Contents lists available at ScienceDirect

## Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

## A novel double-coating approach to prepare fine-grained BaTiO<sub>3</sub>@La<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> dielectric ceramics for energy storage application

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#### ARTICLE INFO

Article history: Received 6 June 2016 Received in revised form 7 August 2016 Accepted 8 August 2016 Available online 9 August 2016

Keywords: Core-shell structure BaTiO<sub>3</sub>@La<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> particle Fine-grained ceramics Energy storage Temperature-stable dielectric properties

### ABSTRACT

We prepared submicron BaTiO<sub>3</sub>@La<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> particles with high uniformity and dispersity using a novel double-coating method. The monodispersed submicron BaTiO<sub>3</sub> particles (diameter about 240 nm) formed a ferroelectric core that was coated with La<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> as a modified layer and a layer with high electrical resistance, respectively, and the thickness of two shells was about 20 nm. We then obtained dense, fine-grained BaTiO<sub>3</sub>-based energy storage ceramics (grain size  $\leq$  300 nm) with the same particle structure by means of sintering in air at 1240 °C for 2 h. As the amount of SiO<sub>2</sub> increased, the content of the tetragonal phase and the densification first increased and then decreased. When the amount of SiO<sub>2</sub> exceeded 9.0 wt%, a secondary phase with Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> appeared, and the core-shell structure disappeared. The BaTiO<sub>3</sub>@La<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> ceramics met the X8R requirements, with a maximum dielectric constant of 3362 at 6.0 wt% SiO<sub>2</sub>, and a low dielectric loss at room temperature (< 0.020, with a minimum of 0.011). The remnant polarization deceased from 13.80 to 1.21  $\mu$ C/cm<sup>2</sup>, while the energy storage density first increased and then decreased as the amount of SiO<sub>2</sub> coating increased from 0.0 to 12.0 wt%. The discharged energy storage density was highest (0.54 J/cm<sup>3</sup>) for samples containing 9.0 wt% SiO<sub>2</sub> under a maximum polarization field of 13.6 kV/mm, and the energy storage efficiency of the ceramic was >85%. © 2016 Elsevier B.V. All rights reserved.

#### 1. Introduction

Ceramic capacitors have many advantages, such as the ability to cycle many times, high reliability, and extremely short charge and discharge periods, and their performance has improved dramatically in recent years [1–3]. Barium titanate (BaTiO<sub>3</sub>) ceramics have been highlighted over the past five decades for use as dielectric materials in capacitors, because of their high dielectric constants [4]. In recent years, high-energy-density applications have led to increasing concern over their dielectric breakdown strength (BDS), which is critical in determining the energy storage capability of dielectric materials [5–7]. Therefore, numerous investigations of BaTiO<sub>3</sub> ceramics have focused on their high BDS, and have found that this property was affected by several factors, such as the existence of a secondary phase, porosity, grain size, and defects [8,9]. S. K. Sarkar et al. [10] studied the effects of adding 2–20 mol% B<sub>2</sub>O<sub>3</sub>

and PbB<sub>2</sub>O<sub>4</sub> glasses on the BDS and the dielectric constant of BaTiO<sub>3</sub> and found that BDS doubled and the dielectric constant decreased from 1500 to 700. A. Young et al. [11] studied the effect of a BaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-H<sub>3</sub>BO<sub>3</sub>-ZrO<sub>2</sub>-SrO glass additive on the BDS of BaTiO<sub>3</sub>, and found that the BDS increased to 2.8 times that of pure BaTiO<sub>3</sub> at 20 vol% glass. Q. Xu et al. [12] added a MgO-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass additive into the Ba<sub>0.95</sub>Sr<sub>0.05</sub>Zr<sub>0.2</sub>Ti<sub>0.8</sub>O<sub>3</sub> ceramics. The best specimen showed an energy density of 0.42 J/cm<sup>3</sup>. The BDS of Ba<sub>0.4</sub>Sr<sub>0.6</sub>TiO<sub>3</sub> ceramics with 10 wt% MgO added improved to 1.6 times that of pure Ba<sub>0.4</sub>Sr<sub>0.6</sub>TiO<sub>3</sub> ceramics [13]. Moreover, the addition of paraelectric SrTiO<sub>3</sub> into BaTiO<sub>3</sub> reduced the nonlinearity of the ceramic's permittivity [14]. Recently, even relaxor ferroelectrics have been receiving much attention due to their high energy storage efficiency, high stability, and environmentally friendly characteristics. BaTiO3-Bi(Mg2/3Nb1/3)O3 (BT-BMN) ceramics with relaxor-like characteristic and narrow polarizationelectric (P-E) field hysteresis loops were prepared with a BMN > 10 mol% [15].

Chemical coating methods have been shown to be more







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effective than solid-state methods as a way to form core-shell structure because they can modify the surface of the particles while maintaining a fine and uniform grain structure [16]. The addition of rare earth elements can increase the permittivity and broaden the peak of the curve at the maximum permittivity. Finegrained BaTiO<sub>3</sub> ceramics coated by La<sub>2</sub>O<sub>3</sub> have temperature-stable dielectric properties, prepared by our group using chemical methods [17]. However, we did not examine the energy storage properties of these materials. The addition of a single glass additive (SiO<sub>2</sub>) both acted as a barrier to dielectric loss by preserving the intrinsic properties of the ferroelectric cores and formed a glass phase with the other substances that had a low melting point and therefore reduced the sintering temperature [6,18]. B. B. Liu et al. [19] prepared BaTiO<sub>3</sub> ceramics with a fine-crystalline structure and an average grain size (< 200 nm) without abnormal grain growth by co-coating the cores with Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, and the BDS increased from 5.6 to 19.0 kV/mm [19]. Nonetheless, the temperature capacitance characteristic (TCC) and dielectric constant of these ceramics decreased. In addition, it was necessary to improve control of the synthesis of nano-sized or submicron-sized powders to produce fine-grained energy storage ceramics so the process could meet the growing demand for high capacitance and miniaturization.

In the present study, we developed a simple system for preparing BaTiO<sub>3</sub>@La<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> ceramics using a double-coating approach. These ceramics are potentially capable of meeting the energy storage needs of the electronics industry due to their fine grains. We selected submicron BaTiO<sub>3</sub>@La<sub>2</sub>O<sub>3</sub> particles for the core owing to their good dielectric properties over a wide temperature range. We then added SiO<sub>2</sub> as the outermost shell to improve the BDS and sintering properties of the ceramics. We studied the effects of the SiO<sub>2</sub> coating on the morphology and properties of the resulting "one core-two shells" particles and their ability to produce dense, fine-grained BaTiO<sub>3</sub>@La<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> energy storage ceramics.

#### 2. Experimental

We prepared the BaTiO<sub>3</sub>@La<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> particles and ceramics with a SiO<sub>2</sub> coating at SiO<sub>2</sub> contents of 0.0, 3.0, 6.0, 9.0, and 12.0 wt %. The starting materials were Ba(CH<sub>3</sub>COO)<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, TiCl<sub>4</sub>, tetraethoxysilane (TEOS), and NaOH, and they were all analytical-grade chemicals (with a minimum purity of 99%) obtained from the Shanghai Chemical Reagent Factory (Shanghai, China). A 0.02 mol/L La(NO<sub>3</sub>)<sub>3</sub> solution was produced by dissolving the La<sub>2</sub>O<sub>3</sub> in nitric acid. The BaTiO<sub>3</sub>@La<sub>2</sub>O<sub>3</sub> powders were prepared using the method described in our previous work [17]. Briefly, we prepared suspension slurries of 1.0 g BaTiO<sub>3</sub>@La<sub>2</sub>O<sub>3</sub> per 300 mL of a 1:1 v/v solution of water and ethanol by means of ultrasonic dispersion for 0.5 h. The TEOS solution was added into the BaTiO<sub>3</sub>@La<sub>2</sub>O<sub>3</sub> suspension slurries and the pH value of the mixed slurry was adjusted to a value greater than 9 by adding ammonia solution. Then, after triggering the suspension slurries for 6 h, the SiO<sub>2</sub> became a coating on the surface of the BaTiO<sub>3</sub>@La<sub>2</sub>O<sub>3</sub> particles. We obtained BaTiO<sub>3</sub>@La<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> powders by drying the total slurry at 80 °C for 10 h and then calcined the residues at 600 °C for 2 h in an air atmosphere. The result was monodispersed submicron BaTiO<sub>3</sub>@-La<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> particles. The powders were pressed into pellets (8 mm in diameter and 4 mm thick) under a pressure of about 6 MPa by means of uniaxial pressing. These pellets were then sintered in air at 1240 °C for 2 h to produce the test samples.

The phase identification was performed by means of X-ray diffraction measurements (XRD; D8 Advance, Bruker, Frankfurt, Germany) at room temperature using Cu K $\alpha$  radiation (1.54059 Å). The morphology of the particles was characterized using field-

emission transmission electron microscopy (FE-TEM; Tecnai G2 F20S-TWIN, FEI, Hillsboro, Oregon, USA) with energy-dispersive spectroscopic (EDS) analysis. The morphology of the ceramic samples was characterized using a field-emission scanning electron microscope (FE-SEM; Model JSM-5800, JEOL, Tokyo, Japan). The DC resistivity was acquired using a high-resistance meter (Model 4339A, HP, Palo Alto, CA) at ambient temperature. The P-E hysteresis loops were measured using a ferroelectric tester (Model 609B, Radiant technology, Washington, USA). Dielectric properties were measured using an LCR meter (Model HP4284A, Hewlett-Packard Company, Santa Clara, California, USA) controlled by a computer. The testing temperature was controlled between -60 °C and 150 °C under test conditions of 1 kHz and 1 V<sub>rms</sub>, with a heating rate of 2 °C/min.

#### 3. Results and discussion

3.1. Phase composition and morphology of the BaTiO<sub>3</sub>@La<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> powders

Fig. 1 shows the XRD results for the BaTiO<sub>3</sub>@La<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> powders. Regardless of the SiO<sub>2</sub> amounts, the main phase of all the BaTiO<sub>3</sub>@La<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> powders was a perovskite phase. The peaks for the tetragonal-phase BaTiO<sub>3</sub> particles in the XRD were indexed based on JCPDS file number 05–0626. Weak diffraction peaks for La<sub>2</sub>O<sub>3</sub> were observed in the XRD patterns based on JCPDS file number 54–0213. The pattern shows a broad hump in the initial range (between  $2\theta = 10^{\circ}$  and  $30^{\circ}$ ) that indicated the presence of an amorphous SiO<sub>2</sub> layer on the particles. However, this hump was not obvious, which could be attributed to the fact that only a small amount of SiO<sub>2</sub> existed in the amorphous form. Compared with the strong intensity of the BaTiO<sub>3</sub> diffraction peaks, the broad humps for SiO<sub>2</sub> were weak [20,21].

Fig. 2 shows the FE-TEM images, EDS results for the line-scan microanalysis, and elemental mapping images of the BaTiO<sub>3</sub>@-La<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> particles. Fig. 2a shows the coating microstructure of the sample that contained 9.0 wt% SiO<sub>2</sub>. The image shows that the particles had a uniform spherical morphology and excellent dispersity. The thickness of the two coating layers was about 20 nm (Fig. 2b), and the mean size of the BaTiO<sub>3</sub>@La<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> particles was about 280 nm. The most important characteristic of these images is that the degree of coverage by the coating is very high,



Fig. 1. XRD patterns for the  $BaTiO_3@La_2O_3$  powders coated with various amounts of  $SiO_2$ : (a) 0.0 wt%, (b) 3.0 wt%, (c) 6.0 wt%, (d) 9.0 wt%, (e) 12.0 wt%.

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