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$(Bi_{1/2}Na_{1/2})TiO_3$ additive effect for improved piezoelectric and mechanical properties in PZT ceramics

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Bismuth sodium titanate, $(Bi_{1/2}Na_{1/2})TiO_3$(BNT) additive effect for the improvement of piezoelectric and mechanical properties in PZT ceramics were discussed from the viewpoint of high-power applications. The addition of 5 wt% BNT in $Pb(Zr_{0.52}Ti_{0.48})O_3$ ceramics showed suppressive effect for electro-mechanical coupling factor (k_p) value. On the other hand, the addition of 0.5 and 1.0 wt% BNT contributed to improve the four point mechanical bending strength when it was sintered at 1150°C.

1. Introduction

Recently, piezoelectric ceramics have been utilized under a high power condition, such as piezoelectric transformers, actuators and ultrasonic motors [1–4]. Generally, large electro-mechanical coupling factors (k_{31}, k_{33} etc.) and large mechanical quality factor (Q_m) are necessary for the conversion efficiency from electrical to mechanical power, and high stability is important in electronic device. In high power applications, large heat generation have been observed. The change of piezoelectric properties and nonlinear heat generation phenomena have been also observed [5, 6].

From the view point of practical uses mentioned above, it is necessary to clear the relations between heat generation and the change of piezoelectric properties, and to clear the nonlinear heat generation phenomena. And it is necessary to produce high mechanical strength piezoelectric ceramics in order to avoid fracture. Yamamoto *et al.* reported the degradation of piezoelectric properties at resonant operational mode by a large input power [3].

Because of high mechanical bending strength, bismuth sodium titanate, $(Bi_{1/2}Na_{1/2})TiO_3$ (abbreviated as BNT) is considered to be one of an excellent lead-free piezoelectric ceramics [7–10].

In this paper, PZT piezoelectric ceramics containing BNT as additive were prepared from the view point of lead-free ceramics and mechanical strength. Piezoelectric and mechanical properties in PZT ceramics were studied.

2. Experimental method

BNT ceramics were fabricated by conventional method. Bi_2O_3, Na_2CO_3 and TiO_2 pure powders were used as raw materials. The raw materials were ball-milled with water for 24 h, and calcined at 800°C for two hours.

Composition of PZT was of the tetragonal ferroelectric phase $Pb(Zr_{0.52}Ti0_{.48})O_3$ in the vicinity of Morphotropic Phase Boundary (MPB). The starting materials were PbO, ZrO_2, TiO_2. PZT was fabricated by conventional method. PZT raw materials were ball-milled with 0.5 wt and 1.0 wt% calcined BNT powders. The mixed powders were pressed into disc of 20 mm and 55 mm in diameter, and sintered at 1150, 1175 and 1200°C for 3 hrs. The specimens were subjected for the measurements of four point bending strength and Vickers hardness, in which $3 \times 4 \times 40$ mm^3 test samples were employed for these mechanical testing. Crystalline phases were indentified and lattice constants were determined by X-ray diffraction analysis. The specimens were polished and examined by means of a scanning electron microscope (SEM). Densities of the specimens were measured by the Archimedes method.

Test pieces with 20 mm Φ were employed for the measurement of piezoelectric property. The specimens were poled at 120°C in a stirred silicone oil bath by applying a D.C. electric field of 3 kV/mm for 30 min. Piezoelectric properties were measured by means of the resonant and anti-resonant frequency by using a

computer-controlled impedance analyzer(HP-4192A) [11]. The electro-mechanical coupling factor, k_p was calculated from the measured results [12].

3. Results and discussion

3.1. Synthesis of BNT ceramics

BNT doped PZT ceramics with high stability under a high power is important. First, the properties of BNT

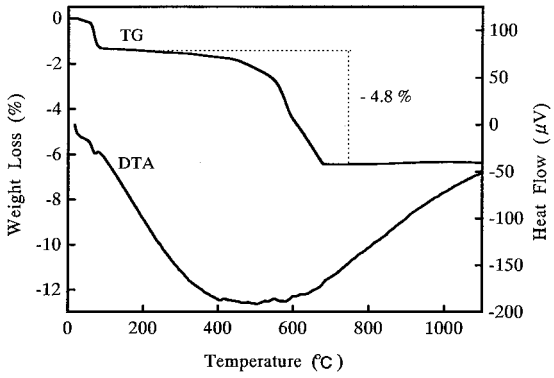


Figure 1 TG-DTA curve of BNT raw material powder.

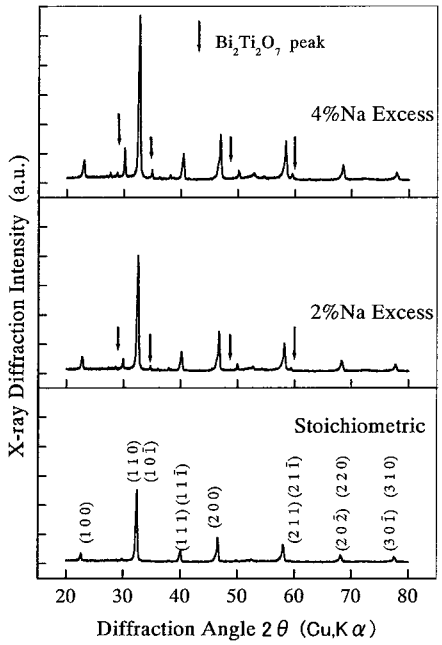


Figure 2 X-ray diffraction patterns of sintered BNT with various Na contents.

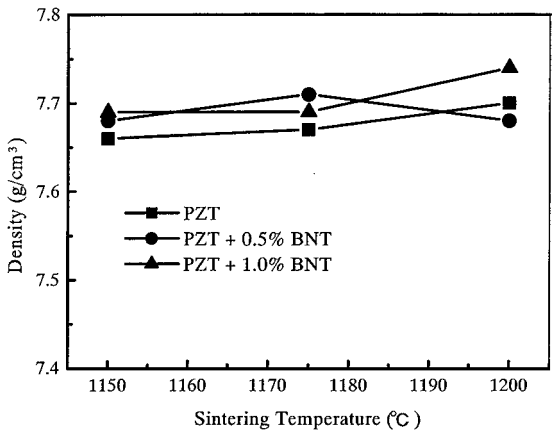


Figure 3 Sintering temperature influence on sintered density with PZT-BNT system.

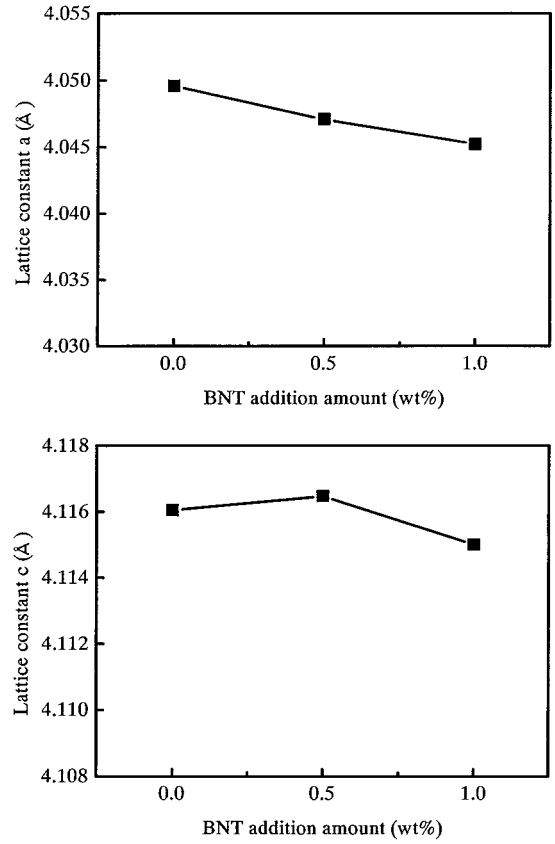


Figure 4 Sintering temperature influence on lattice constants with PZT-BNT system.

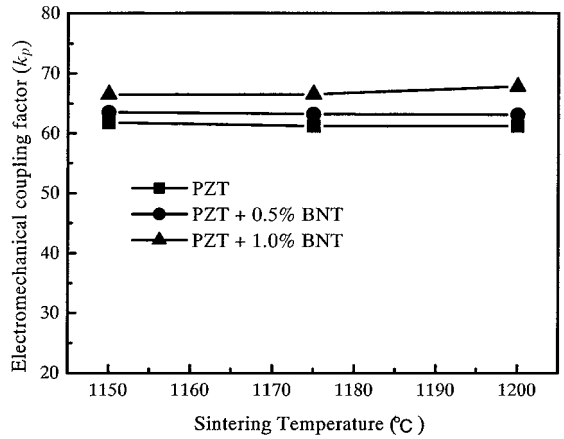


Figure 5 Sintering temperature influence on electro-mechanical coupling factor (k_p) with PZT-BNT.

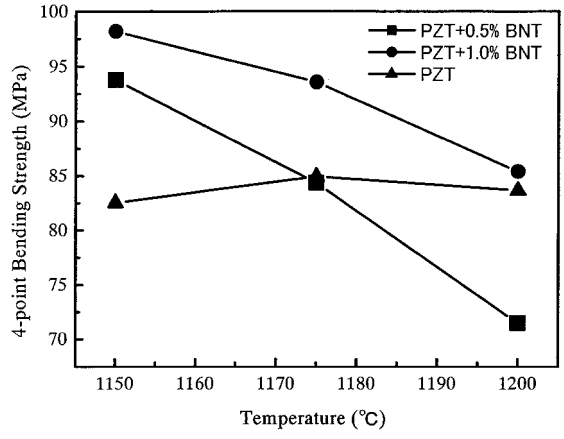


Figure 6 Sintering temperature influence on mechanical bending strength with PZT-BNT.

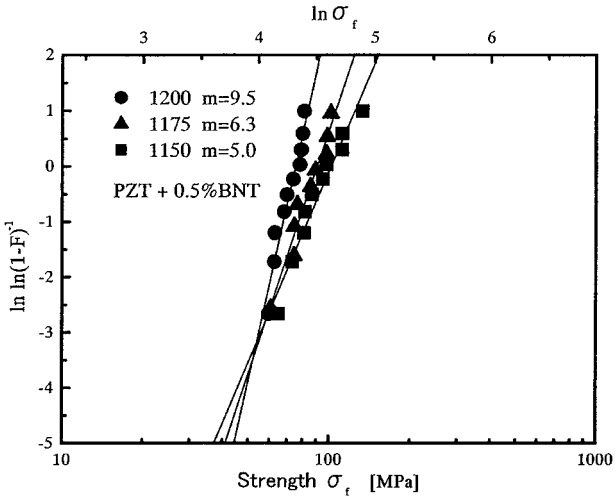


Figure 7 Weibull plots of applied stress until fracture.

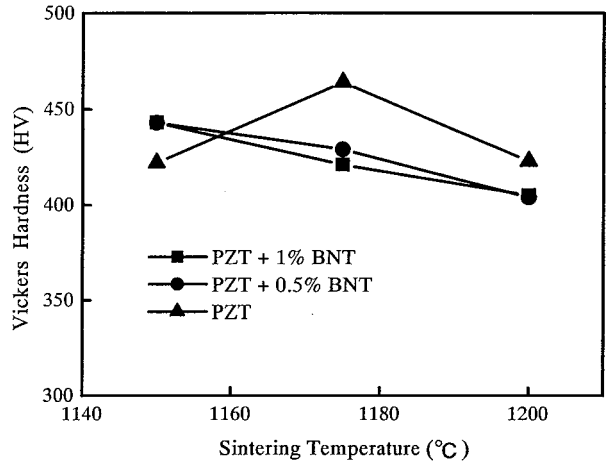


Figure 9 The relationship between sintering temperature and Vickers hardness of PZT-BNT system.

ceramics were studied. The mechanism for chemical synthesis process was discussed by TG-DTA curves (Fig. 1). A broad endothermic peak was observed from 400 to 700°C. Weight loss of 4.8% was observed at this endothermic reaction. It is considered that the endothermic peak results from decarbon dioxide from Na_2CO_3. Perovskite reaction proceeds just after the end of this endothermic reaction.

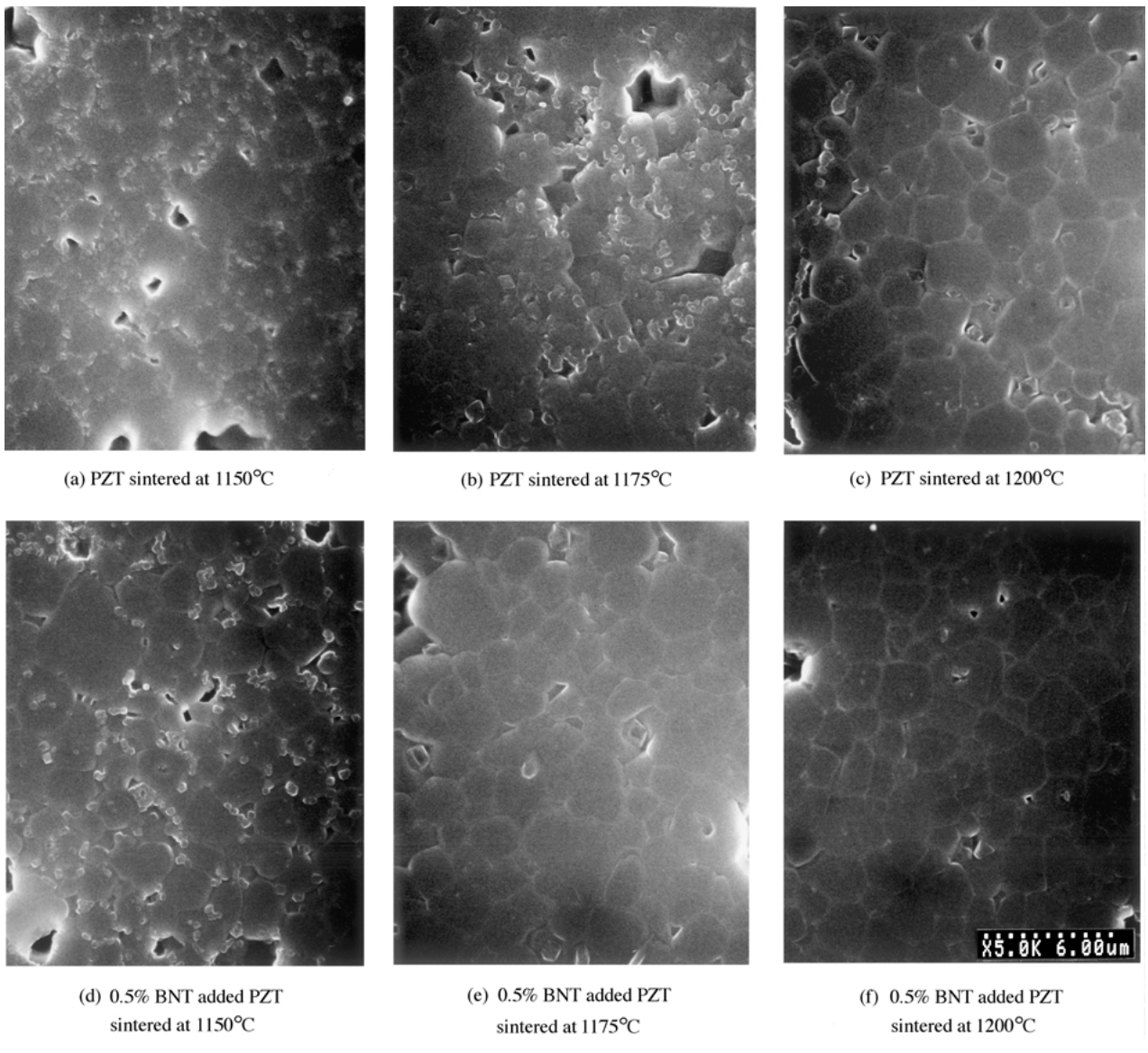
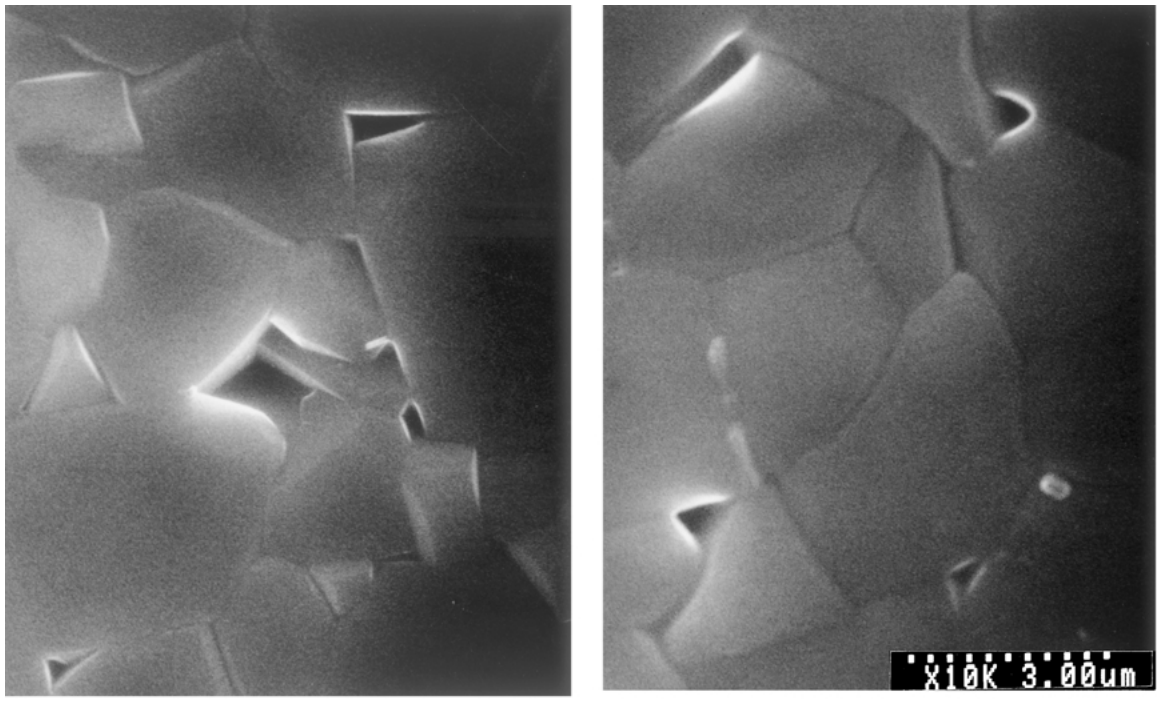


Figure 8 SEM photographs of PZT-BNT system.



(a) BNT sintered at 1150°C

(b) BNT sintered at 1200°C

Figure 10 SEM photographs of BNT sintered at different temperatures.

Fig. 2 shows the X-ray diffraction patterns of BNT with various Na contents (stoichiometric, 2% Na excess, 4% Na excess) sintered at 1150°C. The BNT rhombohedral perovskite phase was prepared by means of conventional method. The diffraction intensity increased by excess 2% and 4% Na containing samples. In the case of excess 2% and 4% Na (4 arrows), secondary $Bi_2Ti_2O_7$ phase was obtained. Therefore it was considered that the perovskite and $Bi_2Ti_2O_7$ synthesis reactions were promoted by excess Na.

3.2. Properties of PZT ceramics containing BNT

The relationship between density and sintering temperature (1150 to 1200°C) in pure PZT and in PZT ceramics with 0.5 and 1.0% BNT are shown in Fig. 3. High densities of PZT were obtained by 0.5% and 1.0% BNT addition, and the sintered densities showed the almost same values by increasing the sintering temperature.

Fig. 4 shows the lattice constants in PZT ceramics sintered at 1175°C containing 0.5, 1.0% BNT. According to XRD analysis, the BNT phase disappeared, and only the PZT tetragonal perovskite phases were observed in each two samples. As the amount of BNT addition increased, lattice constants a and c decreased. In the case of pure BNT, lattice constant is $a = 3.8850$ Å, and those of pure PZT $a = 4.0422$ Å, $c = 4.1085$ Å, respectively. It indicates that BNT dissolves in PZT.

Fig. 5 shows the sintering temperature influence of electro-mechanical coupling factor k_p in PZT ceramics with various BNT contents. The electro-mechanical coupling factor k_p was maintained to 60–70% for 0.5 and 1.0% BNT added samples.

Fig. 6 shows the influence of sintering temperature (from 1150 to 1200°C) on four point mechanical bending strength. The bending strength of the additive-free PZT-specimen was 85 MPa, and almost constant from 1150 to 1200°C. On the other hand, in the case of 0.5% and 1.0% BNT added PZT sintered at 1150°C, the mechanical bending strength was increased about 14%. Usually PZT is sintered at 1250°C, but the high density and mechanical bending strength of BNT is obtained at 1150°C. The difference of optimum temperature between these ceramics is 100°C. It can be explained that BNT played the driving force for the low-temperature sintering of PZT-BNT ceramics, so the bending strength at 1150°C increased. Fig. 7 shows the Weibull plots of applied stress until fracture. The value of Weibull modulus varies from 5.0 to 9.5.

Scanning electron micrographs of polished and thermal etched section of the PZT-BNT specimens are shown in Fig. 8. The average grain sizes of sintered specimens are 2 μm, and the grain sizes remain constant not relating with sintering temperature. In the case of pure PZT, submicron order small particles were also observed at 1150°C and 1175°C. In the case of 0.5% BNT added PZT, small particles were disappeared at 1175°C. Above results also support that BNT promotes the low-temperature sintering of PZT.

Fig. 9 shows the relationship between sintering temperature and vickers hardness of PZT-BNT ceramics. The vickers hardness of additive-free PZT specimen was about 450, and sintering temperature dependence was not observed. On the other hand, in the case of 0.5% and 1.0% BNT added PZT, the vickers hardness apparently decreased as sintering temperature increased. Fig. 10 shows the scanning electron micrographs of BNT sintered at 1150°C and 1200°C. Two specimens had almost the same average grain size. The specimen sintered at 1150°C contained angular grains and had a microstructure different from that of the rounded shape

sintered at 1200°C. The sinterability of the PZT powders was enhanced by BNT. But the microstructure of the specimen sintered at high temperature (1200°C) differed from ones sintered at 1150°C. So the mechanical strength of PZT sintered at 1200°C decreased.

4. Conclusions

Mechanical strength and piezoelectric properties of BNT added PZT composite piezoelectric ceramics have been investigated. The results are summarized below.

1. The BNT rhombohedral perovskite phase was prepared. In the case of excess 2% and 4% Na (4 arrows), secondary $Bi_2Ti_2O_7$ phase was obtained.
2. From XRD analysis, it is found that the BNT phase disappeared, and only the PZT tetragonal perovskite phases were obtained. As the amount of BNT dopant increased, lattice constants a and c decreased.
3. The electro-mechanical coupling factor k_p was not decreased below 60–70% for 0.5 and 1.0% BNT added PZT samples.
4. In the case of 0.5% and 1.0% BNT added PZT, the mechanical bending strengths increased for the samples sintered at 1150°C. BNT played the driving force for the low-temperature sintering of PZT-BNT ceramics, so the bending strength at 1150°C increased.
5. In the case of 0.5% and 1.0% BNT added PZT, the vickers hardness apparently decreased as sintering temperature increased.

Acknowledgments

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