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Letter

Temperature stability of Zn_2SnO_4-doped $BaTiO_3$ ceramics

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ABSTRACT

Zn_2SnO_4-doped $BaTiO_3$ ceramics were prepared as dielectric material though a conventional solid state reaction method. The room temperature dielectric constant was improved by Zn_2SnO_4 doping, with the appearance of diffuse phase transition and reduced dielectric loss. More importantly, the temperature stability of $BaTiO_3$ ceramics ($\Delta C/C_{25^\circ C}$) was modified by varying doping contents. The temperature dependence of sample with 2% doping contents satisfied the Electronic Industries Alliance Y5V temperature characteristic specification and was near the X7R specification. The SEM micrographs indicate that the $BaTiO_3$ solid solution has a homogeneous fine-grained microstructure with grain size < 1 μm and X-ray diffraction pattern suggest that the sample with 2% Zn_2SnO_4 doping contents have a tetragonal phase at RT. DPT was resulted from element substitution of Ti^{4+} with Sn^{4+}, as lattice parameters increasing under inter-grain stress. Results of impedance spectroscopic analysis suggest the presence of two relaxation mechanisms. One was originated from the dipolar polarization in the grain, and the other was related with the hopping charge carriers of oxygen vacancy in the grain boundary. The dielectric loss over a wide temperature range was modified by the activation energies of the two type relaxation mechanisms.

1. Introduction

$BaTiO_3$ is a superior dielectric material with high dielectric constant, ferroelectricity and fine positive-temperature coefficients. This material is widely used in manufacture of multilayer ceramic capacitors. Pure $BaTiO_3$ ceramics has a high sintering temperature of approximately 1300 °C and a considerable grain size of dozens micron. The relative dielectric constant at room temperature (RT) is approximately 1500–2000, and numerous pores result in large dielectric loss of 5% [1,2]. However, $BaTiO_3$ application is greatly limited by the strong dielectric peak derived from the first phase transition. This characteristic imply the necessary to improve temperature stability, regulate the grain size distribution, and reduce the dielectric loss of $BaTiO_3$ by doping proper metal oxides, in the end, the electrical properties of $BaTiO_3$ ceramics should satisfy the standard specified by the Electronic Industries Alliance (EIA).

The two major factors that affecting the $BaTiO_3$ dielectric properties are micro-structural homogeneity [2–4] and distribution of chemical elements [5,6]. The use of ultrafine $BaTiO_3$ powders as raw material could yield ceramics with a relative constant of around 4000 [4]. Dy_2O_3 and ZnO [1,7] are generally adopted to suppress the grain growth of $BaTiO_3$, improve the RT dielectric constant, and reduce dielectric loss for reason that the porosity coalescence and removal was promoted during sintering process. ZrO_2, Nb_2O_5, and SnO_2 [8–10] are usually adopted by single doping or codoping method. The element substitution effect occurred in B-site of perovskite lattice could result in reducing of Curie temperature and diffuse phase transition (DPT) on temperature dependence. Most importantly, the temperature stability of $BaTiO_3$ ceramics would be remarkably enhanced.

In the previous work [11], we have performed Zn_2SnO_4-doped $BaTiO_3$ ceramics and got something outstanding results. In details, pre-synthesized $BaTiO_3$ and Zn_2SnO_4 powders were adopted as raw materials to synthesize Zn_2SnO_4-doped $BaTiO_3$ (ZS-BT) ceramics with different Zn_2SnO_4 doping contents. In this paper, we intend to deeply discuss the temperature stability influenced by doping Zn_2SnO_4, based on the issues of microscopic evolution, crystal lattice parameter variations and impedance spectroscopic analysis. It is mainly because zinc and tin are two excellent addition oxides, i.e., zinc could suppress the $BaTiO_3$ grain growth during sintering and improve the homogeneity micro-structure, while tin could easily replace titanium in B-site of the perovskite lattice, which could result in DPT phenomenon. We assumed that pre-synthesized Zn_2SnO_4 powders could be uniformly distributed around $BaTiO_3$ powder agglomerates by ball-milling process, thereby this special preparation method could provide uniform concentrations of addition sources for sintering process and desired dielectric properties such as temperature stability.

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2. Experimental procedure

The raw materials are analytically pure $BaCO_3$ (98.5%), TiO_2 (98%), SnO_2 (99.5%) and ZnO (99.5%). Firstly, $BaCO_3$ and TiO_2 mixtures with mole ratio 1:1 are prepared by ball-milling process for 6 h using zirconium ball in alcohol, followed by drying, and then pressed into discs with 30 mm in diameter under 100 MPa. The discs were calcined at 1100 °C for 2 h and then ground into $BaTiO_3$ powders. Secondly, the process above was repeated again to obtain Zn_2SnO_4, i.e., ZnO and SnO_2 mixtures with mole ratio 2:1 were prepared by ball-milling process, the drying powders was pressed into discs and calcined at 1000 °C for 2 h, and then ground into Zn_2SnO_4 powders. Finally, pre-synthesized $BaTiO_3$ powders and Zn_2SnO_4 powders were mixed with various $BaTiO_3$:Zn_2SnO_4 mole ratios of $(1-x)$ mol: x mol, while x = 0.002, 0.004, 0.006, 0.008, 0.02, 0.04, 0.06, and 0.08 (named as ZS0.2%, ZS0.4%, ZS0.6%, ZS0.8%, ZS2%, ZS4%, ZS6%, and ZS8%, respectively). The above eight species were mixed by ball-milling process for 6 h in alcohol. Then, the slurry was dried and pressed into discs with 15 mm in diameter and roughly 1 mm in thickness by 200 MPa pressure. The eight species discs were calcined at 1260 °C for 2 h, the obtained ceramics were polished, then coated with silver paste on the upper and bottom surfaces and fired at 600 °C.

The JSM-5610LV scanning electron microscope (SEM) was used to characterize the fracture plane of samples. The crystallographic structure was investigated by X-ray diffraction (XRD) on a D8 ADVANCE diffractometer using Cu Kα radiation. The temperature and frequency dependence of the dielectric constant and loss were measured using the Agilent 4294A precision impedance analyzer in vacuum. Liquid nitrogen was used as cold source and a heater coil was used for heating process.

3. Results and discussion

Zn_2SnO_4 significantly suppress the dielectric peaks and raise dielectric constant between room and Curie temperatures (Fig. 1(a)). The dielectric peaks at Curie temperature present the DPT phenomenon. With increasing dopant contents, the temperature of the tetragonal phase to the cubic phase decrease. The Curie temperatures of sample ZS0.2% and ZS 0.4% were 121.9 °C and 117.3 °C, respectively. Sample ZS2% has a temperature stability of −35% to 12% and dielectric loss is less than 4% between −25 °C and 125 °C (Fig. 1(b)), which is closed to the EIA-X7R specification. The temperature stability between −30 °C and 85 °C is from −21% to 9% while dielectric loss is less than 4.2%, and the dielectric properties meet the requirement of EIA-Y5V. The variation of the Curie temperature may be originated from the element substitution of Ti^{4+} with Sn^{4+} [10]. The dielectric peaks of ZS4% and ZS8% were severely suppressed, which result in poor temperature stability.

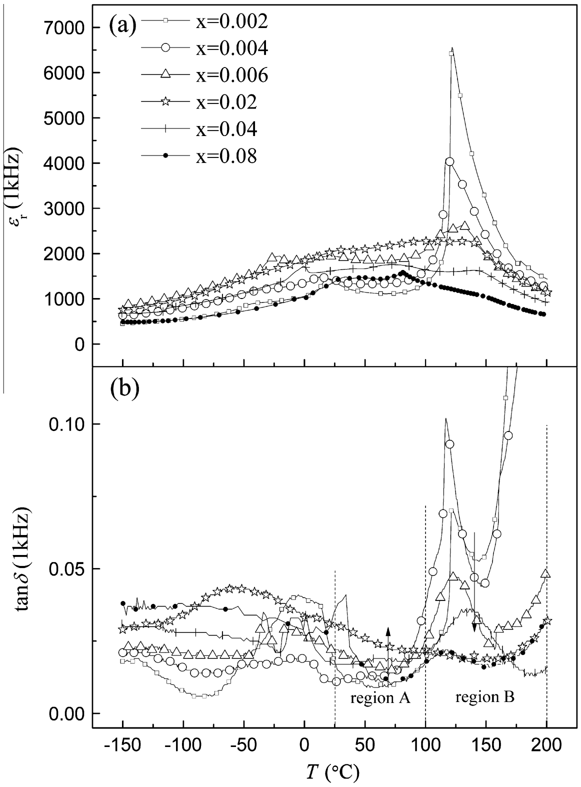

Fig. 1. Temperature dependence of dielectric constant and dielectric loss: (a) temperature dependence of ε_r at 1 k Hz for ZS-BT ceramics, (b) temperature dependence of tan δ at 1 k Hz for ZS-BT ceramics.

In this study, the temperature dependence of dielectric loss was investigated, and whether two different dependences of temperature exist was explored. Different Zn_2SnO_4 doping contents were tested at two temperature regions, marked as regions A (25–100 °C) and region B (100–200 °C) (Fig. 1(b)). Results indicate that the dielectric loss of ZS0.2%, ZS0.4%, ZS0.6% and ZS2% increase with increasing Zn_2SnO_4 contents in region A, on the contrary the loss decrease with doping in region B. This phenomenon will be discussed in detail later.

Distinguishing the microstructure of grain and grain boundary in ZS0.2% is difficult (Fig. 2(a)), while in ZS0.4% (Fig. 2(b)) the fracture plane is apparently rough and has fewer pores compared with sample ZS0.2%. Pores are dramatically reduced in sample ZS0.8% and a rough microstructure of grain and grain boundary is observed (Fig. 2(c)). In sample ZS2% the grain could be well separated from the grain boundary with grain size of roughly 0.5–1 μm, and the pores vanish (Fig. 2(d)). Thus, doping Zn_2SnO_4 could improve grain size distribution, constrain grain growth, promote the porosity removal, and mostly importantly generate a homogeneous microstructure of fine-grained $BaTiO_3$. This phenomenon could be attributed to the Zn_2SnO_4 uniform distribution among the $BaTiO_3$ powder agglomerates during ball-milling process, and zinc element plays a key role in inhibiting uncontrolled growth of $BaTiO_3$ grain during sintering [1].

ZS2% exist in tetragonal phase at RT with second phase Zn_2SnO_4 existing (Fig. 3). The XRD results were analyzed using the software Jade 6.0 [12]. The grain size range from 378 nm to 854 nm by calculating each diffraction peaks, and Zn_2SnO_4 has a huge grain size > 1000 nm. The average stress of the different sizes grain was approximately 0.152% by considering the peak broadening which resulted from inter-grain stress. $BaTiO_3$ exist in tetragonal phase in RT with P4 mm point group, lattice parameters $a = b = 3.986$ Å, $c = 4.026$ Å and axial ratio $c/a = 1.01003$. Ti^{4+} (ionic radius, 0.605 Å) substitution with Sn^{4+} (ionic radius, 0.69 Å) could result in lattice distortion, and the ZS2% lattice parameters were calculated as $a = b = 3.99839$ Å (0.31% increase), $c = 4.02682$ Å (0.00204% increase), and axial ratio $c/a = 1.00711$ (8.4% decrease). The decrease of axial ratio lead to decrease of spontaneous polarization. Therefore, DPT appears around the dielectric peaks.

Dielectric loss is closely related to the charge carriers in dielectric. The relaxation behavior of charge carriers responsed to alternating current could reflect the information of dielectric loss. Two different temperature dependence of dielectric loss exist over a wide temperature range (Fig. 1(b)) as mentioned previous, i.e. the dielectric loss of ZS0.2%, ZS0.4%, ZS0.6% and ZS2% increase with increasing Zn_2SnO_4 contents in region A, on the contrary the dielectric loss decrease with increasing Zn_2SnO_4 contents in region B.

The frequency dependence of complex impedance for sample ZS0.2% and ZS2% over a wide temperature range was measured. The data was converted into relative permittivity complex plane (Fig. 4(a) and Fig. 5(a)) and frequency dependence of tan δ (Figs. 4(b) and 5(b)) based on Eq. (1):

$$\varepsilon^* = \frac{1}{i\omega C_0 Z^*} = \varepsilon' + i\varepsilon'' \tag{1}$$

where ε^* represent the complex dielectric constant, Z^* is complex impedance and C_0 is the vacuum capacitance of sample.

Two types of relaxation behaviors were found from 40 Hz to 10^6 Hz, namely, a low-frequency relaxation (40–10^3 Hz) originated