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Studies of dielectric properties of rare earth (Dy, Tb, Eu) doped barium titanate sintered in pure nitrogen

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Abstract

This paper investigated dielectric properties of rare earth (Dy, Tb, Eu)-doped barium titanate sintered in pure nitrogen. The substituting concentration of rare earth (Dy, Tb, Eu) was 2.0 mol%. The doping behaviors of intermediate rare-earth ions (Dy, Tb, Eu) and their effects on the dielectric property of barium titanate were investigated. Eu^{3+} ion was substituted in the A-site of the perovskite lattice. Dy^{3+} and Tb^{3+} ions substituted partially for Ti^{4+} site and partially for Ba^{2+} site. The different rare earth element had a crucial effect on dielectric properties of rare-earth-doped $BaTiO_3$. Among these doped samples, Tb-doped $BaTiO_3$ had the largest dielectric constant (70,000–80,000); the smallest dielectric loss (less than 4%), and good capacitance-temperature coefficient, which satisfies the X7R specification of the Electronic Industries Association Standards (TCC within ±15% from −55 °C to 125 °C).

Keywords: C. Dielectric properties; D. $BaTiO_3$; E. Capacitors; Pure nitrogen sintering

1. Introduction

There are many papers presenting the doping mechanism and doping effects of barium titanate. In the investigation on anti-reduction ceramic dielectric of barium titanate, Ba/Ti ratio, doping ion radius and valence, oxygen partial pressure are three key factors to influence the doping mechanism and defect structure of barium titanate [1–4]. Rare-earth oxides are important additives for manufacturing multilayer ceramic capacitors with base metal electrodes [4–8]. Trivalent rare-earth ions act as a donor or an acceptor, which depends on the size of the rare-earth ion. Many researches reported that the ionic size is a main factor on the incorporation of rare-earth ions into $BaTiO_3$ ceramics [6–9]. The common understanding is: the larger ions occupy predominantly the Ba^{2+}-site and present the donor behavior, while smaller ions prefer the Ti^{4+}-site and exhibit the acceptor behavior, the intermediate ions can substitute for either the Ba^{2+} or the Ti^{4+} site depending on the Ba/Ti ratio of the initial powder; or the intermediate ions will occupy both sites with different partitioning for each ion [10].

The ionic radii of rare earth elements Dy, Tb, and Eu are about 0.12 nm with 12 coordination, and about 0.09 nm in 6 coordination [11], respectively. These rare earth elements are intermediate ions, and they can substitute for either the Ba^{2+} or the Ti^{4+} site or both. In the case of sintering in air, Eu ions occupy Ba^{2+} site, whereas Tb ions give partial substitution at the Ti^{4+} site [12,13].

In this paper, we assumed that the rare earth elements (Dy, Tb, Eu) substitute in the Ti-site, and the substituting concentration was 2.0 mol%. The difference in doping behaviors of intermediate rare-earth ions (Dy, Tb, Eu) and their effects on the dielectric property and the microstructure of $BaTiO_3$ were investigated. Sintering atmosphere was pure nitrogen. The microstructure and dielectric properties were studied.

2. Experimental procedures

The $Ba(Ti_{0.98}R_{0.02})O_3$ (R = Dy, Tb, Eu) samples were prepared using a conventional powder-sintering technique. The starting materials were hydrothermally synthesized $BaTiO_3$ and high purity Dy_2O_3, Tb_2O_3 and Eu_2O_3. The powders were mixed and ground with ethanol in ZrO_2 ball mill for 8 h. The mixed powders were dried and calcined at 950 °C for 2 h. Then, the

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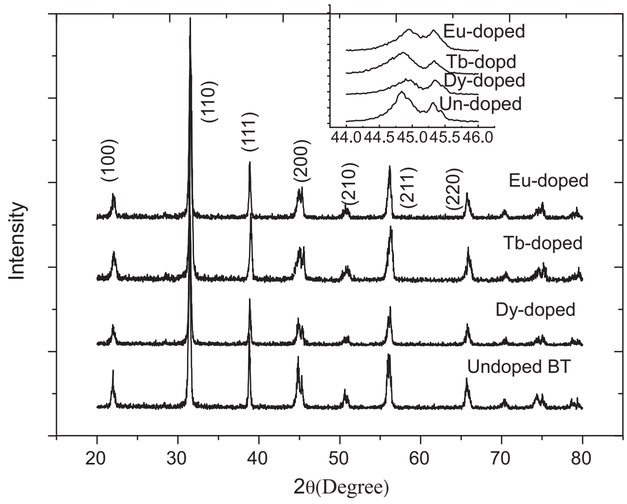

Fig. 1. XRD patterns of rare earth doped $BaTiO_3$ ceramics.

calcined powders were pressed into disks with 10 mm in diameter and about 1 mm in thickness. Finally, after the binder was burned out in air, the disks were fired in pure nitrogen at 1250–1400 °C, followed by furnace cooling. After sintering, silver electrode was coated on both sides of specimens for electrical measurements. Then, the samples with silver electrode were calcined at 520 °C in air. Dielectric properties of sintered disk were measured from −60 °C to 160 °C with an impedance analyzer LCR (HP 4284A) at frequency of 1 kHz and oscillation level of 1 V rms. The heating rate was 2 °C/min and the accuracy was 0.1 °C.

The crystal structure of ceramics was characterized by X-ray diffraction (XRD, Bruker D8 Advance). Microstructures of ceramics were studied on the as-fired surfaces of the sintered ceramics using SEM (JEOL 5510LV) with an accelerating voltage of 10 kV.

3. Results and discussion

Fig. 1 illustrates XRD patterns of rare earth doped $BaTiO_3$ ceramics. No secondary phase was found within the detection limit of XRD. As can be seen from the inset of Fig. 1, the peak (200) had an obvious large angle shift with Eu doping. This reveals the constriction of perovskite lattice by the addition of Eu ion. This construction of perovskite lattice is related to the fact that the ionic radius of Eu^{3+} (0.112 nm) is smaller than that of Ba^{2+} (0.161 nm). The constriction of perovskite lattice shows that the intermediate rare earth element Eu^{3+} was substituted in the A-site of the perovskite lattice [7–10,12]. As also can be seen from the inset of Fig. 1, the peak (200) had no obvious angle shift with Dy and Tb doping. This shows that Dy^{3+} and Tb^{3+} ions give partial substitution at the Ti^{4+} site and partial substitution at the Ba^{2+} site [7–10,13].

Fig. 2 shows SEM micrographs of the surfaces of rare earth doped $BaTiO_3$ ceramics sintered in pure nitrogen. It can be found that the sintering temperature of barium titanate increased with the rare earth (Dy, Tb, Eu) doping. The sintering temperature of un-doped $BaTiO_3$ was about 1250 °C. The sintering temperature of Dy-doped $BaTiO_3$ and Tb-doped $BaTiO_3$ were about 1350 °C and the sintering temperature of Eu-doped $BaTiO_3$ was about 1400 °C. The grains become smaller when the rare earth (Dy, Tb, Eu) entered into barium titanate crystal structure. Especially in the Eu-doped samples,

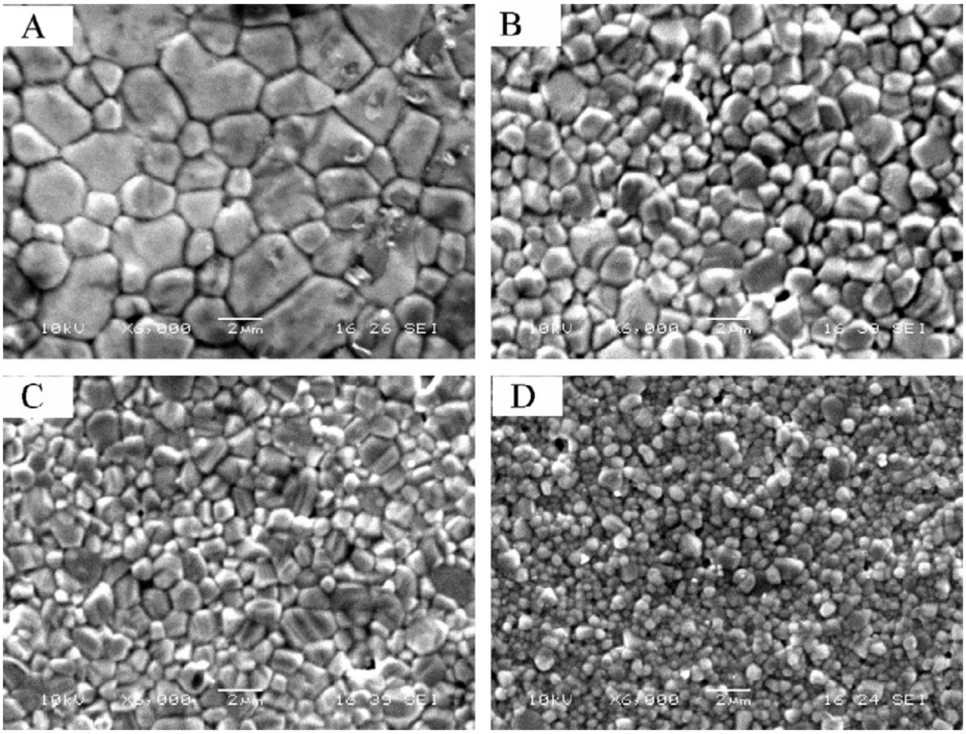

Fig. 2. SEM micrographs of the surfaces of rare earth doped $BaTiO_3$ ceramics sintered in pure nitrogen: (a) un-doped specimen sintered at 1250 °C; (b) Dy-doped specimen sintered at 1350 °C; (c) Tb-doped specimen sintered at 1350 °C; (d) Eu-doped specimen sintered at 1400 °C.

the grains were homogeneous and no more than 1 μm. This may be related to the fact that the intermediate rare earth element Eu^{3+} was substituted in the A-site of the perovskite lattice (8–9, 12).

Fig. 3 illustrates ε–T curves of rare earth (Dy, Tb, Eu)-doped $BaTiO_3$ sintered in pure nitrogen (test frequency is 1 kHz). It can be found that the different rare earth element had a crucial effect on dielectric properties of rare-earth doped $BaTiO_3$. Dy-doped barium titanate and Tb-doped barium titanate had much larger dielectric constant than those of $BaTiO_3$. This may be in accord with the occupation in the perovskite lattice of the rare earth elements. Fig. 4 shows temperature coefficient of rare earth (Dy, Tb)-doped $BaTiO_3$. It can be found from Figs. 3 and 4, Tb-doped $BaTiO_3$ not only obtained the large dielectric constant (70,000–80,000), but also had good capacitance-temperature coefficient, which satisfied X7R specification of the Electronic Industries Association Standards (TCC within ±15% from −55 °C to 125 °C). And Tb-doped $BaTiO_3$ had the smallest dielectric loss either (less than 4%). Dy-doped $BaTiO_3$ had the largest dielectric loss. Eu-doped $BaTiO_3$ had the smallest dielectric constant. When temperature was higher than 100 °C, the dielectric loss of Eu-doped $BaTiO_3$ warped upwards markedly with increasing temperature. Which was caused by the influence of leakage conductivity and temperature had an exponential influence on conductivity.

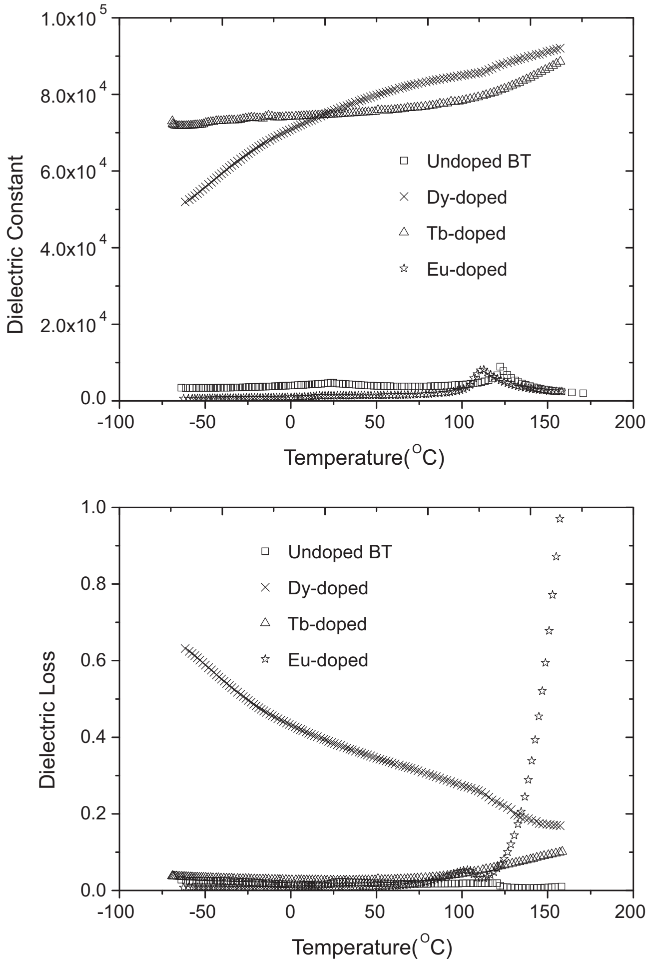

Fig. 3. ε–T curves of rare earth (Dy, Tb, Eu)-doped $BaTiO_3$ sintered in pure nitrogen (test frequency is 1 kHz).

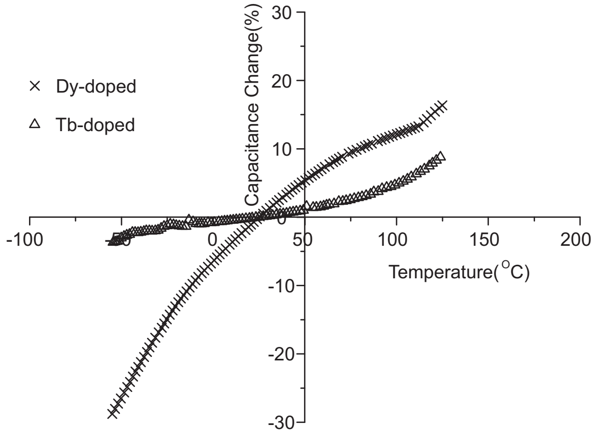

Fig. 4. Temperature coefficient of rare earth (Dy, Tb)-doped $BaTiO_3$.

Insulation resistivity was investigated by means of a high resistance meter (Keithley 6517A) using alternating polarity resistance test method. The alternating polarity resistance was designed to improve high resistance measurements and it was possible to eliminate the effects of the background currents. The test voltage was 100 V. Resistivity of the sintered ceramics samples was 10^9 Ω cm orders of magnitude.

4. Conclusions

The peak (200) had an obvious large angle shift and the grains of samples were refined with Eu doping. Those indicated that the intermediate rare earth element Eu^{3+} entered in the A-site of the perovskite lattice. The peak (200) had no obvious angle shift with Dy and Tb doping. This shows that Dy^{3+} and Tb^{3+} ions give partial substitution at the Ti^{4+} site and partial substitution at the Ba^{2+} site. The sintering temperature of barium titanate increased with the rare earth (Dy, Tb, Eu) doping. The grains become smaller when the rare earth (Dy, Tb, Eu) entered into barium titanate crystal structure. The different rare earth element had a crucial effect on dielectric properties of rare-earth doped $BaTiO_3$. Tb-doped $BaTiO_3$ not only obtained the large dielectric constant (70,000–80,000), the smallest dielectric loss (less than 4%), but also obtained good capacitance-temperature coefficient, which satisfied the X7R specification of the Electronic Industries Association Standards (TCC within ±15% from −55 °C to 125 °C). Dy-doped barium titanate had much larger dielectric constant than those of $BaTiO_3$ and the largest dielectric loss. Eu-doped $BaTiO_3$ had the smallest dielectric constant.

Acknowledgements

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