High Mechanical and Electrical Quality Factors of Nd and V co-substituted $Bi_4Ti_3O_{12}$ Ceramics

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The piezoelectric properties of Nd and V co-substituted bismuth titanate ceramics, $(Bi_{4-y},Nd_y)_{1-(x/12)}(Ti_{3-x},V_x)O_{12}$ [BNTV(x,y) (x=0~0.03, y=0.00~1.00)] ceramics are investigated focusing on a mechanical quality factor, Q_m and electrical quality factor, Q_{emax}. The k_{33} of BNTV(0.01, 0.75) ceramic was 0.21 which is one of the highest values of random oriented BLSF ceramics. Furthermore, the excellent piezoelectric properties of both high Q_m (~7000) and Q_{emax} (~64) were obtained in the BNTV(0.02, 0.75) ceramic by controlling the formation of oxygen vacancies and the subsequent promotion of the domain switching during the poling process. The BNTV(0.02, 0.75) ceramic was sintered at 1070°C. From the thermograph (TG) measurement, a weight loss was not observed in this temperature region. The V substitution for BNTV(0, 0.75) ceramics assisted to make its sintering temperature lower at below 1100°C and thus the control of Bi vaporization seemed to be able to suppress the formation of oxygen vacancies.
Key words: bismuth layer-structured ferroelectrics, mechanical quality factor; domain wall movement, Curie temperature

1. INTRODUCTION

Piezoelectric ceramics have been widely used for several applications, such as those in filters for mobile communications, resonators for microprocessors, actuators for inkjet printers, transformers for back-light inverters of liquid-crystal-displays and sensors for detecting shock to hard disc drives (HDDs). The materials used for these applications are currently based on lead titanate (PbTiO3) and lead zirconate titanate (PZT), which are utilized with several compositional modifications.

The family of bismuth layer-structured ferroelectrics (BLSF) [1-2] is one of attractive lead-free materials from the viewpoint of their application to electronic functional devices such as resonators and high temperature sensors etc [3-4]. In the case of resonator applications, piezoelectric elements are used as inductors, so it is necessary that they have a large electrical quality factor, Q_{emax}, in the inductance frequency region and mechanical quality factor, Q_m, rather than a large electromechanical coupling factors, k. BLSFs are characterized by their high quality factors, Q_m [5-8], and Q_{emax} [9], and low temperature coefficient of resonance frequency, TCF [10-12]. In addition, because of their small coupling factor, they could have higher frequency accuracy with fine tolerance as well [13]. Therefore, we have studied BLSF materials as an excellent candidate of lead-free materials for a ceramic resonator application. Especially, piezoelectric properties have been focused aiming to obtain both high Q_m and Q_{emax} values in BLSF ceramics.

In the case of lead zirconate titanate (PZT) based ceramics, high Q_m values are widely obtained in so-called "Hard PZT" ceramics [14-15]. One of dominant reason for high Q_m in the hard PZT materials is proposed to be the domain wall pinning by oxygen vacancies near the domain boundary [16]. On the other

hand, Q_{emax} is strongly related to the poling process in BLSF ceramics, because BLSF ceramics are basically very difficult to be poled fully. For example, higher applied field and higher temperature during the poling process are necessary for BLSF ceramics to be poled sufficiently as compared with hard PZT ceramics [4-6]. Then, Q_{emax} of BLSF ceramics typically increases with increasing the poling field, E_p and poling temperature, T_p. This result means that the domain wall movement contributes to the Q_{emax} to be enhanced higher [7-8]. Consequently, the domain wall pinning is required for obtaining the high Q_m and the domain wall movement is contrary required for obtaining high Q_{emax}, respectively. From these speculations, a kind of defect engineering which is related to domain wall switching would be one of important and key issues for achieving both high Q_m and Q_{emax}.

Recently, bismuth titanate, $Bi_4Ti_3O_{12}$ (BIT), has been studied widely and actively due to its large spontaneous polarization [2]. Furthermore, Nd substituted BIT (BNT) and V co-substituted BNT (BNTV) have received a great deal of attention since these substitutions lead to larger remanent polarization, P_r [17-20]. In addition, a defect formation mechanism of these systems has been well explored and it is recognized that a defect structure is closely related to the polarization properties [21-24].

In this paper, the piezoelectric properties of $(Bi_{4-y},Nd_y)_{1-(x/12)}(Ti_{3-x},V_x)O_{12}$ [BNTV-x,y (x=0~0.03, y=0.00~1.00)] ceramics are investigated focusing on the Q_m and Q_{emax}. Especially, we prepared V-substituted BNT and un-substituted BNT ceramics and compared these piezoelectric properties in regard to domain wall pinning and movement.

2. EXPERIMENTAL PROCEDURE

Ceramic samples of $(Bi_{4-y},Nd_y)_{1-(x/12)}(Ti_{3-x},V_x)O_{12}$

[BNTV(x,y) (x=0-0.03, y=0.00~1.00)] were prepared by a conventional sintering technique. Reagent-grade oxide and hydroxide powders of Bi_2O_3, TiO_2 V_2O_5 and $Nd(OH)_3$ of more than 99.9% purity were used as the starting materials. These materials were mixed by ball milling and calcined at 600°C for 1 h and 850°C for 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 1070~1150°C for 2 h in air.

The crystal structure was confirmed by X-ray diffraction analysis using CuK_α radiation. Samples were polished and thermally etched for micro structural examination by scanning electron microscopy (SEM, HITACH S-2400). 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 (HP 4275A) in the temperature range from room temperature to 750°C. Specimens for piezoelectric measurements were polarized in stirred silicone oil bath at applied fields of E_p=3~12 kV/mm, temperatures of T_p=100-200°C, and times of t_p=7-15 min. Piezoelectric properties were measured by a resonance-antiresonance method on the basis of IEEE standards, using an impedance analyzer (HP 4294A). A longitudinal vibration of the (33) mode was measured using a rectangular specimen of 4×2×2 mm³. The electromechanical coupling factor, k_{33}, was calculated from the resonance and anti-resonance frequencies. The Q_{emax} is defined by the tangent of maximum phase, θ_{max}, at the inductance frequency region between resonance and anti-resonance frequency.

3. RESULTS AND DISCUSSION

X-ray diffraction patterns of BNTV ceramics show single phase of bismuth layer structured compounds with the layer number, m=3. In BNTV(x, y) (x=0.01, y=0.0~1.0) ceramics, the lattice distortion ratio of a- and b-lattice parameters, a/b, decreased to $a/b \approx 1$ with increasing the amount of Nd. This tendency was good agreement with the examination of rare earth substituted bismuth titanates reported by Wolfe and Newnham [8]. Prepared samples have high relative density ratios more than 95% to the theoretical density.

Figure 1 shows temperature dependence of dielectric constant, ε_r, for the BNTV(x, y) (x=0.01) ceramics measured at 1 MHz. Figure 2 shows Curie temperature, T_c, of BNTV(x, y) (x=0.01) ceramics as a function of Nd concentration. T_c decreased with increasing the amount of Nd which also agreed with rare earth substituted bismuth titanates [8]. It is thought that the decrease of T_c was affected by the decrease of lattice distortion ratio a/b.

Figure 3 shows electromechanical coupling factors, k_{33}, of BNTV(x, y) (x=0.01) ceramics as a function of Nd concentrations. The k_{33} of BNTV ceramics increased with increasing the amount of Nd except for y=1.00. The largest k_{33} of BNTV ceramic was 0.21 at y=0.75 which is one of the highest k_{33} values of randomly oriented BLSF ceramics. This result suggests that the domain wall movement of the BNTV(0.01, 0.75) ceramic is the most promoted during the poling process, which might
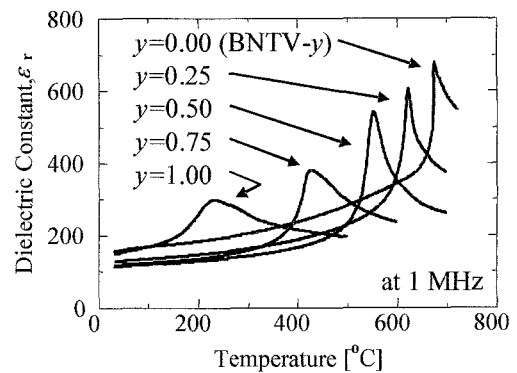

Figure 1 Temperature dependence of dielectric constant, ε_r, for the BNTV(x, y) (x=0.01) ceramics measured at 1 MHz.
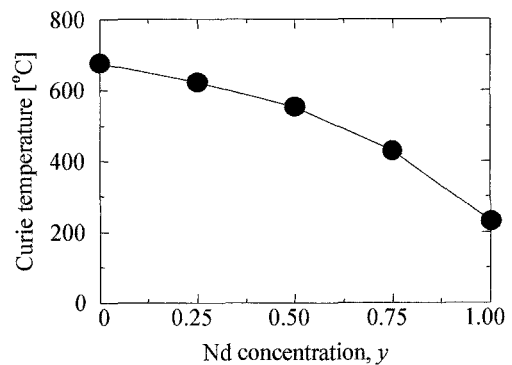

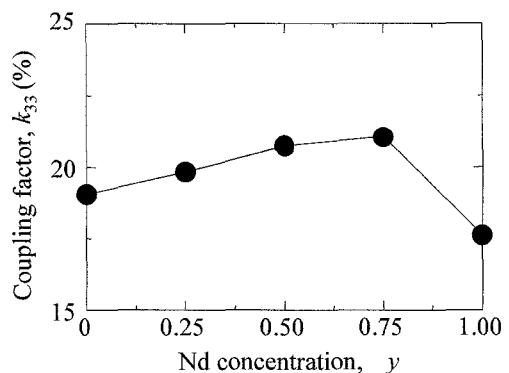Figure 2 Curie temperature, T_c, of BNTV(x, y) (x=0.01) ceramics as a function of Nd concentration.

Figure 3 electromechanical coupling factors, k_{33}, of BNTV(x, y) (x=0.01) ceramics as a function of Nd concentrations.

contribute to the largest k_{33}. Noguchi *et al.* [23] reported that La substitution in BIT crystals is effective for reducing oxygen vacancies and high-pressure oxygen annealing is demonstrated to improve the P_r of La-substituted crystals. This report suggests that the reduction of oxygen vacancies in the BIT based crystals is able to make the domain wall movement accelerated. So, the BNTV(x, 0.75) ceramic is compositionally the best sample for estimating the Q_m value with small amount of oxygen vacancies and the good domain wall
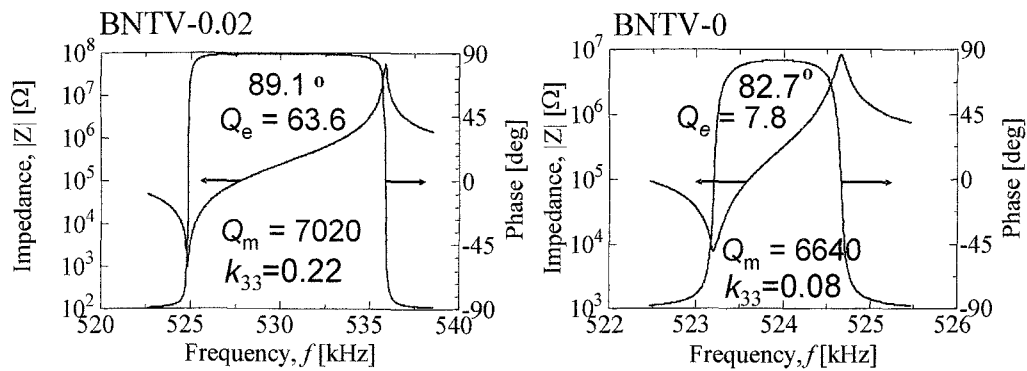
Figure 4 Frequency dependence of impedance, Z (magnitude, $|Z|$, and phase, θ) for BNTV(0, 0.75) [BNTV-0] and BNTV(0.02, 0.75) [BNTV-0.02] ceramics.

movement in the BITV series in this experiment.

There have been some results about the relationship between T_c and Q_m. The high Q_m values more than 9000 have been obtained in some previous reports for BLSF ceramics [5-8]. In these reports, the BLSF ceramics with high Q_m also indicated high T_c. For example, we reported that Nd doped Bi_3TiTaO_9 ceramic with T_c=580°C displayed the extremely high Q_m of 11000 in (33) mode. However this was able to be obtained only by a quite tough poling conditions such as high applied field, E_p=10 kV/mm, and high poling temperature, T_p=300°C [9]. This report showed the excellent Q_m values, however poling state of the samples after the poling was still insufficient so that obtained Q_e value was relatively low of about 20. Generally, the high T_c BLSF materials show a large coercive field, E_c, as well, so that these ceramics are quite difficult to be poled sufficiently. From these speculations of high T_c BLSF materials, a tuning and fixing the T_c down to certain temperature is one of the ways to promote the domain wall movement. Consequently, this consideration also supports that BNTV(x, 0.75) ceramic is compositionally the good sample in the BITV series for estimating the Q_m value with the good domain wall movement.

Figure 4 shows the frequency dependence of impedance, Z (magnitude, $|Z|$, and phase, θ) for BNTV(0, 0.75) [BNTV-0] and BNTV(0.02, 0.75) [BNTV-0.02] ceramics. In terms of Q_{emax}, BNTV-0.02 ceramic shows an extremely good Q_{emax} value of 64 as compared with the BNTV-0 ceramic. This result suggests that the poling state of BNTV-0.02 ceramics after the poling process is much more advanced than that of BNTV-0 ceramics. The reduction of the oxygen vacancies in BNTV-0.02 ceramics is considered to be a dominant reason for making the poling easy and advanced. It is thought that a sintering temperature of these samples is strongly related to the formation of oxygen vacancies in this experiment. Sintering temperatures of BNTV-0 and BNTV-0.02 ceramics are 1150 and 1070°C, respectively. Figure 5 shows the weight loss as a function of the temperature on BNTV-0 and BNTV-0.01 ceramics from the measurement of the thermograph (TG) analysis. Each profile shows the weight loss at higher temperature region nearly 1100°C. Therefore, when samples were sintered at the temperature higher than 1100°C, it is assumed that some component, which is probably Bi ions mainly,
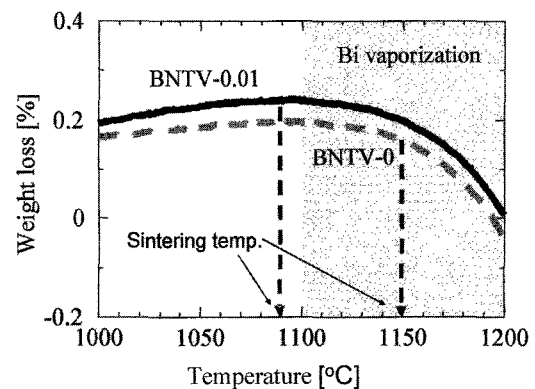

Figure 5 Weight losses as a function of the temperature on BNTV(0, 0.75) [BNTV-0] and BNTV(0.01, 0.75) [BNTV-0.01] ceramics from the measurement of the Thermograph (TG) analysis.
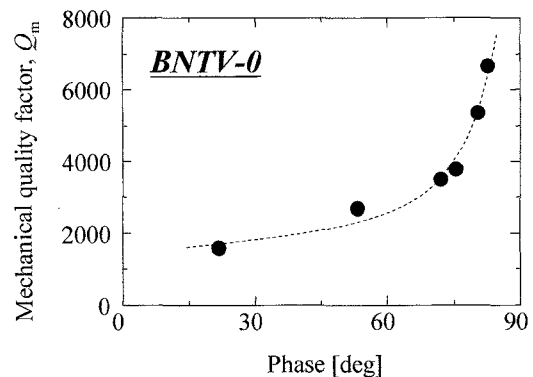

Figure 6 Mechanical quality factor, Q_m, of BNTV (0, 0.75) [BNTV-0] ceramics as a function of the maximum phase, θ, of the inductance region between resonance and anti-resonance frequencies.

evaporates to air during the sintering process. From this result, BNTV-0 ceramics include a lot of oxygen vacancies induced by Bi vaporization. On the other hand, V substitution for BNTV-0.02 ceramics helped to make its sintering temperature lower at below 1100°C and thus the control of Bi vaporization suppressed the formation of oxygen vacancies. Nagata *et al.* [24] investigated a tracer diffusion of ^{18}O into BIT and V-doped BIT

ceramics by means of a secondary ion mass spectrometry (SIMS) and they reported that a volume diffusion coefficient, D_v of ^{18}O into BIT ceramics indicated 2 or 3 orders of magnitude as high as V-doped BIT ceramics. This result suggests that the amount of oxygen vacancies in V-doped BIT ceramics is significantly reduced by the V doping and decreasing the sintering temperature. This report also supports the speculation here about what the formation of oxygen vacancies in BNTV-0.02 ceramics are suppressed as compared with BNTV-0 ceramic and this promotes the domain switching during the poling process. We thought that is the reason why the quite high Q_{emax} of 64 was obtained for BNTV-0.02 ceramics.

In terms of Q_m, BNTV ceramics showed the relatively high Q_m, more than 7000. This value is something remarkable because it is thought that there is less contribution from the domain pinning in BNTV ceramics from the above speculation about oxygen vacancies. Anyhow, the excellent piezoelectric properties of both high Q_m (~7000) and Q_{emax} (~64) were obtained for BNTV-0.02 ceramics by reducing the formation of oxygen vacancies and by promoting the domain switching during the poling process. On the other hand, an interesting result here is that the BNTV-0 ceramics displayed the similar Q_m value of 6600 to BNTV-0.02 ceramics, even though this sample was not fully poled during the poling process. From the TG analysis, the BNTV-0 is supposed to have a lot of pinning centers near the domain boundary due to the formation of oxygen vacancies. This means that this sample is expected to have the higher Q_m value than BNTV-0.02 ceramics as considered with PZT's experience of the domain pinning model. Figure 6 shows Q_m of BNT ceramics as a function of the maximum phase, θ, of the inductance region between resonance and anti-resonance frequencies. The Q_m increased exponentially with increasing the maximum phase closing to 90°. If this sample could be poled sufficiently during the poling process, the huge Q_m value might be obtained. However, it was so difficult for this ceramic to be poled sufficiently because of the domain pinning and lower resisitivity.

4. CONCLUSION

The piezoelectric properties of Nd and V co-substituted bismuth titanate ceramics, $(Bi_{4-y}Nd_y)_{1-(x/12)}(Ti_{3-x}V_x)O_{12}$ [BNTV(x,y) (x=0~0.03, y=0.00~1.00)] ceramics are investigated focusing on a mechanical quality factor, Q_m and electrical quality factor, Q_{emax}. From the viewpoint of the tuning of Curie temperature, T_c, BNTV(y=0.75) with T_c=427°C was chosen for the further measurement of piezoelectric properties. The k_{33} of BNTV(0.01, 0.75) ceramic was 0.21 which was one of the highest values of random oriented BLSF ceramics. Furthermore, the excellent piezoelectric properties of both high Q_m (~7000) and Q_{emax} (~64) were obtained in the BNTV(0.02, 0.75) ceramic by reducing the formation of oxygen vacancies and promoting the domain switching during the poling process. These values are excellent for the ceramic resonator application with higher frequency accuracy with fine tolerance.

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