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Effects of silica coating on the microstructures and energy storage properties of $BaTiO_3$ ceramics

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ABSTRACT

We investigated microstructures and energy storage properties of SiO_2-coated $BaTiO_3$ ceramics that were prepared by the so-called Stöber process. The thickness of coating layer of $BaTiO_3$ powders could be effectively controlled by the silica content. It could be observed that the secondary phases $Ba_2TiSi_2O_8$ appeared in the coated $BaTiO_3$ ceramics due to the interdiffusion reactions between SiO_2 and $BaTiO_3$ components under sintering. $BaTiO_3$ cores in the coated ceramics remained up to the original grain size indicating the coating layer as an inhibitor. The results showed that both breakdown strength and energy density were improved apparently. The homogeneity of silica coating in the ceramics should dominate contribution to breakdown strength, which can reduce the weak-point breakdown under high electric field. The optimized composition for $BaTiO_3$ ceramic coated with 2.0 wt% SiO_2 showed the maximum energy storage density of 1.2 J/cm^3 with energy storage efficiency of 53.8%, which is about three times higher than that of pure $BaTiO_3$ (0.37 J/cm^3).

1. Introduction

Recently, $BaTiO_3$-based ceramics have been widely used in the electronic ceramic industry due to their excellent dielectric and ferroelectric properties, especially as the use of dielectrics for energy storage capacitors [1–3]. However, new applications for energy storage have been driving the demand for dielectric materials which exhibit high breakdown strength (E_b) while still retaining high polarization in order to obtain high energy density [4]. Theoretically, energy storage density (γ) of the three kinds of dielectric materials (linear dielectrics, ferroelectrics, and antiferroelectrics) can be evaluated from their P–E loops, as given by the following equation [5]:

$$\gamma = \int_0^{D_{max}} E dD \quad (1)$$

where E is the applied electric field and D_{max} is the electric displacement (D) at the highest applied field (E_{max}). For the dielectrics with high relative dielectric constant, D can be replaced by the polarization (P). Accordingly, the above formula can be written as follows [5]:

$$\gamma = \int_0^{P_{max}} E dP = \int_0^{E_{max}} P dE \quad (2)$$

Evidently, based on Eq. (2), the energy storage density of nonlinear dielectrics can be evaluated by integrating the area between the polarization axis and the curves of P–E loops. Obviously, both dielectric breakdown strength and polarization should be the key factors for the contribution of energy density of dielectric materials [6]. Although $BaTiO_3$ ceramics exhibit a very large polarization, the energy storage values have been very limited due to the large energy loss from hysteresis with large remnant polarization and the relatively low dielectric breakdown strength of ceramics when in the form of sintered pressed disks [7,8].

In order to improve the dielectric breakdown strength, many methods have been adopted, such as controlling grain size [3,9,10], coating/mixing with low-melting point glass to remove the porosity [11–16], and forming new solid solutions with other compounds to reduce the polarization loss [17]. Among these, coating is a simple but effective method and can be operated at ambient temperature. The resultant particles by coating consist of a core made of the base particles and a shell made of coating materials, therefore, known as a core–shell structure. By coating for dielectric materials, the properties of the core component, such as reactivity and dielectric stability, may be modified.

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SiO_2 has been an effective coating material used in energy storage dielectrics due to high breakdown strength and low dielectric loss. Yu et al. [18,19] have reported the energy storage properties of pure and coated $BaTiO_3$ homogeneous ceramics-polymer nanocomposites, indicating that the coating of SiO_2 can obviously increase energy storage efficiency of the composites. In the present paper, we fabricate $BaTiO_3$ nanoparticles in the ethanol/ammonia medium with the successful coating by silica shell of a few nanometers, and investigate the effects of silica coating on the microstructure and electrical properties of coated $BaTiO_3$ ceramics.

2. Experimental

The selected method was derived from the so-called Stöber process widely used for the synthesis of silica beads from a few tens to a few hundreds of nanometers [20–23]. Here, a series of compositions can be obtained by different silica contents as follows: $BaTiO_3 + x$ wt% SiO_2 ($x = 0$, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 6.0, and 8.0). The silica shell thickness can be tuned by the addition of the amount of tetraethoxysilane (TEOS). $BaTiO_3$ nanoparticles were purchased from Shandong Guoteng Functional Ceramics Co., Ltd., China. The average size of the $BaTiO_3$ nanoparticles is ~300 nm. The other analytical-reagent starting materials, such as TEOS (≥28.4%), acetic acid (≥99.5%), absolute ethanol, and ammonia water (25–28%), are purchased from Sinopharm Chemical Reagent Co., Ltd., China. It was based on the hydrolysis/condensation of tetraethoxysilane (TEOS) catalyzed by ammonia in alcoholic media. Firstly, the surface of $BaTiO_3$ nanoparticles was activated by acetic acid treatment. 20 g of $BaTiO_3$ nanoparticles and 50 ml of absolute ethanol with 3 ml acetic acid were combined in a round-bottomed flask and placed in a water bath (40 °C) with magnetic stirring for 40 min, then sonicated for 30 min. After that, TEOS was added and then redispersed in the same condition. After that, ammonia water was slowly dropped by microburet to form so-called silica-coated $BaTiO_3$ suspension. The obtained BT nanoparticles were washed with deionized water and then dried at 100 °C for 12 h in the air. The coated $BaTiO_3$ powders can be obtained. For comparison, the $BaTiO_3$ + 2.0 wt% SiO_2 composition was prepared by conventional solid-state synthesis (CSSS). Both $BaTiO_3$ and SiO_2 nanoparticles were selected as starting materials. Pellets of 12 mm in diameter and about 0.5 mm thickness were uniaxially pressed at 200 MPa using 5% PVA binder. Slow heating at 600 °C for 2 h burned out the binder. After de-binding, these pellets were sintered in air at temperature 1250 °C for 2 h by heating rate of 2 °C/min.

The crystalline structures of the sintered samples were examined by X-ray diffraction (XRD, PANalytical X'Pert PRO). The microstructures and thickness of coating can be revealed by scanning electron microscopy (SEM, JSM-5610LV) and transmission electron microscopy (JEM-2100F STEM/EDS) measurements, respectively. For the electrical measurements, the sintered ceramics were smoothed and coated with silver electrodes on both faces. The temperature dependence of dielectric nonlinearity was measured by a precision multi-frequency inductance capacitance resistance analyzer (Agilent E4980A) connected with an automated temperature controller with heating rate of 2 °C/min. The dielectric breakdown strength and *P–E* hysteresis loop were examined at room temperature using a Radiant precision workstation (Radiant RT66A) based on the Sawyer-Tower circuit at 10 Hz.

3. Results and discussion

The so-called Stöber process was used to fabricate the coated $BaTiO_3$ powders to form coating layers of a few nanometers. Direct evidence of the coating of SiO_2 shell on the $BaTiO_3$ powder is provided by TEM, as shown in Fig. 1. The continuous and homogeneous coating of $BaTiO_3$ powder can be obtained with a series of silica thickness from 0.5 nm for 1.0 wt% SiO_2 to 12.0 nm for 8.0 wt% SiO_2, as shown in Table 1.

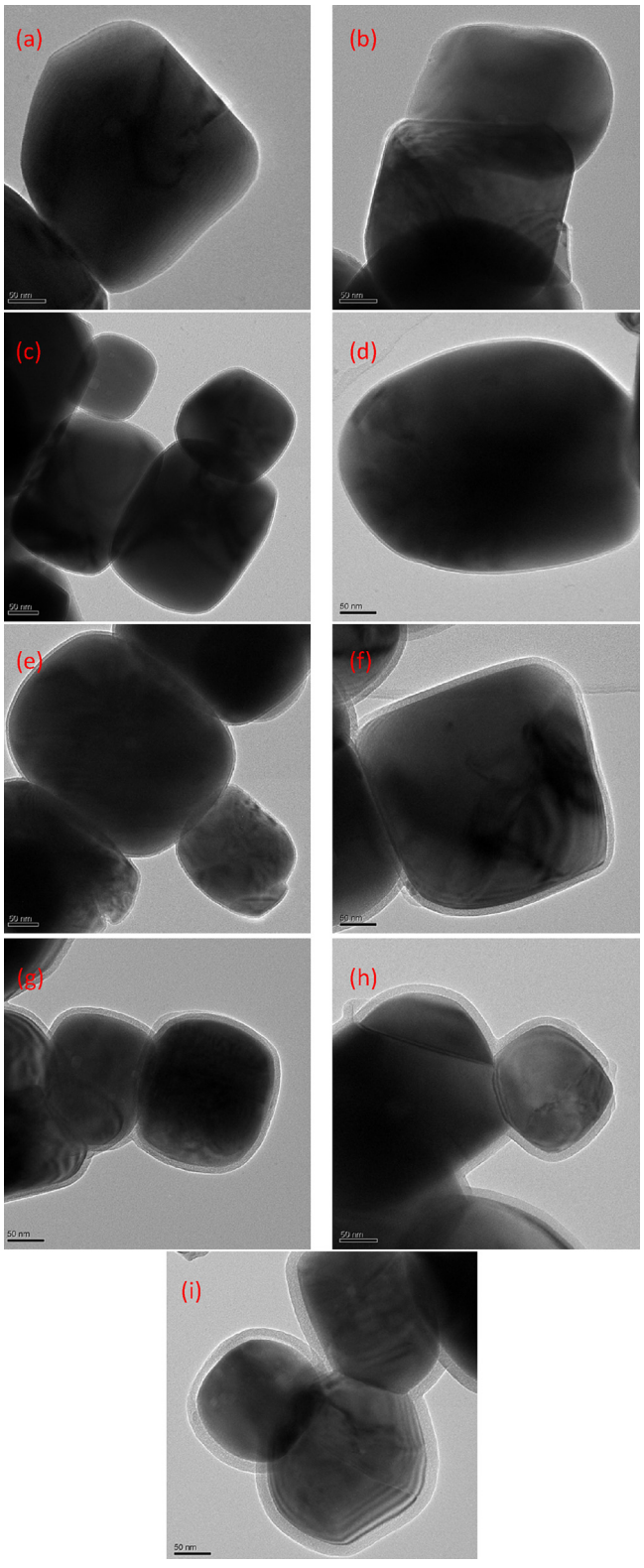

Fig. 1. TEM pictures of $BaTiO_3$ nanoparticles coated with different SiO_2 content (a) $x = 0$; (b) $x = 1.0$; (c) $x = 1.5$; (d) $x = 2.0$; (e) $x = 2.5$; (f) $x = 3.0$; (g) $x = 4.0$; (h) $x = 6.0$; (i) $x = 8.0$. Scale bar is 50 nm for all pictures.