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Low-temperature sintering, structure transition and dielectrical properties of $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ with $Na_{0.5}Bi_{0.5}TiO_3$ addition

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ABSTRACT

$Na_{0.5}Bi_{0.5}TiO_3$-modified $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ ceramics were prepared by solid state route and their structural and dielectric properties were investigated. The sintering temperature of BCTZ ceramics has been significantly decreased from 1460 °C to 1280 °C with NBT addition. All samples showed a pure perovskite structure and a stable solid solution has been formed between BCTZ and NBT. Some tetragonal phase gradually transformed to rhombohedral or cubic phase with the addition of NBT. Dielectric peak gradually becomes broader, revealing that the diffuser behavior was enhanced. The prominent superimposed loss peaks related to thermally activated relaxation process. The values of activation energy of the relaxation process are 1.034, 1.285, 1.308 and 1.353 eV, which could be associated with the migration of oxygen vacancies.

1. Introduction

Lead-containing materials have been used as an essential material for most electronic device. However, the use of lead-containing materials has caused serious lead pollution and some environ- mental issues due to its high toxicity of lead oxide. Therefore, it is necessary to develop lead-free materials for the replacement of these lead-based ceramics [1–4].

Recently, $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ (BCTZ) ceramic with excellent dielectric, piezoelectric and ferroelectric properties was developed by Liu et al. [4] in 2009, which show better dielectric and piezoelectric properties than soft PZT materials, leading to a lot of research in the last few years [5–11]. However, properties like high sintering temperature and low Curie temperature seriously limit their industrial production and practical applications in electronic devices [4–6]. In order to reduce detrimental factors, a lot of works have been done. For example, Bao et al. [7] showed a higher T_c of 114 °C in 0.47BZT–0.53BCT ceramic. Pr_2O_3-doped and $BiFeO_3$-modified BCTZ ceramics prepared by Han et al. [8] and Wu et al. [9] exhibit a low sintering temperature of 1400 °C. Furthermore, Cui et al. [10] and Ma et al. [11] reported a lower sintering temperature of 1350 °C in CeO_2 and $BiYO_3$ modified BCTZ ceramics. However, a slight improvement in sinterability and T_c always accompanied by a great decrease in dielectric and piezoelectric properties for BCTZ-based materials. In addition, most reports were concentrated on the piezoelectric properties of BCTZ-based ceramics rather than the dielectric properties, despite the dielectric properties of BCTZ-based ceramics are better than that of soft PZT [4] and $BaTiO_3$- based ceramics [12].

$Na_{0.5}Bi_{0.5}TiO_3$ (NBT) is an important ferroelectric material with high remnant polarization (P_r=38 μC/cm^2), high Curie temperature (T_c=320 °C) and low sintering temperature (~1150 °C) [1,2]. Therefore, the introduction of NBT into BCTZ might improve the sinterability, T_c, dielectric and ferroelectric properties of BCTZ ceramics.

In the present work, (1-*x*)BCTZ-*x*NBT ceramics were prepared by solid state route. The effects of NBT content on densities, sintering temperature, phase structure, dielectric and relaxtor properties of the samples were investigated.

2. Experiment procedure

(1-*x*)BCTZ-*x*NBT ceramics were prepared by a conventional solid-state reaction method using $BaCO_3$, $CaCO_3$, TiO_2, ZrO_2, Na_2CO_3 and Bi_2O_3 (Sinopharm Chemical Reagent Co., Shanghai) as starting raw materials. First, NBT and BCTZ powders were synthesized separately. Prior to weighing, Na_2CO_3 powders were dried at 110 °C for 12 h. According to their stoichiometric formula, raw materials for NBT and BCTZ were mixed in planetary ball mill using Y_2O_3-stabilized ZrO_2 grinding media for 24 h. After being milled, the mixed powders for NBT and BCZT synthesis were calcined at 850 °C and 1270 °C for 4 h, respectively. After calcinations, the powders were again ball milled separately for 24 h with the above mentioned ball-milling method. According to the chemical formula (1-*x*)BCTZ-*x*NBT (*x*=0, 0.03, 0.05 and 0.08), the NBT and BCTZ powders were weighed and mixed in planetary ball mill for

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24 h. The mixtures were dried in oven at 80 °C for 24 h and granulated with 5 wt% PVA as a binder, and then pressed into green disks with diameters of 12 mm and thickness of 1.5 mm under a pressure of 100 MPa. After burning off PVA at 600 °C for 2 h the disk samples were sintered at 1250–1480 °C for 2 h.

The phase structures of these ceramics were identified by powder X-ray diffraction (CD-MAX 2200pc, Rigaku Co., Tokyo, Japan) at a voltage and current of 40 kV and 30 mA. XRD data were collected in the range of 15 –80° with a 0.02° step and scanning speed of 5°/min. Raman spectroscopy (Renishaw-invia, Renishaw, U. K.) was used to further confirm the phase evolution of these ceramics in the region of 100–900 cm^{-1} at room temperature. For the electrical measurements, the sintered pellets were ground, polished, and painted with silver paste. Their dielectric behavior as a function of measurement temperatures was obtained by using an LCR meter (E4980A, Agilent, U.S.A.). Frequency dependent permittivity and loss tangent of these ceramics were measured at different temperatures by an LCR meter (E4980A, Agilent, U.S.A.).

3. Results and discussions

Fig. 1 shows the densities of (1-*x*)BCTZ-*x*NBT ceramics as a function of sintering temperature, the sintering temperatures of the samples decrease monotonously with the increasing content of NBT, which is due to the fact that the sintering temperature of NBT ceramic [1,2] is lower than that of BCTZ ceramic [4–6]. It is accepted that the oxygen vacancies can enhance the mass transfer and promote the grain growth, finally promote the densification process of (1-*x*)BCTZ-*x*NBT ceramics [8]. The Bi^{3+} and Na^{+} substitution for Ba^{2+} and Ca^{2+} leads to the generation of oxygen vacancies, and then these oxygen vacancies can enhance the mass transfer and promote the grain growth. The optimum sintering temperature and density of the samples is listed in Table 1, it can be seen that the density of the samples increases slightly with the increasing content of NBT because the NBT ceramic has a higher density than that of BCTZ ceramic [13,14].

Fig. 2(a) shows the XRD patterns of (1-*x*)BCTZ-*x*NBT ceramics. The data of all the samples show a pure perovskite phase without secondary phases, indicating that NBT has completely diffused into BCTZ lattices. For better analyze the phase structure of the ceramics, the enlarged XRD patterns of (002)/(200), (202)/(220) and (301)/(310) peaks are given in Fig. 3(a–c), respectively. The (200), (202), (220) and (310) reflection peaks shift to a higher degree indicating the shrink of cell volume according to Bragg's law $2d\sin\theta = n\lambda$, which is due to the substitution of smaller ions (Na^{+} =0.139 nm, Bi^{3+} =0.136 nm, Ti^{4+} =0.605 nm) for bigger ions (Ba^{2+} =0.161 nm and Zr^{4+} =0.072 nm) [15,16].

In perovskite structure, a tetragonal phase is expected to show two peaks at (200) (intensity ratio is 1:2), two peaks at (202) (intensity ratio is 1:1) and two peaks at (301) (intensity ratio is 1:1). Furthermore, a rhombohedral phase is expected to exhibit single (200), split (202) and (301) reflection peaks [17–19]. From Fig. 3, it can be evidently seen that the coexistence of tetragonal and rhombohedral phase in BCTZ composition, this agrees with previous reports in the literatures [4–6,20–23]. The relative intensity of (002), (220) and (301) peaks gradually decrease, indicating that the reduction of the content of tetragonal phase. This

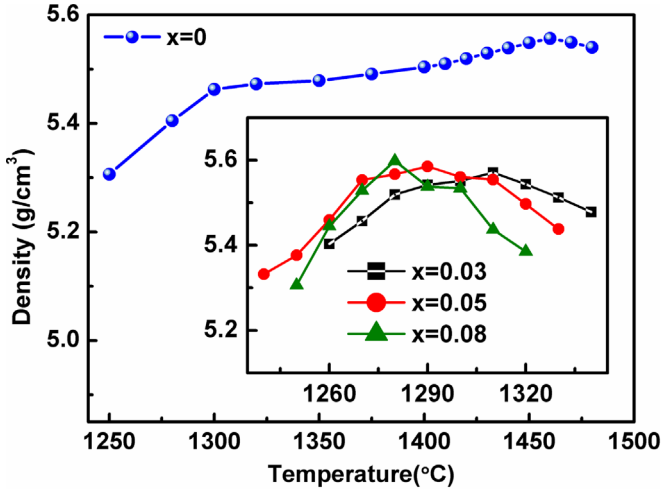

Fig. 1. Densities of (1-*x*)BCTZ-*x*NBT ceramics as a function of sintering temperature.

Table 1
The optimum sintering temperature and density of (1-*x*)BCTZ-*x*NBT ceramics.

x	0	0.03	0.05	0.08
T_s (°C)	1460	1310	1290	1280
Density (g/cm^3)	5.5564	5.5712	5.5854	5.5983

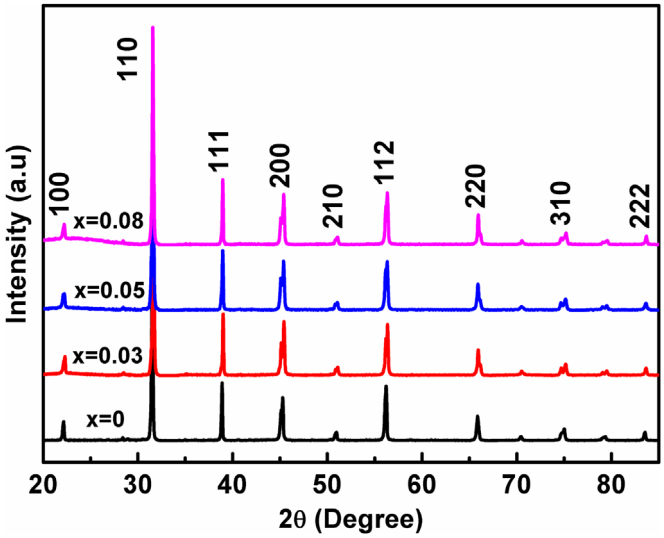

Fig. 2. XRD patterns of (1-*x*)BCTZ-*x*NBT ceramics.

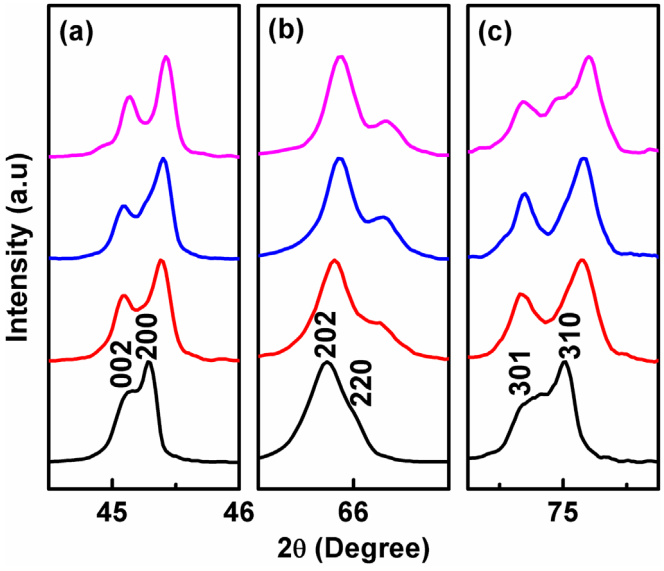

Fig. 3. Enlarged XRD patterns of (a) (002)/(200), (b) (202)/(220) and (c) (301)/(310) peaks.