Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

$Bi_{0.5}Na_{0.5}TiO_3$-$BaTiO_3$-$CaZrO_3$:ZnO high-temperature dielectric composites with wide operational range

Xin Yuan, Xiao-Yu Geng, Ji Zhang, Rui-Xue Wang, Xian-Zhu Deng, Lei Sun, Zheng-Bin Gu, Shan-Tao Zhang*

National Laboratory of Solid State Microstructures & Department of Materials Science and Engineering, College of Engineering and Applied Science, Nanjing University, Nanjing 210093, China

ARTICLE INFO

Keywords:
High-temperature dielectrics
Composite
Relaxor
Permittivity

ABSTRACT

0.82[0.94$Bi_{0.5}Na_{0.5}TiO_3$-0.06$BaTiO_3$]-0.18$CaZrO_3$:xZnO (BNT-BT-CZ:xZnO, x = 0–0.40 with interval of 0.10) high temperature dielectric composites were prepared and the structural and electrical properties were investigated. Significantly improved temperature-insensitive permittivity spectra have been observed in the composites: the temperature range for low variance in permittivity ($\Delta\varepsilon_r/\varepsilon_{r,150\,^\circ C} < 10\%$) is 70–190 °C for x = 0, whereas it is extended at least to 30–250 °C for the optimal x = 0.10 at 1 kHz. Especially, for this optimal composite, the variance of permittivity is less than 4.0% in the temperature range of 30–400 °C with the suitable permittivity value of ~ 600 at 10 kHz. By comparatively investigating the properties of unpoled and poled samples, the improved temperature-insensitive permittivity is rationalized by the ZnO-induced local electric field that can suppress the evolution of polar nanoregions and thus enhance the temperature-insensitivity of permittivity.

1. Introduction

Dielectric materials have important applications in many indispensable electronic components like capacitor, switching and sensing device, thus they are not only the long-term hot research topic but also have strongly growing markets [1–3]. Among various dielectrics-based devices, capacitor is probably one of the most challenging components, mainly due to its need to work under harsh environments like high-temperature [3–5]. For such applications, developing high performance high-temperature dielectrics is of great interest. In general, there are two basic requirements for such high-temperature dielectrics: (1) Extremely temperature-insensitive permittivity, ideally within the variation of 10–15% within a wide temperature range [6]. (2) High permittivity in order to miniaturize device size [7].

Some oxide dielectrics, exemplified by Bi_2O_3-ZnO-Nb_2O_5 system, have been reported for their extremely temperature-stable permittivity in a wide temperature range [8,9]. However, such materials generally show medium permittivity lower than 200. On the other hand, perovskite ferroelectrics usually have large permittivity, whereas their phase transitions, such as ferroelectric-paraelectric phase transition, will result in temperature-sensitive permittivity around the transition temperatures. Chemical doping/substituting can disrupt the long-range ferroelectric order and lead to relaxor ferroelectrics that show improved temperature-stability of permittivity with relatively high permittivity value. Up to now, perovskite $BaTiO_3$ (BT), $K_{0.5}Na_{0.5}NbO_3$ (KNN) and $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) based relaxor ferroelectrics have been studied as the candidates for high-temperature high-permittivity dielectrics [10–17]. Among the reported high-temperature high-permittivity dielectrics, BNT-based materials have attracted great attention due to their particular relaxor characteristic: two successive dielectric relaxational processes corresponding to two different symmetries of polar nanoregions (PNRs) are bridged by a diffused phase transition, which induces temperature-insensitive permittivity in a wide temperature range [14].

However, further optimizing the high temperature dielectric property of perovskite relaxor ferroelectrics is still necessary for actual applications because the existing polar nanoregions (PNRs) makes the fluctuation of permittivity and play a detrimental role in flattening the permittivity. Chemical doping or forming perovskite solid solution is the most widely used method to improve the performance of relaxor-based high-temperature dielectrics. In our opinion, to develop higher performance high-temperature dielectrics, a feasible method other than chemical doping or substituting should be considered. Actually, there are some attempts to improve the dielectric properties by designing novel and particular microstructures, for example, forming duplex core-shell microstructure [18–21], composite microstructure [21–23], etc.

* Corresponding author.
E-mail address: stzhang@nju.edu.cn (S.-T. Zhang).

https://doi.org/10.1016/j.ceramint.2018.04.027
Received 7 March 2018; Received in revised form 4 April 2018; Accepted 4 April 2018

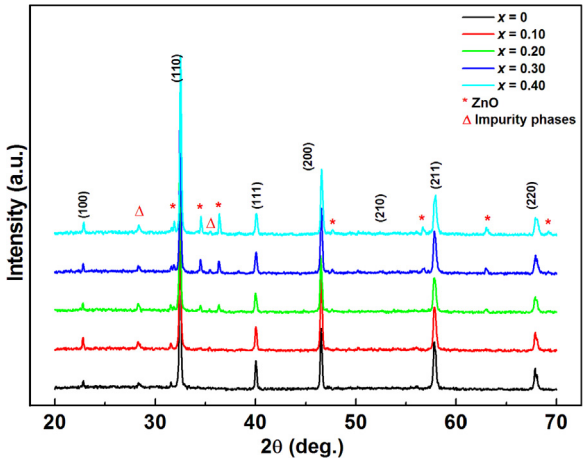

Fig. 1. XRD patterns of BNT-BT-CZ:*x*ZnO composites with $x = 0$, 0.10, 0.20, 0.30, and 0.40.

In order to choose a feasible method to optimize relaxor-based high-temperature dielectrics, one needs to know the possible corresponding mechanism for temperature-insensitivity. In the case of BNT-based relaxor dielectrics, the temperature-induced evolution of PNRs plays a determinable role. That means in order to further enhance the temperature-insensitivity of permittivity, an appropriate method is to construct a local field to suppress the evolution of PNRs. Fortunately, when a semiconductor is introduced into relaxor to form 0–3 type composite, the charges stemmed from semiconductor can form such a local electric field [24]. Accordingly, it is reasonable to expect that if semiconductor ZnO is introduced into BNT-based relaxor to form composite, the high-temperature dielectric performance can be improved.

Based on the above descriptions, we choose $0.82[0.94Bi_{0.5}Na_{0.5}TiO_3\text{-}0.06BaTiO_3]\text{-}0.18CaZrO_3$ (BNT-BT-CZ) as the starting high-temperature dielectrics [14], the BNT-BT-CZ:*x*ZnO composite ceramics with $x = 0$, 0.10, 0.20, 0.30, and 0.40 were prepared and investigated. The *x* represents the mole ratio of ZnO to BNT-BT-CZ. It is found that the optimal composition with $x = 0.10$ has significantly improved thermal stable dielectric performance in a wide temperature range.

2. Experimental procedure

Firstly, the BNT-BT-CZ powders were produced via a mixed oxide route using reagent grade oxides and carbonates (Alfa Aesar). The Bi_2O_3 (99.8%), Na_2CO_3 (99.8%), $BaCO_3$ (99.0%), $CaCO_3$ (99.0%), TiO_2 (99.0%), ZrO_2 (99.5%) were dried and weighed according to the stoichiometric formula. The mixtures were ball milled for 24 h in ethanol, after being dried at 80 °C, the powders were ground, calcined at 850 °C for 3 h, and ball milled for 24 h in ethanol again. The slurry were then dried, ground and subsequently sintered in covered alumina crucibles at 1100 °C for 3 h. Afterwards, both the ground BNT-BT-CZ powders and the commercial ZnO nano particles with the initial size of 25 nm (PlasmaChem) were weighed according to the formula of BNT-BT-CZ:*x*ZnO with $x = 0.10$, 0.20, 0.30, and 0.40. Each mixture was ball milled in ethanol for 24 h. After a drying process at 80 °C, the powders were pressed into disks with a diameter of 10 mm. Sintering of the disks were carried out in covered alumina crucibles at 1000–1050 °C for 1.0 h with the increasing and decreasing temperature rate of 9 °C/min. The $x = 0$ composition (i.e., BNT-BT-CZ) was sintered at 1100 °C for 3 h for comparative investigations.

Powder x-ray diffraction (XRD, Rigaku Ultima III) was performed at room temperature to characterize the crystal structures. Scanning electron microscopy (SEM, FEI Quanta 200) was used for microstructures analysis. For electrical measurements, the circular surfaces of the ground disks (diameter of ~ 8.5 mm and the thickness of ~ 0.5 mm) were covered with a thin layer of silver paste and fired at 550 °C for 30 min. The temperature dependent permittivity and loss factor were measured on both unpoled and poled samples using an impedance analyzer (HP4294A) from room temperature (30 °C) to 400 °C. Poling process was carried out in silicon oil bath at room temperature under a DC electric field of 6.0 kV/mm for 20 min. The temperature dependent impedance spectra were measured on unpoled samples from 300 °C to 400 °C. The polarization-electric field (*P-E*) and current-electric field (*J-E*) curves were measured at 1 Hz by using TF analyzer 1000 (AixACCT, Germany).

3. Results and discussion

Fig. 1 provides the XRD patterns of all samples. Three features should be noted. First, most diffraction peaks can be attributed to either BNT-BT-CZ or ZnO, which indicates the formation of BNT-BT-CZ:*x*ZnO composites. The recorded element distribution confirms the existence of chemical inhomogeneity. For example, the typical SEM micrograph and two-dimensional Zn and Ti distributions of the $x = 0.3$ sample is shown in Fig. 2. It is found that Bi and Ti elements occupy the same areas that connect with each other (Fig. 2(b)) while Zn occupies the isolated areas (Fig. 2(c)). That means for the composite ceramics with $x > 0$, the ZnO grains are embedded in the BNT-BT-CZ matrix to form a 0–3 type composite, in which the BNT-BT-CZ grains form a three-dimensional network, while the ZnO particles are dispersed. Second, BNT-BT-CZ displays perovskite structure with no obvious non-cubic distortion, consistent with other reports on BNT-based high-temperature dielectrics [5,14,15,25]. Actually, at room temperature, the *P-E* curves are very slim and the *J-E* curves have no polarization-induced current peak, both indicate the disappearance of long-range ferroelectric order, which will be discussed below. Third, the weak but detectable diffraction peaks shown by triangle are attributed to impurity phases, the peak locating around 2θ~28.8° corresponds to $Ca_3Bi_8O_{15}$, and that around

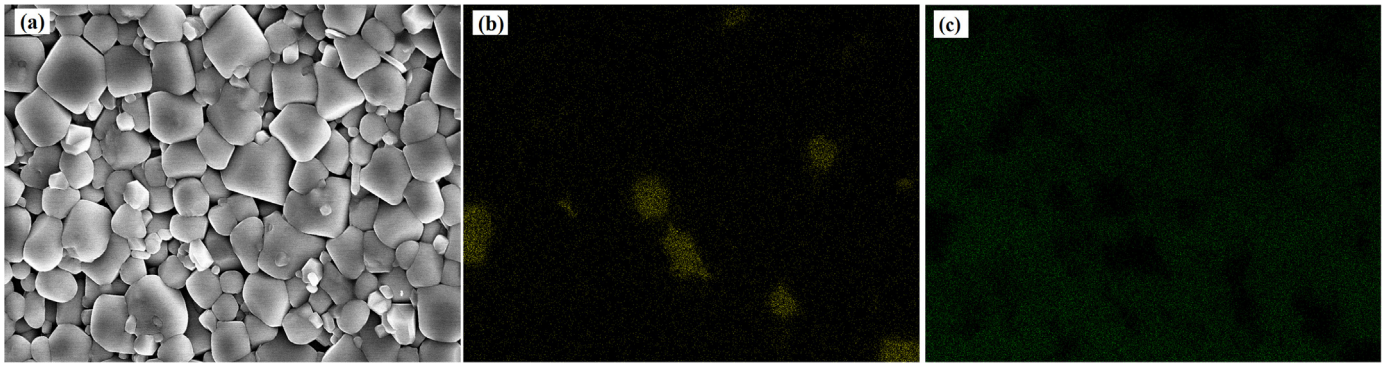

Fig. 2. (a) Typical SEM micrographs of the $x = 0.3$ sample. (b, c) The corresponding distribution of Zn and Ti element.