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Phase composition, microstructure, and dielectric properties of dysprosium-doped $Ba(Zr_{0.1}Ti_{0.9})O_3$-based Y5V ceramics with high permittivity

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Abstract

Barium zirconium titanate, $Ba(Zr_{0.1}Ti_{0.9})O_3$, nanopowders modified with zinc (Zn), niobium (Nb), and dysprosium (Dy) were synthesized by a sol–gel process. The relationships among the phase compositions, microstructures, and properties of sintered ceramics were investigated. The microstructural investigation showed that the grain size of $Ba(Zr_{0.1}Ti_{0.9})O_3$–Zn–Nb ceramics was in the range 30–3 μm when the Dy content increased from 0.0 to 0.6 mol%. Average grain size of the ceramics decreased with increasing concentration of Dy; however, the maximum dielectric constant (ε_{max}) first increased and then decreased. Using a modified version of the Curie–Weiss law, a critical exponent (γ) was calculated. When the Dy concentration was 0.4 mol%, the γ coefficient for the sample equaled approximately 1.43, which confirms that the material shows relaxor behavior. Our results show that these materials met the Electronic Industries Alliance Y5V specifications and that ε_{max} was higher than 20,000, with a dielectric loss (at 25 °C) of only 0.006.

Keywords: A. Sol–gel process; C. Dielectric properties; Barium zirconium titanate; Dysprosium-doped ceramic

1. Introduction

Barium zirconium titanate (BZT) ceramics are eco-friendly and lead-free ferroelectric materials with significant relaxor properties and act as promising candidates for multilayer ceramic capacitor (MLCC) that requires superfine powders containing multiple dielectric layers, each of which must be as thin as possible. Modified BZT composites are promising candidates for Y5V-type MLCCs. In general, a traditional solid-state method is used to prepare Y5V-compliant ceramics; however, the traditional method often produces non-homogeneously doped powders, and the non-homogeneity seriously affects the stability of product performance (Electronic Industries Alliance (EIA) code, Y5V specification: $-82\% \leq \varepsilon - \varepsilon_{25\,^\circ C}/\varepsilon_{25\,^\circ C} \leq 22\%$ in the temperature range from −30 to 85 °C) [1]. Moreover, the method requires high temperature to accelerate the slow solid–solid diffusion forming secondary phases and yielding samples with an uncontrolled particle size and low surface area. Alternative routes to the solid-state method are wet chemical synthesis methods such as the hydrothermal, precipitation, and sol–gel methods. Compared to the solid-state method, the sol–gel method [2,3] has obvious advantages of controlling the composition and achieving nanosized powders at lower heat treatment temperatures because raw ingredients are microscopically homogeneous from the outset. In addition, the sintering temperature of the ceramics can also be decreased because of the high sintering activity of nanopowders with a small grain size, and there would be less risk of the oxygen loss that can be caused by high-temperature sintering. Importantly, the powders and ceramics synthesized by a sol–gel process exhibit a higher dielectric constant, a narrower grain size distribution, a better-controlled morphology, and high purity. Thus, the preparation of

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nanopowders has attracted considerable attention both from a fundamental scientific perspective and to support technological applications [4].

Solid solutions based on $Ba(Zr_xTi_{1-x})O_3$ have been studied widely because of their high maximum dielectric constant (ε_{max}), which is associated with a broad phase transition [5]. The family of $Ba(Zr_xTi_{1-x})O_3$ ceramics also have high voltage resistance because Zr^{4+} is chemically more stable than Ti^{4+} [6]. Furthermore, Ba $(Zr_xTi_{1-x})O_3$ ceramics show a broad dielectric peak near T_m (the temperature of maximum dielectric permittivity) owing to the non-homogeneous distribution of Zr ions at Ti sites and due to the development of mechanical stress in the grains [7–9]. The doping of $Ba(Zr_xTi_{1-x})O_3$ ceramics with impurities has become a common way to improve performance of the material [10]. A series of ε–T (dielectric-temperature) variations and relaxor states was observed in $Ba(Zr_xTi_{1-x})O_3$ ceramics after doping with the Re^{3+} ion (RE=yttrium (Y), erbium (Er), vanadium (V), or lanthanum (La)). For example, the Curie temperature of Ba $(Zr_xTi_{1-x})O_3$ decreased smoothly with increasing Y [11] or Er [12] doping content; however, the ε_{max} of $Ba(Zr_xTi_{1-x})O_3$ first increased and then decreased with increasing V [13] or La [14] doping content. RE elements such as Y, holmium (Ho), and Dy play an important role in the long-term reliability of MLCCs [15]. The X-ray diffraction (XRD) results indicated that Y, Ho, and Dy occupied both Ba and Ti sites in $BaTiO_3$ [16,17]. Compared to Y and Ho ions, Dy ions provided $BaTiO_3$ ceramics with a high rate of densification and greatly enhanced solid solution formation due to their higher solubility; moreover, the microstructure of the Dy-doped specimens was stable at 1280 °C, as was the case for Y and Ho-doped specimens [18], and the dielectric constant increased with increasing dysprosium oxide (Dy_2O_3) content [19,20]. The relative maximum permittivity of $Ba(Zr_xTi_{1-x})O_3$ was observed at 10 mol% of Zr substitution [21–23]. Most studies on $Ba(Zr_xTi_{1-x})O_3$ focused on the temperature dependence of the dielectric permittivity and relaxor behavior.

In this paper, we provide the first report of the fabrication of Ba $(Zr_{0.1}Ti_{0.9})O_3$–Zn–Nb (BZTZN) nanopowders by means of the sol–gel method at a relatively low temperature. Furthermore, the effects of different Dy concentrations on the phase composition, microstructure, and dielectric properties of multicomponent BZTZN ceramics were investigated. We used a modified version of the Curie–Weiss law to clarify the influence of the dopant on the dielectric properties of the BZTZND ceramics.

2. Experimental section

2.1. Synthesis

We synthesized $Ba(Zr_{0.1}Ti_{0.9})O_3$ nanopowders modified with Zn, Nb, and Dy, and produced sintered ceramics from these powders using the sol–gel process. The precursor reagents were barium acetate [$Ba(CH_3COO)_2$, 99%], zirconium nitrate [$Zr(NO_3)_4 \cdot 5H_2O$, 99.5%], zinc acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$, 99%], tetrabutyl titanium [$Ti(C_4H_9O)_4$, 99%], and dysprosium oxide [Dy_2O_3, 99.9%]. The Dy_2O_3 was dissolved in nitric acid to form a dysprosium nitrate ($Dy(NO_3)_3$) solution. The $Dy(NO_3)_3$ solutions with different Dy content (0.2, 0.4, 0.6, 0.8, and 1.0 mol%) were used for doping BZTZN, forming BZTZND1, BZTZND2, BZTZND3, BZTZND4, and BZTZND5, respectively. $H_3[Nb(O_2)_4]$ solutions were prepared according to the method reported by Das and Pramanik [24]. Other reagents were all analytical-grade chemicals. General procedure for the synthesis of BZTZNDs was as follows: A stoichiometric quantity of Ti $(C_4H_9O)_4$ was dissolved in a mixture of absolute ethanol (10 mL) and acetic acid (15 mL) with constant stirring using a magnetic stirrer for 1 h at room temperature to form a uniform $Ti(C_4H_9O)_4$ solution. Next, $Ba(CH_3COO)_2$, $Zn(CH_3COO)_2 \cdot 2H_2O$, $H_3[Nb(O_2)_4]$, $Zr(NO_3)_4 \cdot 5H_2O$, and a stoichiometric quantity of Dy $(NO_3)_3$ solution were dissolved in deionized water (50 mL). Finally, the freshly prepared solutions were slowly added into the above mentioned $Ti(C_4H_9O)_4$ solution and stirred vigorously for 2 h to form a homogeneous transparent sol. Gelling was performed on the resulting transparent sol for 40 min in a water bath at 80 °C, followed by aging for 12 h. The xerogels acquired after this step were then dried at 80 °C for 12 h.

The xerogels were calcined at 900 °C for 2 h. This process is intended to decompose any organic components that formed during the sol–gel process and to achieve crystalline nanopowders. The heat-treated nanopowders were then compressed into pellets (8 mm in diameter and 6 mm in thickness) under a uniaxial pressure of about 6 MPa. These pellets were fired at a rate of 2 °C min^{-1} up to 500 °C, were then held at 500 °C for 30 min to expel the binder, and were then sintered in air at 1280 °C for 2 h. Finally, the sintered discs were polished, and a silver paste was applied to both sides of each disc for dielectric measurements.

2.2. Characterization

Thermal behavior of the xerogels was studied using an SDT Q600 thermal analyzer (TA Instruments, New Castle, DE, USA) in the temperature range 50–1000 °C (at a rate of 10 °C min^{-1}) under dynamic air atmosphere. The phases of the powders and ceramics were determined by XRD (D8 Advance; Bruker, Frankfurt, Germany). The XRD data were collected in the 2θ range 10–70°. Angle correction was carried out using an external silicon standard. The lattice parameters were determined using least-square refinement based on the XRD patterns in the *JADE* software (version 5.0).

The characterization of the microstructure of the Ba $(Zr_{0.1}Ti_{0.9})O_3$-based ceramics was performed using an S-570 scanning electron microscope (SEM; Hitachi) to investigate the homogeneity of the pellets and estimate the grain sizes. The dielectric properties were measured using an HP 4284A LCR (Hewlett-Packard, Palo Alto, CA, USA) meter controlled by a computer with data recorded in the frequency range 10^3–10^6 Hz, and the testing temperature was controlled in the range from −30 °C to 85 °C using high and low gimbals.

3. Results and discussion

3.1. Formation and characterization of BZTZN nanopowders

Fig. 1 shows the results of the thermogravimetric and differential thermogravimetric (TG-DTG) analysis for the xerogel of the

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