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# The effect of thulium doping on the electrical properties of barium titanate ceramics for multilayered ceramic capacitors

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The effect of thulium oxide  $(Tm_2O_3)$  doping on the electrical properties of barium titanate  $(BaTiO_3)$  ceramics was investigated in terms of the crystallinity and core-shell structure. The electrical properties of the  $Tm_2O_3$  doped  $BaTiO_3$  were evaluated by measurements of the dielectric constant and temperature coefficient of capacitance (TCC) in addition to insulation resistance (IR). The dielectric constant and the IR of an undoped dielectric specimen were about 30% and 20%, respectively, lower than the values of a 1 mol%  $Tm_2O_3$  doped specimen which met the reliability test condition in the range from -55 to 125 °C. The addition of  $Tm_2O_3$  in  $BaTiO_3$  contributed to the enhanced electrical properties; however, an excessive addition had bad effects on the characteristics of  $BaTiO_3$  due to the formation of a second phase and the expansion of the shell region. This could be explained by the fact that the improved dielectric properties and IR according to the appropriate doping of  $Tm_2O_3$ , were revealed by an increase of the crystallinity and the reinforcement of the core-shell structure in  $BaTiO_3$ .

Keywords: BaTiO<sub>3</sub>, Thulium, Electrical properties, Crystallinity, Core-shell structure.

#### Introduction

BaTiO<sub>3</sub>-based ceramics have been widely used as dielectric layers in manufacturing multilayered ceramic capacitors (MLCCs), one of the most important applications of these materials [1, 2]. To meet the specifications of MLCCs application, the temperature dependence of the dielectric constant must be well controlled so that the dielectric degradation of MLCCs will not appear over their applied temperature range. For instance, the conventional X7R specification which was set by the Electronic Industries Association (EIA) requires that the capacitance variation with respect to that at room temperature should be within  $\pm 15\%$  over the temperature range from -55 °C to 125 °C [2].

Rare earth oxides are known to exhibit useful functions of stabilizing the temperature dependence of the dielectric properties and lower dissipation factor in dielectric ceramics [3]. It is also well known that electrical properties of BaTiO<sub>3</sub>-based MLCCs can be drastically improved by the addition of rare earth ions. In particular, these ions with intermediate values of ionic radii can be simultaneously substituted at both the Ba and Ti sites and act as donor and acceptor ions in the lattice [4]. It has been Jung *et al.* reported that rare earth elements such as Dy, Y, and Ho are effective dopants to increase the crystallinity of BaTiO<sub>3</sub> as well as to shift the T<sub>c</sub> toward a higher temperature [5-7]. Moreover, rare earth elements were dominant additives in forming

core-shell structures associated with grain boundaries affecting the insulation resistance property [8].

In a previous investigation, the rare earth ions, such as  $Dy^{3+}$ ,  $Y^{3+}$ , and  $Ho^{3+}$ , were shown as effective materials to improve the electrical properties for MLCCs [7]. However, the influences of  $Tm_2O_3$  additions in BaTiO<sub>3</sub> ceramics have not been studied. Therefore, candidate rare earth additives which have similar properties are required for high performance MLCCs. For this goal, the doping effect of thulium additions on the electrical properties of BaTiO<sub>3</sub> has been studied through a crystal structure analysis and microstructural characterization.

### **Experimental**

In the  $(Ba_{1-x}Tm_x)(Ti_{1-x}Tm_x)O_3$  system with  $0.00 \le x \le 0.03$ , BaTiO<sub>3</sub> powders (Samsung Fine Chemicals, NBT-03) with a mean particle size of 300 nm were mixed with Tm<sub>2</sub>O<sub>3</sub> (Aldrich, 99.9%), and sintering aids, MgO (Aldrich, 98%), V<sub>2</sub>O<sub>5</sub> (Junsei chemical Co. Ltd, 99.0%), SiO<sub>2</sub> (Aldrich, 99.9%), and MnO (Aldrich, 99%). The raw materials were mixed in a ball mill with zirconia balls and ethanol. The ball-milled powders were dried in an oven, granulated with PVA binder, and formed into disk shapes under a uniaxial pressure of 100 MPa. The powder compacts were sintered at 1320 °C for 2 h in a N<sub>2</sub> reducing atmosphere with an oxygen partial pressure  $Po_2 = 10^{-13}$ - $10^{-11}$  MPa. Silver paste was printed as conducting electrodes on the surfaces of sintered bodies, followed by firing in a reducing atmosphere at 750 °C for 2 h.

The dielectric constant and temperature coefficient of capacitance (TCC) were examined in the temperature range

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from -55 °C to 150 °C using a LCR meter (Agilent, E4980A) at 1 kHz/1.0 V and the insulation resistance (IR) was measured using a high resistance meter (Agilent, 4339B) at 25 V. In order to identify the crystalline phase and tetragonality, the samples were analyzed by an X-ray diffractometer (XRD, MAC Science, M18XHF) and the lattice constants of the BaTiO<sub>3</sub> powders were determined using the Rietveld method (RIETAN-RF) [9]. Furthermore, the relative density change as a function of Tm<sub>2</sub>O<sub>3</sub> contents was measured by a gas pycnometer (Micromeritics, AccuPyc-1340). The core-shell structure of BaTiO<sub>3</sub> grains was observed by transmission electron microscopy (TEM, JEOL 2010) and energy dispersive X-ray spectrometry (EDS) line profiling over a grain was performed to analyze the elements in shell regions.

#### **Results and Discussion**

Fig. 1(a) shows the variation in dielectric constant of undoped BaTiO<sub>3</sub> and various mol%  $Tm_2O_3$  doped BaTiO<sub>3</sub> specimens as a function of temperature. The specimen doped with 1 mol%  $Tm_2O_3$  exhibited the highest dielectric constant in the temperature range from -55 °C to 150 °C

with an enhancement of 40% compared to the undoped specimen. However, when the  $Tm_2O_3$  content was above 1 mol%, the dielectric constants of  $Tm_2O_3$  doped specimens decreased abruptly. The specimens doped with 2 and 3 mol%  $Tm_2O_3$  exhibited about 30% and 45% lower dielectric constants than the specimen doped with 1 mol%  $Tm_2O_3$ , respectively, and these values were even lower than that of undoped one. The dependence of the dielectric constant on temperature substantially increased with an increase in the  $Tm_2O_3$  content by more than 1 mol%. Fig. 1(b) shows the variation in temperature coefficient of capacitance (TCC) of all specimens. The specimens with 1 and 2 mol%  $Tm_2O_3$  doping satisfied the X7R reliability specification as well as the undoped specimen, whereas the specimen with 3 mol%  $Tm_2O_3$  did not.

Fig. 2 shows the variation in IR of  $(Ba_{1-x}Tm_x)(Ti_{1-x}Tm_x)O_3$  system with  $0.00 \le x \le 0.03$ . The specimen doped with 1 mol%  $Tm_2O_3$  exhibited the highest IR value of  $5.2 \times 10^{10} \Omega$ , and it decreased with an increase in the  $Tm_2O_3$  content when it was more than 1 mol%. To investigate the relation between the electrical properties and crystallinity, a structural analysis of specimens was performed with the XRD patterns.

As shown in Fig. 3, specimens with 2 and 3 mol% Tm<sub>2</sub>O<sub>3</sub>



**Fig. 1.** Variation in (a) dielectric constant (K) and (b) temperature coefficient of capacitance (%) of  $(Ba_{1-x}Tm_x)(Ti_{1-x}Tm_x)O_3$  ceramics with  $0.00 \le x \le 0.03$  as a function of temperature.



**Fig. 2.** Variation in insulation resistance (IR) of  $(Ba_{1-x}Tm_x)(Ti_{1-x}Tm_x)O_3$  ceramics with  $0.00 \le x \le 0.03$ .



**Fig. 3.** XRD patterns of  $(Ba_{1-x}Tm_x)(Ti_{1-x}Tm_x)O_3$  ceramics : (a) x = 0.00, (b) x = 0.01, (c) x = 0.02, and (d) x = 0.03.

had a secondary phase, while undoped and  $1 \text{ mol}\% \text{ Tm}_2\text{O}_3$ doped specimens had just the perovskite structure. This stemmed from the reaction between excess  $\text{Tm}_2\text{O}_3$  and  $\text{TiO}_3$  forming a  $\text{Tm}_2\text{Ti}_2\text{O}_7$  phase when the  $\text{Tm}_2\text{O}_3$  content exceeds its solubility limit in the  $(\text{Ba}_{1-x}\text{Tm}_x)$   $(\text{Ti}_{1-x}\text{Tm}_x)\text{O}_3$ system. It has been reported that the formation of the oxygen vacancies caused by the secondary pyrochlore phase generally had undesirable effects on the electrical properties [10, 11].

The crystallinity of BaTiO<sub>3</sub> dielectrics was analyzed from the XRD data in the 2 $\theta$  range from 44.5° to 46°, covering (002) and (200) peaks of the tetragonal BaTiO<sub>3</sub>, as shown in the inset in Fig. 3. It is known that the reaction of a rare earth element with BaTiO<sub>3</sub> enhances the intensity between the (002) peak and (200) peak [12, 13]. Fig. 3 also illustrates that the peaks were merged into a single (200) peak with an increase in the Tm<sub>2</sub>O<sub>3</sub> content by more than 1 mol%. As the content of Tm<sub>2</sub>O<sub>3</sub> increased by more than 1 mol%, however, the peak-to-peak separation was gradually degraded with a further increase of the Tm<sub>2</sub>O<sub>3</sub> content to 3 mol%, revealing the phase transformation from the tetragonal to cubic structure.

In addition, the tetragonality of the BaTiO<sub>3</sub> powders was calculated using the Rietveld refinement method. Table 1 shows the variations of lattice parameters a and c as a function of  $Tm_2O_3$  content in the  $(Ba_{1-x}Tm_x)(Ti_{1-x}Tm_x)O_3$ system. The lattice parameters of Tm-doped BaTiO<sub>3</sub> powders decreased with an increase in the Tm content, for x > 0.01. It seems that Tm<sup>3+</sup> ions would have an amphoteric behavior in perovskite sublattices because the size of the thulium ion is almost intermediate between those the Ba<sup>2+</sup> ion and Ti<sup>4+</sup> ion. Therefore, the lattice parameter may increase with a decrease in the thulium substitution for Ti sites, and decrease with an increase in the thulium substitution for Ba sites. This suggestion was experimentally verified with the XRD data shown in Fig. 3. In particular, a crystalline decay in dielectrics reduces the internal electrical dipoles of a ferroelectric material (BaTiO<sub>3</sub>). Therefore, it is clear that the BaTiO<sub>3</sub> specimen doped with 1 mol% Tm<sub>2</sub>O<sub>3</sub> had the highest crystallinity and dielectric properties and that the formation of the pyrochlore phase in the BaTiO<sub>3</sub> dielectrics changes the XRD peaks from a tetragonal structure to a pseudocubic structure [12]. These results are consistent with the variation of the dielectric constant and the insulation resistance, as shown in Fig. 1 and Fig. 2.

The density of dielectric specimens was measured to

**Table 1.** Lattice constant and tetragonality of  $(Ba_{1-x}Tm_x)$   $(Ti_{1-x}Tm_x)O_3$  ceramics measured by Rietveld refinement method.

Tm content	Lattice constant (Å)		Tetragonality
х	а	с	c/a
0.00 (undoped)	4.0008	4.0213	1.0051
0.01 (1 mol%)	4.0009	4.0219	1.0052
0.02 (2 mol%)	4.0013	4.0210	1.0049
0.03 (3 mol%)	4.0022	4.0210	1.0047



Fig. 4. Density of  $(Ba_{1-x}Tm_x)(Ti_{1-x}Tm_x)O_3$  ceramics with  $0.00 \le x \le 0.03$ .

analyze the correlation between electrical properties and densification, as illustrated in Fig. 4. The density of  $Tm_2O_3$  doped specimens ranged from 5.54 g/cm<sup>3</sup> to 5.88 g/cm<sup>3</sup>, while that of the undoped specimen was 5.85 g/cm<sup>3</sup>. The 1 mol% Tm<sub>2</sub>O<sub>3</sub> doped specimen showed a slightly higher density than the undoped specimen, and it gradually decreased with an increase of the Tm<sub>2</sub>O<sub>3</sub> content. It is well known that an excessive addition of rare-earth ions inhibits the densification caused by pore inclusion in BaTiO<sub>3</sub> grains. This reveals that the low density of dielectric specimens can reduce the dielectric properties and insulation resistance [14].

Fig. 5 shows that the TEM observations and the EDS line profiles as microstructural analysis provide a more detailed insight into the core-shells of Tm<sub>2</sub>O<sub>3</sub> doped specimens and a compositional analysis for core-shell regions. It is well known that core-shell structure generated from the extra rare-earth ions is associated with grain boundaries affecting the insulation resistance and breakdown voltage [8]. The degradation of insulation resistance strongly depends on the microstructure, especially on the density of grain boundaries [14]. The specimens doped above 1 mol% Tm<sub>2</sub>O<sub>3</sub> showed well-developed and easily observed coreshell grains and typical grains observed in 1 mol% specimen are shown in Fig. 5(a). The core region is clearly distinguished from the shell in terms of the existence of domain boundaries. As shown in Fig. 5(b), the EDS line profiles indicated that the concentration of thulium was preserved to a certain depth from the grain boundaries and decreased abruptly across the shell-to-core boundaries. Although the shell composition was slightly varied from grain to grain, it was generally confirmed that thulium was a dominant element in forming shell structures. The results revealed that the shell portion in a dielectric grain tends to increase with an increase in the amount of  $Tm_2O_3$  additive. Therefore, the higher insulation resistance of the specimen doped with 1 mol% Tm<sub>2</sub>O<sub>3</sub> can be understood based on grain boundary reinforcement caused by shell formation. However, the lower values of the specimens doped above 1 mol% Tm<sub>2</sub>O<sub>3</sub> primarily stemmed from their relatively lower densities.



Fig. 5. TEM images and EDS line profiles of typical core-shells in the  $BaTiO_3$  specimens doped with (a) 1 mol%, (b) 2 mol%, and (c) 3 mol%  $Tm_2O_3$ .

#### Conclusions

This paper shows that the effects of thulium doping on the dielectric properties and the insulation resistance were verified by an increase of the crystallinity and the formation of core-shell structure in dielectrics. The BaTiO<sub>3</sub> specimen doped with 1 mol% Tm<sub>2</sub>O<sub>3</sub> gave a the higher dielectric constant and IR values compared to specimens doped with 2 and 3 mol% Tm<sub>2</sub>O<sub>3</sub>, and the TCC of 1 mol% Tm<sub>2</sub>O<sub>3</sub> doped specimen met the X7R reliability requirement. However, the electrical properties of specimens with 2 and 3 mol% Tm<sub>2</sub>O<sub>3</sub> declined due to a decrease of the density and the low crystallinity. This can be explained by the fact that an excessive addition of Tm<sub>2</sub>O<sub>3</sub> beyond the solubility limit in BaTiO<sub>3</sub> caused the generation of the Tm<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> secondary phase and the expansion of the shell region. It could be concluded that the addition of Tm<sub>2</sub>O<sub>3</sub> below its solubility limit gradually enhanced the electrical properties through an increase of the crystallinity and the formation of core-shell structure in BaTiO<sub>3</sub> by a simultaneous substitution. Therefore, it is apparent that thulium doped BaTiO<sub>3</sub> ceramics have a good potential to be used as a candidate materials and this approach could be applied to the designing of high performance MLCCs.

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