

Effects of Y_2O_3 Addition on the Microstructure and Electrical Property of TiO_2 -excess $BaTiO_3$

Jong Han Kim^{1,2,a} and Young Ho Han^{1,b}

¹Department of Advanced Material Engineering, Sungkyunkwan University, 300 Chunchun-dong, Jangan-gu, Suwon 440-746, Korea

²Samsung Electro-mechanics, 314 Maetan3-dong, Youngtong-gu, Suwon 443-803, Korea
^akjh007.kim@samsung.com, ^bCorresponding author: yhhan@skku.ac.kr

Abstract

When Y_2O_3 was added to Ti-excess $BaTiO_3$ ($(Ba+Y)/Ti = 1$), the area occupied by Y^{3+} ion was confirmed by its microstructure development, electrical conductivity behavior and lattice constant. Grain growth inhibition was observed when the content of donor dopant exceeded a critical value ($x \approx 0.01$) in $BaTiO_{3+x}(0.5Y_2O_3+TiO_2)$ system. A donor-doped behavior was observed at various Y contents (0.2~3.0 mol% Y) when Y_2O_3 was added to TiO_2 -excess $BaTiO_3$. As Y content was increased, (002) and (200) peaks shifted to higher angles and the lattice constant (a and c axis) decreased gradually.

Keywords: $BaTiO_3$, Y, electrical conductivity, defects, lattice constant

1. Introduction

The ionic radius of Y^{3+} ion (0.09nm) is somewhere between that of Ba^{2+} ion (0.14nm) and Ti^{4+} (0.06nm) ion. Thus, Y^{3+} can be used on either cation site of $BaTiO_3$ sub-lattice, depending on the Ba/Ti ratio [1]. Recent results showed that Y^{3+} acts like a donor impurity when Y_2O_3 is added to the stoichiometric $BaTiO_3$ ($Ba/Ti=1$) or BaO-excess $BaTiO_3$ [2-3]. Furthermore, according to our recent results, Y_2O_3 addition to Ba-excess $BaTiO_3$ showed a donor-doped behavior at low levels of Y_2O_3 (≤ 1.0 mol%) and an acceptor-doped behavior at higher levels (> 1.0 mol%). This result imply that below 1 mol% Y, Y^{3+} ions preferentially occupy Ba sites even in $BaTiO_{3+x}(BaO+0.5Y_2O_3)$, with excess BaO.

In this paper, the effect of yttrium addition on electrical conductivities of Ti-excess $BaTiO_3$ ($(Ba+Y)/Ti = 1$) is investigated. The occupancy of the [] site by yttrium will be discussed in terms of microstructure development, equilibrium electrical conductivity and lattice constant.

2. Experimental and Results

Samples were prepared by a conventional ceramic processing and using $BaTiO_3$ (Sakai BT04), TiO_2 (Aldrich) and Y_2O_3 (NanoTek). These samples were sintered at 1300 °C for 3 h in air. The conductivity was measured at 1100 °C using a four point d.c. method. The desired oxygen partial pressure was obtained by using N_2-O_2 and $CO-CO_2$. The oxygen activity was measured using a closed-end tube of stabilized zirconia. Figure 1 shows the microstructures of specimens having nominal compositions of

$BaTiO_{3+x}(0.5Y_2O_3+TiO_2)$ where $x = 0, 0.002, 0.005, 0.01, 0.02, \text{ and } 0.03$. At lower levels of Y addition, larger grains were developed as shown Fig. 1(a) ~ (c), whereas the grain growth was suppressed at higher Y levels as shown in Fig. 1(d) ~ (f). A significant grain growth inhibition was observed at the doping level of 1.0 mol% Y, compared with 0.5 mol% Y. This result is similar to the window of grain growth inhibition threshold (GGIT) of donor doped $BaTiO_3$ with TiO_2 excess [2-5]. Figure 2 shows the electrical conductivity profiles measured as a function of oxygen partial pressure at 1100 °C. The electrical conductivity profiles of TiO_2 -excess $BaTiO_3$ with 0.5 mol% or 1.0 mol% Y showed a donor-doped behavior as in Fig. 2. When Y^{3+} ions used as donor in the Ba sites, Y_{Ba} is compensated either by electrons or by cation vacancies [6-7]. The electrical conductivity at low P_{O_2} (reduced atmosphere) increases with Y contents, which indicates that Y_{Ba} is compensated by electrons. At the ambient atmosphere, electrical conductivities follow the $-1/4^{\text{th}}$ power of P_{O_2} [6,8,9]. This implies that Y^{3+} ions effectively substituted for Ba sites and are compensated by cation vacancies at higher P_{O_2} . Figure 3 shows partial X-ray diffractograms for $BaTiO_3$ doped with various levels of Y_2O_3 . As Y content was increased, (002) and (200) peaks shift to higher angles, leading to the contraction of $BaTiO_3$ unit cell. These samples were quenched after sintering at 1300°C for 3 h, preventing significant diffusion and segregation of dopants and defects. Since the ionic radius of Y^{3+} ion (0.09nm) is somewhere between that of Ba^{2+} ion (0.14nm) and Ti^{4+} (0.06nm) ion, the lattice constant may decrease with increasing the yttrium substitution for Ba sites (Y_{Ba}). This result supports that Y^{3+} ions replace Ba sites in $BaTiO_{3+x}(0.5Y_2O_3+TiO_2)$.

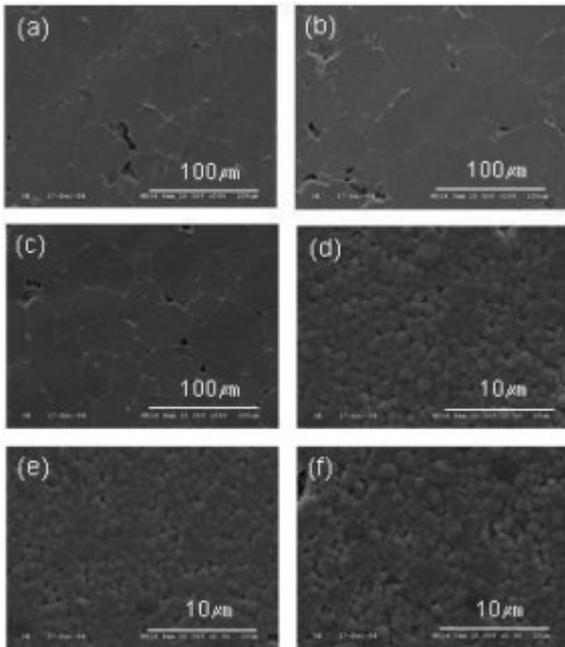


Fig. 1. SEM photomicrographs of $\text{BaTiO}_3 + x(0.5\text{Y}_2\text{O}_3 + \text{TiO}_2)$ sintered at 1300°C for 3 h: (a) un-doped BaTiO_3 (b) $x = 0.002$, (c) $x = 0.005$, (d) $x = 0.01$, (e) $x = 0.02$, (f) $x = 0.03$

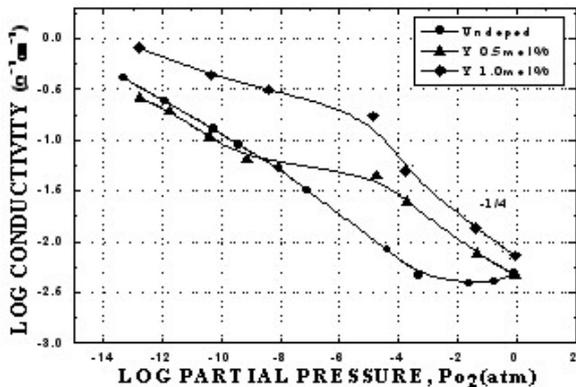


Fig. 2. Electrical conductivity at 1100°C of $\text{BaTiO}_3 + x(0.5\text{Y}_2\text{O}_3 + \text{TiO}_2)$

This data is compatible with the equilibrium electrical conductivity behavior shown in Fig. 2, where the donor doped-behavior was clearly obvious.

3. Summary

The Y_2O_3 addition to Ti-excess BaTiO_3 ($(\text{Ba} + \text{Y})/\text{Ti} = 1$) showed a typical microstructure development; larger grains were observed at low levels (≤ 0.5 mol% Y) and small and uniform grain size distribution, at high levels (≥ 1.0 mol %). Equilibrium electrical conductivity data followed the $-1/4^{\text{th}}$ sloped of oxygen partial pressure dependence at near ambient. As Y content was increased, (002) and (200) peaks

shifted to higher angles and the lattice constant (a and c axis) decreased gradually. These results confirms that Y^{3+} ions preferentially occupy Ba sites when $\text{Ba}/\text{Ti} < 1$.

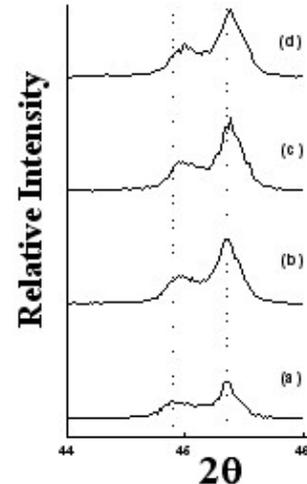


Fig. 3. Partial X-ray diffractogram for $\text{BaTiO}_3 + x(0.5\text{Y}_2\text{O}_3 + \text{TiO}_2)$: (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.03$.

4. References

1. Y. Tsur, T. D. Dunbar and C. A. Randall : J. Electroceram. Vol.7 (2001), p. 25
2. L. A. Xue, Y. Chen and J. Brook : Materials Science and Engineering Vol. B1 (1988), p. 193
3. M. H. Lin and H. Y. Lu : Mater. Sci. Eng. Vol. A335 (2002), p. 101
4. C. J. Peng, and H. Y. Lu : J. Am Ceram. Soc. Vol. 71[1] (1988), p. C44
5. C. J. Ting, C. J. Peng, H. Y. Lu and S. T. Wu : J. Am Ceram. Soc. Vol. 73 (1990), p. 329
6. J. H. Jeong, M. G. Park and Y. H. Han : J. Electroceram. Vol. 13 (2004), p. 805
7. K. Takada, E. Chang and D. M. Smyth : Adv. in Cera. Vol. 19 (1986), p. 147
8. N. H. Chan, and D.M. Smyth : J. Am. Ceram. Soc. Vol. 67 (1984), p. 285
9. J. Daniels and K. H. Härdtl : Philips Res. Repts. Vol. 31 (1976), p. 489