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Structural, dielectric, and piezoelectric properties of fine-grained NBT–$BT_{0.11}$ ceramic derived from gel precursor

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Abstract

$(Na_{1/2}Bi_{1/2})TiO_3$ doped *in situ* with 11 mol% $BaTiO_3$ (NBT–$BT_{0.11}$) powders were synthesized by a sol–gel method, and the electrical properties of the resulting ceramics were investigated. The powders consisting of uniform and fine preliminary particles of about 50 nm were prepared by calcining the gel precursor at 700 °C. $(Na_{1/2}Bi_{1/2})_{0.89}Ba_{0.11}TiO_3$ ceramics, sintered at temperatures up to 1150 °C have a rhombohedral symmetry, while the ceramic sintered at 1200 °C exhibits a tetragonal crystalline structure. The ceramics show high dielectric constant ($\varepsilon_r \sim 5456$), dielectric loss of 0.02, depolarization temperature $T_d \sim 110$ °C and temperature corresponding to the maximum value of dielectric constant $T_m \sim 262$ °C. The dielectric constant (ε_{33}) and the piezoelectric constant (d_{33}) attain the maximum values of 924 and 13 pC/N, respectively, while the electromechanical coupling factor (k_p) value is 0.035. The NBT–$BT_{0.11}$ ceramics derived from sol–gel present high mechanical quality factor ($Q_m \sim 860$). The dielectric and piezoelectric properties values of NBT–$BT_{0.11}$ ceramics derived from sol–gel are smaller than those of samples produced by the conventional solid state reaction method, due to the grains size and oxygen vacancies that generate dipolar defects.

Keywords: A. Sol–gel processes; C. Dielectric properties; C. Piezoelectric properties; D. $BaTiO_3$ and titanates

1. Introduction

Lead zirconate titanate (PZT) ceramics exhibit excellent electric properties and are extensively used in numerous electronic devices, such as actuators, sensors, capacitors, and high-power transducers.[1,2] On the other hand, PZT ceramics have been continuously modified with different additives, which make them more attractive for specific applications. Thus, incorporating ZnO to PZT ceramics contributes to an obvious improvement of the fracture properties.[3] ZnO whiskers and Sb_2O_3 co-modified lead zirconate titanate composites show enhanced piezoelectric and mechanical properties,[4] while Nb_2O_5 enhance piezoelectric and ferroelectric properties of the monolithic PZT.[5]

With the increasing environmental concerning, lead-free piezoelectric ceramics have turned to be a certain trend in the sustainable development. Lead-free piezoelectric materials include $BaTiO_3$, $(Na,Bi)TiO_3$, $(Na,K)NbO_3$ system and so on.[6]

$Na_{1/2}Bi_{1/2}TiO_3$ (NBT) is a ferroelectric compound with perovskite structure and rhombohedral symmetry.[7] Usually, the NBT ceramic exhibits weak piezoelectric properties.[8] In order to improve the piezoelectric properties of this ceramic, a large number of NBT-based solid solutions, including NBT–$BaTiO_3$ (NBT–BT), have been prepared and intensively studied in recent years.[9–20] The partial substitution of $(Na_{0.5}Bi_{0.5})^{2+}$-site ions by Ba^{2+} contributes to the decrease of Curie temperature and to the improvement of sintering and piezoelectric properties. The $(1-x)$NBT–xBT (abbreviated as NBT–BT_x) ceramics with 1–20 mol% $BaTiO_3$ were studied. NBT–BT_x system has attracted considerable attention, because of the existence of a rhombohedral–tetragonal morphotropic phase boundary (MPB) near $x = 0.06$. Compositions close to the MPB provide

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substantially improved poling and piezoelectric properties.[18,21] Similar to pure NBT, NBT–BT_x ($x < 0.06$) ceramic has a rhombohedral perovskite structure. As x increases, a tetragonal phase appears and increases continuously. At $x \sim 0.10$, the ceramic becomes a pure tetragonal phase. These suggest that a MPB of rhombohedral and tetragonal phases resides for $0.06 < x < 0.10$.[7] In this paper, we investigated the piezoelectric properties of NBT–BT_x ($x = 0.11$) ceramic outside the MPB domain, where this ceramic should present a tetragonal structure.

NBT-based ceramics are usually fabricated by the conventional solid-state method. Recently, considerable research efforts have been devoted to the preparation of materials by various wet chemical methods, such as citrate method,[22,23] emulsion method,[24] hydrothermal process,[25] sol–gel techniques[26,27] and stearic acid gel route.[28] It was found that NBT-based ceramics made from powders synthesized by alternative methods exhibit improved sinterability, poling process and piezoelectric properties. In the present study, NBT–$BT_{0.11}$ ceramics were produced by the sol–gel method, and their structure and electrical properties were examined.

2. Experimental procedures

Precursor sol of $0.89[(Na_{0.5}Bi_{0.5})TiO_3]$–$0.11[BaTiO_3]$ was prepared by a sol–gel technique starting from sodium acetate [$Na(CH_3COO)$], barium acetate [$Ba(CH_3COO)_2$], bismuth (III) acetate [$Bi(CH_3COO)_3$] and titanium (IV) isopropoxide, 97% solution in 2-propanol [$Ti\{OCH(CH_3)_2\}_4$], acetic acid and isopropanol. All reagents (Aldrich) are of analytical grade purity. The procedure is described in detail in a previous publication.[27] After drying the gel at 100 °C, the resulting powder was treated at different temperatures in order to obtain a single-phase powder. The ceramic samples were prepared by uniaxial pressing at 100 MPa. The as-obtained pellets with 10 mm diameter and 1 mm thickness were then sintered at various temperatures, in the 1100–1200 °C range, for 1 h, in air. Samples with apparent densities of 94–96% of the theoretical density were obtained. The calcined powder was investigated by scanning and transmission electronic microscopy (SEM, TEM) and X-ray diffraction (XRD). The microstructure of the samples was investigated using a FEI Quanta Inspect F scanning electron microscope and a Tecnai^{TM} G^2 F30 S-TWIN transmission electron microscope with a line resolution of 1 Å, in high resolution transmission electron microscopy (HR-TEM) mode and selected area electron diffraction (SAED). For diffraction analysis, a Bruker-AXS tip D8 ADVANCE diffractometer with Cu $K_{\alpha 1}$ radiation (wavelength 1.5406 Å), LiF crystal monochromator and Bragg–Brentano diffraction geometry was used. The data were acquired at 25 °C, with a step-scan interval of 0.020° and a step time of 10 s. The electrical measurements were carried out in the metal-ferroelectric-metal (MFM) configuration, where the electrodes M consist of silver. Dielectric measurements at fixed frequencies in the 120 Hz to 1 MHz frequency intervals have been performed on a temperature range between room temperature of about 25 °C and 300 °C. A Hioki 3532-50 type automatic RLC bridge and Kethley 2000 voltmeter, with chromel–alumel thermocouple type for temperature measurements, were controlled by a computer through the GPIB interfaces for automatic experimental data registration and further investigations. P–E loops were measured using a Radiant (Premier II) System. For the piezoelectric measurements, the samples were poled under an applied field of 3 kV/mm, at 120 °C, for 40 min. Piezoelectric properties were measured by a resonance-antiresonance method on the basis of IEEE 176-1987 standards, using an impedance analyzer (HP 4194A). The electromechanical coupling factor (k_{33}), was calculated from the resonance and antiresonance frequencies. The dielectric constant (ε_{ii}^{T}), was determined from the capacitance of the poled specimen at 1 kHz. The elastic constants (s_{jj}^{E}), was calculated using the frequency constant (N_{ij}) and the measured density (ρ_o), by the relation $s_{11}^{E} = 10^9/(^2N_P^2\rho_o)$. Finally, the piezoelectric constants (d_{ij}) were calculated using the k_{ij}, ε_{ii}^{T} and s_{jj}^{E} values, by the equation

$$d_{ij} = k_{ij}(\varepsilon_{ii}^{T} s_{jj}^{E})^{1/2}.$$

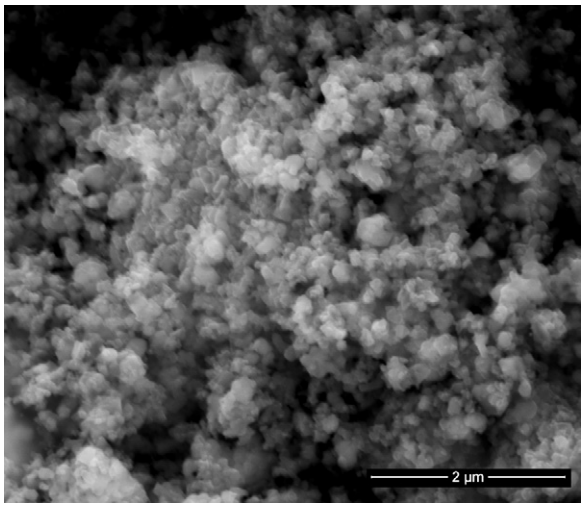

Fig. 1. SEM photomicrograph of 11 mol%$BaTiO_3$ doped-$Na_{1/2}Bi_{1/2}TiO_3$ precursor gel, heated at 700 °C, 3 h.

3. Results and discussion

3.1. Microstructure

The SEM micrograph of $Na_{0.5}Bi_{0.5}TiO_3$ doped with 11 mol% $BaTiO_3$ powder calcined at 700 °C, 3 h, in air, is presented in Fig. 1.

It can be seen that the sol–gel derived powder has a regular morphology, as a result of the agglomeration of preliminary particles of 40–60 nm.

The TEM and HR-TEM images and SAED pattern of the powder calcined at 700 °C, 3 h, in air, are shown in Fig. 2. The TEM image (see Fig. 2(a)) reveals that the powder is composed of spherical and polyhedral particles with the tendency to form agglomerates; the average size of the nanocrystallites is about 50 nm.