



## Electrical Properties of Acceptor Doped BaTiO<sub>3</sub>

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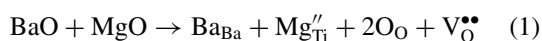
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**Abstract.** Electrical properties of acceptor (Mn, Mg or Mn + Mg)-doped BaTiO<sub>3</sub> ceramic have been studied in terms of oxygen vacancy concentration, various doping levels and electrical degradation behaviors. The solubility limit of Mn on Ti sites was confirmed to be close to or less than 1.0 mol%. Oxygen vacancy concentration of Ba(Ti<sub>0.995-x</sub>Mg<sub>0.005</sub>Mn<sub>x</sub>)O<sub>2.995-y</sub> ( $x = 0, 0.005, 0.01$ ) was estimated to be ~50 times greater than that of the un-doped BaTiO<sub>3</sub>. The leakage current of 0.5 mol% Mn-doped BaTiO<sub>3</sub> was stable with time, which was much lower than that of the un-doped BaTiO<sub>3</sub>. The BaTiO<sub>3</sub> specimen co-doped with 0.5 mol% Mg and 1.0 mol% Mn showed the lowest leakage current below 10<sup>-10</sup> A. It was confirmed that leakage currents of Mg-doped and un-doped BaTiO<sub>3</sub> under dc field are effectively suppressed by Mn co-doping as long as the Mn doping level is greater than Mg contents.

**Keywords:** Mg, Mn, BaTiO<sub>3</sub>, MLCC, degradation

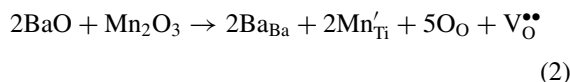
### Introduction

Magnesium (Mg) or/and Manganese (Mn), together with rare earth elements (Dy, Er, Ho, Y) have been widely used as a doping element for BaTiO<sub>3</sub> ceramic. Since the sizes of Mg and Mn ions are 0.053–0.083 nm, they can be substituted for Ti ions (0.061 nm) of BaTiO<sub>3</sub> [1]. Negatively charged defect (Mg<sub>Ti</sub>'') in BaTiO<sub>3</sub> will be formed with the simple substitution of Mg<sup>2+</sup> for Ti<sup>4+</sup> and the corresponding number of positively charged oxygen vacancies will be required to satisfy the site balance and charge neutrality conditions as follows:



The defect notation is that suggested by Kröger and Vink [2]. The valence state of Mn ion is known to vary from divalent (Mn<sup>2+</sup>) to trivalent (Mn<sup>3+</sup>) or to tetravalent (Mn<sup>4+</sup>) with increasing oxygen activity (P<sub>O<sub>2</sub></sub>), while Mg ion maintains a constant divalent [3–7]. The incorporation reaction of Mn<sub>2</sub>O<sub>3</sub> into BaTiO<sub>3</sub> lattices can be written near the conductivity minimum P<sub>O<sub>2</sub></sub> as

follows:



The solubility limit of Mg<sub>Ti</sub>' and Mn<sub>Ti</sub>' were reported to be 1.0 mol% [6, 8–11]. Within the solubility limit, the addition of Mg<sup>2+</sup> and Mn<sup>3+</sup> ions increases oxygen vacancies as expressed in Eqs. (1) and (2). The increase in oxygen vacancy suppresses the reduction of BaTiO<sub>3</sub> specimens and moves the *n*-type range to lower P<sub>O<sub>2</sub></sub>, resulting in the highly insulating *p*-type material. However, the oxygen vacancy is the most mobile species in BaTiO<sub>3</sub> lattices and the electromigration of charged oxygen vacancies in dc field is accountable for the electrical degradation of BaTiO<sub>3</sub>-based ceramic capacitors [12–15].

Effects of Mn doping in BaTiO<sub>3</sub> have been studied because of extensive changes in electrical and dielectrical properties [3–7, 16–18]. Numerous workers measured the equilibrium electrical conductivity as a function of P<sub>O<sub>2</sub></sub> and confirmed that the *p*-type conductivity at the P<sub>O<sub>2</sub></sub> near stoichiometric composition is proportional to the 1/6th power of P<sub>O<sub>2</sub></sub> [5–7]. Okazaki et al. reported that the mean time to failure (MTTF) of BaTiO<sub>3</sub>

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doped with 0.4 wt% MnO<sub>2</sub> was improved by more than three orders of magnitude compared to the un-doped BaTiO<sub>3</sub> [17]. An increase of lifetime in BaTiO<sub>3</sub>-Ho<sub>2</sub>O<sub>3</sub>-MgO system doped with Mn was also found by Morita and Kishi [18]. However, the defect chemistry and degradation mechanism of Mn-doped BaTiO<sub>3</sub> have not been clarified yet. In this paper, the equilibrium electrical conductivities of Mn or/and Mg-doped BaTiO<sub>3</sub> at 1100°C will be presented and the related defect chemistry will be discussed in terms of solubility, oxygen vacancy concentration, and various doping combinations. Furthermore, effects of co-doping of Mg and Mn will be discussed on microstructural development, phase transition and degradation behavior.

### Experimental Procedure

Powders of BaTiO<sub>3</sub> doped with acceptors (Mg, Mn, Mg + Mn) were synthesized using the liquid mix method developed by Pechini [19]. Each sample composition were prepared by polymerization and calcination of an organometallic solution containing precisely determined amounts of the metallic components as described in the previous work [20]. The specimens were then sintered at 1320°C for 5 h in air and furnace-cooled. The conductivity was measured at 1100°C using a four-point d.c. technique. The desired oxygen partial pressures (P<sub>O<sub>2</sub></sub>) were obtained from the mixture of N<sub>2</sub>-O<sub>2</sub> and CO-CO<sub>2</sub>. An X-ray diffraction analysis was carried out on a Rigaku X-ray powder diffractometer with Cu-Kα radiation. The microstructure development was investigated using a scanning electron microscope (Hitachi S2150). Leakage currents were measured by using a dc fields at 150°C.

### Results and Discussion

Equilibrium electrical conductivity profiles as a function of oxygen partial pressure (P<sub>O<sub>2</sub></sub>) at 1100°C for Ba(Ti<sub>1-x</sub>Mn<sub>x</sub>)O<sub>3-y</sub> are shown in Fig. 1. As the manganese content is increased, the conductivity increases in the *p*-type region and decreases in the *n*-type region around the conductivity minimum. This behavior indicates that the oxygen vacancy due to manganese ion retards the reduction reaction at lower P<sub>O<sub>2</sub></sub> and expedites oxidation at higher P<sub>O<sub>2</sub></sub>. At a given temperature, Smyth suggested that the conductivity minimum moves to lower P<sub>O<sub>2</sub></sub> by two orders of magnitude for each order of magnitude increase in acceptor content

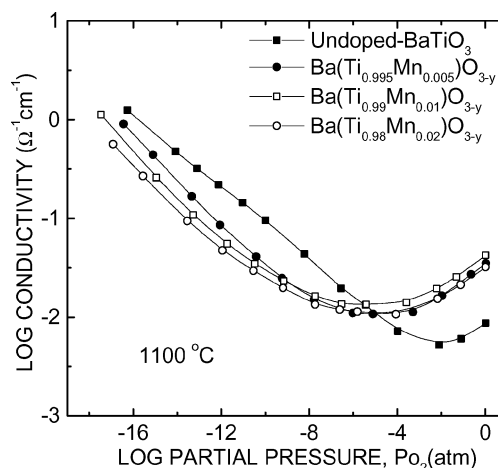


Fig. 1. Equilibrium electrical conductivity of Ba(Ti<sub>1-x</sub>Mn<sub>x</sub>)O<sub>3-y</sub> specimens at 1100°C.

and this shift serves as a measure of the relative contents of oxygen vacancies [21, 22]. As Mn content was increased above 1.0 mol%, no difference was observed in the position of conductivity minimum (P<sub>O<sub>2</sub></sub>)<sup>o</sup> between Ba(Ti<sub>0.99</sub>Mn<sub>0.01</sub>)O<sub>3-y</sub> and Ba(Ti<sub>0.98</sub>Mn<sub>0.02</sub>)O<sub>3-y</sub>, but the latter showed a general suppression of the entire conductivity curve compared with the former. This indicates that the solubility for Mn<sub>Ti</sub> on the Ti site is close to or less than 1.0 mol%, even though the observed solubility is dependent on the precise processing details such as measuring time and temperature.

Figure 2 shows the equilibrium electrical conductivities of Mn- or/and Mg-doped BaTiO<sub>3</sub> as a function

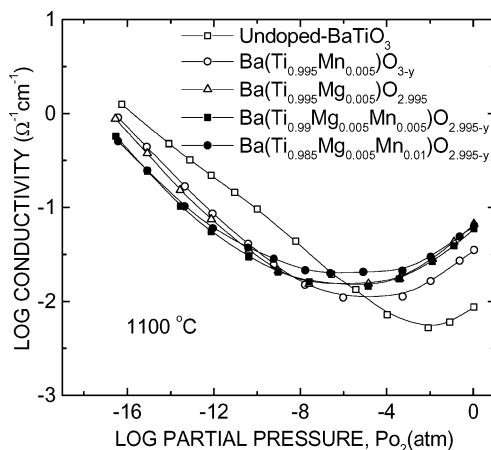


Fig. 2. Equilibrium electrical conductivity of Mn or/and Mg-doped BaTiO<sub>3</sub> at 1100°C.

of Po<sub>2</sub> at 1100°C. Conductivity minimum of Ba(Ti<sub>0.995</sub>Mn<sub>0.005</sub>)O<sub>3-y</sub> and Ba(Ti<sub>0.995</sub>Mg<sub>0.005</sub>)O<sub>2.995</sub> moved to lower Po<sub>2</sub> by 2.8 and 3.4 orders of magnitude, respectively, compared with that of the un-doped BaTiO<sub>3</sub>. However, co-doped specimens do not show any significant shift to lower Po<sub>2</sub> compared with the Mg-doped specimen, Ba(Ti<sub>0.995</sub>Mg<sub>0.005</sub>)O<sub>2.995</sub>. This indicates that the solubility limit of (Mg + Mn) on Ti sites is less than 1.0 mol% and does not exceed that of Mg or Mn on Ti sites. It is thus believed that only a slight difference in oxygen vacancy concentration exists between Ba(Ti<sub>0.995</sub>Mg<sub>0.005</sub>)O<sub>2.995</sub>, Ba(Ti<sub>0.99</sub>Mg<sub>0.005</sub>Mn<sub>0.005</sub>)O<sub>2.995-y</sub> and Ba(Ti<sub>0.985</sub>Mg<sub>0.005</sub>Mn<sub>0.01</sub>)O<sub>2.995-y</sub>. Their oxygen vacancy concentration was estimated to be ~50 times greater than that of un-doped BaTiO<sub>3</sub> according to the relationship proposed by Smyth [21, 22]. It was assumed that the un-doped BaTiO<sub>3</sub> inherently includes ~100 ppm of oxygen vacancies due to the background acceptor impurities [23, 24]. Difference in the conductivity minimum shift between the specimens with same acceptor doping level is ascribed to the difference of oxygen vacancy concentration due to the valence state of Mg<sup>2+</sup> and Mn<sup>3+</sup> ions. In addition, it should be also noted that the difference in electrical conductivities between Ba(Ti<sub>0.995</sub>Mn<sub>0.005</sub>)O<sub>3-y</sub> and Ba(Ti<sub>0.995</sub>Mg<sub>0.005</sub>)O<sub>2.995</sub> at the low Po<sub>2</sub> region is negligible and at the high Po<sub>2</sub> region is significant. This is consistent with the previous reports that the valence state of Mn ions changes from trivalent/tetravalent in the high Po<sub>2</sub> region to divalent in the low Po<sub>2</sub> region [5–7].

X-ray diffraction data and scanning electron microscope photography for Mn- or/and Mg-doped BaTiO<sub>3</sub> are shown in Figs. 3 and 4, respectively. The un-doped and 0.5 mol%-Mn doped specimens showed the tetragonal phase BaTiO<sub>3</sub> and microstructures with globular grains. However, Ba(Ti<sub>1-x</sub>Mn<sub>x</sub>)O<sub>3-y</sub> ( $x = 0.01, 0.02$ ) and Ba(Ti<sub>0.995-x</sub>Mg<sub>0.005</sub>Mn<sub>x</sub>)O<sub>2.995-y</sub> ( $x = 0.005, 0.01$ ) exhibited an extra phase, identified as hexagonal type BaTiO<sub>2.977</sub>, together with a rod-like grains [25]. The phase transition from tetragonal/cubic to hexagonal of the stoichiometric BaTiO<sub>3</sub> was reported to occur above 1320°C under the reducing condition giving rise to a slight oxygen deficiency [25, 26]. However, the phase transition of the un-doped BaTiO<sub>3</sub> specimen sintered in air or oxidation atmosphere was confirmed only at the temperature higher than 1460°C [27]. In oxidizing atmosphere, it was suggested that the driving force for phase transition of Mn-doped BaTiO<sub>3</sub> is due to the effect of Jahn Teller distortion, which is

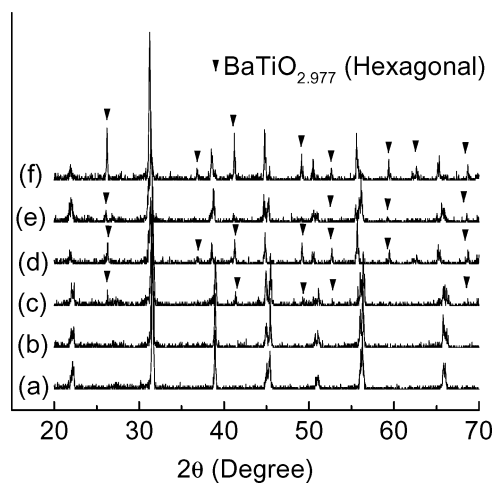


Fig. 3. XRD diffractograms of Mn or/and Mg-doped BaTiO<sub>3</sub>. (The extra reflections are due to the hexagonal phase of BaTiO<sub>2.977</sub>.) (a) Un-doped BaTiO<sub>3</sub>, (b) Ba(Ti<sub>0.995</sub>Mn<sub>0.005</sub>)O<sub>3-y</sub>, (c) Ba(Ti<sub>0.98</sub>Mn<sub>0.01</sub>)O<sub>3-y</sub>, (d) Ba(Ti<sub>0.98</sub>Mn<sub>0.02</sub>)O<sub>3-y</sub> (e) Ba(Ti<sub>0.99</sub>Mg<sub>0.005</sub>Mn<sub>0.005</sub>)O<sub>2.995-y</sub>, (f) Ba(Ti<sub>0.985</sub>Mg<sub>0.005</sub>Mn<sub>0.01</sub>)O<sub>2.995-y</sub>.

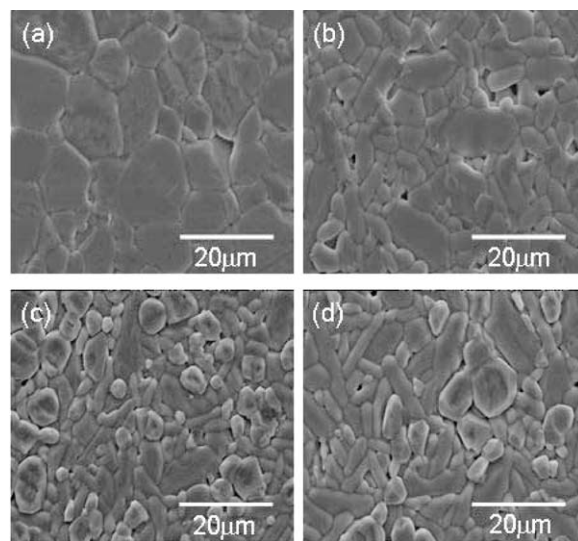


Fig. 4. Microstructures of Mn or/and Mg-doped BaTiO<sub>3</sub> sintered at 1320°C for 5 hr in air. (a) Ba(Ti<sub>0.995</sub>Mn<sub>0.005</sub>)O<sub>3-y</sub>, (b) Ba(Ti<sub>0.98</sub>Mn<sub>0.02</sub>)O<sub>3-y</sub>, (c) Ba(Ti<sub>0.99</sub>Mg<sub>0.005</sub>Mn<sub>0.005</sub>)O<sub>2.995-y</sub>, (d) Ba(Ti<sub>0.985</sub>Mg<sub>0.005</sub>Mn<sub>0.01</sub>)O<sub>2.995-y</sub>.

caused by the substitution of trivalent Mn ions for Ti sites [28, 29]. The stabilization of hexagonal BaTiO<sub>3</sub> would require a sufficiently high concentration of oxygen vacancies stemmed from the substitution of acceptor ions for Ti sites [28]. The hexagonal BaTiO<sub>3</sub> was also reported at the specimens doped with such

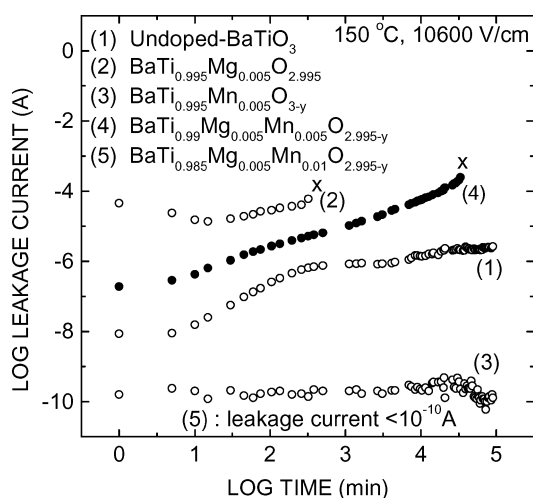


Fig. 5. Leakage currents of Mn or/and Mg-doped BaTiO<sub>3</sub> as a function of time at 150 °C, 10,600 V/cm

acceptors as Mg, Ca and Ga [10, 30–32]. Mg<sup>2+</sup> and Mn<sup>3+</sup> ions effectively increase the oxygen vacancies, as shown in Eqs. (1) and (2). It is thus believed that the oxygen vacancy due to the acceptor impurities would expedite the formation of hexagonal BaTiO<sub>3</sub>.

Figure 5 shows the leakage currents under a continuously applied dc field of 10,600 V/cm at 150 °C as a function of time. The specimen of 0.5 mol%-Mg doped BaTiO<sub>3</sub> exhibited the highest leakage current and failure occurred in 6.3 h. The leakage current of 0.5 mol% Mn-doped BaTiO<sub>3</sub> was stable with time and was much lower than that of the un-doped BaTiO<sub>3</sub>, and the specimen co-doped with 0.5 mol% Mg and 1.0 mol% Mn showed the lowest leakage current below 10<sup>-10</sup> A. However, the specimen equally co-doped with 0.5 mol% Mg and Mn showed higher leakage currents and failure occurred earlier than the un-doped BaTiO<sub>3</sub>. The high leakage current with short lifetime of 0.5 mol% Mg-doped BaTiO<sub>3</sub> is due to the electro-migration of oxygen vacancy from anode to cathode under the continuous dc field [12–15]. This result demonstrates that leakage currents of acceptor doped BaTiO<sub>3</sub> under dc field are effectively suppressed by Mn doping as long as the Mn doping level is greater than Mg contents. The remarkably low leakage current of Ba(Ti<sub>0.985</sub>Mg<sub>0.005</sub>Mn<sub>0.01</sub>)O<sub>2.995-y</sub> with longer life times might be ascribed to the valence change of Mn ions and the microstructural development with rod-like grains as shown in Fig. 4. The valence states of Mn ions change from divalent to trivalent/tetravalent

with increasing oxygen partial pressure, and most Mn ions exist as a trivalent/tetravalent state in air or oxidation atmosphere [4]. Merkle et al. reported that the association of oxygen vacancies (V<sub>O</sub><sup>••</sup>) together with acceptor cations (Mn<sub>Ti</sub><sup>′</sup>) could significantly reduce the ionic conductivity of the SrTiO<sub>3</sub> at the temperatures up to 270 °C [15]. It is thus believed that the defect association of {Mn<sub>Ti</sub><sup>′</sup> – V<sub>O</sub><sup>••</sup>} could more effectively suppress the electro-migration of oxygen vacancies than any other combination of defect associates.

## Conclusions

The solubility of Mn on the Ti site was confirmed to be close to or less than 1.0 mol% through electrical conductivity measurements. Oxygen vacancy concentration of Ba(Ti<sub>0.995-x</sub>Mg<sub>0.005</sub>Mn<sub>x</sub>)O<sub>2.995-y</sub> ( $x = 0, 0.005, 0.01$ ) was estimated to be ~50 times greater than that of un-doped BaTiO<sub>3</sub>. The un-doped and 0.5 mol%-Mn doped specimens showed the tetragonal phase BaTiO<sub>3</sub> and microstructures with globular grains. However, Ba(Ti<sub>1-x</sub>Mn<sub>x</sub>)O<sub>3-y</sub> ( $x = 0.01, 0.02$ ) and Ba(Ti<sub>0.995-x</sub>Mg<sub>0.005</sub>Mn<sub>x</sub>)O<sub>2.995-y</sub> ( $x = 0.005, 0.01$ ) exhibited an extra phase, identified as hexagonal type BaTiO<sub>2.977</sub>, together with a rod-like grains. The leakage current of Ba(Ti<sub>0.995</sub>Mn<sub>0.005</sub>)O<sub>3-y</sub> was stable with time and was much lower than that of the un-doped BaTiO<sub>3</sub>, and the Ba(Ti<sub>0.985</sub>Mg<sub>0.005</sub>Mn<sub>0.001</sub>)O<sub>2.995-y</sub> showed the lowest leakage current below 10<sup>-10</sup> A. It was also confirmed that leakage currents of Mg-doped and un-doped BaTiO<sub>3</sub> under dc field are effectively suppressed by Mn doping as long as the Mn doping level is greater than Mg contents.

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