{33} was obtained on the tetragonal region around the MPB composition. It is thought that the 0.852BNT-0.12BKT- 0.028BT (BNBK2-0.4) ceramic seems to be one of the candidate material for lead-free actuator applications with the relatively large d_{33} (=191 pC/N) and high T_c (= 301 °C).

(3) KNbO₃-based ceramics

Potassium niobate, KNbO₃ (KN), has an orthorhombic symmetry at room temperature, and has phase transition at –10, 225 and 425 °C for rhombohedral →orthorhombic→tetragonal →cubic, respectively. KN single crystals are known to have high piezoelectric activities [15-17]. However, it is difficult to obtain a dense ceramic body of KN by the ordinary firing process. To obtain the dense KN-based ceramic, the hot-press (HP) method or liquid phase sintering by additive dopants were investigated [18-19]. At present, the dense KN-based ceramic can be obtained, however, good piezoelectric properties cannot be displayed due to the difficulties in poling treatments.

On the other hand, electrical properties of potassium-sodium niobates, KNbO₃- NaNbO₃ system, were reported by Egerton *et al.* [20-21]. Their works on ceramics in the system indicated that relatively low dielectric constants and high electromechanical coupling factors could be obtained over a wide compositional range. However, it is difficult to realize the desired structure in a ceramic form because the sintering of these materials in an air requires long soaking periods to achieve sufficient densification. Tashiro *et al.* reported that (K_{0.47}Pb_{0.03}Na_{0.5})NbO₃ ceramic fired at 1170 °C for 40 h showed high density, coupling factor, $k_p=0.44$ and $Q_m=152$ [22]. The resonance-antiresonance characteristic of this ceramic is shown in **Fig. 7**.

3.2 Bismuth layer-structured ferroelectrics

The family of bismuth layer-structured ferroelectrics (BLSF) [23-26] is very attractive from the viewpoint of their applications as electronic materials such as dielectrics, piezoelectrics and/or pyroelectrics, because BLSF are characterized by their low dielectric constant, ϵ_s , high Curie temperature, T_c , and large anisotropy in the electromechanical coupling factor k_t/k_p or k_{33}/k_{31} [23-28]. Therefore, the BLSF ceramics are seen as superior candidates for lead-free piezoelectric applications for high- T_c piezoelectric sensors, filters, resonators and/or pyroelectric sensors with large figures of merit.

(1) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ -based system

Bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT), is a typical well-known BLSF [24-27]. Concerning the anisotropy, Cummins and Cross reported that spontaneous polarizations of a BIT single crystal along the a- and c-axes are 50 and 4 $\mu\text{C}/\text{cm}^2$, respectively [27]. Therefore, it is thought that the BIT single crystal has good piezoelectricity. However, it is difficult to measure piezoelectric properties on the BIT single crystal because the shape of prepared BIT single crystals is always platelet and usually very thin. On the other hand, fully reliable piezoelectric properties of BIT ceramics have not been reported because of some problems such as the low resistivity and the large coercive field [28-35]. To solve these problems, Nb^{5+} and V^{5+} ions were doped into BIT ceramic to obtain higher resistivities [36-37]. In this paper, $\text{Bi}_4\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$ [BITN- x] and $\text{Bi}_4\text{Ti}_{3-x}\text{V}_x\text{O}_{12}$ [BITV- x] ceramics are studied regarding on their dielectric, ferroelectric and piezoelectric properties. Furthermore, the grain orientation effects of BITN and BITV ceramics on their piezoelectric properties are discussed using the grain-oriented ceramics prepared by the hot-forging (HF) method.

X-ray diffraction patterns for BITN and BITV ceramics (OF) show single phase of bismuth layer-structured compounds with the layer number, $m=3$. No peaks of Nb_2O_5 and V_2O_5 were observed within $x \leq 0.12$. Both BITN and BITV ceramics have high relative density ratios more than 95 % to the theoretical density.

Figure 8 shows the Curie temperature, T_c , as a function of Nb and V concentration. The T_c of the BIT ($x=0$) ceramic is 683 °C and gradually becomes lower with increasing Nb and V concentration. Therefore, it is thought that Nb and V ions occupy the B-site of the pseudo-perovskite cell in the bismuth layer-structure. However, the T_c of BITV has the tendency to saturate with increasing the V concentration comparing to the BITN ceramics. Therefore, it is thought that V ions are difficult to substitute Ti ions. Excess V ions seem to exist on the grain boundary and/or the triple point when the V concentration increases. This consideration is estimated by the ionic radii of Ti, Nb and V ions. The ionic radii of Ti^{4+} (IV coordination), Nb^{5+} (IV coordination) and V^{5+} (IV coordination) ions reported by R. D. Shannon [39] are 0.605, 0.64 and 0.54 Å, respectively. It is thought that the ionic radius of the V ion is too small to substitute to B-site of the pseudo-perovskite cell in the bismuth layer-structure. The resistivity, ρ , of BIT ($x=0$) is about 10^{10} - 10^{11} $\Omega\cdot\text{cm}$, and, those of BITN and BITV ceramics are about 10^{13} - 10^{14} $\Omega\cdot\text{cm}$. It is clear that the ρ is enhanced by some donor-dopings. The optimum charge neutrality was observed for the each composition of BITN-0.08 and BITV-0.01, respectively.

Figure 9 shows the compositional dependences of the electromechanical coupling factor, k_{33} on the dopant Nb and V concentration (x). The k_{33} of BITN reaches the saturated value (0.20) for the composition of $x=0.08$ while, the k_{33} of BITV-0.02 is 0.25, which is the relatively high value for BLSF ceramics with a random orientation.

Figure 10 shows X-ray diffraction patterns of BITN-0.08 and BITV-0.04 ceramics for the perpendicular plane (polished) of the HF ceramics and the OF ones. It is very clear that grains in the HF ceramics were oriented along the c-axis because intensities of the 00 l planes of the HF samples are very high. The grain

orientation factor, F , of BITN-0.08 and BITV-0.04 were 0.91 and 0.75, respectively.

Figure 11 shows the frequency dependence of the impedance, Z (magnitude $|Z|$, and phase θ), of HF BITN-0.08 and HF BITV-0.04 ceramics. Good profiles were obtained and their k_{33} values were enhanced to 0.39 and 0.38 for BITN-0.08 and BITV-0.04, respectively. These values are about twice as large as than those of non-oriented (OF) ones, and are larger than reported value ($k_{33}=0.27$) [34] of HF BIT ceramics. In this investigation, a saturated k_{33} value of the BIT ceramic was not observed because of an electrical breakdown during the poling process.

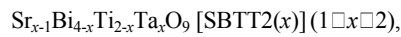
Figure 12 shows the k_{33} of the HF BITN-0.08 and the BITV-0.04 as a function of the orientation factor, F . Accurate F was obtained using the X-ray diffraction patterns for the k_{33} specimen, that is, XRD was performed directly on the k_{33} specimen shown in **Fig. 13**. From this measurement, the relationship between k_{33} and F is clear. The k_{33} increases linearly with increasing the orientation factor, F . From this figure, the k_{33} value for the specimen with a perfect orientation ($F = 1$) could be extrapolated to be almost 0.42.

Figure 14 shows the temperature dependence of the k_{33} and a ratio of impedance peak/deep, P/D , obtained from the resonance and antiresonance curve on the HF BITN-0.08 ceramic. The k_{33} higher than 0.35 was maintained from RT to 650 °C. However, the P/D decrease rapidly at temperatures higher than 350 °C. In other words, sharp resonance and antiresonance peaks with high P/D more than 1000 was kept up to 350 °C. It is clear that HF BITN-0.08 ceramic maintains high piezoelectric properties from RT to 350°C. The donor doped-BIT ceramics seem to be a superior candidate for lead-free high-temperature piezoelectric materials.

(2) $\text{Bi}_3\text{TiTaO}_9$ -based system

The high mechanical quality factor, Q_m , was obtained for BLSF ceramics in some previous reports. For example, Nanao *et al.* [40] and Shibata *et al.* [41] reported that the Q_m shows 9000 in (t)-mode for $\text{Bi}_3\text{TiNbO}_9$ - $\text{BaBi}_2\text{Nb}_2\text{O}_9$ solid solution and 11000 in (p)-mode for $\text{SrBi}_2\text{Ta}_2\text{O}_9$ - $\text{CaBi}_2\text{Ta}_2\text{O}_9$ solid solution, respectively. The common features of these reports are that the end members of these systems, $\text{Bi}_3\text{TiNbO}_9$ and $\text{CaBi}_2\text{Ta}_2\text{O}_9$, have the very high T_c above 800 °C. These data suggest the possibility of the high Q_m is able to be obtained by BLSF materials with high T_c . By this concept, dielectric, ferroelectric and piezoelectric properties of $\text{Bi}_3\text{TiTaO}_9$ (BTT) ($m=2$) based solid solution system with a high Curie temperature, T_c were investigated. Three ceramic systems were selected as follows.

□ $\text{Bi}_3\text{TiTaO}_9$ (BTT) - $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBTa) system,



□ La or Nd- modified $\text{Bi}_3\text{TiTaO}_9$ (BTT) system,



About the SBTT2 system, the T_c of the SBTa ceramic is 280 °C and becomes higher with increasing the amount of modified BTT that T_c is higher than 900 °C. The Q_m and k_p were enhanced the maximum value of 9000 and 0.12, respectively, on the SBTT2 (1.375) with poling conditions of $E_p=7\text{-}10$ kV/mm, $T_p=250$ °C and $t_p=7$ min. On the other hands, SBTT2 (1.25) with the poling condition of $T_p=300$ °C shows the maximum Q_m of 13500 in the planar (p) mode. This value is extremely high in usual piezoelectric ceramics. **Figure 15** shows the frequency dependence of impedance, Z (magnitude $|Z|$, and phase θ), of (p)-, (33)- and (15)- vibration modes for the SBTT2 (1.25) ceramic. In the same poling conditions, Q_m values of (33) and (15) modes for SBTT2 (1.25) were about 8800 and 6000, respectively. Temperature coefficients of the resonance frequency, $\text{TC-}f_r$, of SBTT2

(1.25) were -82 ppm/□ for (33) mode and -97 ppm/□ for (15) mode, respectively. Both BLTT2 (0.25) and BNTT2 (0.5) ceramics show the extremely high Q_m value of 11000 in (33)-mode, and the results were summarized in **Table 2**.

4. CONCLUSIONS

Dielectric, ferroelectric and piezoelectric properties of perovskite ferroelectric and bismuth layer-structured (BLSF) ceramics were investigated as superior candidates for lead free piezoelectric materials to reduce environmental damages. Perovskite type ceramics seem to be a suitable for actuator and high power applications that were required large piezoelectric constants, d_{33} (>300 pC/N) and a high Curie temperature, T_c (>200 °C) [43]. While, BLSF ceramics seem to be excellent candidates as piezoelectric sensors for high temperature and ceramic resonators with high mechanical quality factor, Q_m , and low temperature coefficient of resonance frequency, $TC-f_r$ [42, 44]. To replace PZT systems, it is necessary that special features of each lead-free material correspond to required piezoelectric properties for each application.

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Figure captions:

- Fig. 1 Temperature dependence of dielectric constant, ϵ_r and loss tangent, $\tan\delta$ for the BTBK ceramics measured at 1 MHz.
- Fig. 2 Curie temperature, T_c , of BTBK ceramics as a function of the amount of $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ measured at 1 MHz.
- Fig. 3 Resistivity, ρ , of BTBK ceramics as a function of the doped Mn content (wt%).
- Fig. 4 Frequency dependence of impedance, Z (magnitude $|Z|$, and phase θ , of the (33)-mode for the BTBK20+Mn (0.1 wt%).
- Fig. 5 Phase relation of the $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3 - \text{BaTiO}_3 - (\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ (BNBK) system around the MPBs.
- Fig. 6 Piezoelectric constant, d_{33} , of BNBK1 and BNBK2 as a function of the amount (a) of BNBT-6 for BNBK1 and BNBT-7 for BNBK2.
- Fig. 7 Resonance-antiresonance characteristic of $(\text{K}_{0.47}\text{Pb}_{0.03}\text{Na}_{0.5})\text{NbO}_3$ ceramic fired at 1170 °C for 40 h [22].
- Fig. 8 Curie temperature, T_c , of BITN and BITV ceramics as a function of Nb and V concentrations.
- Fig. 9 Electromechanical coupling factor, k_{33} of BITN (OF) and BITV (OF) as a function of the dopant concentration (x).
- Fig. 10 X-ray diffraction patterns of BITN-0.08 and BITV-0.04 ceramics for the perpendicular plane (polished) of the HF and the OF.
- Fig. 11 Frequency dependence of the impedance, Z (magnitude $|Z|$, and phase θ), of HF BITN-0.08 and HF BITV-0.04.
- Fig. 12 Coupling factor, k_{33} , of HF BITN-0.08 and BITV-0.04 as a function of orientation factor, F .
- Fig. 13 Shape for measuring of the orientation factor, F , and the coupling factor, k_{33} .
- Fig. 14 Temperature dependence of the k_{33} and the ratio of impedance peak/deep, P/D , of the HF BITN-0.08.
- Fig. 15 Frequency dependence of impedance, Z (magnitude $|Z|$, and phase θ), of (p)-, (33)- and (15)-modes for the SBT2 (1.25) ceramic.

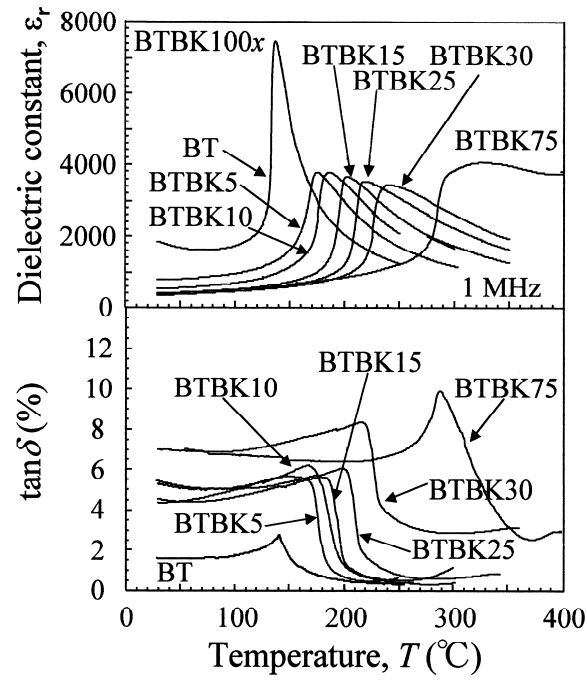


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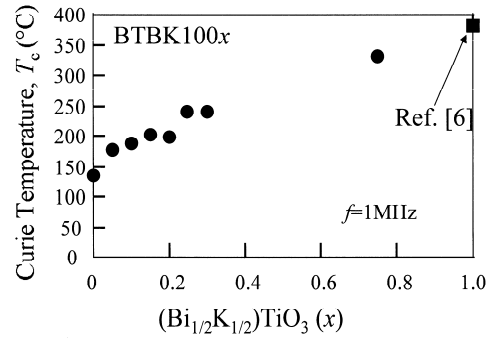


Fig. 2 Curie temperature, T_c , of BTBK ceramics as a function of the amount of $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ measured at 1 MHz.

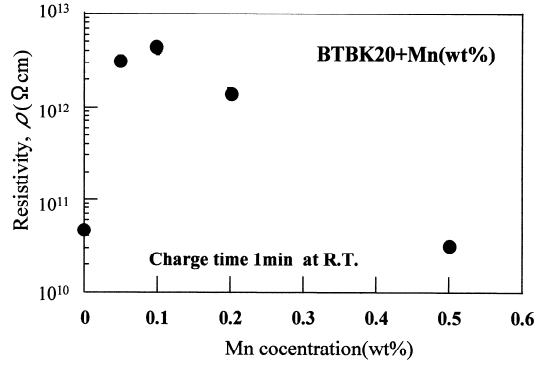


Fig.3 Resistivity, ρ , of BTBK ceramics as a function of the doped Mn content (wt%).

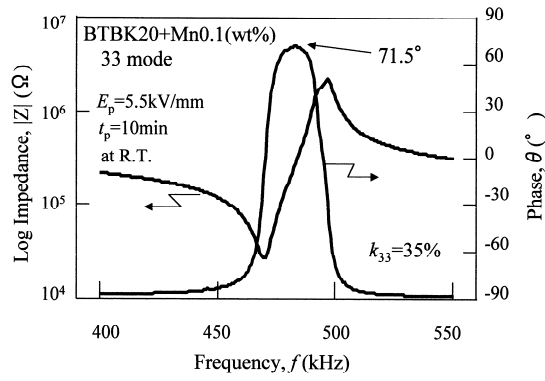


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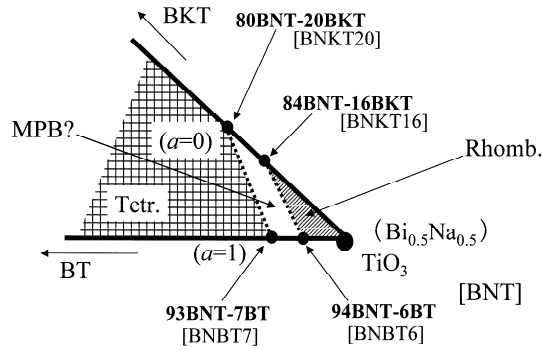


Fig. 5 Phase relation of the $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3 - \text{BaTiO}_3 - (\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ (BNBK) system around the MPBs.

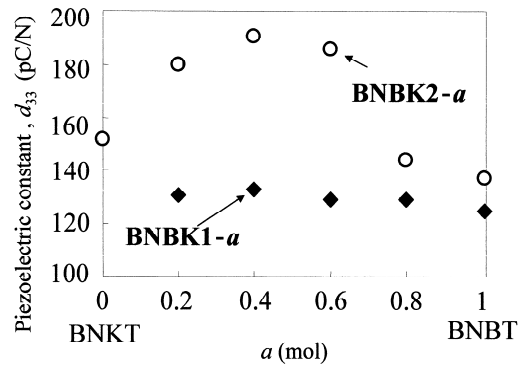


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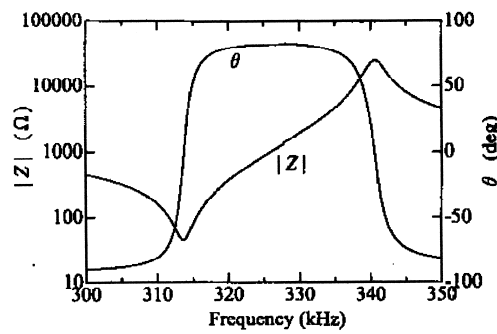


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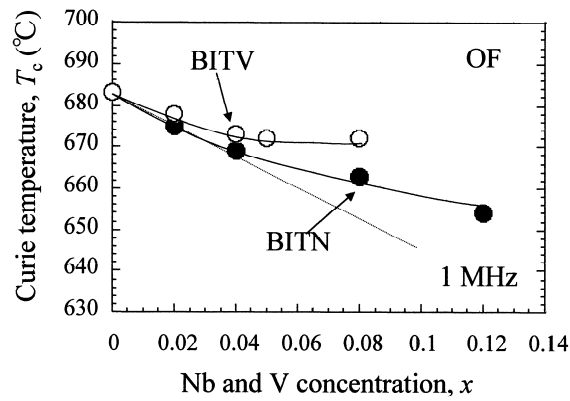


Fig. 8 Curie temperature, T_c , of BITN and BITV ceramics as a function of Nb and V concentrations.

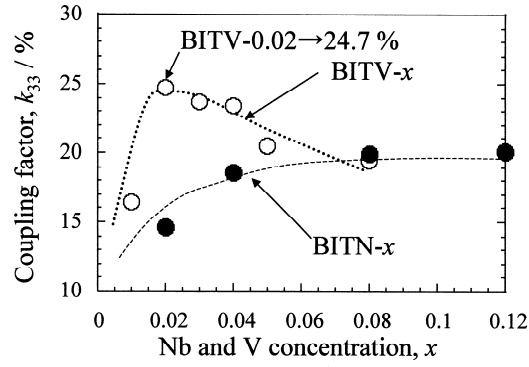


Fig. 9 Electromechanical coupling factor, k_{33} of BITN (OF) and BITV (OF) as a function of the dopant concentration (x).

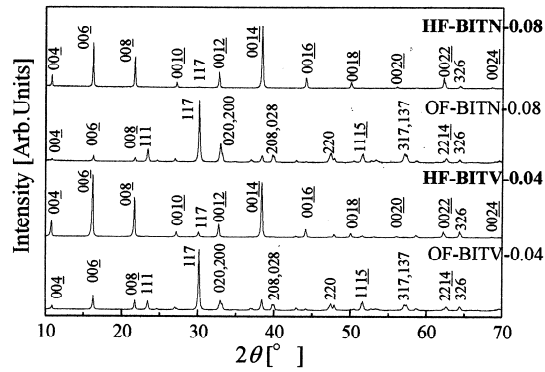


Fig. 10 X-ray diffraction patterns of BITN-0.08 and BITV-0.04 ceramics for the perpendicular plane (polished) of the HF and the OF.

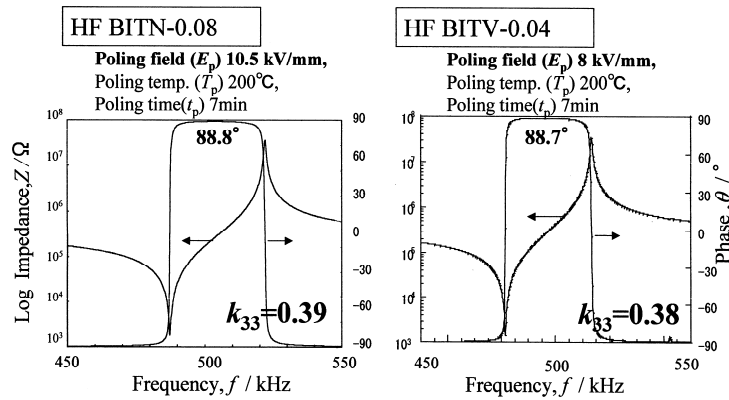


Fig. 11 Frequency dependence of the impedance, Z (magnitude $|Z|$, and phase θ), of HF BITN-0.08 and HF BITV-0.04.

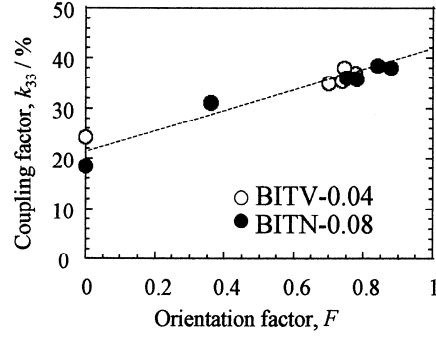


Fig. 12 Coupling factor, k_{33} , of HF BITN-0.08 and BITV-0.04 as a function of orientation factor, F .

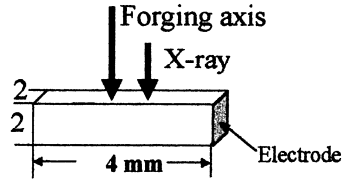


Fig. 13 Shape for measuring of the orientation factor, F , and the coupling factor, k_{33} .

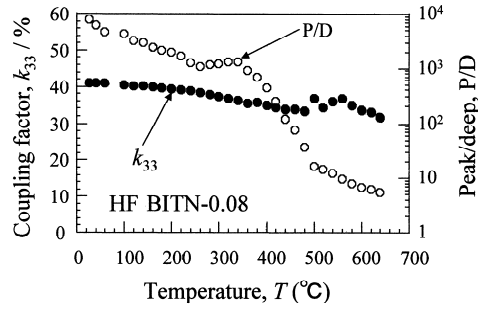


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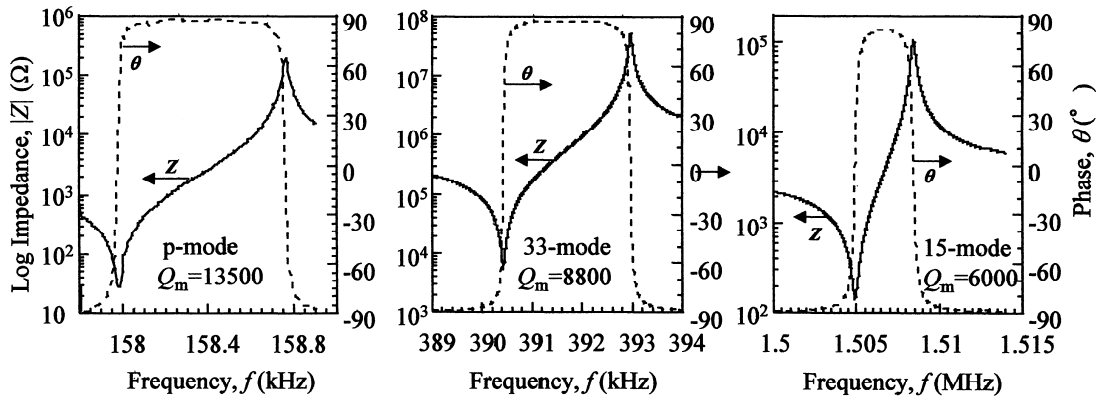


Fig. 15 Frequency dependence of impedance, Z (magnitude $|Z|$, and phase θ), of (p)-, (33)- and (15)-modes for the SBTT2 (1.25) ceramic.

Table 1 Curie temperature, T_c , and piezoelectric properties of BTBK ceramics.

	T_c (°C)	k_{33} (%)	$\epsilon_{33}^T/\epsilon_0$	d_{33} (pC/N)
BTBK20M	223	35	467	58.9
BTBK5M	170	28	849	71.0
BTBK5M (Reduced)	174	27	2300	117

Table 2 Piezoelectric properties such as coupling factor, k , and mechanical quality factor, Q_m , of SBTT2 (1.25), BLTT2 (0.25) and BNTT2 (0.5) ceramics.

composition	mode	k (%)	Q_m	$TC-f_r$ (ppm/°C)
SBTT2 (1.25)	33 (OF)	15.0	8800	- 82
	15 (OF)	7.3	6000	- 97
	15 (HF)	8.4	3000	- 79
	24 (HF)	5.9	8500	- 132
BLTT2 (0.25)	33 (OF)	10.5	11000	- 91
BNTT2 (0.50)	33 (OF)	11.3	11000	- 85