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Defect Chemistry of BaTiO₃ under Nonstoichiometric Ba/Ti Ratio

Jin Hyun HWANG and Young Ho HAN

Department of Materials Engineering, Sungkyunkwan University (Suwon, 440-746 Korea)

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The equilibrium electrical conductivity of polycrystalline BaTiO₃ with nonstoichiometric Ba/Ti ratio was studied over the oxygen partial pressure of 10⁻¹⁵ to 1 atm, at temperatures higher than 1200°C. Conductivity results showed that more TiO₂ was incorporated into BaTiO₃ solid solution, resulting in the conductivity minimum shift. The oxygen vacancy content due to the extra TiO₂ was about three times as high as that of the stoichiometric composition, estimating from the relative position of the conductivity minimum. In contrast, the conductivity minimum of BaO excess samples was not shifted, which implies that the solubility of extra BaO in BaTiO₃ could not significantly exceed the background acceptor impurity (100 ppm). It is believed that the extrinsic oxygen vacancy due to the excess TiO₂ in BaTiO₃ could affect the microstructure development and dielectric degradation behavior.

Key Words : BaTiO₃, Conductivity, Microstructure, Degradation

1 Introduction

The effect of cation nonstoichiometry *i.e.*, BaO or TiO₂ excess on the defect chemistry of BaTiO₃ has been studied by several investigators.¹⁻³⁾ Sharma *et al.* studied the effect of excess TiO₂ on the equilibrium conductivity at 1000°C, confirming that the solubility of excess TiO₂ is no more than 100 ppm in BaTiO₃.²⁾ They also reported Ba₆Ti₁₇O₄₀ as a second phase in polycrystalline samples with Ba/Ti ≤ 0.999, and whatever amount does go into the solid solution could not affect the equilibrium electrical conductivity. Hu *et al.*¹⁾ pointed out that the solubility of excess BaO could not exceed 100 ppm and BaO is practically insoluble, which is in agreement with the phase work of Rase and Roy⁴⁾ who showed no solubility for BaO in BaTiO₃ over the temperature range 1200°C to 1600°C. The most probable incorporation reactions of excess BaO and TiO₂ into the BaTiO₃ lattice are given as, respectively,

It is assumed that V_{Ba}' , V_{Ti}'' , and V_{O}'' are the preferred defects for the incorporation of excess BaO and TiO₂, the alternative choices of Ti_{Ti}'' and O_i' , Ti_{Ba}' and O_i' , or Ba_i' and O_i' being less probable in the close-packed structure.

Masurement of the equilibrium conductivity as a function of oxygen partial pressure is a sensitive test for changes in the concentration of extrinsic oxygen vacancy, $[V_{\text{O}}'']_{\text{ext}}$. This oxygen vacancy stems from the compensation of acceptor impurities or from excess BaO and TiO₂ as depicted in Eqs. (1) and (2). The shift of $\text{Po}_2(\text{min})$ with extrinsic oxygen vacancy content, $[V_{\text{O}}'']_{\text{ext}}$, can be expressed as⁵⁻⁸⁾

$$\frac{d \log \text{Po}_2(\text{min})}{d \log [V_{\text{O}}'']_{\text{ext}}} = -2 \quad (3)$$

At a given temperature, the minimum moves to lower Po_2 by the square of the factor increase in $[V_{\text{O}}'']_{\text{ext}}$. Thus, its relative position as a function of oxygen partial pressure is a convenient measure of the incorporation of excess BaO and TiO₂ according to Eqs. (1) and (2).

Based on the equilibrium conductivity data at 1000°C by several investigators, the absence of significant solubility for either BaO or TiO₂ have indicated that none of the possible incorporation reactions including Eqs. (1) and (2) conserving the basic perovskite structure are very favorable. However, this seems to be a little qualitative. In other words, we should confirm the accommodation of excess BaO and TiO₂ into BaTiO₃ lattice by measuring the equilibrium conductivity at temperatures higher than 1200°C, close to the sintering temperature, leading to the better understanding of the defects and structural changes in the BaTiO₃ system. A study has shown that BaTiO₃ containing cation vacancies for the compensation of donor impurities is likely to follow the equilibrium state with atmosphere at the high temperatures between 1200°C and 1400°C.⁹⁾

In this paper, we present conductivity measurements on BaTiO₃ with cation nonstoichiometry at temperatures higher than 1200°C to see whether excess BaO and TiO₂ could be incorporated into BaTiO₃ lattice, resulting in additional oxygen vacancies even though the previous equilibrium conductivity data measured at 1000°C shows no solubility for either cation excess in BaTiO₃.¹⁻³⁾ Microstructure and leakage current as a function of cation nonstoichiometry were also investigated.

2 Experimental Procedure

Powders of precisely determined composition of BaTiO₃ with different Ba/Ti ratios were prepared by the liquid mix method developed by Pechini.¹⁰⁾ Each sample was prepared by polymerization and calcination of an organometallic solution containing exact amounts of the in-

gradient components as described in the previous work.^{2, 5)} The calcined powders were pulverized into fine powder and pressed into rectangular bars at 1.5 ton/cm² followed by air sintering at 1380°C for 5 h. Platinum paint was applied onto both ends of each sample and fired at 900°C to serve as current leads. The conductivity was measured using a four-point d.c. technique in the temperature range 1000°C to 1300°C. The desired oxygen partial pressures were obtained from the mixture of N₂-O₂ or CO-CO₂. The resulting oxygen activity was determined by the emf measurement of a closed-end tube of stabilized zirconia. The effect of cation nonstoichiometry on grain size was investigated on the as-fired surface of sintered body using a scanning electron microscope. Leakage currents were measured under a continuously applied dc field.

3 Results and Discussion

Figure 1 shows the equilibrium electrical conductivities of undoped BaTiO₃ as a function of oxygen activity, $P(\text{O}_2)$, at a series of temperatures, which are similar to the previous report of SrTiO₃.¹¹⁾ The oxygen excess p-type region and oxygen deficient n-type region is separated by the conductivity minima which correspond to the completely compensated stoichiometric state, neglecting mobility differences. As the sample is reduced in the n-type condition region, any oxygen leaving a normal oxygen site forms oxygen vacancies and adds two electrons to the crystal while the conductivity increases with decreasing $P(\text{O}_2)$. In the p-type conduction region, extrinsic oxygen vacancies due to background acceptor impurities are filled and electron holes for the incorporation of oxygen are formed while the conductivity increases with increasing $P(\text{O}_2)$. At the conductivity minimum, intrinsic electronic disorder contributes to electrical conduction and there is no contribution from excess or deficient oxygen. As can be seen in Fig. 1, the n-type region prevails with increasing temperature and the p-type region disappears at the temperature higher than 1300°C. This indicates that electrical conductivity is proportional to the degree of oxygen deficiency all over the $P(\text{O}_2)$ measured.

Fig. 1 Equilibrium electrical conductivity of undoped BaTiO₃ (Ba/Ti = 1.000). Lines having ideal slope are indicated for reference.

Equilibrium electrical conductivity profiles measured at 1200°C and 1300°C for samples having Ba/Ti ratios of 1.000, 0.998, 0.996, and 0.994 are shown in Figs. 2(a) and (b), respectively. To a lesser extent, a slight shift in $P_{\text{O}_2}(\text{min})$ has been observed in both cases. Cation nonstoichiometry with excess TiO₂ shifts the conductivity minima to lower oxygen pressures, implying an increase in the concentration of extrinsic oxygen vacancy according to Eq. (2). There is no difference in the position of $P_{\text{O}_2}(\text{min})$ for the samples with Ba/Ti = 0.998 to 0.994, but rather a general increasing of the entire conductivity curve for Ba/Ti = 0.996 and 0.994. This generally upward movement may result from the difference in microstructure by increasing amounts of excess TiO₂. The position of $P_{\text{O}_2}(\text{min})$ for the sample with 0.2 mol% excess TiO₂ relative to that of the undoped BaTiO₃ with stoichiometric composition corresponds to an increase in oxygen vacancy content. It is approximately estimated at 300 ppm if $[V_{\text{O}}^{\bullet}]_{\text{ext}}$ due to accidental acceptor impurities was assumed 100 ppm molar in the undoped sample, calculating from the relative position of the conductivity minima given by Eq. (3). It appears that the samples are saturated with TiO₂ since the total amount of excess TiO₂ available with this composition is 2000 ppm. These phenomena are already seen in SrTiO₃⁷⁾ and CaTiO₃¹²⁾ to much more extent, but contradict the findings of Sharma *et al.*²⁾ and Chan *et al.*,³⁾ who found $P_{\text{O}_2}(\text{min})$ to lie at

Fig. 2 a) Equilibrium electrical conductivity as a function of Ti-excess at 1200°C.

Fig. 2 b) Equilibrium electrical conductivity as a function of Ti-excess at 1300°C.

the same position for BaTiO_3 with excess TiO_2 . They reported that the solubility of TiO_2 was less than 100 ppm and had no effect on the conductivity profiles at 1000°C . Comparing with their results, the measuring temperature of higher than 1200°C could increase the solubility of TiO_2 and lead the subtle movement of conductivity minima which results from the cation nonstoichiometry.

The effect of excess BaO on the conductivity profiles of BaTiO_3 measured at 1200°C and 1300°C are shown in Figs. 3(a) and (b), respectively. Unlike excess TiO_2 cases, there is no discernible shift in $\text{Po}_2(\text{min})$ due to the solubility of excess BaO according to Eq. (1). None of the conductivity minimum shift indicates that the concentration of oxygen vacancy due to excess BaO is negligibly small, which is in agreement with the previous results measured at 1000°C and below.¹⁾ According to the theoretical calculations of defect energetics in BaTiO_3 by Lewis and Catlow,^{13,14)} excess BaO could be more easily accommodated by the formation of relatively favorable defects involving V_{Ti}'' rather than V_{Ba}'' for the case of excess TiO_2 . However, the measured low solubility of BaO in BaTiO_3 indicates that the accommodation of excess BaO by point defect formation is energetically unfavorable and the maximum concentration of free oxygen vacancies created by the solution of excess BaO in BaTiO_3 could not exceed 100 ppm. Comparing the shift in the conduc-

tivity minima resulting from 0.2 mol% excess TiO_2 with from 0.4 mol% excess BaO as shown in Figs. 2 and 3, it appears that TiO_2 is slightly more soluble than BaO in BaTiO_3 as in the case of SrTiO_3 .⁷⁾

A microstructure development was investigated on the samples with excess TiO_2 to see whether any increase in the oxygen vacancy content by the accommodation of TiO_2 in BaTiO_3 could expedite the sintering rate. As shown in Figs. 4(a) to (c), grain size was slightly increased with excess TiO_2 . This small difference could account for the presence of V_{O}'' . Since sintering was done at 1215°C , far below eutectic temperature, eutectic and twin-assisted growth mechanisms¹⁵⁾ can be ruled out. Thus, the oxygen vacancy concentration resulting from the incorporation of TiO_2 as depicted in Eq. (2) is likely to affect the diffusion rate, which is in reasonable agreement with the experimentally obtained conductivity data in Fig. 2. Figs. 4(d) to (f) show the micrographs of the samples having excess BaO, Ba/Ti ratios of 1.002, 1.004, and 1.006, respectively. The grain size of the samples with excess BaO becomes smaller comparing with the stoichiometric composition (Fig. 4(a)). This is in agreement with the observation of Kulscar that BaO acts as a grain-refiner.¹⁶⁾ No significant change in grain size was observed with excess BaO contents from 0.2 to 0.6 mol %, supporting the electrical conductivity profiles. The conductivity and micrograph results in Figs. 2 and 4 support a slight solubility of excess TiO_2 in BaTiO_3 .

It is well known that oxygen vacancies are the most mobile species in BaTiO_3 lattice and the electromigration of charged oxygen vacancies in dc fields is accountable for the electrical degradation of BaTiO_3 -based ceramic capacitors.¹⁷⁻¹⁹⁾ The degradation behavior of undoped BaTiO_3 at 100°C under a continuously applied dc field of 4.5 kV/cm is presented as a function of Ba/Ti ratios in Fig. 5. The TiO_2 -rich composition, especially Ba/Ti = 0.996, degraded more rapidly than stoichiometric or BaO-rich compositions. This is in accord with the study of the leakage current of BaTiO_3 with excess TiO_2 by Harmer *et al.*¹⁸⁾ They suggested that a second phase identified as $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ might be responsible for the observed degradation. However, the exact roles of the second phase to

Fig. 3 a) Equilibrium electrical conductivity as a function of Ba-excess at 1200°C .

Fig. 3 b) Equilibrium electrical conductivity of BaTiO_3 and $\text{Ba}_{1.002}\text{TiO}_3$ at 1300°C .

Fig. 4 Microstructure of Ti-excess and Ba-excess BaTiO at 1215°C for 38 hr (bar: $20\mu\text{m}$). a) stoichiometric comp. (Ba/Ti: 1.000), b) 0.2mol% Ti excess (Ba/Ti: 0.998), c) 0.4mol% Ti excess (Ba/Ti: 0.996), d) 0.2mol% Ba excess (Ba/Ti: 1.002), e) 0.4mol% Ba excess (Ba/Ti: 1.004), f) 0.6mol% Ba excess (Ba/Ti: 1.006).

Fig. 5 Degradation behavior of undoped BaTiO₃ at 100°C, 4.5 kV/cm as a function of Ba/Ti ratio.

Fig. 6 Microstructure of BaTiO₃ with different Ba/Ti ratios at 1350°C for 5 hr. a) Ba/Ti = 0.996 ($\times 400$, bar: 100 μm), b) Ba/Ti = 1.000 ($\times 2000$, bar: 20 μm), c) Ba/Ti = 1.002 ($\times 2000$, bar: 20 μm).

ionic conduction are not known yet. Since it was reported that grain boundaries play an important role in impeding the diffusion of oxygen vacancies,²⁰⁾ larger grain size of excess TiO₂ shown in Fig. 6(a) could be taken into consideration for degradation. In addition to these effects, considering the effect of oxygen vacancy on degradation, as described above, the explanation based on a change in the point defect concentration is also likely since the accommodation of excess TiO₂ into the BaTiO₃ lattice upto 300 ppm in molar could be available. A recent study²¹⁾ that the onset of resistance degradation is in concurrence with $V_{O^{\bullet\bullet}}$ motion within the oxygen octahedron in the perovskite lattice also supports this interpretation. As can be seen in Fig. 5, the BaO-excess sample (Ba/Ti = 1.002) remains stable throughout the test, which is consistent with the previous studies.²²⁾ As described previously, the decrease in grain size yields an increase in the area of grain boundaries, which is effective for suppressing degradation. It is believed that the small grain size in the sample with Ba/Ti = 1.002 (Fig. 6(c)) seems to be responsible for the improved degradation behavior.

4 Conclusions

1. For BaTiO₃ with excess TiO₂, it is confirmed that the

equilibrium electrical conductivity is consistent with the incorporation reaction *i.e.*, $\text{TiO}_2 \rightarrow V_{\text{Ba}}^{\bullet\bullet} + \text{Ti}_{\text{Ti}} + 2\text{O}_o + V_{\text{O}}^{\bullet\bullet}$ with the formation of extrinsic oxygen vacancy.

2. For BaTiO₃ with excess BaO, the conductivity profile is not changed, which indicates that the solubility of excess BaO in BaTiO₃ could not affect the concentration of the background oxygen vacancy.

3. It is believed that the increased extrinsic oxygen vacancy due to TiO₂ in BaTiO₃ solid solution could affect the microstructure development and degradation behavior.

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