Journal of the European Ceramic Society 21 (2001) 2599–2604

www.elsevier.com/locate/jeurceramsoc

Effect of chemical element doping and sintering atmosphere on the microwave dielectric properties of barium zinc tantalates

J.S. Kim[a,*], J.-W. Kim[a], C.I. Cheon[a], Y.-S. Kim[b], S. Nahm[c], J.D. Byun[c]

[a]*Department of Materials and Mechanical Engineering, Hoseo University, Chungnam, 336-795, South Korea*
[b]*Department of Radio Science and Engineering, Korea University, Seoul, South Korea*
[c]*Department of Materials Engineering, Korea University, Seoul, South Korea*

Abstract

The microwave dielectric properties, long range ordering (LRO) of Zn/Ta sites, and extra phase formation were studied in $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics doped with 0–4 mol% $BaWO_4$ under varying sintering conditions. The sintering atmosphere was either air or ZnO-powder muffling. The LRO were analyzed by Rietveld refinement method using X-ray diffraction data. The $Q{\cdot}f$ values were extremely low for samples prepared under ZnO-muffling regardless of the degrees of LRO. Maximum $Q{\cdot}f$ values were 160,000–200,000 GHz at 0.5–1.5 mol% $BaWO_4$ doping. The extra phases formed during sintering in air and under ZnO-muffling were analyzed in detail. The air sintered specimens showed $Ba_7Ta_6O_{22}$ as a major extra phase accompanied by ZnO-loss; in ZnO-muffled specimens $BaWO_4$ was a dominant extra phase. During the ZnO-loss process point defects in the Zn/O sites could be introduced into BZT.

Keywords: BZT; Cation ordering; Extra phase; Loss quality; ZnO-loss

1. Introduction

$Ba(Zn_{1/3}Ta_{2/3})O_3$(BZT) is a compound having ultra-high quality Q value. It has potential for applications in satellite broadcasting at high frequency (>10 GHz) and as a super-high Q DR (dielectric resonator) in a combiner filter for PCS applications.[1,2] The factors influencing Q-values of the perovskites $Ba(M^{2+}_{1/3}Ta^{5+}_{2/3})O_3$ (M = Mg, Zn) have been considered to be long range ordering (LRO) of cations, zinc oxide evaporation, point defects, and stabilization of micro domain boundaries.[3–6]

The LRO of B-site cations is the most frequently asserted parameter since the high-Q values could be obtained typically after an extended high-temperature annealing step. Conversely Davies[6] showed that Q-values of BZT could be enhanced even with the reduction of LRO by $BaZrO_3$ doping. Similarly, Ra et al.[1] showed that despite LRO reduction in BMT by the doping of $BaZrO_3$, the Q-values did not decrease substantially. On the other hand, Kawashima[4,5] and Desu et al.[3] reported that the high-Q values are linked to the ZnO-loss. The possible mechanisms for the ZnO-loss were proposed by Desu et al.[3,5] and Kawashima [4] as follows.

$$Ba_3(ZnTa_2)O_9 \rightarrow (1-x)Ba_3(ZnTa_2)O_9 + xBa_3Ta_2O_8 + xZnO\uparrow \quad (1)$$

$$Ba_3(ZnTa_2)O_9 \rightarrow (1-x)\{Ba_3(Zn_{1-x}Ba_xTa_2)O_9\} + 4/3xZnO\uparrow + x/3Ta_2O_5 \quad (2)$$

$$Ba(_xZn_{1/3-5x/3}Ta_{2/3+2x/3})O_3 \quad (3)$$

However, no further study on either the defect structure or the extra phases formed by above equations have been pursued.

In this study the aim was to clarify the relation between the microwave dielectric properties and the factors previously discussed; the LRO and the formation of second phase accompanying the ZnO-loss were analyzed in detail. In this study $BaWO_4$ was used to dope BZT ceramics to enhance LRO and sinterability via the study of BaO/WO_3 doping in $Ba(Mg_{1/3}Ta_{2/3})O_3$.[7] The effect of $BaWO_4$ doping in BZT ceramics on the micro-

* Corresponding author. Tel.: +82-418-540-5472; fax: +82-418-548-3502.
E-mail address: kimjungs@office.hoseo.ac.kr (J.S. Kim).

0955-2219/01/$ - see front matter
PII: S0955-2219(01)00323-5

wave dielectric properties was analyzed under varying processing conditions, specifically sintering atmosphere, i.e. air and ZnO-powder muffling, sintering time, and temperature. Optimum processing and doping contents for achieving high-Q values in BZT were also studied.

2. Experimental

Commercially available $Ba(Zn_{1/3}Ta_{2/3})O_3$ powder, which is a single-phase material without additives, was used for this study. The dopant $BaWO_4$ was prepared by

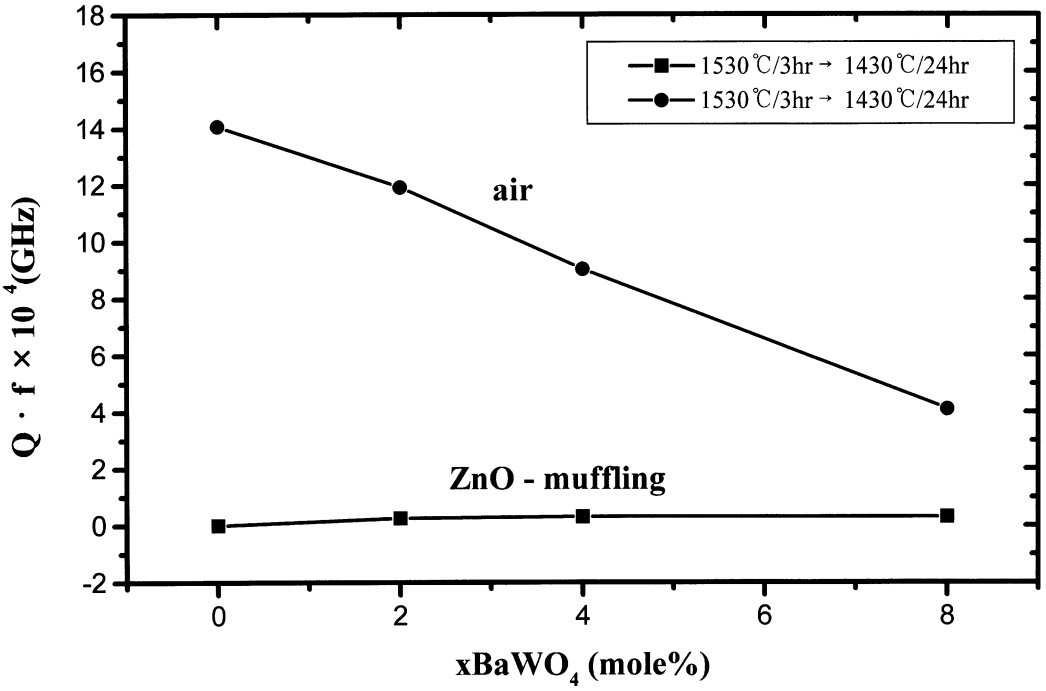

Fig. 1. Effect of sintering atmosphere on the $Q{\cdot}f$ values. Samples were sintered at 1530 °C for 3 h and post-annealed at 1430 °C for 24 h either in air or ZnO-powder muffling.

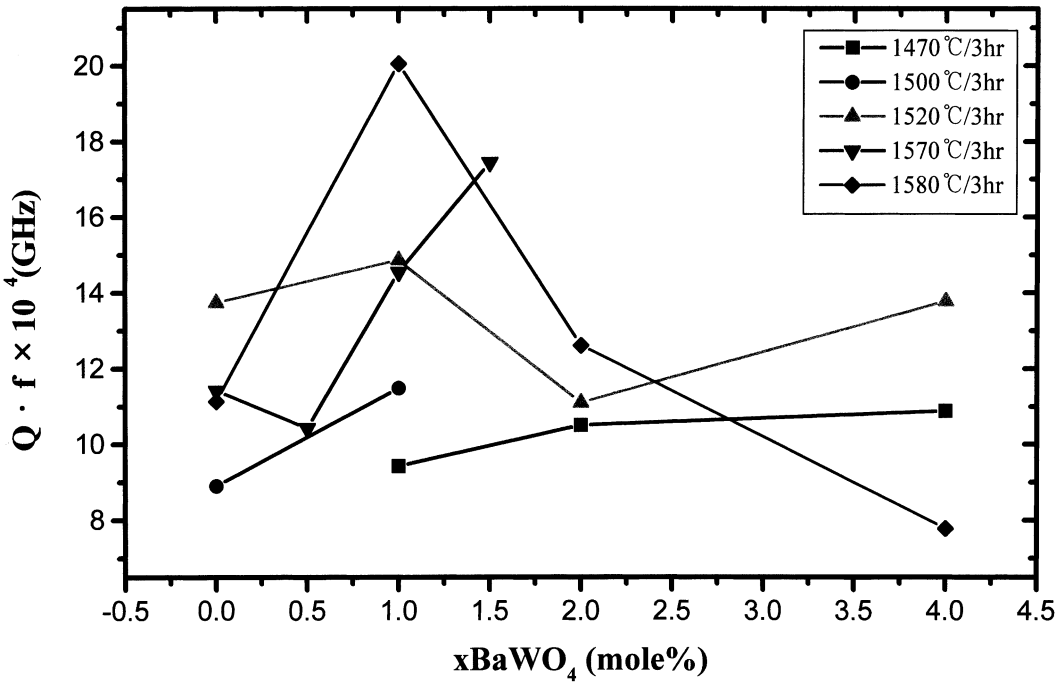

Fig. 2. Variation of $Q{\cdot}f$ values with sintering temperature and the $BaWO_4$ content. The specimens were sintered for 3 h at each temperatures.

mixing and calcining the raw materials, $BaCO_3$ and WO_3, in appropriate proportions at temperatures in the range of 800–900 °C. The calcined $BaWO_4$ was added at 0–4 mol% to the commercially available BZT powder and ball milled after adding 1 wt.% PVA. After drying and granulating on an 80-mesh screen, the powder was pressed into disks of 15 mm diameter. Microwave dielectric properties of the specimens were measured by post resonator technique by the Hakki and Coleman method at the frequency of 8 GHz. After stripping off the as-sintered surfaces, X-ray diffraction data for the specimens were collected. The degree of LRO was calculated using the occupational parameters of Zn and Ta obtained by Rietveld refinement method using X-ray diffraction data. The formation of additional crystalline phases due to the addition of $BaWO_4$ and ZnO-loss was also analyzed.

3. Results

3.1. Microwave dielectric properties

The effect of sintering atmosphere on the $Q{\cdot}f$ values is shown in Fig. 1. The commercial BZT ceramic powder was doped with 0, 2, 4 and 8 mol% $BaWO_4$ and sintered either in air or ZnO-powder muffling at 1530 °C for 3 h and post-annealed at 1430 °C for 24 h. As shown in the figure, ZnO-muffling drastically lowers the $Q{\cdot}f$ values of

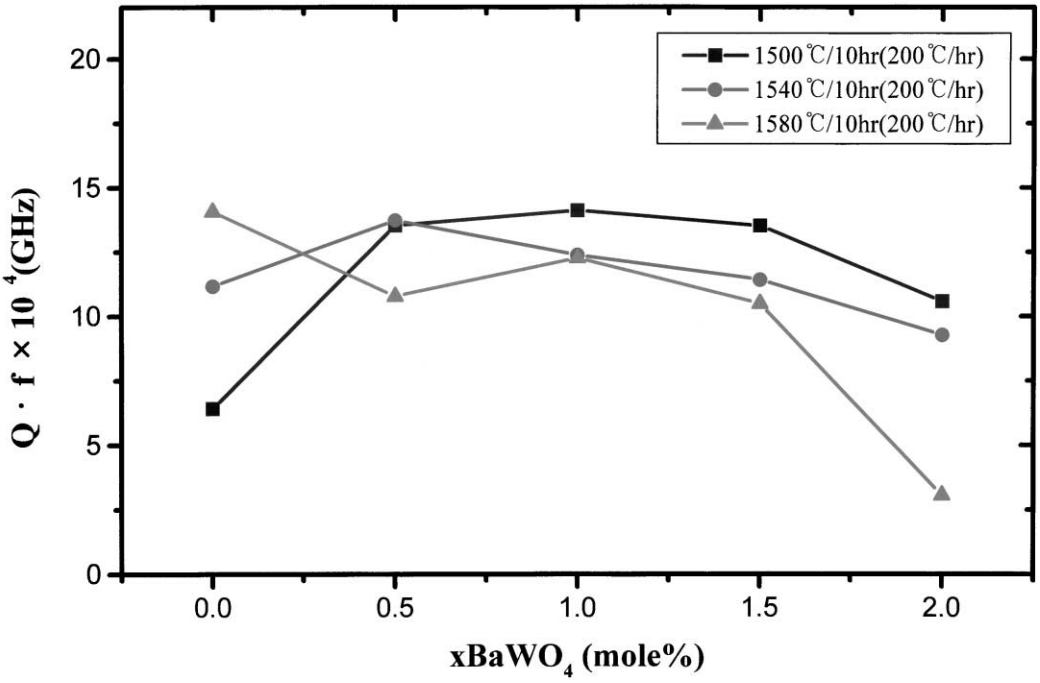

Fig. 3. Effect of sintering temperature and $BaWO_4$ doping on the $Q{\cdot}f$ values. The specimens were sintered for 10 h at each temperatures; the heating rate was 200 °C/h.

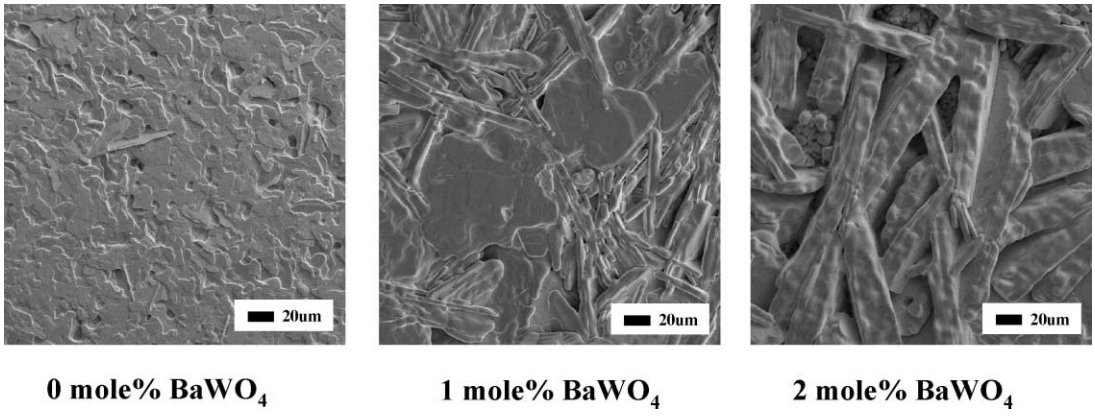

Fig. 4. SEM micrographs of the BZT–(0, 1, 2) mol% $BaWO_4$ sintered in air for 10 h at 1540 °C.

all the samples while sintering in air produces the high $Q{\cdot}f$ values. The increase of $BaWO_4$ doping to larger than 2 mol% substantially reduced the $Q{\cdot}f$ values even in air-sintered samples.

Fig. 2 shows the effect of $BaWO_4$ doping (0–4 mol%) on the $Q{\cdot}f$ (GHz) of the specimens sintered in air at temperature range of 1470–1580 °C for 3 h. The heating rate from 1000 °C to the sintering temperature was 200 °C/h. The $BaWO_4$ doping enhances the sinterability of BZT specimens. At low temperatures (1470 and 1500 °C) the $Q{\cdot}f$ values tend to increase with the amount of $BaWO_4$. At high temperatures the $Q{\cdot}f$ values reach a maximum figure of 150,000–200,000 GHz at about 1.0 mol% and decrease with further addition of $BaWO_4$.

Fig. 3 shows the $Q{\cdot}f$ values of the specimens sintered at temperatures in the range of 1500–1580 °C for 10 h. The heating rates from 1000 °C to the sintering temperatures was 200 °C/h. Similarly to Fig. 2 the $Q{\cdot}f$ values of the pure BZT increases with the sintering temperature, while the specimens doped with $BaWO_4 \geqslant 1.0$ wt.% show lower $Q{\cdot}f$ values in the high temperature range. SEM micrographs of the specimens sintered in air are shown in Fig. 4. The doping of $BaWO_4$ accelerates the grain growth and the grain shape becomes anisotropic. The grain growth occurs in an abnormal manner. The microstructures of the doped specimens appear to be less dense than undoped one. The linear shrinkage of the sintered specimens also decreased with the increase of $BaWO_4$ in accordance with the SEM micrographs.

3.2. Structural analysis

Crystal structures of the specimens doped with varying amounts of $BaWO_4$, which were sintered either in air or ZnO-muffling were refined by the Rietveld method using X-ray diffraction data. The crystal structure was hexagonal with space group P-3m1, and with lattice parameters of $a = b = 5.766$ Å and $c = 7.071$ Å. The lattice parameter ratio c/a remained nearly constant (1.2261–1.2263) in all the specimens, showing slight deviation from the ideal hexagonal (1.2247). Fig. 5 shows the degree of LRO calculated using the refined occupation parameters of Zn/Ta-sites. The LRO of Zn- and Ta-sites in ZnO-muffling conditions drastically decreased with the increase of $BaWO_4$. At 0 mol% $BaWO_4$ the degrees of LRO of Zn- and Ta- sites were nearly the same regardless of the sintering atmosphere. In air-sintered specimens the degree of LRO of the Zn-site decreases by about 0.1 with the increase of $BaWO_4$ from 0 to 4 mol%. The order parameter S of the Ta-site in air-sintered specimens shows a maximum at 1 mol% and then decreases to that of the Zn-site.

Fig. 6 shows the X-ray diffraction patterns of the specimens with varying $BaWO_4$ sintered either in air or ZnO-muffling. The BZT-0 mol% $BaWO_4$ specimen in ZnO-muffling showed no extra-peak while the air-sintered samples showed some extra peaks. The extra lines were identified to be from $Ba_7Ta_6O_{22}$ or $BaWO_4$. The peak intensities of $BaWO_4$ were stronger than those of $Ba_7Ta_6O_{22}$ in the ZnO-muffled specimens while in air-

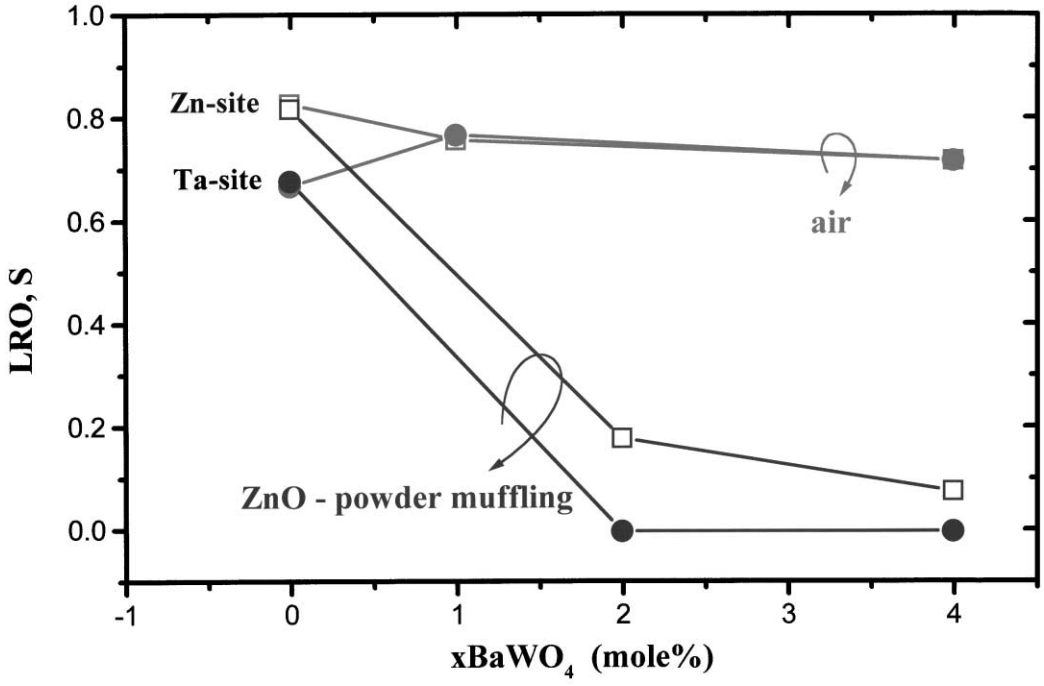

Fig. 5. Effect of sintering atmosphere and $BaWO_4$ dopant on LRO parameter (S). S was calculated from the refined occupancies of the Zn and Ta-sites. [$S = (R_A - F_A)/(1-F_A)$; R_A, A atom on the ordered position; F_A, fraction of A atoms].

sintered specimens vice versa. The extra-lines were allocated to either $BaWO_4$ or $Ba_7Ta_6O_{22}$ phase by comparing the *d*-spacing and intensities of each extra phase. As shown in Fig. 6 the extra lines under ZnO-muffling arises mostly from $BaWO_4$ and negligibly from $Ba_7Ta_6O_{22}$. However, in air-sintered specimens the major extra phase was $Ba_7Ta_6O_{22}$.

Table 1 showed the summarized results of second phase identification. The relative intensity ratio (%) of the extra peaks to that of I_{max} of BZT (100%) are represented in Table 1. The relative intensity of the $BaWO_4$ peaks increases with the increase of $BaWO_4$ doping. However, the formation of $Ba_7Ta_6O_{22}$ is favoured only in the air-sintered specimens and the $BaWO_4$ phase is strongly favoured in ZnO-muffling.

4. Discussion

The LRO is the most frequently discussed factor in the literature affecting $Q{\cdot}f$ values of BZT ceramics. Without $BaWO_4$ doping the degree of LRO for air and ZnO-muffling is nearly identical regardless of sintering atmosphere. However, $Q{\cdot}f$ values for ZnO-muffling are extremely low compared to air sintered specimens. This confirms that the LRO is not a major factor contributing to $Q{\cdot}f$ values.

The second-phase analyses show that the $Ba_7Ta_6O_{22}$ phase is formed as a major extra-phase in the air-sintered specimens while in the ZnO-muffling specimens the $Ba_7Ta_6O_{22}$ becomes minor and even completely suppressed. The effect of $Ba_7Ta_6O_{22}$ on $Q{\cdot}f$ values in $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics has been also reported by Byun et al.[8] In BMT the presence of $Ba_7Ta_6O_{22}$ or $Ba_2Ta_2O_7$ were also found to improve $Q{\cdot}f$ values. Since the formation of $Ba_7Ta_6O_{22}$ is attributed to ZnO-loss in BZT, the mechanism proposed by Desu et al.[3] can be correctly modified as follows.

$$Ba_3(ZnTa_2)O_9 \Rightarrow (1-x)Ba_3(ZnTa_2)O_9 + x/3Ba_7TaO_{22} + xZnO\uparrow + 2x/3BaO \quad (4)$$

During the ZnO-evaporation, the BZT crystal structure could have point defects on the Zn/O-sites [$Ba(_xZn_{1/3-5x/3}Ta_{2/3+2x/3})O_3$] which is undetectable by the X-ray diffraction. Recently Gong et al. [2] proposed a point defect mechanism for the microwave loss mechanism in NiO-doped BZT ceramics. They observed

Table 1
Result of second-phase analysis. Relative intensity ratios (I'_{max}/I_{max}) of each extra phase to that of BZT in the specimens of BZT + xBaWO$_4$ (x = 0, 1, 2 and 4 mol%) are indicated

Sintering atmosphere	In air (%)			In ZnO-muffling (%)		
x (%) Extra-phase	0	1	4	0	2	4
BaWO4	0	0.8	3.5	0	1.2	2.4
Ba7Ta6O22	0.68	2.3	5.0	0	0.3	0.2

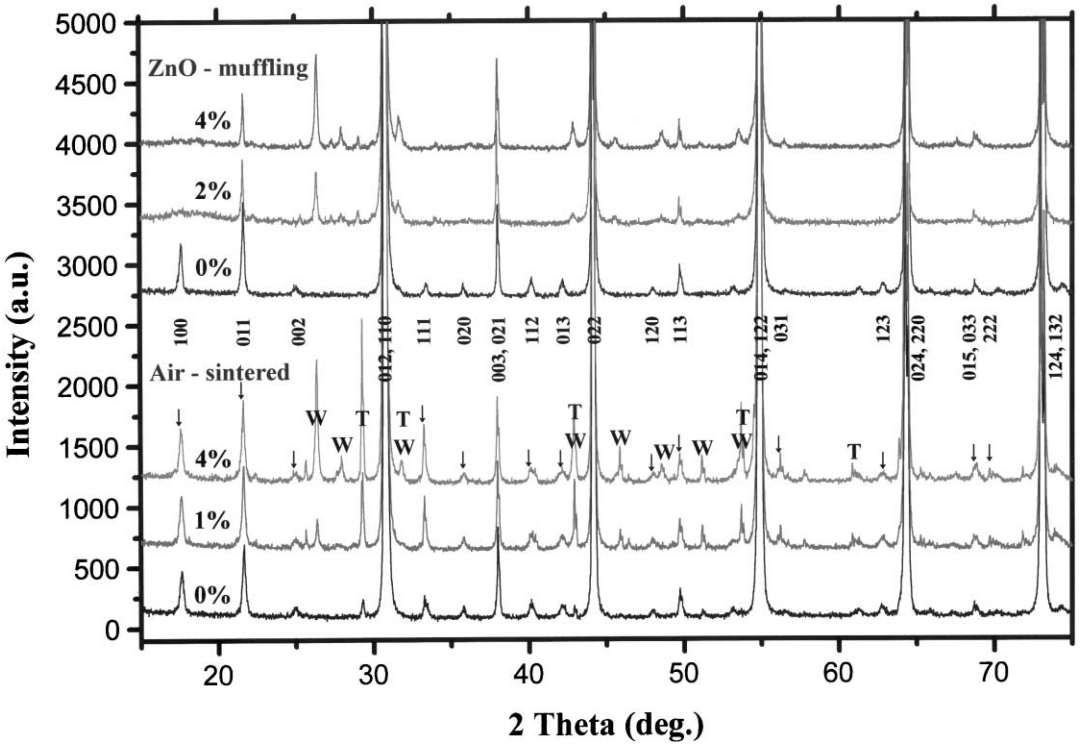

Fig. 6. X-ray diffraction patterns of the BZT–(0, 1, 2, 4) mol% $BaWO_4$ sintered in either air or in ZnO-powder muffling at 1530 °C for 3 h and post annealed at 1430 °C for 24 h. (T, $Ba_7Ta_6O_{22}$; W, $BaWO_4$).

the optical spectra in the visible range of Ni ions showing the characteristic of the local electrostatic environment of point defects, and suggested that point defects, such as impurity point defects and oxygen vacancies can enhance microwave loss through their influence on anharmonic vibrations.

The results in this study clearly demonstrated that the formation of $BaO–Ta_2O_5$ compounds, e.g. $Ba_7Ta_6O_{22}$ is a prerequisite for the high $Q{\cdot}f$ values in BZT as well as in BMT. During the ZnO-evaporation, point defect in the Zn and/or O-sites could be introduced in BZT ceramics. However, at this moment, it cannot be clearly said which factor is more directly related to the loss quality of BZT ceramics.

5. Conclusion

The doping by $BaWO_4$ increased the sinterability of BZT ceramics. The highest $Q{\cdot}$f values (15,000–200,000 GHz) were obtained at 0.5–1.5 mol% $BaWO_4$ in samples sintered at 1570–1580 °C for 3 h in air. Further increase of $BaWO_4$ lowered the $Q{\cdot}f$ values. The ZnO-muffled specimens showed extremely low $Q{\cdot}$f values independently of the degree of LRO. The $Ba_7Ta_6O_{22}$ phase was a major extra phase in all the air-sintered specimens, while in ZnO-muffled specimens the formation of $Ba_7Ta_6O_{22}$ was suppressed. Either the point defects introduced by the ZnO-loss or the formation of $Ba_7Ta_6O_{22}$ could be one of the possible mechanisms for assisting $Q{\cdot}f$ values in BZT ceramics.

Acknowledgements

This work was supported by a grant from the Korea Research Foundation in the 1999 program year. The authors deeply appreciate the support.

References

1. Ra, S.-H. and Phule, P. P., Processing and microwave dielectric properties of barium magnesium tantalate ceramics for high-quality-factor personal communication service filters. *J. Mater. Res*., 1999, **14**, 4259–4265.
2. Rong, G., Newman, N., Shaw, B. and Cronin, D., Role of Ni and Zr doping on the electrical properties of barium zinc tantalates ceramics. *J. Mater. Res*., 1999, **14**, 4011–4019.
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. Kawashima, S., Influence of ZnO evaporation on microwave dielectric loss and sinterability of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics. *Am. Ceram. Soc. Bull*., 1993, **72**, 120–126.
5. 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.
6. Davies, P. K., Influence of structural defects on the dielectric properties of ceramic microwave resonators. *Ceramic Trans*., 1995, **53**, 137–149.
7. Yoon, K. H., Yoo, S. J., Kim, W. S., Kim, J. B. and Kim, E. S., Effect of BaO/WO_3 on the Microwave Loss Quality of $Ba(Mg_{1/3}Ta_{2/3})O_3$. *Jpn. J. Appl. Phys*., 1999, **38**, 5616–5620.
8. Byun, J. D., Choi, I.K., Lee, D. W., Ko, S. W. and Kim, J. S., A low loss microwave dielectric composition and a method of preparing the same. Patent Pending, Korea Patent Office, 2000, 10-2000-0017474.