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Temperature dependence of dielectric properties of rare-earth element doped $BaTiO_3$

Eunsang Na, Sung-Churl Choi and Ungyu Paik*
Department of Ceramic Engineering, Hanyang University, Seoul 133-791, Korea

The influence of rare earth elements (Pr, Gd, Ho, Er, Yb, and Lu) on the dielectric constant-temperature characteristics of the $BaTiO_3$-MgO-MnO_2 system for automotive applications was investigated. In the case of Yb- and Lu-doped $BaTiO_3$, the Curie point shifted to a higher temperature and the peak widths were broadened by the addition of smaller radii rare earth elements. It was found that the ionic radius of rare earth elements had a major effect in controlling the temperature coefficient of capacitance. The addition of rare-earth elements with smaller ionic radii led to an improvement in the temperature dependence of dielectric properties

Key words: $BaTiO_3$, dielectric, rare-earth element, temperature-capacitance characteristics (TCC).

Introduction

In recent years, multilayer capacitors (MLCs) with Ni electrodes have been widely used in electronic components to meet requirements for high volumetric efficiency and reduced manufacturing cost. In non-reducible dielectrics based on $BaTiO_3$, it is well known that the resistance degradation of dielectrics strongly depends on the A/B ratio and the ratio of donor dopant to acceptor dopant [1, 2]. Electronic parts in the control module for automotive applications must maintain their performance at high temperatures [3].

As one of the specifications for electronic applications, X8R specifications demand temperature-stable dielectric behavior (less than 15% deviation) over the temperature range -55°C to 150°C. The Bi_2O_3-PbO-TiO_2 composition has been commonly used for X8R MLCs. However, the Bi_2O_3-PbO-TiO_2 type MLCs could not be fabricated in thinner layers, and also they employed Pd or Ag-Pd as inner electrodes. In order to attain down-sizing, cost reduction, and environmental protection (Pb free), X8R MLCs with Ni electrodes (Ni-MLCs) for automotive applications are needed.

In order to obtain a moderate temperature coefficient of capacitance, rare-earth elements were introduced to $BaTiO_3$-based dielectrics with base metal electrodes (BMEs) in the fabrication of MLCs. Okino *et al*. [4] reported that highly reliable Ni-MLCs conforming to the X7R specification were obtained by the addition of a smaller ionic size rare-earth oxide (R_2O_3) such as Dy, Ho and Er into the $BaTiO_3$-MgO-R_2O_3 based system. However, few studies have focused on the conventional $BaTiO_3$ system doped with various rare earth elements. Therefore, it is necessary to investigate the electrical properties of MLCs, in particular the temperature dependence of dielectric properties.

In this paper, we present the effects of rare-earth elements on the temperature dependence of dielectric properties of non-reducible dielectrics with base metal electrodes (BME).

Experimental Procedure

Hydrothermally synthesized $BaTiO_3$ with a mean particle size of 0.4 μm (Sakai Chemical Co., Ltd, Japan) and fine-grained rare-earth oxides (High Purity Chemicals, Japan) were used as starting materials. Reagent grade $MgCO_3$ and MnO_2 were used as dopants and $BaSiO_3$ was used as a sintering additive. Along with 2.0 atomic% rare-earth elements (Pr_2O_3, Gd_2O_3, Ho_2O_3, Er_2O_3, Yb_2O_3 and Lu_2O_3), 1.5 atomic% $MgCO_3$ and 0.7 atomic% MnO_2 were added into $BaTiO_3$ to modify the electrical properties. Ceramic slurries were prepared using toluene/ethanol mixture of 8:2 (vol%). In the first milling stage, dispersant, rare-earth oxides, $MgCO_3$, MnO_2 and $BaTiO_3$ were weighed and mixed with the solvent by ball milling for 3 hrs. In the second stage, poly(vinyl butyral) (PVB) as a binder and dioctyl phthalate (DOP) as a plasticizer were added to the suspension and milled for another 18 hrs.

Ceramic sheets were formed by tape casting. The tape-casting machine was a home-made one with a stationary carrier that moved at a controlled speed. The slip passes through a doctor blade system assuring uniform tape thickness, whose height could be adjusted

*Corresponding author:
Tel: +82-2-2290-0502
Fax: +82-2-2281-0502
E-mail: upaik@hanyang.ac.kr

through the use of a micrometer screw. To prevent dry cracks, green sheets were slowly passed through the heating zone. The dried tapes were cut into 16×16 cm^2 and stacked as 35 layers without an electrode. Stacked sheets were laminated into a die heated at 60°C, under an external pressure of 600 kgf/cm^2 for 5 minutes. Laminated blocks were cut into 1×1 cm^2. First, the green blocks were heated at 250°C for 22 hrs in air to burnout the binder. After burning out the binder, the blocks were sintered at 1310°C for 2 hrs in a reducing atmosphere (P_{O_2}=10-12 atm) controlled by levels of N_2, H_2, O_2, and H_2O.

The sintered blocks were crushed and ground into powder, and then the phase transition of samples were characterized by an X-ray diffractometer (XRD) and a differential scanning calorimeter (DSC). The capacitance was measured using an HP4284A precision LCR meter (Hewlett-Packard, U.S.A.), and the resistivity was measured using an HP4339B high resistance meter. The microstructure of the ceramics was observed by scanning electron microscopy (SEM).

Results and Discussion

Figure 1 shows the XRD profile for various rare earth doped $BaTiO_3$ specimens. We selected the (002) and (200) diffraction peaks of the $BaTiO_3$ solid solution for the determination of the crystal system. The (002) and (200) diffraction lines were separated from each other with the addition of smaller ionic radii elements, such as Ho, Er, Yb and Lu. By contrast, as the dopants with larger ionic radii were added, the diffraction lines became merged. This result indicated that rare-earth elements with different radii caused a lattice parameter alteration that induced internal stress in the so-called core and shell structure of grains [5, 6]. Addition of large radii ions to the $BaTiO_3$ matrix gave a high level of residual stress induced in the grains with accompanying development of the pseudo-cubic phase. By contrast, small radii ions induced small internal stresses

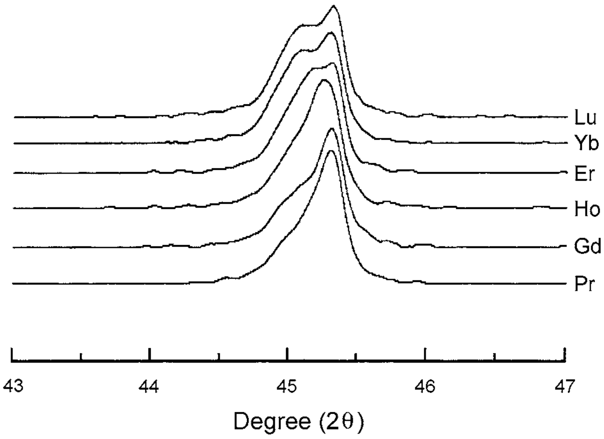

Fig. 1. X-ray (002), (200) diffraction lines of various rare-earth doped $BaTiO_3$.

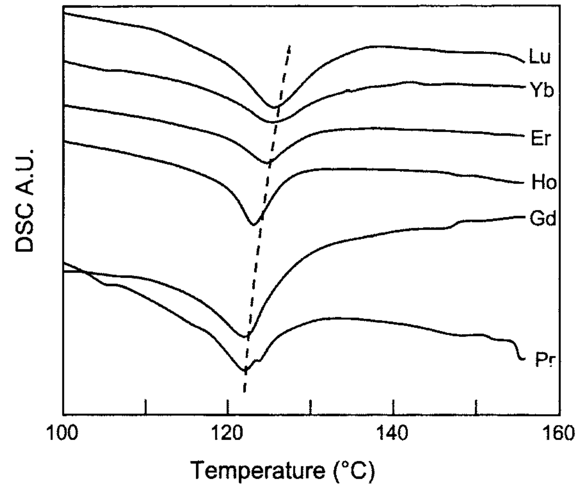

Fig. 2. Differential scanning calorimeter profile of $BaTiO_3$ doped with various rare-earth elements.

that was suppressed the phase transition in the core shell structure.

The Curie temperature of various rare-earth doped $BaTiO_3$ samples was measured using DSC. DSC results also show a change in crystal structure as presented in Fig. 2. In the case of the Lu-doped sample, a Curie point was observed at around 125.8°C. The peaks shifted toward higher temperatures and the peak widths were broadened by doping with the rare-earth elements with smaller ionic radii such as Ho, Er, Yb and Lu. The shift in peaks towards high temperatures indicated that the tetragonal phase became stable at the high temperatures [7]. The broadening of peak widths suggested that the tetragonal to cubic phase transition became dispersive. It is considered that the increase of Curie temperature and dispersive characteristics of the phase transition are suitable for the high temperature capacitance stability of MLCs.

These DSC peaks were due to the Curie temperature of the core phase. The DSC peaks of Pr, Gd, Ho and Er doped samples were sharp compared with Yb and Lu doped samples. It is considered that the diffusivity of Pr, Gd, Ho and Er ions into the core phase is much lower than that of smaller ionic radii rare-earth elements such as Yb and Lu [2]. Diffusivity of doped elements must be in conjunction with the core volume and the presence of the internal stress in samples composed of the core-shell microstructure [8].

Figure 3 shows the temperature-capacitance characteristics (TCC) of dielectric doped with rare-earth elements. The TCC became linear with rare-earth elements under 25°C. However, TCC became larger with elements with smaller ionic radii such as Pr, Gd, Ho, Er, Yb and Lu, and satisfied the X8R specifications. Especially, it should be noted that Yb, Lu doped samples satisfy the specifications very well.

SEM images of $BaTiO_3$ specimens doped with various rare earth elements are shown in Fig. 4. A little change

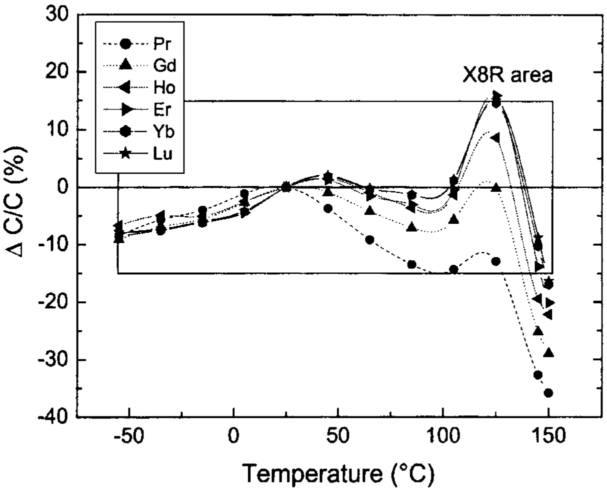

Fig. 3. Temperature dependence of capacitance change for various rare-earth doped $BaTiO_3$.

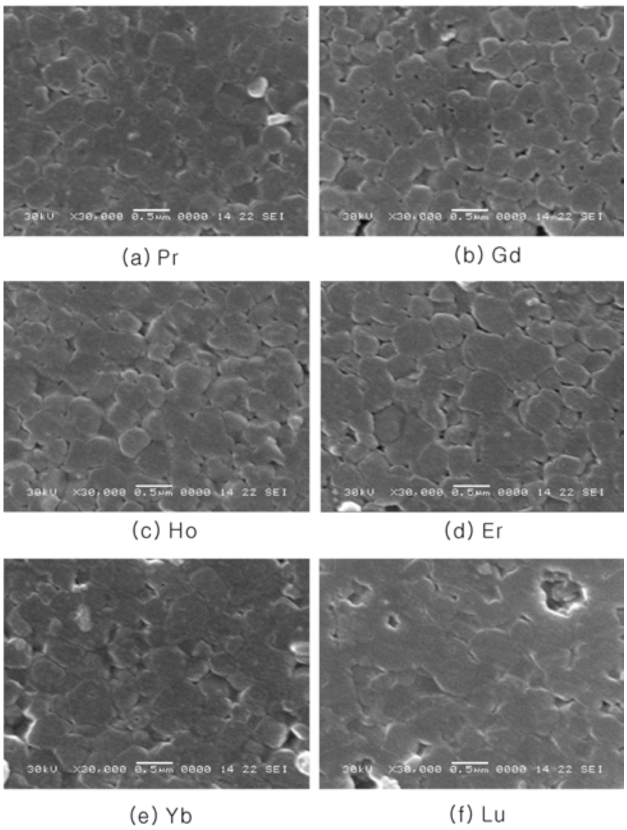

Fig. 4. SEM images of various rare-earth doped $BaTiO_3$ specimens.

in grain size was observed among $BaTiO_3$ specimens doped with various rare earth elements with different ionic radii. But the grain size of specimens was decreased with the larger ionic radii rare earth elements. It was previously reported that the dielectric-temperature characteristic was dependent on the starting $BaTiO_3$ particle size and grain size [9], which is in good agreement with the microstructural observations. These images revealed the typical core shell structure, whose grains were composed of a grain core of ferroelectric domains and a surrounding grain shell. The volume fractions of grain core of pure $BaTiO_3$ are likely to be roughly proportional to the grain size. Thus, it is supposed that a decrease in the average grain size enhanced the temperature dependence of the dielectric properties.

Table 1. Electrical Properties of Rare-Earth Doped $BaTiO_3$

Dopant	ε_r	DF [%]	Resistivity [Ω·cm]
Pr	2130	0.49	4.53×10^{12}
Gd	2094	0.53	3.44×10^{12}
Ho	2201	0.55	2.82×10^{12}
Er	2235	0.51	1.33×10^{12}
Yb	2022	0.62	8.14×10^{11}
Lu	2064	0.75	3.39×10^{11}

Table 1 summarizes the electrical properties of Ni-MLCs with the X8R characteristics, which were prepared in this study. Elements with an intermediate ionic size such as Ho, Er exhibited the highest capacitance and relative low dissipation factor (DF). Note that all samples showed high resistivity ($>10^{11}$ Ω·cm). Therefore, it is found that both the electrical properties and the Curie temperature of rare-earth element doped $BaTiO_3$ are strongly affected by the change in occupational sites of rare-earth elements in the perovskite structure. Larger ionic radii rare-earth elements occupied A sites, and smaller ones B sites considering the relative ionic size ratio of rare earth elements to matrix ion.

Conclusions

The influence of rare-earth elements on the temperature dependence of the dielectric properties of non-reducible dielectrics with base metal electrodes (BME) was investigated. In the case of elements with larger ionic radii (Pr, Gd), the Curie temperature was lower than where the elements had smaller ionic radii (Yb, Lu) of the rare earth element doped $BaTiO_3$-MgO-MnO_2 system. However in the case of elements with smaller ionic radii (Yb, Lu), the Curie temperature shifted towards higher temperatures and the tetragonality (a/c) was increased. In particular, the smaller ionic radii of rare-earth elements such as Yb and Lu were effective in developing novel temperature-stable dielectrics based on the $BaTiO_3$-MgO-MnO_2 system. The temperature-capacitance characteristic of Ni-MLCs for the X8R specification could be controlled using various rare earth elements, and these results could be related to microstructural features such as grain size and core-shell structure.

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References

1. A.C. Caballero, J.F. Fernández, M. Villegas, C. Moure, P. Durán, P. Florian, and J.P. Coutures, J. Am. Ceram. Soc. 83 (2000) 1499-1505.
2. H. Kishi, Y. Okino, M. Honda, Y. Iguchi, M. Imada, Y. Takahashi, H. Ohsato, and T. Okuda, Jpn. J. Appl. Phys. 36 (1997) 5954-5957.
3. F.D. Morrison, D.C. Sinclair, and A.R. West, J. Am. Ceram. Soc. 84 (2001) 474-476.
4. Y. Okino, H. Shizuno, S. Kusumi, and H. Kishi, Jpn. J. Appl. Phys. 33 (1994) 5393-5396.
5. T.R. Armstrong, L.E. Morgens, A.K. Maurice, and R.C. Buchanan, J. Am. Ceram. Soc. 72 (1989) 605-611.
6. H.Y. Lu, J.S. Bow, and W.H. Deng, J. Am. Ceram. Soc. 73 (1990) 3562-3568.
7. H. Kishi, N. Kohzu, Y. Mizuno, Y. Iguchi, J. Sugino, H. Ohsato, and T. Okuda, Jpn. J. Appl. Phys. 38 (1999) 5452-5456.
8. T.R. Armstrong and R.C. Buchanan, J. Am. Ceram. Soc. 73 (1990) 1268-1273.
9. Y. Park, Y. Kim, and H. Kim, J. Phys. D: Appl. Phys. 29 (1996) 2483-2491.