



Defect Chemistry of Y Doped BaTiO₃

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Abstract. Defect chemistry of Y doped BaTiO₃ was investigated as a function of the Ba/Ti ratio. When the Ba/Ti ratio was greater than unity, Y³⁺ was substituted for the normal Ti site and the equilibrium conductivity showed a strong evidence of acceptor-doped behavior. With the Ba/Ti ratio < 1, Y³⁺ was substituted for the Ba site and the equilibrium conductivity showed donor-doped behavior. In the case excess Y₂O₃ was added to the stoichiometric BaTiO₃ (Ba/Ti = 1), the conductivity profile showed a donor-doped behavior at low concentrations (<1.0 mol%), whereas, at higher donor levels (>2.0 mol%), the equilibrium conductivity minimum shifted toward lower P_{O₂}, indicating acceptor doped behavior.

Keywords: BaTiO₃, Y₂O₃, conductivity, nonstoichiometry, solubility

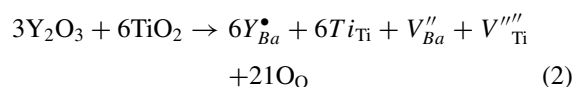
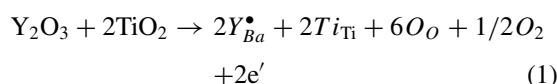
1. Introduction

Y₂O₃ is known as an effective additive for improving the insulating resistance of multilayer ceramic capacitor (MLCC) with Ni-electrodes [1]. There have been reported two different models to explain the improvement in the life time of Y₂O₃ doped BaTiO₃. Nakano et al. suggested the A-site model that Y³⁺ ion acts as donor and reduces the concentration of the oxygen vacancies accompanied by acceptor type dopant such as MnO [1]. Hitomi et al. proposed the B-site model that Y³⁺ ion acts as acceptor and reduces the bulk diffusivity of oxygen vacancies through strain and electric field interactions [2]. It is thus necessary to understand the defect chemistry of Y-doped BaTiO₃ and define the role of Y₂O₃ on the degradation behavior of MLCC with Ni-electrodes.

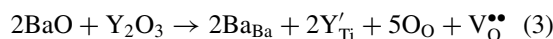
The size of Y³⁺ ion (0.9 Å) is almost halfway between Ba²⁺ ion (1.4 Å) and Ti⁴⁺ ion (0.6 Å). Thus, Y³⁺ could be accommodated on either cation site in BaTiO₃ lattices, depending on the Ba/Ti ratio [3]. It was reported that Y³⁺ acts as acceptor in the presence of excess BaO (Ba/Ti > 1) and as a donor in the pres-

ence of excess TiO₂ (Ba/Ti < 1) [4, 5]. It was also suggested that Er³⁺ can occupy both Ba²⁺ site and Ti⁴⁺ site simultaneously, bringing about the donor-acceptor self-compensation [4, 6]. However, Xue et al. reported that Y³⁺ shows a clear donor character when Y₂O₃ is added to the stoichiometric BaTiO₃ (Ba/Ti = 1) [5], while Er³⁺ exhibits predominantly self-compensating behavior [6]. Possible modes of incorporation reaction of Y³⁺ ions into BaTiO₃ lattices are as follows:

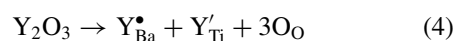
(i) Y substitution for Ba sites (Ba/Ti < 1): donor



(ii) Y substitution for Ti sites (Ba/Ti > 1): acceptor



(iii) Equal population of Y ions on Ba sites and Ti sites (Ba/Ti = 1): self-compensation



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The defect notation is that proposed by Kroger and Vink [7]. According to Eqs. (1) and (2), Y ion carries an excess positive charge relative to the ideal Ba lattice. Thus, for the maintenance of charge neutrality condition, Y_{Ba}^{\bullet} could be compensated by electrons or by cation vacancies such as Ba vacancy and/or Ti vacancy [8–10]. However, for the cation vacancy compensation, a consistent defect model is not established yet. The defect species, Y_{Ti}' is compensated by the corresponding number of oxygen vacancies as shown in Eq. (3) [11, 12]. Equation (4) shows that Y^{3+} may replace both cation sites and give rise to self-compensation, i.e. donor-acceptor compensation [4, 5]. In this paper, the defect chemistry of Y doped $BaTiO_3$ will be discussed in terms of the solubility, acceptor and donor behavior, and mode of substitution of Y into $BaTiO_3$ lattices.

2. Experimental Procedure

Y-doped $BaTiO_3$ powders were prepared using the liquid mix method developed by Pechini [13]. Each sample composition was prepared by polymerization and calcination of an organometallic solution containing precisely determined amounts of the metallic components as described in the previous work [14]. The calcined powders were pressed into rectangular bars at 150 MPa. The samples were sintered at 1320°C for 5 h in air and furnace-cooled. The conductivity was measured with a four-point dc technique, using constant applied current to maintain a voltage drop of ~ 0.5 V in the temperature range 1200°C to 1300°C. The desired oxygen partial pressures were obtained from mixtures of N_2 - O_2 and CO - CO_2 . The effect of Y_2O_3 addition on the microstructure development was investigated for the as-fired surface of the sintered body using a scanning electron microscope.

3. Results and Discussion

Figure 1 shows the equilibrium electrical conductivity profiles measured as a function of oxygen partial pressure, at 1200°C, for the samples of $Ba(Ti_{1-x}Y_x)O_{3-0.5x}$ with $x = 0, 0.002, 0.02, 0.03$ and 0.05 . As Y^{3+} is substituted for the Ti sites up to 2.0 mol%, the conductivity increases in the p -type region and decreases in the n -type region around the conductivity minimum, and the conductivity minimum shifts to lower P_{O_2} , which

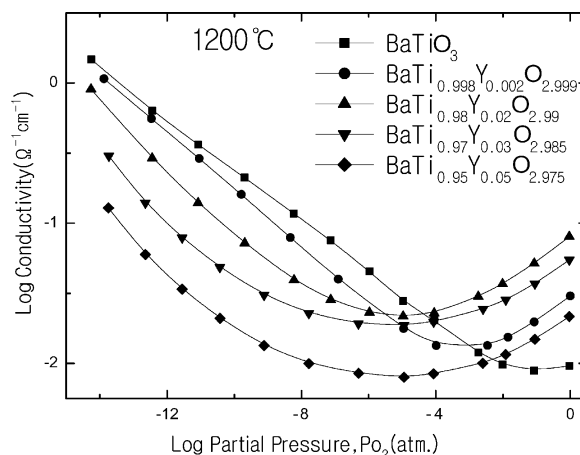


Fig. 1. Equilibrium electrical conductivity of $Ba(Ti_{1-x}Y_x)O_{3-0.5x}$ ($x = 0, 0.002, 0.02, 0.03$ and 0.05).

is similar to the previous reports of acceptor-doped $BaTiO_3$ [11, 12]. The substitution of Y^{3+} for Ti^{4+} generates charged defects, the negatively charged defect Y'_{Ti} will be formed, and the corresponding number of positively charged oxygen vacancies will satisfy the site balance and charge neutrality condition according to Eq. (3). Addition of Y_2O_3 as acceptor impurities also causes the conductivity minima to be flattened as shown Fig. 1. The broad and flattened conductivity minimum is typical for acceptor-doped samples and due to the contribution of the P_{O_2} -independent ionic conduction which results from the extrinsic oxygen vacancies introduced by the acceptor impurity [11, 15]. As the Y content was increased further to 3.0 mol% and greater, the conductivity showed a general suppression of the entire curve compared with $Ba(Ti_{0.98}Y_{0.02})O_{2.99}$. This indicates that the solubility limit for Y'_{Ti} is assumed to be equal to ~ 3.0 mol% or less, even though the observed solubility is dependent on the precise processing details such as sintering time and temperature [6].

It is well known that $BaTiO_3$ doped with small amounts of donor impurities (<0.5 mol%) on either A or B sites exhibits a semiconducting behavior due to the electronic compensation as expressed in Eq. (1), and then reverts to the cation vacancy compensation mode as shown in Eq. (2), such as V''_{Ba} and V''_{Ti} , resulting in insulating materials for donor concentrations greater than 0.5 mol% [8, 9]. It was reported that the equilibrium electrical conductivity follows the $-1/4$ th power dependence of P_{O_2} when the donor impurities are compensated by cation vacancies such as Ba vacancy and/or Ti vacancy [16]. Figure 2 shows the

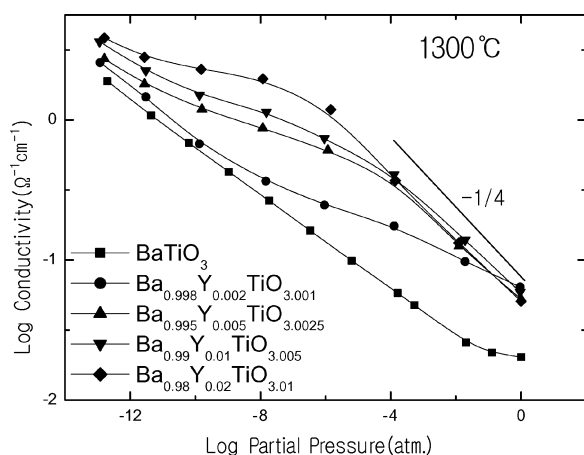


Fig. 2. Equilibrium electrical conductivity of $(\text{Ba}_{1-x}\text{Y}_x)\text{TiO}_{3+0.5x}$ ($x = 0, 0.002, 0.005, 0.01$ and 0.02).

equilibrium electrical conductivity profiles measured as a function of oxygen partial pressure, at 1300°C , for the samples of $(\text{Ba}_{1-x}\text{Y}_x)\text{TiO}_{3+0.5x}$ with $x = 0, 0.002, 0.005, 0.01$ and 0.02 . When Y^{3+} is substituted for Ba sites as a donor, Y^{3+} is compensated either by electrons or by cation vacancies. At a heavily reduced atmosphere, Y^{3+} is compensated by electron, whereas in ambient atmosphere, Y^{3+} is compensated by metal vacancies and the conductivity profile shows the $-1/4$ th dependence of oxygen partial pressure. This conductivity behavior is similar to the previous results on the donor doped BaTiO_3 [10, 16]. The electrical conductivity at low Po_2 gradually increases with Y content, which indicates that $\text{Y}_{\text{Ba}}^\bullet$ is compensated by electrons according to Eq. (1). At the ambient atmosphere, conductivities follow the $-1/4$ th power Po_2 dependence by the cation vacancy compensation.

Figure 3 shows the equilibrium electrical conductivities as a function of oxygen partial pressure, at 1300°C , for the samples of $(\text{BaY}_x)(\text{TiY}_x)\text{O}_3$ with $x = 0, 0.005$, and 0.01 . When 1.0 mol% ($x = 0.005$) Y was added to the stoichiometric BaTiO_3 , the conductivity profile showed a donor-doped behavior. However, with 2.0 mol% ($x = 0.01$), the equilibrium conductivity is separated by a minimum and the conductivity minimum shifts toward lower Po_2 , indicating the acceptor doped behavior. This implies that at lower levels of Y_2O_3 addition, Y^{3+} ions effectively incorporate into Ba sites instead of Ti sites, whereas at higher levels (>0.5 mol%) the cation vacancy compensation mode as shown in Eq. (2) is predominant for the Ba site defect ($\text{Y}_{\text{Ba}}^\bullet$) and the Ti site substitution of $\text{Y}(\text{Y}_{\text{Ti}}')$ will

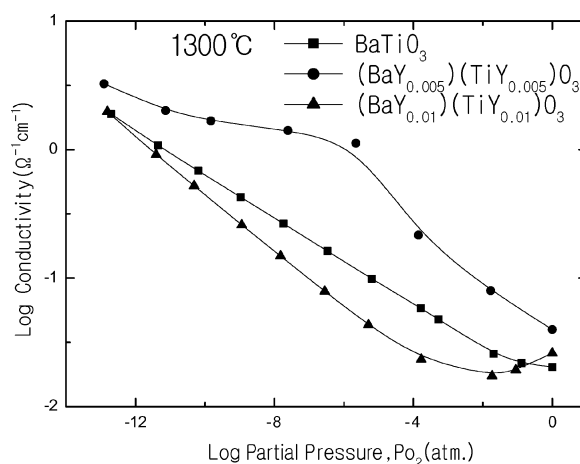


Fig. 3. Equilibrium electrical conductivity of $(\text{BaY}_x)(\text{TiY}_x)\text{O}_3$ ($x = 0, 0.005$ and 0.01).

accompany oxygen vacancies. Thus when 1.0 mol% Y was added to BaTiO_3 with $\text{Ba}/\text{Ti} = 1.000$, this was within the solubility limit on both sites, and the results indicate some small preference for A-sites, which gave donor-doped behavior. When 2.0 mol% Y was added, however, the A-sites could accept less than half of this, while the B-sites could accept more than 1.0 mol%, so the net result was acceptor-doped behavior. This explains why the behavior switched from donor-doped to acceptor-doped when the Y level was increased from 1.0 to 2.0 mol%. This incorporation behavior is totally different from the self-compensation mode of the Er-substitution into BaTiO_3 [6].

The microstructures of $\text{Ba}(\text{Ti}_{1-x}\text{Y}_x)\text{O}_{3-0.5x}$ samples with $x = 0, 0.002, 0.02, 0.03$ and 0.05 are shown in Fig. 4. When Y content was greater than 2.0 mol%, poor densifications were observed with a large amount of residual porosity. The overall suppression of electrical conductivities of the specimen ($x = 0.03$ and 0.05) in Fig. 1 may be attributed to the interference with conduction processes by the poor densification of sintered specimens (75% theoretical density for $x = 0.03$ and 52% for $x = 0.05$). This also supports that the solubility limit of Y on the Ti site is less than 3.0 mol%. It is well known that BaTiO_3 doped with more than 0.5 mol% of donor impurities yields cation vacancy compensation and results in the material being fine-grained (1–2 μm) [17]. In Fig. 5, at the low level of Y-substitution ($x = 0.2$ mol%), the grain size is fairly large, whereas at the Y-substitution larger than 0.5 mol%, the grain size significantly decreases. This is in good agreement with the previous results [17, 18]

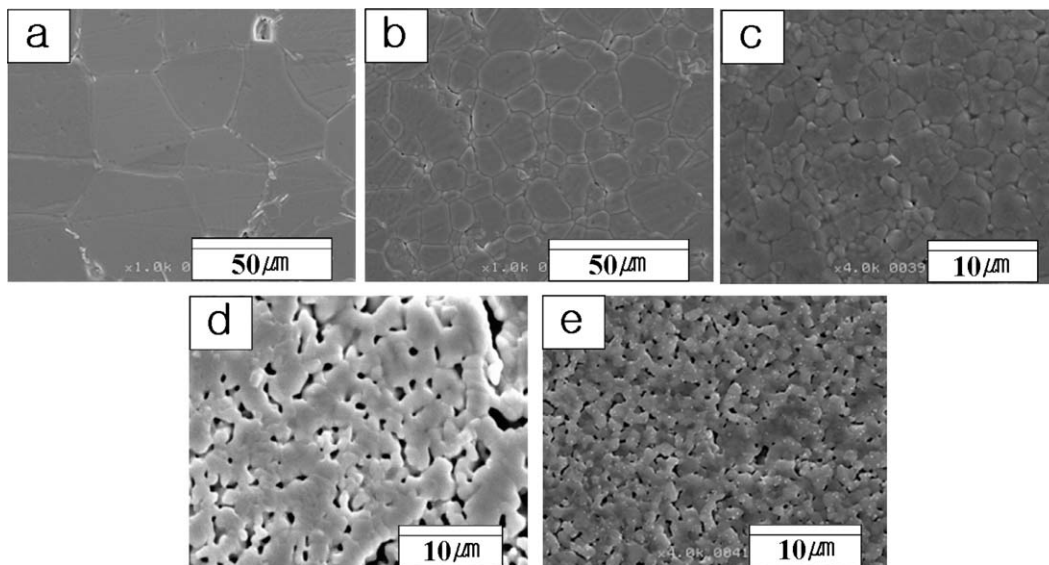


Fig. 4. Microstructure of (a) BaTiO₃, (b) BaTi_{0.998}Y_{0.002}TiO_{2.999}, (c) BaTi_{0.98}Y_{0.02}O_{2.99}, (d) BaTi_{0.97}Y_{0.03}O_{2.985} and (e) BaTi_{0.95}Y_{0.05}O_{2.975} sintered at 1320°C for 5 hr.

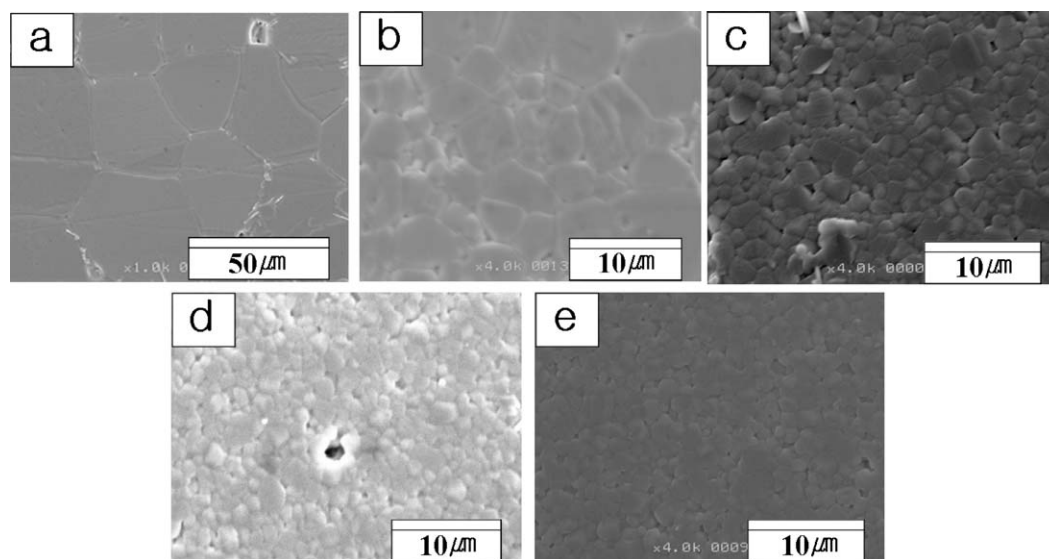


Fig. 5. Microstructure of (a) BaTiO₃, (b) Ba_{0.998}Y_{0.002}TiO_{3.001}, (c) Ba_{0.995}Y_{0.005}TiO_{3.0025}, (d) Ba_{0.99}Y_{0.01}TiO_{3.005} and (e) Ba_{0.98}Y_{0.02}TiO_{3.01} sintered at 1320°C for 5 hr.

and confirms the Y substitution for Ba sites as a donor impurity. Figure 6 shows the microstructures of (BaY_x)(TiY_x)O₃ having $x = 0, 0.005$ and 0.01 . The sample doped with 1.0 mol% ($x = 0.005$) showed small grain sizes about 2μm, whereas the sample doped with 2.0 mol% ($x = 0.01$) exhibited larger

grain sizes. This microstructural development is consistent with electrical conductivities shown in Fig. 3. The specimen with small grains ($x = 0.005$) exhibits donor-doped behavior, whereas the large grained microstructure ($x = 0.01$) in Fig. 6(c) is compatible with the acceptor-doped behavior.

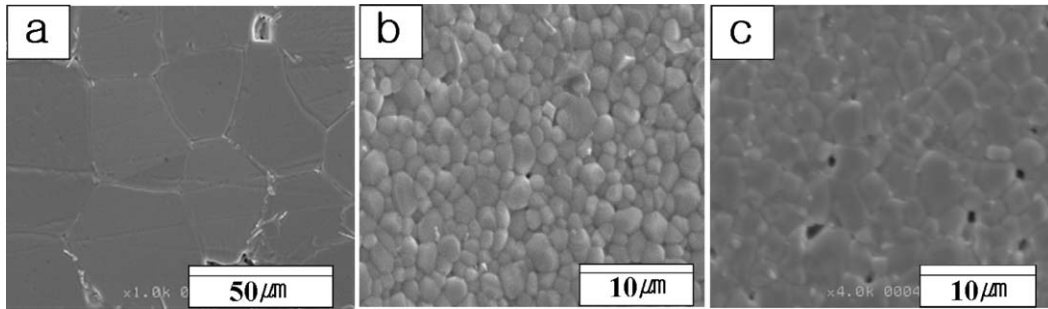


Fig. 6. Microstructure of (a) BaTiO₃, (b) (BaY_{0.005})(TiY_{0.005})O₃ and (c) (BaY_{0.01})(TiY_{0.01})O₃ sintered at 1320°C for 5 hr.

4. Conclusions

The substitution of Y³⁺ for the Ti site in Ba(Ti_{1-x}Y_x)O_{3-0.5x} led to a significant shift in the conductivity minimum and showed an acceptor-doped behavior. When Y content was larger than 2.0 mol%, poor densifications were observed with a large amount of residual porosity. The solubility of Y on the Ti site was confirmed to be less than 3.0 mol%. The equilibrium electrical conductivity of (Ba_{1-x}Y_x)TiO_{3+0.5x} follows the -1/4th power Po₂ dependence at the high oxygen activity region, which indicates that Y³⁺ is compensated by metal vacancies in ambient atmosphere. When 1.0 mol% Y was added to the stoichiometric BaTiO₃, the conductivity profile showed a donor-doped behavior, whereas with 2.0 mol%, the equilibrium conductivity is separated by a minimum and the conductivity minimum shifts toward lower Po₂, indicating acceptor doped behavior. It was thus confirmed that Y can be substituted for Ba or/and Ti sites depending on the Ba/Ti ratio because of the intermediate ionic radius.

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