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Microstructure and dielectric properties of Dy/Mn doped $BaTiO_3$ ceramics

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Abstract

Dy/Mn doped $BaTiO_3$ with different Dy_2O_3 contents, ranging from 0.1 to 5.0 at% Dy, were investigated regarding their microstructural and dielectric characteristics. The content of 0.05 at% Mn was constant in all the investigated samples. The samples were prepared by the conventional solid state reaction and sintered at 1290°, and 1350 °C in air atmosphere for 2 h. The low doped samples (0.1 and 0.5 at% Dy) exhibit mainly fairly uniform and homogeneous microstructure with average grain sizes ranged from 0.3 μm to 3.0 μm. At 1350 °C, the appearance of secondary, abnormal, grains in the fine grain matrix and core–shell structure were observed in highly doped Dy/$BaTiO_3$. Dielectric measurements were carried out as a function of temperature up to 180 °C. The low doped samples sintered at 1350 °C, display the high value of dielectric permittivity at room temperature, 5600 for 0.1Dy/$BaTiO_3$. A nearly flat permittivity–temperature response was obtained in specimens with 2.0 and 5.0 at% additive content. Using a Curie–Weiss and modified Curie–Weiss low, the Curie constant (C), Curie like constant (C'), Curie temperature (T_C) and a critical exponent (γ) were calculated. The obtained values of γ pointed out the diffuse phase transformation in highly doped $BaTiO_3$ samples.

Keywords: A. Sintering; B. Microstructures; C. Dielectric properties; D. $BaTiO_3$

1. Introduction

Rare earth oxides are widely used as doping materials for $BaTiO_3$ based multilayer capacitors [1–4]. The incorporation of trivalent rare-earth cations Dy^{3+}, Sm^{3+} and Ho^{3+}, which replaces predominately A sites in perovskite $BaTiO_3$ structure, modifies the microstructural and electrical properties of doped $BaTiO_3$. For lower donor concentration, up to 0.5 at%, named as grain growth inhibition threshold (GGIT), the bimodal microstructure is formed and anomalous grain growth occurred which leads to semiconductive properties of ceramics [5–9]. The substitution of Dy^{3+} on Ba^{2+} sites requires the formation of negatively charged defects. There are three possible compensation mechanisms: barium vacancies (V''_{Ba}), titanium vacancies (V''''_{Ti}) and electrons (e'). For samples sintered in air atmosphere, which are the electrical insulators, the principal doping mechanism is the ionic compensation mechanism. The controversy remains concerning whether the dominant ionic mechanism is through the creation of barium or titanium vacancies [10–13].

MnO_2 are frequently added to $BaTiO_3$ together with other additives in order to reduce the dissipation factor. In heavily, codoped $BaTiO_3$ ceramics, with small grained microstructure the resistivity is in the order of 10^{10} Ω cm. Manganese belongs to the valence unstable acceptor type dopant which may take different valence states, Mn^{2+}, Mn^{3+} or even Mn^{4+} during the post sintering annealing process. For codoped systems [14–16] the formation of donor–acceptor complexes such as $2[Dy^{\bullet}_{Ba}]$–$[Mn''_{Ti}]$ prevent a valence change from Mn^{2+} to Mn^{3+}.

The purpose of this paper is to study the microstructure and dielectric properties of Dy-doped $BaTiO_3$ in function of different amount of dopant concentration and sintering temperature. The Curie–Weiss and modified Curie–Weiss laws were used to clarify the influence of dopant on the dielectric properties of $BaTiO_3$.

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2. Experimental procedure

The doped $BaTiO_3$ samples were prepared starting from reagent grade powders $BaTiO_3$, Rhone Poulenc (Ba/Ti= 0.996 ± 0.004, average particle size of 0.10–0.5 μm), and as additive Dy_2O_3 (Merck, Darmstadt). The content of additive oxides ranged from 0.1 to 5.0 at%. The content of MnO_2 (Merck, Darmstadt) was kept constant at 0.05 at% in all the samples. Raw materials were homogenized and ball milled in ethyl alcohol medium for 24h. The powders were milled by using polypropylene bottle and Al_2O_3 balls (10 mm balls diameter) as the milling media. After milling the slurries were dried in an oven at 200 °C for several hours until constant weigh and PVA was added as a binder. The dried powders were then pressed under a uniaxial pressure of 120 MPa into disk of 10 mm in diameter and 2 mm of thickness. The samples were sintered at 1290 °C and 1350 °C for 2 h in air atmosphere. The temperature regime during sintering was adjusted for 5 °C/min during heating and 10 °C/min during cooling in air atmosphere. The bulk density was measured by the Archimedes method. The specimens are denoted such as 0.1 Dy/BT for specimen with 0.1 at% Dy and 0.05 at% Mn and so on. The microstructures of the sintered or chemically etched samples were observed by scanning electron microscope JEOL-JSM 5300 equipped with EDS (QX 2000 S) system. X-ray diffraction (XRD) analyses were carried out by Rigaku-Miniflex diffractometer. Capacitance was measured by using HP 4276 LCZ meter in frequency range from 100 Hz to 20 kHz and the variation of dielectric constant with temperature was measured in a temperature interval from 20° to 180 °C.

3. Results and discussion

3.1. Microstructure characteristics

The relative density of Dy doped samples ranged from 78% of theoretical density (TD) for 0.1 Dy/BT samples sintered at 1290 °C to 90% TD for 0.1 Dy/BT samples sintered at 1350 °C. With increase of sintering temperature and decrease of additive content the density of investigated samples increase. The homogeneous and completely fine-grained microstructure, with grain size ranged from 0.5 to 3.0 μm, of fairly narrow size distribution, are the main characteristics of low doped ceramics, sintered at 1290 °C, as it is shown in Fig. 1a and b. With the increase of dopant amount, the increase of porosity is evident. For all samples the addition of Dy greatly inhibits the grain growth. At 1350 °C the microstructure for specimens with 0.1 and 0.5 at% Dy is similar to that, ones obtained for lower sintering temperature, as illustrated in Fig. 1c and d.

For higher content of additive, apart from the fine grained matrix, some local areas, with grains sized around 15 μm, were observed (Fig. 2a and b). Also, in grain size over 15 μm, the domain structure is detected (Fig. 2c). The domain width varies from 0.5 to 1 μm and the wall thickness is ranged from

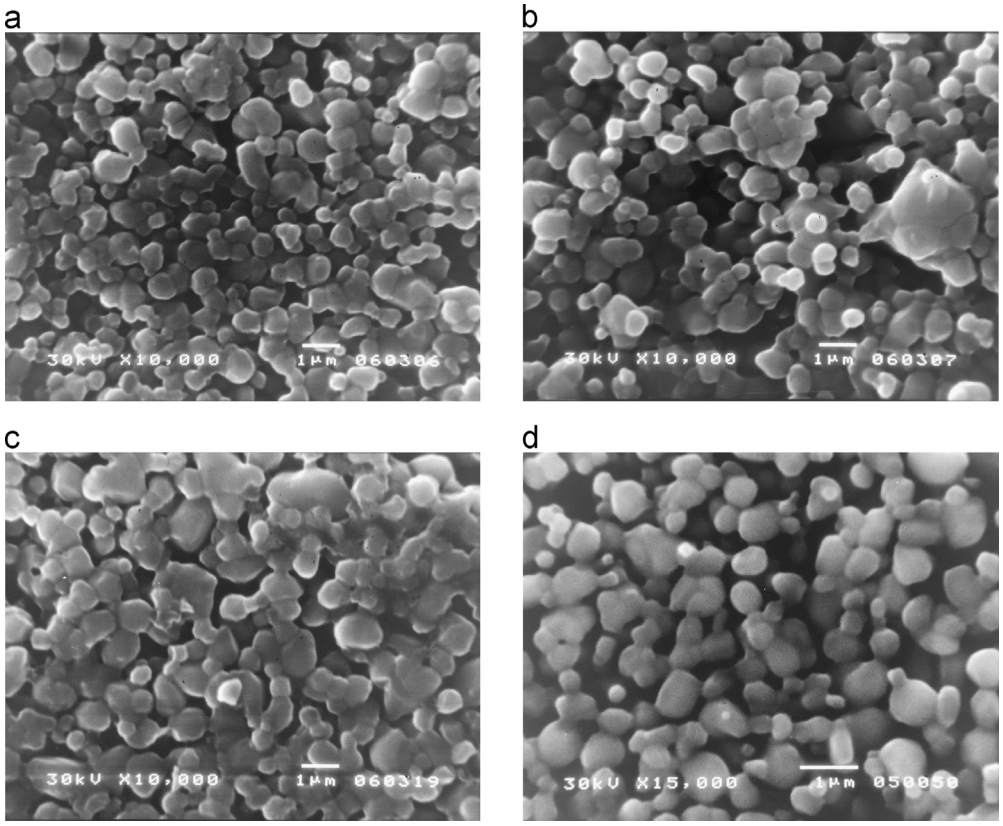

Fig. 1. SEM images of $Dy/BaTiO_3$, (a) 0.1 and (b) 0.5 at% Dy sintered at 1290 °C and (c) 0.1 and (d) 0.5 at% Dy sintered at 1350 °C.