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Microstructure and dielectric properties of $Ba_xSr_{1-x}TiO_3$ ceramics

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Abstract

The crystalline structure and dielectric properties of $Ba_xSr_{1-x}TiO_3$ ceramics with $x = 0.45$, 0.5, 0.6, 0.65, 0.8, 0.9 were investigated. The *a*- and *c*-axis lattice constants of $Ba_xSr_{1-x}TiO_3$ ceramics were calculated and it is found that the crystal structures are tetragonal phase when $x \geq 0.65$ at room temperature. The Curie–Weiss temperature (T_0) is always lower than Curie temperature (T_C) and the linear relation between the Curie temperature and the stoichiometric percentage of barium can be observed and expressed as T_C (°C) = −195.0 + 322.2*x*. The values of coercive electric field (E_C) and remanent polarization (P_r) increase as Ba/Sr ratio of $Ba_xSr_{1-x}TiO_3$ ceramics increases except for $x \leq 0.5$, which are due to the decrease in grain size and the difference between the radius of Ba^{2+} and that of Sr^{2+}.

Keywords: Barium strontium titanate; Ceramics; Lattice constant; Curie temperature; Hysteresis loop

1. Introduction

Barium titanate ceramics have been used extensively as capacitor dielectrics for the past decades years. Pure $BaTiO_3$ undergoes a paraelectric to ferroelectric phase transition at 130 °C, which is accompanied by a sharp peak in the permittivity. Isovalent dopants, such as strontium or lead, are often employed to lower or raise the Curie point for particular applications. For example, barium strontium titanate (BST) ceramics are very attractive for microwave devices such as phase shifters, tunable filters, delay lines, tunable oscillators, etc. [1–3]. Therefore, the microstructure and properties of BST ceramics have to be investigated in detail [4–6]. However, the dielectric properties of $Ba_xSr_{1-x}TiO_3$ ceramics have not been reported systematically.

In this paper, the microstructure and dielectric properties of $Ba_xSr_{1-x}TiO_3$ ceramics with $x = 0.45$, 0.5, 0.6, 0.65, 0.8, 0.9 were studied. The Ba/Sr ratio dependence of the structural and dielectric properties, including the lattice constant, Curie temperature (T_C), Curie–Weiss temperature (T_0), coercive electric field (E_C) and remanent polarization (P_r), were discussed.

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2. Experiment

2.1. Preparation of ceramics

The starting chemicals were high-purity $BaCO_3$, $SrCO_3$ and TiO_2 powders. The composition prepared was $Ba_xSr_{1-x}TiO_3$ with $x = 0.45$, 0.5, 0.6, 0.65, 0.8, 0.9. Specimens were prepared by the conventional mixed-oxide method. The raw material was weighed out in stoichiometric proportions, ball-milled in water, dried and then calcined at 1180 °C for 2 h. The obtained powders were pressed into pellets with a diameter of 10.0 mm and thickness of 1.0 mm prior to sintering at 1320 °C for 2 h.

2.2. X-ray measurements

After sintering, X-ray diffraction (XRD) with Cu Kα radiation ($\lambda = 0.1541$ nm) was performed to examine the phase constitution of the specimens at room temperature.

2.3. Dielectric measurements

In order to measure the dielectric property, silver paste was painted on the polished samples as the electrodes and fired at 830 °C for 15 min.

The dielectric properties of the ceramics were determined with a HIOKI 3532-50 LCR at 1 V/mm during cooling the samples from 150 to –60 °C with 0.5 °C/min. The dielectric constant was calculated from the capacitance using the following equation:

$$\varepsilon = \frac{Cd}{\varepsilon_0 A} \quad (1)$$

where C is the capacitance (F), ε_0 the free space dielectric constant value (8.85×10^{-12} F/m), A the capacitor area (m^2) and d the thickness (m) of the ceramics. The dielectric constant-dc bias field tunabilities of the materials were studied. The % tunability of the material is determined by the following equation:

$$\%\,\text{tunability} = \frac{\{\varepsilon(0) - \varepsilon(V_{\text{app}})\}}{\varepsilon(0)} \quad (2)$$

where $\varepsilon(0)$ is the dielectric constant without dc bias field applied, and $\varepsilon(V_{\text{app}})$ is the dielectric constant with maximum dc bias field applied. The polarization–electric field (P–E) hysteresis characteristics were performed out using a Radiant Precision LC material analyzer.

3. Results and discussion

3.1. Crystalline structure

The X-ray diffraction patterns of $Ba_xSr_{1-x}TiO_3$ ceramics with various Ba/Sr ratios are shown in Fig. 1. It is observed from the X-ray patterns that the crystal structures are cubic phase for $x = 0.45$ and 0.5 and tetragonal phase for $x = 0.65$, 0.8 and 0.9. The Curie temperature of the transition cubic-tetragonal decreases with the decreasing Ba concentration and crosses the room temperature at the composition $x \approx 0.65$.

The a- and c-axis lattice constants of $Ba_xSr_{1-x}TiO_3$ ceramics were calculated and plotted in Fig. 2. The lattice constants increased gradually with increasing stoichiometric percentage of barium. This is attributed to the ionic radius of barium being larger than that of strontium. When $x \leq 0.5$, the a- and c-axis lattice constant values are very close to each other, i.e., $c/a = 1$. This implied that the crystal structures of the BST ceramics are very close to cubic. However, when $x \geq 0.65$, the c-axis lattice constant is larger than a-lattice constant, i.e., $c/a > 1$. This suggested that at room temperature the crystal structures are tetragonal phase when $x \geq 0.65$.

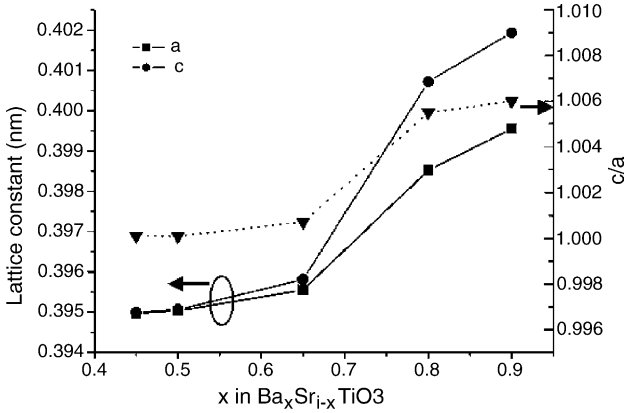

Fig. 2. Dependence of the a- and c-axis lattice constant and c/a ratio (right hand side ordinate) on Ba/Sr ratio at room temperature.

3.2. Temperature dependence

To investigate the dielectric properties of our BST ceramics, we fabricated capacitors using sliver paste as the electrode. The temperature dependence of the relative permittivity for BST ceramics with various stoichiometric percentage of barium is shown in Fig. 3. It was found that the dielectric constant of every sample has a maximum and the Curie point temperature (T_C), corresponding to this maximum of the dielectric constant increases as the Ba/Sr ratio increases.

The change of inverse dielectric constant with respect to temperature is shown in Fig. 4. It can be seen that the dielec-

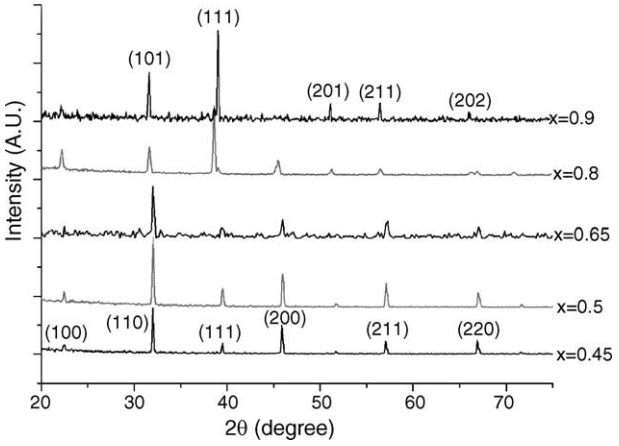

Fig. 1. The X-ray diffraction patterns of $Ba_xSr_{1-x}TiO_3$ ceramics at room temperature.

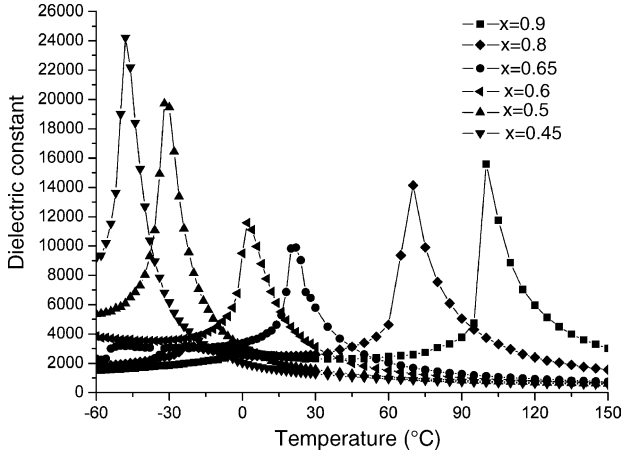

Fig. 3. Temperature dependence of the relative permittivity for $Ba_xSr_{1-x}TiO_3$ ceramics at 1 kHz.