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Structural variation and microwave dielectric properties of TiO_2-doped $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics

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Abstract

The effect of TiO_2 on microstructure and microwave dielectric properties of $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) ceramics was investigated. The addition of TiO_2 did not disturb the 1:2 ordering structure of the BZT ceramic. The average grain size significantly increased with the addition of TiO_2, which was attributed to the liquid phase formation. A small amount of TiO_2 increased the relative density. However, relative density decreased with the addition of the large amount of TiO_2 and it might be due to the abnormal grain growth. The Q value of the BZT significantly improved with the addition of the TiO_2 for the specimens sintered at 1580 °C and it could be explained by the increased relative density. However, for the specimens sintered at 1630 °C, Q value decreased with the addition of the TiO_2 which is attributed to the decrease of the relative density. The maximum $Q \times f$ value achieved in this investigation was about 135,000 GHz for the BZT with 1.0 mol.% TiO_2 sintered at 1580 °C for 10 h.

Keywords: Microstructure; Dielectric properties; TiO_2; Ba(Zn, Ta)O_3

1. Introduction

$Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics is known to have a high Q value, a small temperature coefficient of resonant frequency (τ_f) and a high dielectric constant (ε_r), all of which are important properties for the application of dielectric ceramics to microwave devices.[1,2] It is known that the microwave dielectric properties of BZT ceramics are greatly affected by their structure. In particular, the 1:2 chemical ordering of B site cations has been reported to influence the Q value of BZT ceramics.[2] However, Desu and O'Bryan suggested that the high Q value of BZT ceramics is related to the crystallographic distortion which is related to the evaporation of ZnO.[3] Long-time sintering at high temperature is required to obtain the lattice distortion or 1:2 ordering for high Q value. On the other hand, Tamura et al. showed that the $(1-x)$BZT–xBaZrO$_3$[$(1-x)$BZT–xBZ] solid solution sintered at 1500 °C for 4 h exhibited high Q value but they did not clearly explain the Q value increase.[4] Recently, Davies and Tong explained the improvement of the Q value in BZT–BZ ceramics in terms of the stabilization of the domain boundary and lowering of the free energy of the antiphase boundary.[5] An improvement in the Q value was also found in $(1-x)$BZT–x[$Ba_{(1-y)}Sry$]($Ga_{1/2}Ta_{1/2}$)O_3 ceramics, but it was not completely understood.[6]

Previously, we reported that the Q value of BZT was greatly improved when a small amount of M_2O_3 ($A = Ga^{3+}$ or Al^{3+}) was added.[7,8] For Ga_2O_3-added BZT, Ga^{3+} ions entered the vacant Zn sites and disturbed the 1:2 ordering structure, resulting in the disordering structure.[7] An increase in grain size and Ba–Ga liquid phase were observed and the Q value improvement was explained by the increase in the grain size and relative density.[7] For the Al_2O_3-added BZT, Al^{3+} ion is too small to replace the Zn vacancy thus, the 1:2 ordering structure was maintained. For the Al_2O_3-added BZT, even if the variation of the ordering structure is different from that of Ga_2O_3-added BZT, grain growth and liquid phase were also observed and the improvement in Q value was explained in terms of grain growth and density.[8] The variation of ordering structure and improvement in Q value were also observed in the ZrO_2-added BZT.[9,10] When

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ZrO_2 was added to BZT ceramics, the 1:2 ordering structure changed to the 1:1 ordering structure. Grain growth and liquid phase were observed and the improvement in the Q value was also explained by the increase in the grain size and relative density.

In this work, we investigated the structural and microwave dielectric properties of TiO_2-added BZT ceramics. Especially, the variation in the ordering structure, the formation of a liquid phase and grain growth were studied and the variation of the Q value was understood in terms of the density and gram size.

2. Experimental details

BZT + xTiO$_2$ ceramics with 0.0 mol.% ≤ x ≤ 8.0 mol.% were prepared from oxides of >99% purity using conventional solid-state synthesis. Oxide compounds of $BaCO_3$ (Aldrich Chemical Co., Milwaukee, WI), ZnO (Junsei Chemical Co., Tokyo, Japan) and Ta_2O_5 (Junsei Chemical Co., Tokyo, Japan) were mixed for 24 h in a nylon jar with zirconia balls, then dried, and calcined at 1200 °C for 2 h. The calcined BZT powder was ground and calcined again at 1200 °C for 2 h. After remilling with a TiO_2 (Junsei Chemical Co., Tokyo, Japan) additive, the powder was dried and pressed into discs and sintered at 1580–1630 °C for 10 h. The microstructure of the specimens was studied by using X-ray diffraction (Rigaku D/max-RC, Japan), Transmission electron microscopy (TEM; Hitachi H-9000NAR, Ibaraki, Japan) and Scanning electron microscopy (SEM; Hitachi S-4300, Japan). Densities of the sintered specimens were measured by a water-immersion technique. The dielectric properties in the microwave frequency range were measured by a dielectric post-resonator technique suggested by Hakki and Coleman and Courtney.[11,12] The temperature coefficients of the resonant frequency was measured at 6.5 GHz in the temperature range of 25 and 85 °C.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of BZT + xTiO$_2$ ceramics with 0.0 mol.% ≤ x ≤ 8.0 mol.% sintered at 1580 °C for 10 h. All the peaks were indexed in terms of simple a perovskite unit cell. BZT has the $Ba_5Ta_4O_{15}$ second phase which might be formed due to the evaporation of ZnO during sintering. Peak intensity for $Ba_5Ta_4O_{15}$ second phase did not decrease with the addition of TiO_2. For the ZrO_2-added BZT, Zr^{4+} ions which entered the Zn vacant site decreased the amount of $Ba_5Ta_4O_{15}$ second phase but assisted the formation of $Ba_{0.5}TaO_3$ second phase.[9] However, the $Ba_{0.5}TaO_3$ second phase was not found in the TiO_2-added BZT. The peak for a 1:2 ordering structure indicated by asterisk in Fig. 1 was found in the all the specimens and the intensity of the 1:2 ordering peak did not change with the addition of TiO_2 implying that

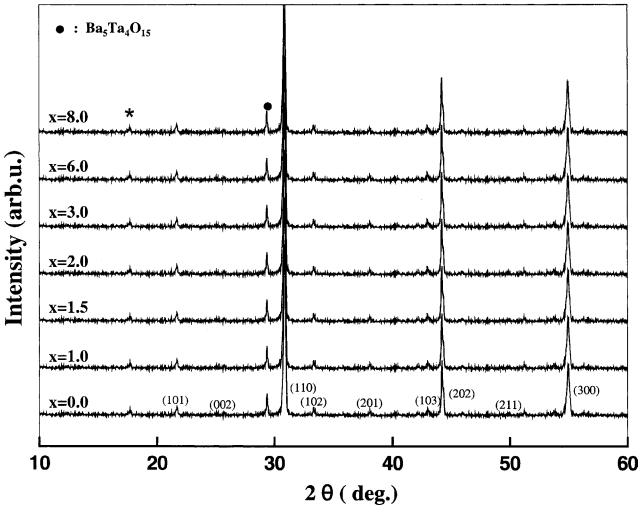

Fig. 1. X-ray diffraction patterns of Ba($Zn_{1/3}Ta_{2/3}$)O_3 + xTiO$_2$ ceramics with 0.0 mol.% ≤ x ≤ 8.0 mol.% sintered at 1580 °C for 10 hrs.

the 1:2 ordering structure was maintained in spite of the addition of the TiO_2. Electron diffraction analysis was also carried out on the TiO_2-added BZT to study the ordering structure of the specimens. Fig. 2a illustrates the electron diffraction pattern of the BZT ceramics and the 1:2 ordering superlattice reflection at 1/3 (1 1 1) position indicated by arrowhead were observed. BZT ceramics with 4 mol.% TiO_2 also has the 1:2 ordering reflections as shown in Fig. 2b. The 1:1 ordering or disordering structure was not found in the TiO_2-added BZT ceramics. Electron diffraction analysis confirms that the TiO_2-added BZT has the 1:2 ordered hexagonal structure. According to the previous research, for the ZrO_2-added BZT and the (1 − x)BZT–xBaZrO$_3$ systems, Zr^{4+} ions replaced Zn vacancies and altered the 1:2 ordering structure to the 1:1 ordering structure.[5,9,10] Moreover, replacement of Zn vacancies by the Zr^{4+} ions also changed $Ba_{0.5}Ta_4O_{15}$ second phase existed in pure BZT to $Ba_{0.5}TaO_3$ second phase.[9] On the contrary, when Ti was added, variations of the 1:2 ordering and $Ba_5Ta_4O_{15}$ second phase were not observed. The ionic radius of the Zr^{4+} is about 0.072 nm, which is similar to that of Zn^{2+} ion (0.074 nm) thus, Zr^{4+} ion can easily enter the vacant Zn^{2+} site and alter the ordering structure and the second phase. However, the ionic size of Ti^{4+} (=0.0605 nm) is much smaller than that of the Zn^{2+} ion.[13] Therefore, since the Ti^{4+} ion could not enter a Zn vacant site, the 1:2 ordering structure and $Ba_5Ta_4O_{15}$ second phase were maintained.

Fig. 3a–c show the SEM images of the fracture surface of the BZT + xTiO$_2$ ceramics with 0.0 mol.% ≤ x ≤ 2.0 mol.% sintered at 1580 °C for 10 h. BZT ceramics has homogeneous microstructure with an average grain size of 1.5 μm. According to the X-ray diffraction pattern, $Ba_5Ta_4O_{15}$ second phase exists in BZT ceramics but it was difficult to identify the $Ba_5Ta_4O_{15}$ second phase using SEM. When x = 1.0 mol.%, grain growth started and some of the grains were already grown as shown in Fig. 3b. As the amount of TiO_2

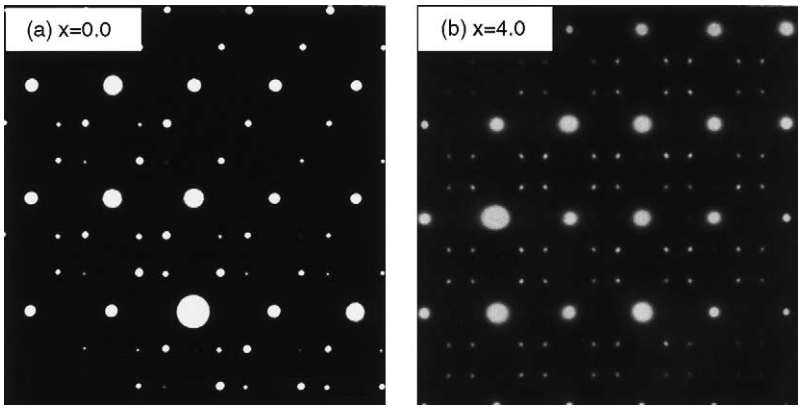

Fig. 2. Electron diffraction patterns of $Ba(Zn_{1/3}Ta_{2/3})O_3 + xTiO_2$ ceramics with (a) $x = 0.0$ mol.% and (b) $x = 4.0$ mol.% sintered at 1580 °C for 10 h.

additive exceeded 1.0 mol.%, grain growth was completed. For the specimens sintered at 1600 and 1630 °C, variation of the microstructure was similar to that of the specimens grown at 1580 °C but grain growth already occurred when $x = 0.7$ and 0.3 mol.%, respectively (see Fig. 4a and b). Moreover, a considerable amount of the liquid phase indicated by the arrow in Fig. 4c was observed for the specimens with a large amount of the TiO_2. Therefore, the presence of the liquid phase could be responsible for the grain growth. The amount of liquid phase increased with the increases of the sintering temperature and the amount of TiO_2 content.

Fig. 5 shows the relative density of the BZT + $xTiO_2$ ceramics with 0.0 mol.% $\leq x \leq$ 8.0 mol.% as a function of TiO_2. Relative density of the specimens sintered at 1580 and 1600 °C slightly increased with the addition of TiO_2 but significantly decreased when TiO_2 content increased. These

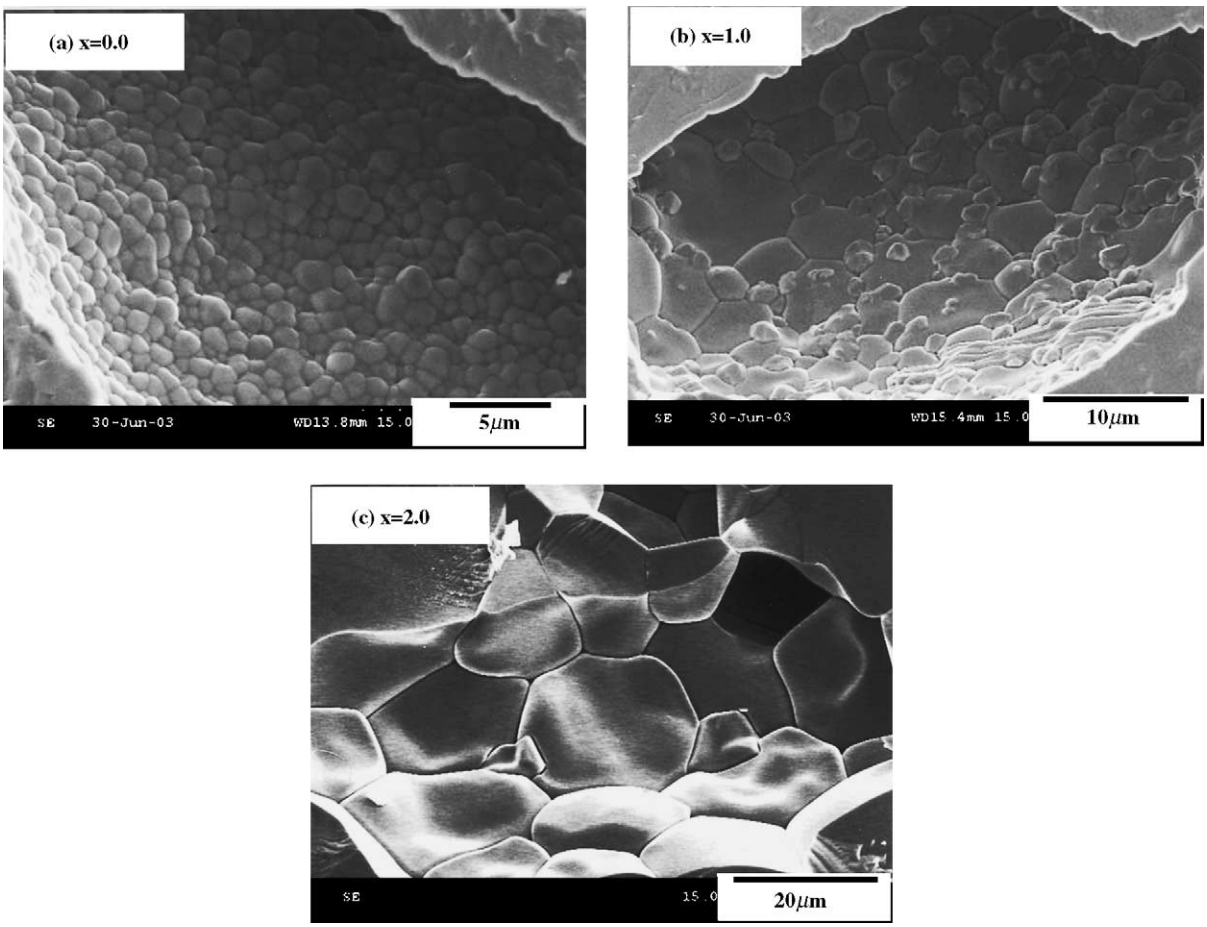

Fig. 3. SEM images of $Ba(Zn_{1/3}Ta_{2/3})O_3 + xTiO_2$ ceramics with (a) $x = 0.0$ mol.%, (b) $x = 1.0$ mol.%, and (c) $x = 2.0$ mol.% sintered at 1580 °C for 10 h.

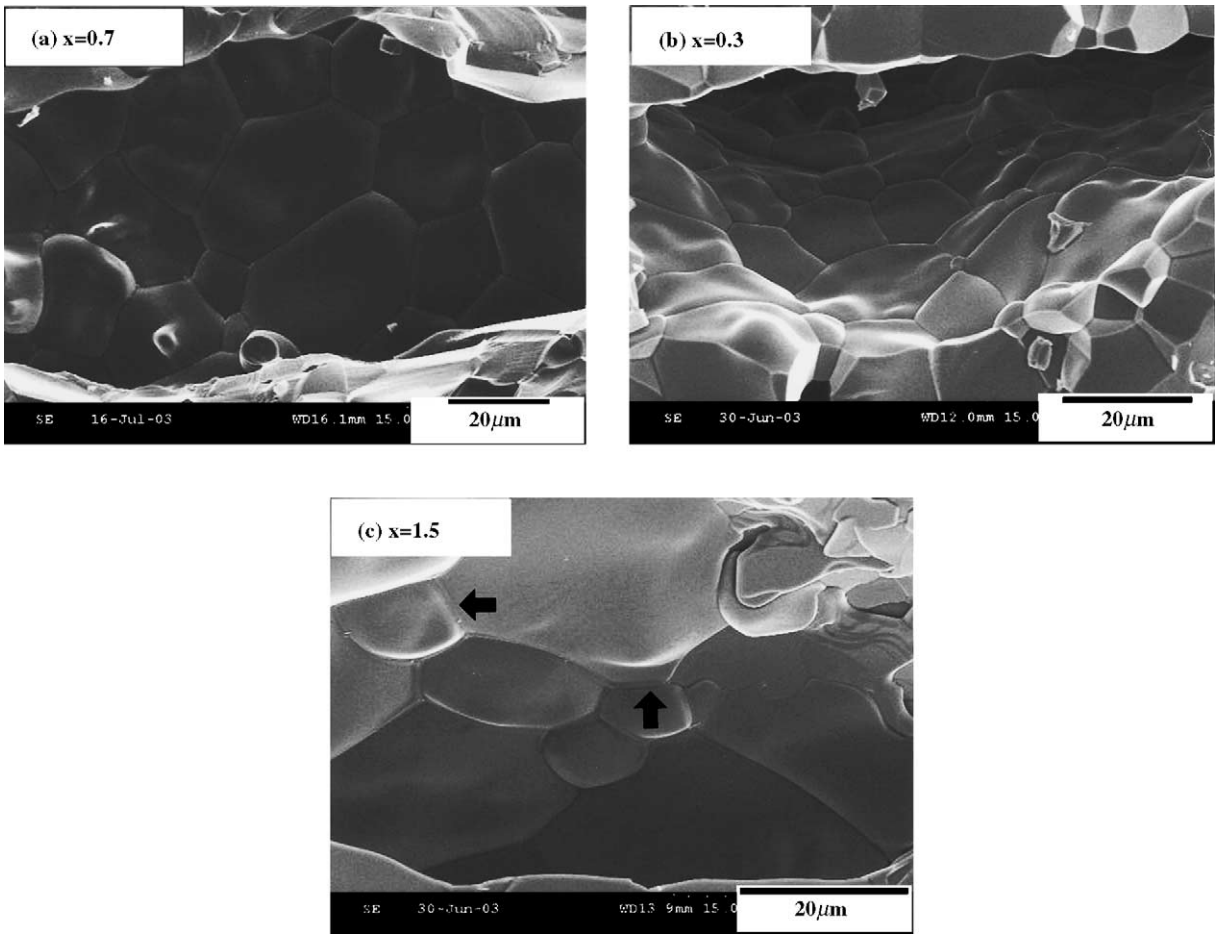

Fig. 4. SEM images of $Ba(Zn_{1/3}Ta_{2/3})O_3 + xTiO_2$ ceramics with (a) $x = 0.7$ mol.%, sintered at 1600 °C for 10 h, (b) $x = 0.3$, and (c) $x = 1.5$ mol.% sintered at 1630 °C for 10 h.

results imply that a small amount of TiO_2 might act as a sintering aid which increases the density of the specimens. However, when a large amount of TiO_2 was added, abnormal grain growth occurred resulting in the decrease of the relative density. For the specimens sintered at 1630 °C, however, relative density decreased with the addition of TiO_2 because abnormal grain growth occurred even if a very small amount of TiO_2 was added. This result is also shown in Fig. 5.

Fig. 6 illustrates the variation of the dielectric constant of $BZT + xTiO_2$ ceramics with $0.0\,\text{mol.\%} \leq x \leq 8.0\,\text{mol.\%}$ as a function of TiO_2 content. When x is less than 2.0 mol.%, variation of the dielectric constant is similar to that of relative density. However, as x exceeded 1.5 mol.%, it increased even if density was low. The increase of the dielectric constant could be attributed to the increase of the amount of TiO_2 because TiO_2 has a high dielectric constant.

Fig. 7 shows the variation of $Q \times f$ value with the addition of TiO_2 at various temperatures. For the BZT sintered at 1580 °C, the $Q \times f$ value was about 85,000 GHz and increased with the addition of TiO_2, and showed a maximum value when $x = 1.0$ mol.%. The $Q \times f$ value significantly decreased as x exceeded 1.0 mol.% and it could be explained by the low relative density and presence of the large amount of the liquid phase. According to the X-Ray and TEM results, the degree of 1:2 ordering did not change with the addition of the TiO_2. Therefore, 1:2 ordering is not related to the increase in Q value. For 1:1 ordered single-phase

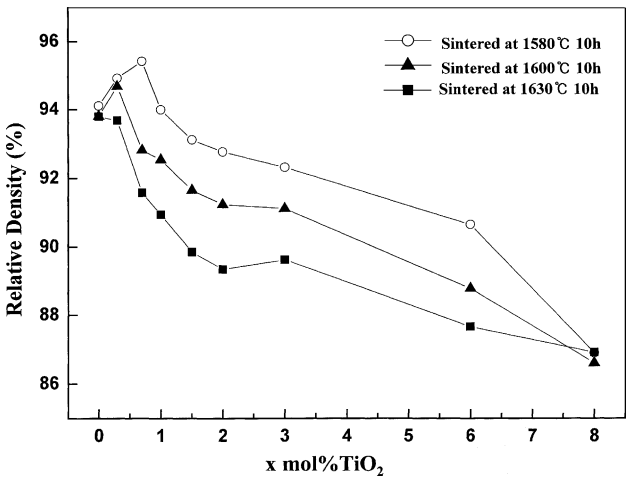

Fig. 5. Variation of the relative density with TiO_2 for $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics sintered at various sintering temperatures for 10 h.

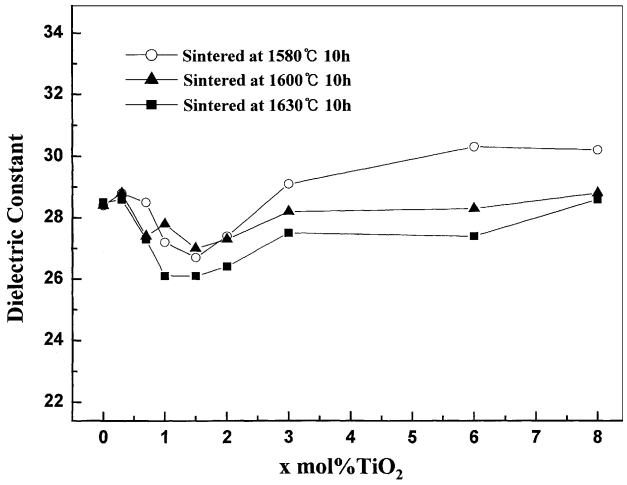

Fig. 6. Variation of the dielectric constant with TiO_2 for $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics sintered at various sintering temperatures for 10 h.

$(1-x)$BZT–xBZ ceramics, the improvement in Q value was explained in terms of the stabilization of anti-phase boundary by the random layer.[5] However, 1:1 ordering was not found in the Ti-added BZT. Therefore, the improvement in Q value cannot be explained by the stabilization of the anti-phase boundary. On the other hand, since the relative density increased with the addition of a small amount of TiO_2, the increase of the density could be responsible for the improvement of $Q \times f$ value. Moreover, the decrease of $Q \times f$ value with the addition of a large amount TiO_2 can be explained by the decrease of the relative density. Therefore, density is important for the Q value of BZT ceramics. For the specimens sintered at 1600 °C, variation of Q value is similar to that of the specimens sintered at 1580 °C but the maximum Q value was obtained for the BZT with 0.7 mol.% TiO_2. In addition, it is interesting to note that the maximum Q value was obtained when grain growth was completed even though the density was slightly low. Therefore, grain size might also be important for the improvement in Q value of TiO_2-added BZT. For the specimens sintered at 1630 °C, the Q value decreased with the addition of TiO_2 and it is due to the low relative density and the presence of the large amount of the liquid phase.

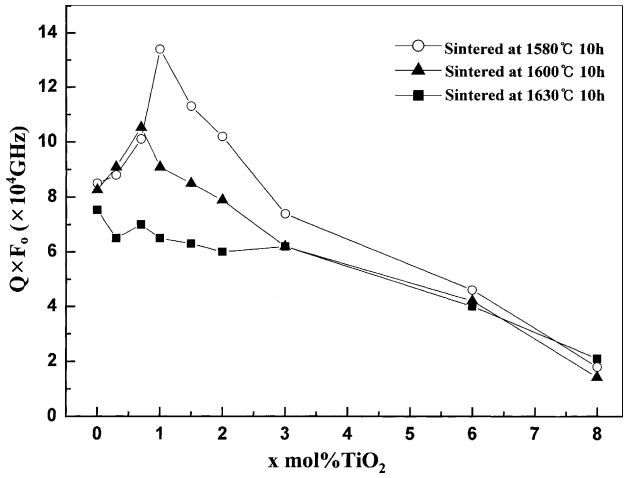

Fig. 7. Variation of the $Q \times f$ with TiO_2 for $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics sintered at various sintering temperatures for 10 h.

4. Conclusions

Microstructure and microwave dielectric properties of BZT + xTiO$_2$ ceramics with 0.0 mol.% $\leq x \leq$ 8.0 mol.% were investigated. BZT has a 1:2 ordered hexagonal structure. The addition of TiO_2 did not change the 1:2 ordering structure. For the BZT sintered at 1580 °C, grain growth occurred when TiO_2 was added. The grain growth occurred in TiO_2-added BZT could be explained by the presence of the liquid phase. The $Q \times f$ value of BZT significantly increased with the addition of the TiO_2. Since the 1:2 ordering structure was not changed with the addition of TiO_2, and the 1:1 ordering was not observed, the increase in the $Q \times f$ value cannot be explained by the 1:2 ordering or the stabilization of anti-phase boundary. On the other hand, relative density increased and grain growth occurred when a small amount of TiO_2 was added. Therefore, the increase in the relative density and grain size could be responsible for the improvement in the Q value of BZT ceramics.

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References

1. Kawashima, S., Nishida, M., Ueda, I. and Ouchi, H., Dielectric properties ceramics of $Ba(Zn_{1/3}Nb_{2/3})O_3$–$Ba(Zn_{1/3}Ta_{2/3})O_3$. *Proc. Ferroelect. Mater. Appl.* 1977, **1**, 293–296.
2. Kawashima, S., Nishida, M., Ueda, I. and Ouchi, H., $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics with low dielectric loss at microwave frequencies. *J. Am. Ceram. Soc.* 1983, **66**, 421–423.
3. Desu, S. B. and O'Bryan, H. M., Microwave loss quality of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics. *J. Am. Ceram. Soc.* 1985, **68**, 546–551.
4. Tamura, H., Konoike, T., Sakabe, Y. and Wakino, K., Improved high Q dielectric resonator with complex perovskite structure. *J. Am. Ceram. Soc.* 1984, **67**, C59–C61.
5. Davies, P. K. and Tong, J., Effect of ordering-induced domain boundaries on low-loss $Ba(Zn_{1/3}Ta_{2/3})O_3$-$BaZrO_3$ perovskite microwave dielectrics. *J. Am. Ceram. Soc.* 1997, **80**, 1727–1740.
6. Kageyama, K., Crystal structure and microwave dielectric properties of $Ba(Zn_{1/13}Ta_{2/3})O_3$–(Sr, Ba)$(Ga_{1/2}Ta_{1/2})O_3$ ceramics. *J. Am. Ceram. Soc.* 1992, **75**(7), 1767–1771.
7. Yang, J. I., Nahm, S., Choi, C. H., Lee, H. J., Kim, J. C. and Park, H. M., Effects of Ga_2O_3 on the microstructure and microwave dielectric properties of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics. *Jpn. J. Appl. Phys.* 2002, **41**, 702–706.

8. Kim, M.-H., Nahm, S., Lee, W.-S., Yoo, M.-J., Park, J.-C. and Lee, H.-J., Effect of the microstructure on the microwave dielectric properties of the $A1_2O_3$ added $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics. *Jpn. J. Appl. Phys.*, in press.
9. Yang, J. I., Nahm, S., Choi, C. H., Lee, H. J. and Park, H. M., Microstructure and microwave dielectric properties of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics with ZrO_2 addition. *J. Am. Ceram. Soc.* 2002, **85**, 165–168.
10. Yang, J. I., Nahm, S., Yoon, S. J., Park, H. Y. and Lee, H. J., Structural variation and microwave dielectric properties of ZrO_2 added $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics. *Jpn. J. Appl. Phys.* 2004, **43**, 211–214.
11. Hakki, B. W. and Coleman, P. D., A dielectric resonator method of measuring inductive in the millimeter range. *IEEE Trans. Microwave Theor. Tech.* 1960, **8**, 402–410.
12. Courtney, W. E., Analysis and evaluation of a method of measuring the complex permittivity and permeability of microwave insulators. *IEEE Trans. Microwave Theor. Tech.* 1970, **18**, 476–485.
13. Shannon, R. D., Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.* 1976, **A32**, 751–767.