

Zinc Vacancy Ordering in $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ Ceramics

Seong-Jin Choi, Sahn Nahm, Myong-Ho Kim* and Jae-Dong Byun

Department of Materials Science and Engineering, Korea University, Seoul 136-701, Korea

*Department of Materials Science and Engineering, Changwon National University, Changwon 641-773, Korea

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The microstructure of $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BZT) was investigated using X-ray diffractometry (XRD) and transmission electron microscopy (TEM). $\text{Ba}_{0.5}\text{TaO}_3$ and $\text{Ba}_3\text{TaO}_{5.5}$ (BT) phases were observed on the surface of the sintered specimen by XRD. Furthermore, a new type of ordering along the [110] direction was found in sintered specimen by the XRD and TEM analysis. The wavelength of ordering was 0.9 nm which is three times larger than the interplanar distance of (110) plane and new type of ordering is considered to be a result of Zn vacancy ordering. The creation of Zn vacancies and formation of BT phases are attributed to the evaporation of volatile ZnO. A new mechanism for ZnO loss is suggested. In this mechanism, only Zn vacancies are created only when the amount of ZnO loss is small and as the amount of ZnO loss increases, BT phases are formed at the same time. A new unit cell of ordered structure is suggested as the superlattice containing three BZT unit cells.

Key words : BZT, Ordering, Zn vacancy, $\text{Ba}_3\text{Ta}_2\text{O}_7$

I. Introduction

Several investigators have studied the relation between microwave dielectric properties and crystalline structure of $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BZT) because of its application to satellite communication.¹⁻⁹ According to the previous work, the microwave dielectrics of superior properties were achieved by sintering at high temperature or prolonged sintering at low temperature.^{3,4} However, prolonged sintering results in the formation of new phases at the surfaces of specimens caused by evaporation of volatile ZnO.⁴ Two mechanisms for ZnO loss were suggested by previous investigators.¹ For small amount of ZnO loss, large Ba ions were assumed to be transferred to small Zn vacant sites with lattice distortion. The increase of c/a ratio and the splitting of (422) and (226) peaks after prolonged sintering were considered to be the results of lattice distortion. However, the transfer of large Ba ion to small Zn vacant site was not fully explained. In this mechanism, the Ta_2O_5 is formed inevitably. However, the presence of Ta_2O_5 was not clear. For large amount of ZnO loss, the existence of $\text{Ba}_3\text{Ta}_2\text{O}_7$ phase was assumed without only clear experimental evidence.

In this work, microstructure and as-sintered surface of BZT specimen was studied using XRD and TEM. The phases observed at the as-sintered surface of the specimen were identified as $\text{Ba}_{0.5}\text{TaO}_3$ and $\text{Ba}_3\text{TaO}_{5.5}$. Ordering of Zn vacancy was observed by TEM and a new unit cell of ordered structure is suggested. Computer simulation was carried out using this unit cell. New mechanisms for ZnO loss are suggested.

II. Experimental Procedure

$\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ pellets were prepared using the reagent grade BaCO_3 , ZnO, and Ta_2O_5 powders. These powders were mixed in polyethylene jar for 24 hr and calcined for 2 hr at 1100°C. The calcined samples were ball-milled for 12 hr and pressed into disc under a pressure of 1500 kg/cm². Finally, discs were sintered at 1400°C for 10, 30, 50, 70, and 90 hr. The microstructure of BZT samples were studied using TEM and XRD. TEM samples were prepared by mechanical grinding and subsequent ion milling. Microscopes (Philips CM20T/STEM and Hitachi H-9000 NAR) were used to observe the specimens and X-ray diffractometer (Rigaku D/max-RC) was used for the X-ray measurements.

III. Results and Discussion

Figure 1 shows the X-ray spectra of BZT specimens prepared at various processing conditions. As can be seen from Fig. 1(a), ordered hexagonal structure represented by the (100) peak appeared in the specimen calcined at 1100°C for 2 hr. Thus, ordered hexagonal phases are considered to be formed in the specimen at the early stage of processing. Figures 1(b), (c), and (d) are the X-ray spectra taken from the as-sintered surfaces of the specimens. Besides the BZT peaks, extra peaks were observed in these spectra indicating the presence of new phases. The extra peaks were identified as those of $\text{Ba}_{0.5}\text{TaO}_3$ and $\text{Ba}_3\text{TaO}_{5.5}$ phases. $\text{Ba}_{0.5}\text{TaO}_3$ has the tetragonal unit cell with $a=b=1.26$ nm, $c=0.395$ nm, and $\text{Ba}_3\text{TaO}_{5.5}$ has the cubic unit cell with $a=b=c=0.869$ nm. However, we could not detect any Ta_2O_5 phase. The presence of new phases at the sintered surface is attributed to the evaporation of volatile ZnO during the sintering.

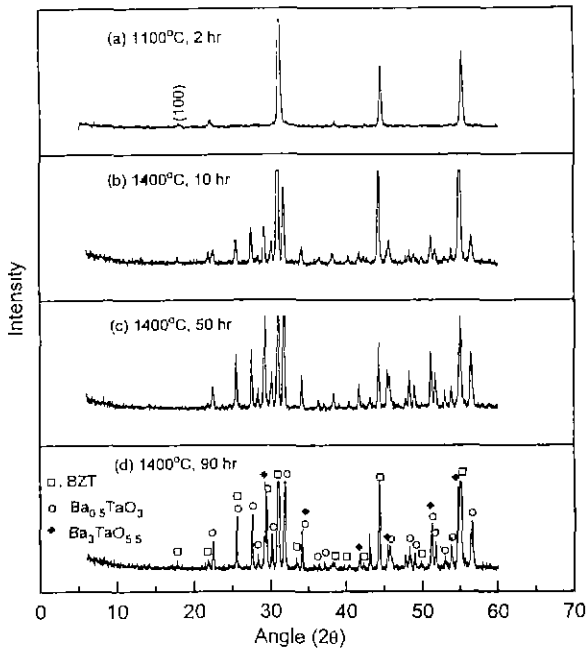


Fig. 1. X-ray spectra of BZT specimens prepared at various processing conditions. (b) (c), and (d) are the spectra taken from the as-sintered surfaces.

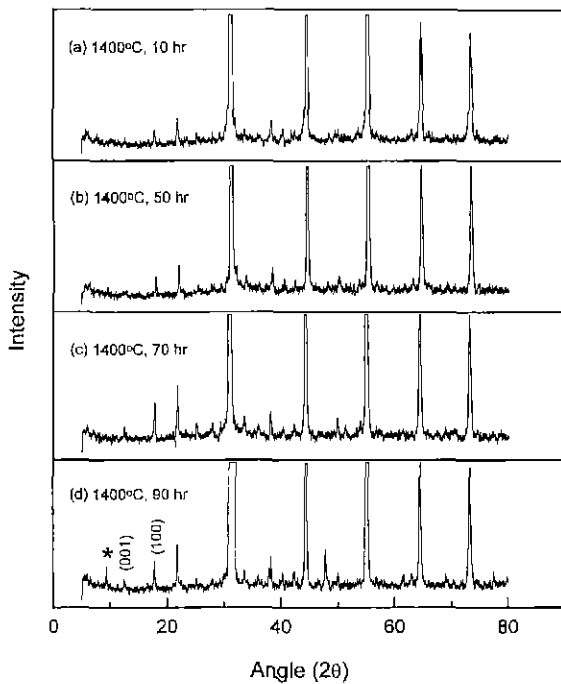


Fig. 2. X-ray spectra taken from the polished surfaces of BZT specimens sintered for various times. Peak indicated by * represents the new type of modulation with approximately 0.9 nm wavelength.

Figure 2 shows X-ray spectra taken from the polished surfaces of the sintered BZT specimens. The intensity of (100) peak increases with the sintering time as observed by previous investigators. (001) peak at 12.9° was also observed in the specimen sintered at 1400°C for 90 hr. Be-

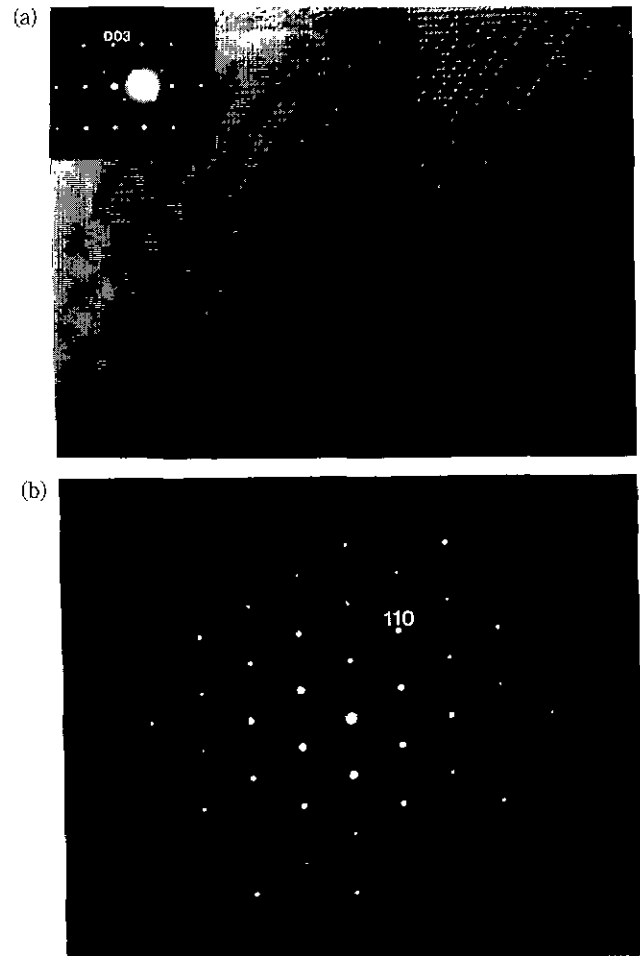


Fig. 3. (a) The [010] zone axis high resolution lattice image and diffraction pattern of specimen sintered at 1400°C for 90 hr. (b) The diffraction pattern of the same specimen with [001] zone axis that is taken from Fig. 3(a).

sides these ordered hexagonal peaks usually observed in prolonged sintered specimen, a new peak indicated by asterisk was observed. The interplanar distance calculated from this extra peak was about 0.9 nm. The existence of this extra peak implies the presence of a new type of modulation with the wavelength of 0.9 nm. In some cases, the extra peak was observed even on the surface of the specimen sintered for 70 hr.

Figure 3(a) is the [010] zone axis high resolution lattice image of specimen sintered at 1400°C for 90 hr. The inset shows the diffraction pattern taken from the same area. As shown in this figure, 1:2 (Zn:Ta) ordering is developed along the c-direction with the wavelength of 0.7 nm. Figure 3(b) shows the diffraction pattern of the same specimen with [001] zone axis. Most of the grains in the specimen have the diffraction patterns shown in Fig. 3 (a) and (b). However, diffraction pattern shown in inset of figure 4 was also observed in the limited area. The analysis revealed that it is the [001] zone axis diffraction pattern with extra reflection at 1/3(110) position. The interplanar distance calculated from the extra re-

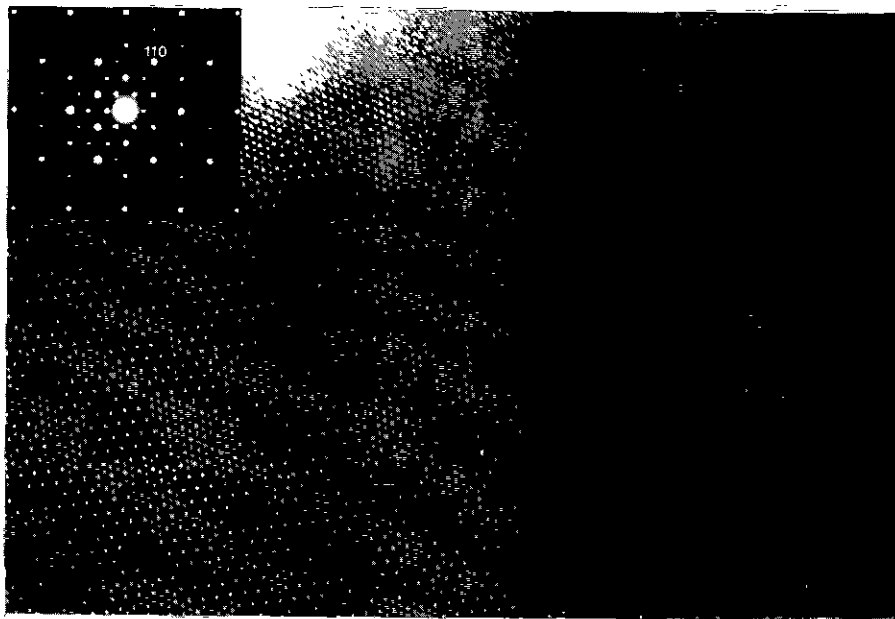


Fig. 4. High resolution lattice image with [001] beam direction showing the modulation along the [110] direction taken from BZT sintered at 1400°C for 90 hr.

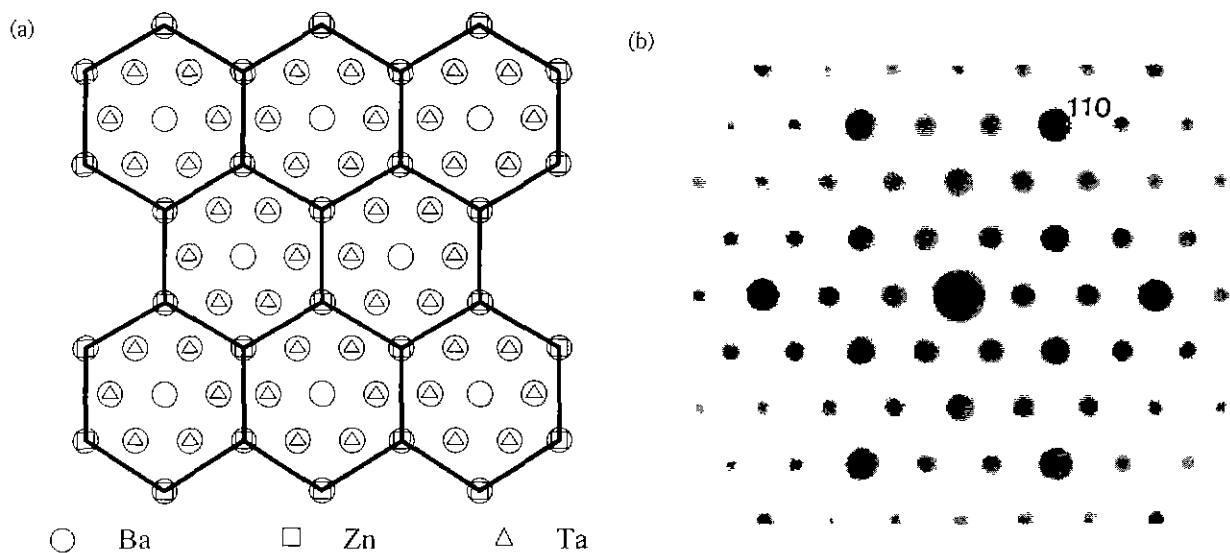


Fig. 5. (a) Ordered Zn vacancy structure projected along the [001] direction. Oxygen atoms were not shown in this figure for convenience, but they were considered for the computer simulation. (b) Computer simulated diffraction pattern with [001] beam direction using the structure shown in Fig. 5(a).

flection was about 0.9 nm which is three times larger than the interplanar distance of (110) plane. The interplanar distance obtained from diffraction pattern was comparable with the result from X-ray measurement. In order to check the possibility of double diffraction, the specimen was tilted about 10° from [001] zone axis exciting only the spots along [110] direction. With this tilting, the intensity of extra reflections increased, and thus it is obvious that the extra reflections were not artifacts caused by double diffraction. High resolution lattice image with [001] beam direction also showed about 0.9 nm modulation along [110] direction (see Fig. 4). Thus, we

come to a conclusion that a new type of ordering exists along [110] direction which is different from 1:2 (Zn:Ta) ordering. The wavelength of the new ordering is about 0.9 nm.

In order to develop a new ordered structure along the [110] direction observed in this study, one of the defects in cation sites should be ordered. We proposed that the new type of ordering along [110] direction is due to the Zn vacancy ordering. Previous works reported that ZnO compound was volatile and the ZnO loss was observed in the specimens sintered at high temperature (>1400°C) or for long time (>60 hr) at 1400°C.¹⁶ Moreover, Desu *et al.*

also suggested that the splitting of (422) and (226) reflections after accomplishment of Zn:Ta ordering is due to the replacement of Zn vacancies by Ba atoms.⁴ Therefore, it is thought that Zn vacancies exist in the specimens sintered at 1400°C for long time (>60 hr) and these vacancies are ordered. A superlattice containing three BZT unit cells is suggested as the unit cell of ordered structure. In this unit cell, Zn vacant sites were located at $(00\frac{1}{2})$. Figure 5(a) shows the ordered Zn vacancy structure projected along the [001] direction. The computer simulation of diffraction pattern was carried out using the structure shown in Fig. 5(a) and the simulation result is shown in Fig. 5(b). The simulated diffraction pattern matches exactly the experimental result shown in inset of Fig. 4. Oxygen atoms were randomly removed to keep the charge neutrality, but the effect on diffraction pattern was negligible.

According to the above analysis of TEM results, Zn vacancies are considered to exist in sintered BZT ceramics. On the basis of this argument, the BZT ceramic body is considered to consist of Zn deficient BZT ($\text{Ba}_3(\square_x\text{Zn}_{1-x}\text{Ta}_2)\text{O}_3$) and $\text{Ba}_x\text{Ta}_y\text{O}_z$ phases (where, \square is vacancy). For the small amount of ZnO loss, only Zn-deficient BZT phases exist. When the amount of ZnO loss increases, new $\text{Ba}_x\text{Ta}_y\text{O}_z$ phases with various values of x, y, and z are considered to be formed. In our specimens, $\text{Ba}_{0.5}\text{TaO}_3$ and $\text{Ba}_3\text{TaO}_{3.5}$ phases were observed. However, we do not exclude the possibility of existence of $\text{Ba}_x\text{Ta}_y\text{O}_z$ phases with other values of x, y, and z.

IV. Conclusions

$\text{Ba}_{0.5}\text{TaO}_3$ and $\text{Ba}_3\text{TaO}_{3.5}$ phases were observed on the as-sintered surface of BZT specimen. This formation of new phases is attributed to the evaporation of volatile ZnO. A new type of ordering was found in BZT specimen

and it is due to Zn vacancies. The direction of ordering is [110] and the wavelength of ordering was about 0.9 nm which is three times larger than the interplanar distance of (110) plane. The unit cell of ordered structure was suggested as superlattice containing three BZT unit cells. Computer simulation of diffraction pattern was carried out using the unit cell and the simulated diffraction pattern matches the experimental result. ZnO loss was explained using a new mechanism.

Acknowledgments

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