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Dielectric characteristics of donor-acceptor modified $BaTiO_3$ ceramics

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ABSTRACT

Sm/Mn codoped $BaTiO_3$ ceramics were investigated for their microstructure and dielectric characteristics. The powders were prepared by the conventional solid state procedure. The concentration of Sm_2O_3 as a donor dopant has been kept from 0.1 up to 5.0 at%. The content of MnO_2 as acceptor was kept constant at 0.05 at% Mn in all samples. The specimens were sintered at 1290 °C, 1320 °C and 1350 °C in an air atmosphere for two hours.

A mainly uniform and homogeneous microstructure with average grain size ranging from 0.3 μm to 2.0 μm was observed in low doped samples. In highly doped samples, apart from the fine grained matrix, the appearance of local area with secondary abnormal grains was observed.

The dielectric properties were investigated as a function of frequency and temperature. The low doped samples exhibit the high value of dielectric permittivity at room temperature and the greatest change at the Curie temperature. The highest value of dielectric constant ($\varepsilon_r = 6800$) was measured for $0.1Sm/BaTiO_3$ samples sintered at 1350 °C. A nearly flat permittivity-temperature response and lower values of ε_r were obtained in specimens with 2.0 and 5.0 at% additive content. The dielectric constant increases with the increase of sintering temperature. The dissipation factor ranged from 0.01 to 0.22 and decreases with the increase of sintering temperature. The Curie constant (C), Curie-Weiss temperature (T_0) and critical exponent of nonlinearity (γ) were calculated using a Curie-Weiss and modified Curie-Weiss law. The highest value of Curie constant ($C = 9.06 \cdot 10^5$ K) was measured in 0.1 at% doped samples. The Curie constant decreased with increasing dopant content. The γ values, ranging from 1.001 to 1.58, point out the sharp phase transition in low doped samples, and the diffuse phase transition in heavily doped $BaTiO_3$ samples.

1. Introduction

Tetragonal $BaTiO_3$ is a ferroelectric perovskite at room temperature and one of the most important ceramic materials in electronics. The significance of this material is mainly based on its wide variety of applications such as multilayer ceramic capacitors (MLCCs), PTC thermistors, varistors, dynamic random access memories (DRAM) in integrated circuits, piezoelectric devices, optoelectronic elements and semiconductors [1–4]. For MLCCs, dielectric materials need to be electrically insulating and exhibit high permittivity values at room temperature. Overload protection devices are required to be semiconductors at room temperature and undergo a sharp rise in resistivity at the Curie temperature [5].

The dielectric properties of $BaTiO_3$ depend on the synthesis method, density, porosity, grain size, and sintering procedure. Consequently, there is a considerable interest in the preparation the powder of high homogeneity in order to get ceramics of high density, low porosity and small grain sizes. A low sintered density is related to the presence of porosity which decreases the dielectric constant and increases the dielectric loss [6]. The presence of porosity also lowers the breakdown strength of ceramic material. According to the literature data [7,8], density and grain sizes of the porous ceramics increases with sintering temperature while porosity decreases. Also, the relative permittivity increases with decreasing material porosity. Thus, by controlling porosity can be obtained ceramics with a high dielectric constant and low dielectric loss.

The dielectric properties of $BaTiO_3$ ceramics can be modified by using various types of donor or acceptor dopants [9]. Substitution of the barium or titanium ion with small concentrations of ions with a similar radius could lead to structure and microstructure changes, and furthermore, modify the dielectric properties. Also rare earth ions have been used as doping elements to improve the dielectric properties of $BaTiO_3$ based materials [10–13]. The electrical properties are strongly dependent on the site preference of

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rare earth ions in $BaTiO_3$ sublattices [14]. The ions with large radius and low valence like Nd^{3+} and La^{3+}, predominantly occupy the Ba^{2+}sites, giving donor doped behavior, while ions with small radius like Yb^{3+}, prefer the Ti^{2+} sites, conferring acceptor doped behavior [15,16]. The rare earth ions with intermediate range of ionic radius like Ho^{3+} and Dy^{3+}, can simultaneously occupy both Ba and Ti sites and can act as either donor or acceptor [17–20].

According to literature data [21–24], the addition of Sm as a donor dopant in $BaTiO_3$ decreases the grain size and enhances the dielectric constant. Also, the addition of Sm causes lowering of the Curie temperature and a decrease of the dielectric losses.

The incorporation of samarium (Sm^{3+}) ions in $BaTiO_3$ is also strongly dependent on the Ba/Ti ratio. During sintering in air, if the Ba/Ti ratio is smaller than 1 and the doping level is under 0.5 mol%, Sm^{3+} ions occupy the Ba sites giving donor doped behavior.

$$Sm_2O_3 \overset{-2BaO}{\Longrightarrow} 2Sm_{Ba}^{\bullet} + 2O_O + \frac{1}{2}O_2 + 2e^{/} \tag{1}$$

Eq. (1) represent the donor action of rare earth ions at the Ba site, providing electron charges and oxygen gas.

When the dopant content is higher than a certain value (>0.5 mol%) the dopant can be compensated by negatively charged cation vacancies. Therefore, the concentrations of conductor band electron decrease, resulting in the increase of the resistivity in the sample. The incorporation of Sm into Ba site at Ba/Ti < 1, forms the corresponding number of barium vacancy as described in:

$$Sm_2O_3 \overset{-3BaO}{\Longrightarrow} 2Sm_{Ba}^{\bullet} + 3O_O + V_{Ba}^{//} \tag{2}$$

If the Ba/Ti ratio is larger than 1, Sm^{3+} ions substitute for Ti and act as acceptors. In this case of incorporation of Sm ions into Ti sites, oxygen vacancies are created as a compensating defect through the equation

$$Sm_2O_3 \overset{-2TiO_2}{\Longrightarrow} 2Sm_{Ti}^{//} + 3O_O + V_O^{\bullet\bullet}. \tag{3}$$

In order to reduce the dielectric losses, Mn is frequently added to $BaTiO_3$ ceramics. As an acceptor dopant incorporated at Ti^{4+} site, Mn is used to counteract the effect of the oxygen vacancies introduced by donors [25–27]. As an additive, segregating at grain boundaries, Mn prevents exaggerated grain growth. Manganese belongs to the valence unstable acceptor type dopants. The valence state of Mn ion varies from divalent (Mn^{2+}) to trivalent (Mn^{3+}) or tetravalent (Mn^{4+}) with increasing oxygen activity. For codoped systems [10,11,28,29], formation of $2[Sm_{Ba}^{\bullet}]$-$[Mn_{Ti}^{//}]$ donor-acceptor complexes, prevents a valence change from Mn^{2+} to Mn^{3+}.

In codoped ceramics [28,29], the controlled incorporation of donor (Sm) in combination with an acceptor (Mn) leads to the formation of electric ceramics with homogeneous microstructure and high dielectric constant. Also, in modified $BaTiO_3$ ceramics the additives affect the Curie temperature through shifting towards lower values.

The present study deals with comparative investigations of microstructure features and dielectric properties of Sm/Mn codoped $BaTiO_3$ ceramics as a function of different dopant concentrations and sintering temperatures.

2. Experimental procedure

The Sm/Mn codoped $BaTiO_3$ samples were prepared by the conventional solid state reaction. Reagent grade powders $BaTiO_3$, Rhone Poulenc (Ba/Ti $= 0.996 \pm 0.004$, average particle size of 0.10–0.5 μm), and as additives Sm_2O_3 (Merck, Darmstadt) and MnO_2 (Merck, Darmstadt) were used as a starting materials. The content of Sm_2O_3 has been kept from 0.1 to 5.0 at%. The content of MnO_2 was kept constant at 0.05 at% in all samples. The starting powders were homogenized and ball milled in ethyl alcohol for 24 h using polypropylene bottle and Al_2O_3 balls as the milling media. After drying at 200 °C for several hours, powders were isostatically pressed at 120 MPa into 10 mm diameter and 2 mm of thickness disk form. The compacts were sintered at 1290 °C, 1320 °C and 1350 °C in an air atmosphere for two hours. The temperature regime during sintering was adjusted for 5 °C/min during heating and 10 °C/min during cooling in an air atmosphere. The bulk density was measured by the Archimedes method. The samples are denoted such as 0.1 Sm/$BaTiO_3$ for specimen with 0.1 at% Sm and 0.05 at% Mn, and so on.

The microstructures of sintered samples were observed by the scanning electron microscope JEOL-JSM 5300, equipped with an energy dispersive x-ray analysis spectrometer (EDS-QX 2000 S) system. Prior to electrical measurements silver paste was applied on flat surfaces of specimens. Capacitance and dissipation factor were measured using the HP 4276 LCZ -meter in the frequency range from 100 Hz to 20 kHz. The variation of dielectric constant with temperature was measured in the temperature interval from 20 °C to 180 °C. The Curie temperature, Curie-Weiss temperature and Curie constant were calculated according to Curie-Weiss and a modified Curie-Weiss law.

3. Results and discussion

3.1. Microstructure characteristics

The relative density of the Sm/Mn codoped samples varies from 70% to 93% of theoretical density (TD), depending on the additive amount and sintering temperature. For 0.1Sm/$BaTiO_3$ doped samples, the relative density ranged from 80% TD for samples sintered at 1290 °C to 93% TD for samples sintered at 1350 °C. With an increase of the dopant amount, the density value decreases while porosity increases. For 5.0 at% doped samples sintered at 1290 °C the density was 70% of theoretical density.

Regarding microstructure feature, for the samples doped with 0.1 and 0.5 at% of Sm (low doped samples) sintered at 1290 °C or 1320 °C, a homogeneous and completely small-grained microstructure is observed, without any evidence for explicit bimodal grain growth. The average grain size in these samples ranged from 0.3 to 2.0 μm as illustrated in Figs. 1 and 2. The similar microstructure with grain size around 2.0 μm is observed in 0.1 and 0.5 at% Sm-$BaTiO_3$ samples sintered at 1350 °C as illustrated in Fig. 3. With an increase of the additive content and sintering temperature the average grain size increased.

In contrast to the uniform microstructure of the low doped samples, the grain structure of the high doped samples (2.0 and 5.0 at% Sm) sintered at 1350 °C was bimodal. It consists of coarse grains, sized around 10 μm, dispersed in a fine-grained matrix with grains sized from 1 to 2.0 μm (Fig. 4(a) and (b)). After etching, in 2.0 and 5.0 at% Sm/$BaTiO_3$ samples, the core-shell microstructure was found (Fig. 4(c)). The grain core indicates the undoped ferroelectric region. The grain shell is the outer region. The grain shell has a dopant gradient concentration towards the grain core. Since the dopant is not homogeneously distributed in $BaTiO_3$, the quantity of core-shell grains is limited. Also, in highly Sm doped samples sintered at 1350 °C, in grains size over 10 μm the domain structure is detected (Fig. 4(d)). The domain width varies from 0.5 to 1.0 μm and the wall thickness ranges from 0.10 to 0.25 μm.

The EDS spectra taken from different areas of the same sample,