

Relaxor characteristics of ferroelectric $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics

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The crystalline microstructure, surface morphology, and the dielectric properties of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (BZT) ceramics are investigated. From the X-ray diffraction pattern, it is found that the c -axis lattice parameter of the BZT ceramics is greater than the a -axis one. The temperature dependence of the electric permittivity indicates that there exists a diffuse transition in BZT ceramics. According to a modified Curie-Weiss law, it is calculated that the diffuseness constant (γ) equals 1.93. From the hysteresis loops, it is found that the remanent polarization ($2P_r$) and the coercive field ($2E_C$) of BZT ceramics both increase as the applied maximum voltage increases.

Key words: barium zirconium titanate; ceramics; diffuse phase transition; hysteresis loop

1. Introduction

Barium titanate (BaTiO_3) ceramics have been used extensively as capacitor dielectrics for decades. Pure BaTiO_3 undergoes a paraelectric-to-ferroelectric phase transition at 130 °C, appearing as a sharp peak in the permittivity curve. Isovalent dopants, such as strontium and zirconium, are often employed to shift the Curie point for particular applications. The $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) has a high electric permittivity, low leakage current and low dielectric dispersion against frequency [1–3]. However, the leakage current often abruptly shoots up by several orders of magnitude as the applied field exceeds a critical value of several hundred kV/cm, and breakdown occurs at a field around 2MV/cm [2, 3]. Recently, $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ (BZT) has been chosen as an alternative to BST in the fabrication of ceramic capacitors. The Zr^{4+} ion (0.087 nm) is chemically more stable than Ti^{4+} (0.068 nm) and has a larger ionic size to expand the lattice. Therefore, the conduction by electron hopping between Ti^{4+} and Ti^{3+} would be reduced by the substitution of Ti by Zr [4].

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In past years, some preliminary results on the preparation, microstructure and properties of BZT ceramics have been reported [5-11]. For example, BZT powders were synthesized through a hydrothermal reaction by using amorphous $\text{BaZr}_x\text{Ti}_{1-x}$ -peroxo-hydroxide and there is diffuse transition in $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics [5]. Moreover, a relaxor ferroelectric characteristic was observed for $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics [5-7]. However, descriptions of the relaxor characteristics of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics by the conventional mixed-oxide method have not been found in the literature.

In this paper, the crystalline microstructure, surface morphology, relaxor characteristics and hysteresis loops of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics are investigated by the conventional mixed-oxide method.

2. Experimental

The starting chemicals were 99.5% BaCO_3 , ZrCO_3 and TiO_2 powders used as received. A series of samples of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics were prepared by the conventional mixed oxide method. The raw material was weighed in stoichiometric proportions, ball-milled in water, dried and then calcined at 1200 °C for 2 h. The obtained powders were pressed at 20 MPa into disks 10.0 mm in diameter, 1.5 mm thick prior to sintering at 1350 °C for 4 h. After sintering, X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation ($\lambda = 0.1541$ nm) was used to examine the phase composition of the specimens at room temperature. The morphology of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics was investigated by the scanning electron microscopy (SEM). Before measurements of electric capacitances, polished samples were covered with silver paste and fired at 830 °C for 15 min. Then a HIOKI 3532-50 LCR at 1 V/mm was used while the samples were heated from -55 °C to 200 °C at the rate of 0.5 °C/min. The electric permittivity was calculated based on the capacitance from the equation:

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

where C is the capacitance (F), ε_0 the free space electric permittivity (8.85×10^{-12} F/m), A the capacitor area (m^2) and d the thickness (m) of the ceramics. The polarization-electric voltage (P - V) hysteresis characteristics were determined using a radiant precision LC material analyzer.

3. Results and discussion

3.1. Crystal structure

The X-ray diffraction pattern of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics is shown in Fig. 1. It is evident that the ceramics are of perovskite crystal structure. No other phases are ob-

served in the spectra. The lattice constants of BZT ceramics were calculated from the following equation:

$$d_{hkl} = \left[\left(\frac{h}{a} \right)^2 + \left(\frac{k}{a} \right)^2 + \left(\frac{l}{c} \right)^2 \right]^{-1/2} \quad (2)$$

where d_{hkl} is the interplanar distance, h , k and l are the crystallographic indices. The c axis lattice parameter ($c = 0.4107$ nm) of the BZT ceramics is greater than the a axis one ($a = 0.4101$ nm), the ratio c/a being 1.001. It is suggested that the crystal structure of the ceramics belongs to tetragonal phase and is close to cubic phase.

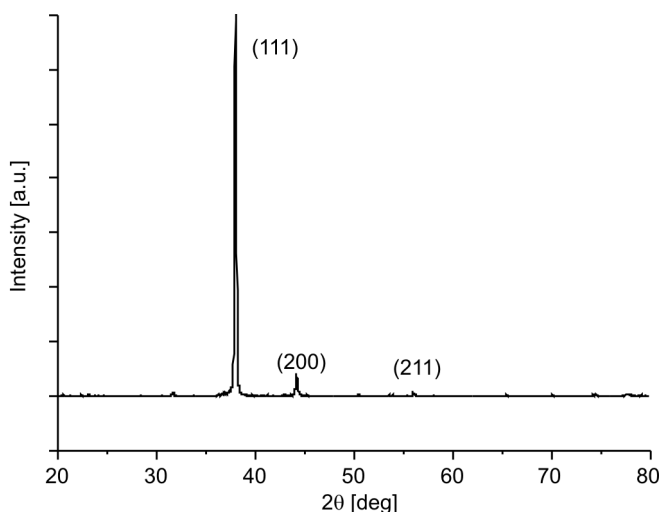


Fig. 1. XRD pattern of BaZr_{0.2}Ti_{0.8}O₃ ceramics

3.2. Surface morphology

Figure 2 shows a typical SEM micrograph of BaZr_{0.2}Ti_{0.8}O₃ ceramics. It is seen that it is very dense and crack-free. The average grain size of the ceramics is ca. 45 μ m.

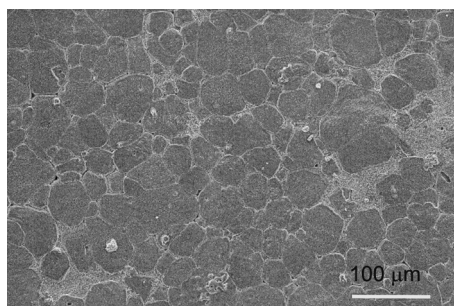


Fig. 2. Scanning electron micrograph of BaZr_{0.2}Ti_{0.8}O₃ ceramics

3.3. Temperature dependence

The temperature dependence of the electric permittivity of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics is shown in Fig. 3. The maximum value of the electric permittivity occurs at 50 °C.

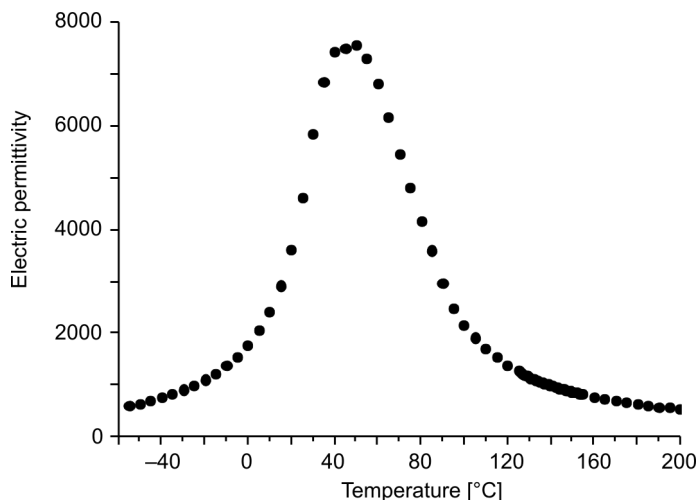


Fig. 3. Temperature dependence of the electric permittivity of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics at 1 kHz

Compared with BST ceramics [12], the electric permittivity of BZT ceramics exhibited broad peaks indicating occurrence of a diffuse phase transition from ferroelectric to paraelectric phase.

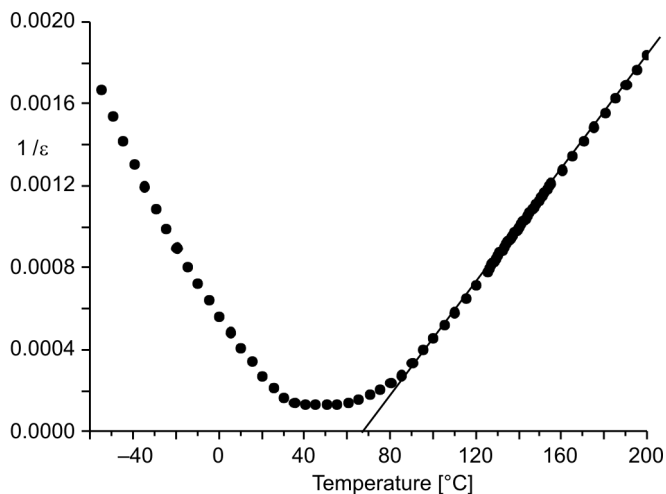


Fig. 4. Temperature dependence of the reciprocal value of the permittivity for $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics at 1 kHz

For a normal ferroelectric, at a temperature T above T_C , the dielectric behaviour follows the Curie–Weiss law:

$$\frac{1}{\varepsilon} = \frac{T - T_0}{C} \quad (3)$$

where T_0 is the Curie–Weiss temperature and C the Curie–Weiss constant. The temperature dependence of the reciprocal of the electric permittivity is shown in Fig. 4. It can be seen that the dielectric behaviour does not completely follow the Curie–Weiss law at temperatures above T_C . The Curie–Weiss temperature can be obtained from linear extrapolation of the reciprocal values of the electric permittivities in the high-temperature range.

A modified Curie–Weiss law was proposed to describe the diffuseness of the ferroelectric phase transition [6, 7]:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^\gamma}{C_1} \quad (4)$$

where ε_m and T_m represent the maximum of electric permittivity and the corresponding temperature. Here, γ and C_1 are assumed to be constant. The parameter γ provides information about the character of the phase transition: for $\gamma = 1$, the normal Curie–Weiss law is followed, whereas $\gamma = 2$ describes a complete diffuse phase transition.

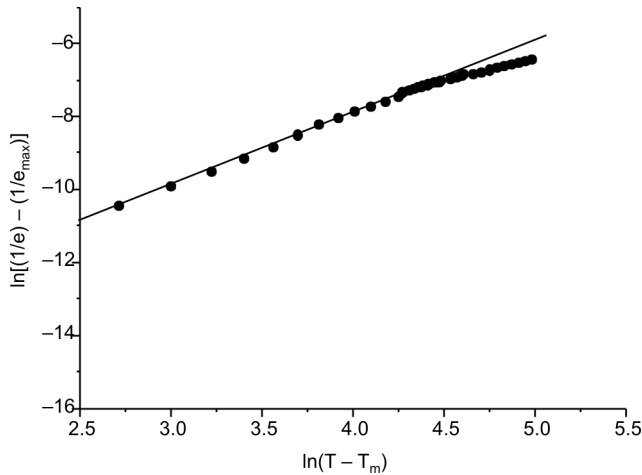


Fig. 5. Dependence of $\ln(1/\varepsilon - 1/\varepsilon_m)$ on $\ln(T - T_m)$ at 1 kHz

T_m and $1/\varepsilon_m$ of BaZr_{0.2}Ti_{0.8}O₃ ceramics are 50 °C and 1.325×10^{-4} . The dependence of $\ln(1/\varepsilon - 1/\varepsilon_m)$ on $\ln(T - T_m)$ is shown in Fig. 5. According to Eq. (4), the slope of the curve gives the diffuseness constant γ . A nearly linear relationship is observed and the γ value equals 1.93. It implies that the BaZr_{0.2}Ti_{0.8}O₃ ceramics exhibits a strong diffuse phase transition, which may be due to the high Zr content.

3.4. Hysteresis loop

Figure 6 shows the polarization curves of the same ceramics with various applied maximum voltages at the frequency of 1 kHz. Typical hysteresis loops can be observed. This suggests that at room temperature the crystal structures are in the ferroelectric phase, which is consistent with the XRD patterns and the temperature dependence of the relative permittivity. Moreover, it is found that the remanent polarization ($2P_r$) and the coercive field ($2E_C$) of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics both increased as the applied maximum voltage increased. As the applied maximum voltage increased from 500 V to 1000 V and 1500 V, the remanent polarization increased from $1.69 \mu\text{C}/\text{cm}^2$ to $3.10 \mu\text{C}/\text{cm}^2$ and $3.60 \mu\text{C}/\text{cm}^2$.

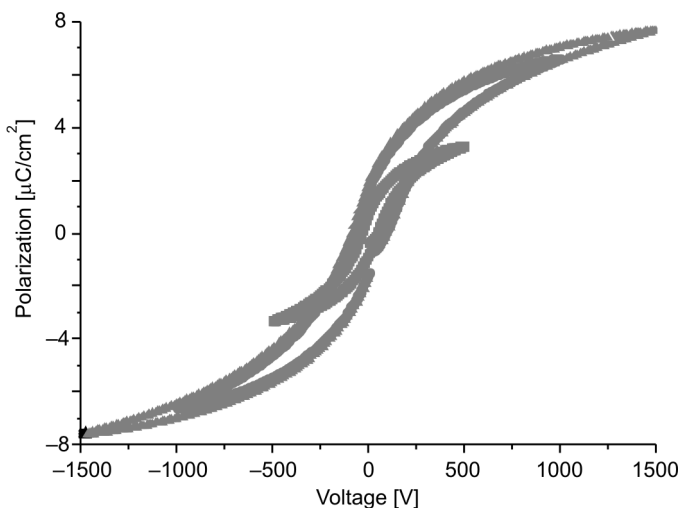


Fig. 6. Hysteresis loops for $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics with various applied maximum voltages at 1 kHz

Furthermore, the coercive field increased from $0.88 \text{ kV}/\text{cm}$ to $1.19 \text{ kV}/\text{cm}$ and $1.35 \text{ kV}/\text{cm}$. The number of ferroelectric domains along the direction of the applied electric field increased as the applied voltage increased. Therefore, the remanent polarization increased gradually. Accordingly, under reverse bias, the number of reversal domains increased. Consequently, the coercive field increased gradually.

4. Conclusions

The microstructures and dielectric properties of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ceramics were investigated. The c axis lattice parameter ($c = 0.4107 \text{ nm}$) of the BZT ceramics is greater than the a axis one ($a = 0.4101 \text{ nm}$). It was found that the crystal structure of the ceramics belongs to tetragonal phase and is close to cubic phase. There is a diffuse tran-

sition in BaZr_{0.2}Ti_{0.8}O₃ ceramics, and the diffuseness constant γ equals 1.93. It is found that the remanent polarization ($2P_r$) and the coercive field ($2E_C$) of BaZr_{0.2}Ti_{0.8}O₃ ceramics both increased as the applied maximum voltage increased.

Acknowledgements

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