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Effect of firing temperatures on properties of BNT-BCTZ-0.007mol%BFCO lead free piezoelectric ceramics synthesized by the solid state combustion method

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ABSTRACT

In this study, the effects of calcination temperature (550–750 °C for 2 h) and sintering temperature (1100–1200 °C for 2 h) on the phase formation, microstructure, electric and magnetic properties of the $0.94Bi_{0.5}Na_{0.5}TiO_3$-$0.06(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})$ lead-free piezoelectric ceramic doped with 0.007 mol% Bi_2FeCrO_6 (BNT-BCTZ-BFCO) were investigated. These ceramics were prepared by the solid state combustion technique using glycine as fuel. The pure perovskite phase was observed in the BNT-BCTZ-BFCO powders attained at the calcined temperature of 650 °C for 2 h. The morphology of the BNT-BCTZ-BFCO powders exhibited an almost-spherical shape and the average particle size increased when the calcination temperature increased from 550 to 750 °C. TEM results of pure BNT-BCTZ-BFCO powder calcined at 650 °C for 2 h showed rounded shapes and the average particle size was ~ 200 nm. The XRD results of all ceramics exhibited a single perovskite structure with the co-existence of the rhombohedral and tetragonal phases. The average grain size increased with increasing sintered temperature. The density, dielectric constant (ε at T_r and T_m) and piezoelectric constant (d_{33}) increased when the sintered temperature increased up to 1150 °C and then reduced in values. At a sintered temperature of 1150 °C, BNT-BCTZ-BFCO ceramic showed the highest relative density (97.2%), maximum dielectric properties (ε at T_r = 1783 and ε at T_m = 5117), d_{33} value (178 pC/N), d^*_{33} (549 pm/V) and the remnant polarization (P_r = 34.66 μC/cm^2). At higher sintering temperatures, the properties of BNT-BCTZ-BFCO ceramics decreased due to the evaporation of Bi and Na. All ceramics exhibited the paramagnetic behavior and the magnetization increased with increasing sintering temperature.

1. Introduction

Lead-based piezoelectric ceramics that have a perovskite structure, for example (Pb, Zr)TiO_3 and Pb(Mg, Nb)O_3, have been widely used and applied in electronic devices such as sensor, transducer etc. owing to their large piezoelectric coefficient (d_{33} ≥ 400 μC/N) and high dielectric constant (≥ 8000) [1–3]. However, it is well known that the preparation process of Pb-based materials generates PbO during high sintering temperatures. PbO is very toxic and is a serious threat for human health and the environment. In this scenario, the development and creation of new lead free piezoelectric ceramics is essential in order to replace Pb-based piezoelectric ceramics. Lead-free $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) ceramics are one of the most important of the piezoelectric materials due to BNT possessing a rhombohedral perovskite structure at room temperature and a large remnant polarization (P_r ≈ 38 μC/cm^2) [4]. At high temperatures (around 320 °C), the BNT ceramics show a broad maximum of dielectric constant, which may be initiated from dielectric relaxor behavior owing to the response of electro-mechanical interaction between polar regions and non-polar matrix [5]. However, BNT exhibits a low piezoelectric constant (d_{33} ≈ 90 pC/N) and has difficultly poling because of a large coercive field (E_c ≈ 73 kV/cm) and high leakage current. These defects lead to limits on their possible applications in electronic devices [4]. Moreover, the preparation of BNT usually involves a high sintered temperature (> 1120 °C) which evaporates Bi and Na during the sintering process [6]. Therefore, many researchers have attempted to modify the electrical

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properties of BNT ceramics by adding other compounds such as: $BaTiO_3$ (BT) [7], $BiKTiO_3$ (BKT) [8], $Bi(Ni_{0.5}Ti_{0.5})O_3$ (BNiT) [9], $KNaNbO_3$ (KNN) [10], and $(BaCa)(TiZr)O_3$ (BCTZ) [11].

Qian Gou et al. [11] prepared a binary system of (1-x) $Bi_{0.5}Na_{0.5}TiO_3$-x$(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O_3$ [(1-x)BNT-xBCTZ] ceramics by the conventional solid reaction method (calcined at 850 °C for 6 h and sintered at 1150 °C for 2 h). It was found that at x = 0.06, the coexistence of rhombohedral-tetragonal morphotropic phase boundary (MPB), together with the highest dielectric constant at room temperature ($\varepsilon_r \approx 1165$) and piezoelectric constant ($d_{33} \approx 158$ pC/N) were obtained. After this, Cheng et al. [12] reported doping small amount of Bi_2FeCrO_6 (BFCO) compound into the $0.94Bi_{0.5}Na_{0.5}TiO_3$-$0.06BaTiO_3$ [0.94BNT-0.06BT] ceramics forming a solid solution by the conventional solid reaction method. It was observed that the ceramics presented large remnant polarization ($P_r \approx 42.3$ μC/cm^2), high piezoelectric constant ($d_{33} \approx 214$ pC/N) and low coercive field ($E_c \approx 28.7$ kV/cm) at BFCO doping of 0.007 by mol%. Hence, the addition of BCTZ and doped BFCO compounds in a reasonable ratio are an effective route to modify the electrical properties of BNT ceramics. Following this route, the synthesis of 0.94BNT-0.06BCTZ solid solution with doped 0.007 mol%BFCO may have improved electrical properties and is of considerable interest and worthy of investigation.

Another point of interest in piezoelectric ceramics is the fabrication technique, which is one of the main factors for production of high quality lead free piezoelectric ceramics. Recently, T. Bongkarn and coworkers have successfully fabricated high quality lead free piezoelectric ceramics of BZT [13], BNKLT [14], BNT-BKT-BLT [15], KNLNTS [16], and BNKLLT-BCTZ [17] by the solid state combustion technique. An important feature of the combustion technique is that it relies on the energy released from the fuel to accelerate the chemical reaction between raw materials and reduces the reaction temperature. Moreover, the reaction can easily occur in a liquid system because the diffusion coefficient is higher than in a solid medium [18]. Ceramics with a high density and excellent electrical properties were obtained using a low firing temperature and a short soaking time [18–20].

From a review of literature, the preparations of 0.94BNT-0.06BCTZ ceramic doped with 0.007 mol%BFCO [BNT-BCTZ-BFCO] fabricated via the solid state combustion technique have not been reported. This paper characterizes the ceramics made from the binary system of 0.94BNT-0.06BCTZ doped with 0.007 mol%BFCO prepared via the solid state combustion technique. The effect of firing conditions on crystal structure, morphology, electric and magnetic properties of BNT-BCTZ-BFCO ceramics was investigated.

2. Experiment

The $0.94Bi_{0.5}Na_{0.5}TiO_3$-$0.06(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})$-0.007 mol% Bi_2FeCrO_6 (BNT-BCTZ-BFCO) samples were prepared by the solid state combustion technique with glycine as the fuel. High purity, reagent grade powders of $Bi(NO_3)_3{\cdot}5H_2O$, $NaNO_3$, $Ba(NO_3)_2$, $Ca(NO_3)_2{\cdot}4H_2O$, ZrO_2, TiO_2, $Fe(NO_3)_3{\cdot}9H_2O$ and $Cr(NO_3)_3{\cdot}9H_2O$ were used as raw materials. All raw materials were weighed to the suitable stoichiometry and ball mixed in ethanol for 24 h. The slurry was then dried and pulverized (500 mesh). The dried powder was mixed with glycine in a ratio of 1:0.41 and then calcined at 550–750 °C for 2 h using a heating/cooling rate of 2 °C/min. The pure calcined powder was mixed with 3 wt% polyvinyl alcohol (PVA) as a binder and ball milled again for 12 h. The mixture of calcined powders was pressed into discs with a diameter of 15 mm and a thickness of 2 mm under 80 MPa pressure. The samples were covered in an alumina crucible and sintered between 1100 and 1200 °C for 2 h in ambient atmosphere with a binder burnout at 600 °C for 1 h. The crystalline structure of the powders and ceramics was confirmed by X-ray diffractometer (XRD, Philip PW 3040/60 X'pert pro). The sintered samples were thermally etched by annealing at 100 °C below the sintering temperature for 20 min, then the microstructures were investigated by scanning electron microscopy (SEM, Leo1455VP). The linear interception method was used to calculate the average particle size of the calcined powders and the average grain size of the sintered ceramics. More than 300 particles or grains were measured to calculate their sizes. The bulk density of the ceramics were measured using the Archimedes principle. For electrical properties, the sintered samples were polished and coated with silver paste (Heraeus, D11402), to act as electrodes, on both faces and then fired at 500 °C for 30 min. The dielectric constant and loss of the poled and unpoled samples were investigated using a LCR meter (HP, 4284A) with temperatures ranging from room temperature to 400 °C at difference frequencies. Impedance spectroscopy (IS) measurements were conducted over a wide temperature (480–540 °C) and frequency range (20 Hz to 1 MHz) using Keysight impedance gain/phase analyzer (model 4194A). The obtained impedance data were analyzed by utilizing a combination of the impedance complex plane plot (Z* plot) and the spectroscopic plot of the imaginary part of the impedance (Z" spectroscopic plot). For piezoelectric testing, the specimens were poled under a dc field of 50 kV/cm for 30 min in silicon oil at 60 °C. A quasi-static d_{33}-meter (Sinocera, YE2730A) was used to measure the piezoelectric constant d_{33} value of the samples. The ferroelectric behaviors were measured at room temperature with a computer-controlled modified Sawyer-Tower circuit (Radiant, PLC2-1014346). Magnetization curve measurements were carried out at room temperature using a vibrating sample Magnetometer (Versa Lab, Quantum Design).

3. Results and discussion

Fig. 1 shows the XRD pattern of the BNT-BCZT-BFCO powders as a function of calcined temperature between 550 and 750 °C for 2 h. As can be seen, the impurity phases of TiO_2 (JCPDS: 00-002-0387), Bi_2O_3

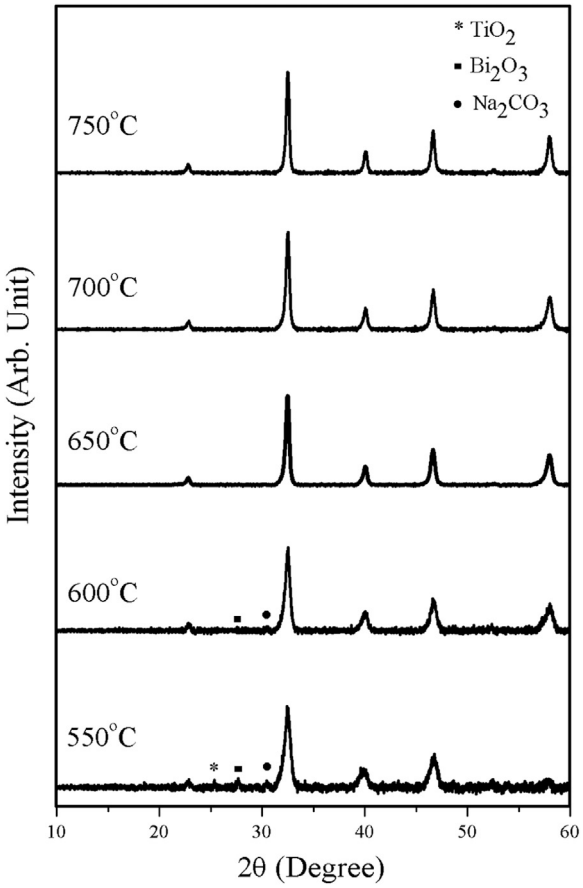

Fig. 1. XRD patterns of the BNT-BCZT- BFCO powders calcined at 550–750 °C.