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Synthesis and electrical properties of CeO_2-added $(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$ ceramics

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Abstract

$(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$-xwt.%$CeO_2$ ($x = 0$, 0.2, 0.4, 0.6, 0.8, 1.0) powders were synthesis by a citrate method, and the piezoelectric and ferroelectric properties of the ceramics were investigated. The results indicate that the citrate method is an advantageous route in producing $(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$-xwt.%$CeO_2$ ($x = 0$, 0.2, 0.4, 0.6, 0.8, 1.0) ceramics. Homogeneous and fine powders with a pure perovskite structure were derived from precursor solutions with a mole ration of citric acid to total metal cation content (C/M) of 1.3 by calcining at 650 °C for 1 h. The sample containing 0.6 wt.%CeO_2 made by the citrate method shows superior piezoelectric properties and a strong ferroelectricity: high piezoelectric constant ($d_{33} = 157$ pC/N), high electromechanical coupling factor ($k_p = 31.2\%$), enhanced dielectric constant ($\varepsilon_{33}^T/\varepsilon_o = 819$) and relatively low dissipation factor ($\tan\delta = 2.72\%$) at 1 kHz, corresponding to a relatively large remanent polarization of $P_r = 38.0$ μC/cm^2 and a relatively low coercive field of $E_c = 37.4$ kV/cm.

Keywords: A. Ceramics; A. Oxides; B. Chemical synthesis; D. Piezoelectricity; D. Ferroelectricity

1. Introduction

In recent years, lead-free piezoelectric ceramics has attracted considerable attention as an important piezoelectric material because of its outstanding advantages in no lead pollution. Sodium bismuth titanate, $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT), is a kind of perovskite-type ferroelectric with complex A-site cations, showing a relatively large remanent polarization ($P_r = 38$ μC/cm^2) at room temperature and a relatively high Curie temperature ($T = 320$ °C) [1]. Due to its strong ferroelectricity at room temperature, NBT has been considered to be a promising candidate material for lead-free piezoelectric ceramics. However, it is difficult to pole due to the high coercive field ($E_c = 73$ kV/cm) and the high conductivity of NBT, making it unsuccessful in obtaining the desired piezoelectric properties. To solve these problems, various NBT-based solid solutions have been developed [2–9]. Among these solid solutions, the $(Na_{0.5}Bi_{0.5})_{1-x}Ba_xTiO_3$ material has attracted considerable attention owing to an existence of a rhombohedral (F_α)-tetragonal (F_β) morphotropic phase boundary (MPB). Takenaka et al. reported that the $(Na_{0.5}Bi_{0.5})_{0.94}TiO_3$-

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$0.06BaTiO_3$ (NBT-BT6) composition near the MPB have a relatively low dielectric constant and a relatively high electromechanical coupling factor [2]. The further enhancement on the piezoelectric and ferroelectric properties of NBT-BT6 ceramics is reported by Wang and Li [10,11]. However, there have been limited reports about rare-earth element doping to NBT-BT6 composition for the further enhancement on the piezoelectric and ferroelectric properties. It has been proved that the synthesis process has an obvious influence on NBT and NBT-based solid solutions in terms of chemical stoichiometry, lattice distortion and electrical properties [12–14]. However, there have been limited investigations into this subject. Therefore, it is necessary to investigate the synthesis and preparation of NBT-based ceramics. In view of this, we reported the synthesis of $(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$-xwt.%$CeO_2$ ($x = 0$, 0.2, 0.4, 0.6, 0.8, 1.0) (NBT-BT6-x%CeO_2) powders by a citrate method. In addition, CeO_2 was added into NBT-BT6 ceramics as an additive based on the formula NBT-BT6-x%CeO_2 and its effects on the piezoelectric and ferroelectric properties of the ceramics were investigated.

2. Experimental procedures

The citrate method was used to prepare NBT-BT6-x%CeO_2 powders with the nominal composition of $(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$-xwt.%$CeO_2$ ($x = 0$, 0.2, 0.4, 0.6, 0.8, 1.0). Reagent grade $NaNO_3$, $Bi(NO_3)_3{\cdot}5H_2O$, $Ba(NO_3)_2$, $Ce(NO_3)_3{\cdot}6H_2O$, tetrabutyl titanate and citric acid were used as starting materials. Citric acid was first dissolved into deionized water in a beaker. After adjusting the pH value of the solution to 7–9 by dripping an appropriate amount of ammonia solution, tetrabutyl titanate was added under a stirring at 60 °C. After stirring at 60 °C for 1 h, a yellowish two-layer liquid was obtained, comprising a transparent aqueous solution at the lower layer and an oil-like liquid at the upper layer. The aqueous solution was separated from the mixing liquid. Various nitrates were then added into the solution one after another, respectively, followed by a stirring at 80 °C for 1 h to generate a precursor solution with a pH value of about 6. The precursor solution was dehydrated in an oven at 100 °C to form a sol. Subsequent heating at a higher temperature of 160 °C yielded a gel. The gel was pulverized and then calcined at 550–700 °C for 1 h in air. The calcined powders were granulated with PVA as a binder. The granulated powders were pressed into discs in diameter of 19 mm and thickness of 1 mm. The compacted discs were sintered at 1150 °C for 2 h in air.

Thermogravimetry (TG) analysis and differential scanning calorimetry (DSC) analysis of the gel were performed using a netzsch STA449C simultaneous thermal analyzer in air. The crystal structure of calcined powders and ceramic specimens was examined by a Rigaku D/MAX-RB X-ray diffractometer using Cu H k_α radiation. A scanning electron microscope (SEM, Jeol JSM-5610LV) was used to investigate the morphology of calined powders. Silver paste was fired on both faces of the discs at 650 °C as electrodes. The specimens for measurement of piezoelectric properties were poled in silicon oil at 60 °C under 3 kV/mm for 15 min. After poling, the piezoelectric constant d_{33} was measured using a quasistatic d_{33} meter based on the Berlincourt method. The resonance measurements were performed using a HP4294 impedance analyzer. The electromechanical coupling factor k_p was calculated from the resonance and the anti-resonance frequencies according to Onoe's formulas [15]. Dielectric properties were determined using a HP4192A impedance analyzer at 1 kHz. The coercive field E_c and remanent polarization P_r were determined from P–E hysteresis loops obtained by a Radiant precision workstation at room temperature. The measurement frequency of P–E loops is 20 Hz.

3. Results and discussion

During the synthesis process, it was found that the mole ratio of citric acid to the total metal cation content (C/M) is a main contributing factor to the formation of the sol and gel. It was ascertained that a C/M in the range of 1.1–1.5 produced homogeneous, transparent sol and gel. Fig. 1 shows the TG-DSC curves of NBT-BT6-0.6%CeO_2 gel derived from the precursor solution with C/M = 1.3. The faint endothermic peak at 84.4 °C was caused by the evaporation of residual citric acid and water. The successive endothermic peak at 180.3 °C is attributed to the melting of the citric acid. The exothermic peak at 280.6 °C is assigned to the thermal decomposition of excessive citric acid. The exothermic peak at 477.5 °C is ascribed to the thermal decomposition of the citrate complex. The front four peaks correspond to a total weight loss of 57.14%. The strong exothermic peak at 565.8 °C is attributed to the combustion of remaining organic components. No further DSC peak or weight loss can be seen, indicating the completion of the thermal decomposition of the gel before 600 °C. Fig. 2 shows the X-ray diffraction (XRD) patterns