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Letter

Positive temperature coefficient of resistivity behavior of Niobium-doped $(1-x)BaTiO_3$–$xBi_{0.5}Li_{0.5}TiO_3$ ceramics

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ABSTRACT

As an appreciable lead-free positive temperature coefficient of resistivity (PTCR) material, Niobium (Nb)-doped $(1-x)BaTiO_3$–$xBi_{0.5}Li_{0.5}TiO_3$ [$(1-x)$BT-xBLT] ceramics with $0 \le x \le 0.03$ were prepared by solid-state reaction method. XRD results indicated that the raw material formed a solid solution during sintering and the lattice parameters of BT–BLT samples changed with the BLT content. With a little addition of Nb, the BT ceramics without BLT-doping possessed low room-temperature resistivity ($\rho_{RT} \le 10^3\ \Omega\,cm$). However, with the increasing addition of BLT, the ρ_{RT} raised sharply. Temperature dependences of resistivity and permittivity of the prepared ceramic showed its ferroelectric and paraelectric phase transition temperatures (Curie temperature, *Tc*) were enhanced by 30 °C than that without BLT-doping.

1. Introduction

In recent years, to meet the demand of environmental protection, lead-free barium titanate ($BaTiO_3$, BT)-based ceramics have been developed rapidly, such as lead-free piezoelectric ceramics and lead-free positive temperature coefficient of resistivity (PTCR) ceramics [1–3]. It is well known that BT-based PTC ceramics showed a rapid increase in resistivity near the ferroelectric Curie temperature, *Tc*. Many applications, such as constant temperature heater, over-current limiter make use of this PTC effect. However, the current commercial high $Tc > 130\ ^\circ C$ PTC ceramics all contain Pb element. It is currently believed that Pb is the only effective element to shift the *Tc* of BT to a higher temperature (>130 °C). For this reason, many researchers recently devote their efforts to exploit lead-free PTC ceramics. Xiang et al. [4] and Shimada et al. [5] have reported that $BaTiO_3$–$Bi_{0.5}Na_{0.5}TiO_3$ (BT–BNT) ceramics is a new lead-free PTC material with $Tc > 130\ ^\circ C$. Subsequently, Leng et al. [6] and Takeda et al. [7] showed that $BaTiO_3$–$Bi_{0.5}K_{0.5}TiO_3$ (BT–BKT) system also possessed good PTC effect above 130 °C. These reports indicate that the BT–BNT and BT–BKT system reveal an excellent PTC characteristic. Therefore, incorporation of $Bi_{0.5}Li_{0.5}TiO_3$ (BLT) into the semiconducting BT-based ceramics is considered a possible way to raise the *Tc* to a high temperature. BLT as an addition agent was always used for fabricating lead-free piezoelectric ceramic [8–10]. The research of PTC phenomena in Nb-doped BT–BLT system was not reported before.

In this study, we selected Bi_2O_3, Li_2CO_3 and TiO_2 as other end members of BT-based solid solutions. Furthermore, the Nb^{5+} ion as a donor [11] which can reduce the room-temperature resistivity (ρ_{RT}) was also added into BT. We prepared Nb-doped BT–BLT ceramics successfully and investigated on the electric properties in terms of BLT and Nb content.

2. Experimental procedures

Firstly, high purity $BaCO_3$ and TiO_2 powders were thoroughly mixed according to the formula of $BaTiO_3$ and calcined at 1150 °C for 2 h to obtain a pure BT phase. Then, the synthesized BT powder and high purity Nb_2O_5 were weighted and thoroughly mixed in distilled water according to the formula of yNb_2O_5–$BaTiO_3$ ($0 \le y \le 0.0015$). After drying and granulating with PVA, the well mixed powders were pressed into a disk ($\Phi 10\ mm \times 1.5\ mm$) at 120 MPa and then sintered at 1310–1340 °C for 2 h in air. In this step, we measured the ρ_{RT} of prepared ceramics with different Nb_2O_5 content and found that the ceramic with the addition of $y = 0.001$ Nb_2O_5 revealed the lowest ρ_{RT}.

Secondly, high purity Bi_2O_3, Li_2CO_3, TiO_2, Nb_2O_5 and the synthesized BT powder according to the nominal composition $(1-x)BaTiO_3$–$xBi_{0.5}Li_{0.5}TiO_3$–$0.001Nb_2O_5$ ($0 \le x \le 0.03$) were weighted, mixed and calcined at 700 °C for 1 h. Then, the calcined powder was mixed in distilled water using a zirconia ball mill in polyethylene pot for 6 h. After drying and granulating with PVA, the well mixed powders were pressed into a disk ($\Phi 10\ mm \times 1.5\ mm$) at 120 MPa and then sintered at 1250–1280 °C for 2 h in air.

The In–Ga paste was applied to both surfaces of the sintered samples as the electrode to ensure the contact between electrode and sample was ohmic contact; the temperature dependences of resistivity and permittivity were determined by direct measurement of resistivity and permittivity of samples applied on the electric field of 1 V/mm (Agilent E4980A) from room temperature to 300 °C at a heating rate of 2 °C/min. A scanning electron microscope (JSM-6460) was used to investigate the microstructure of the Nb-doped BT–BLT ceramics.

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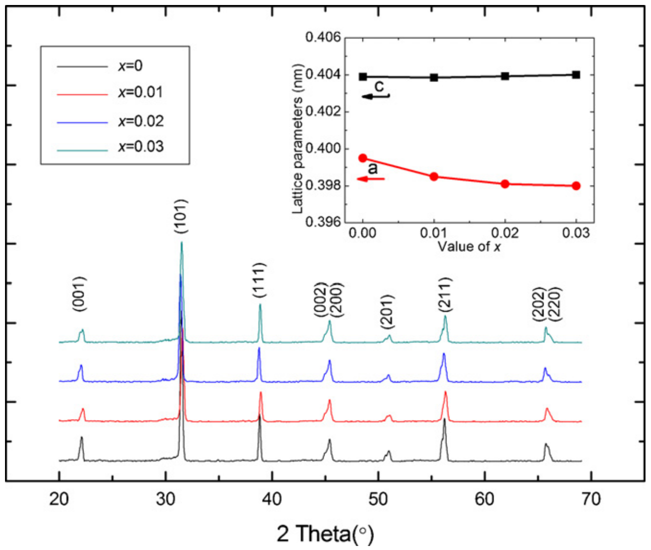

Fig. 1. X-ray diffraction patterns of the $(1-x)$BT–xBLT–0.001Nb_2O_5 ceramics sintered in air at 1260 °C for 2 h.

3. Results and discussion

Fig. 1 shows the XRD patterns of the $(1-x)$BT–xBLT–0.001Nb_2O_5 ceramic samples sintered in air at 1260 °C for 2 h. There was no secondary phase appeared from XRD results. All the peaks of the sintered sample were similar to that of the published date of the host BT, indicating the sample consisted of a single perovskite phase. The fact that the lattice parameters of sintered samples changed with the BLT content (as shown in the inset of Fig. 1) demonstrates that the raw materials had formed a solid solution during sintering. This result was reasonable from the viewpoint of ionic size effects. The Bi^{3+} (96 pm) cation replaced the Ba^{2+} (134 pm) site. No report existed that Li^+ occupied A-site of perovskite ABO_3 structure and that Li^+ contained complex oxides from perovskite-type structure, therefore, Li^+ may not enter the crystal lattice but segregated at grain boundary.

Table 1
Variations of ρ_{RT} for different compositions sintered in air for 2 h.

Composition	ρ_{RT} (Ω cm)
BT–0.0005Nb_2O_5	1023
BT–0.001Nb_2O_5	316
BT–0.0015Nb_2O_5	534
0.99BT–0.01BLT–0.001Nb_2O_5	265
0.98BT–0.02BLT–0.001Nb_2O_5	1893
0.97BT–0.03BLT–0.001Nb_2O_5	$\geq 10^6$

Fig. 2 shows the SEM micrographs of the as-sintered surface of $(1-x)$BT–xBLT–0.001Nb_2O_5 ceramics sintered in air at 1260 °C for 2 h. It is shown that the sample without BLT-doping possessed clear-cut grain boundary, but the other samples' grain were of irregular shape and distribution. Furthermore, the average grain size of BLT-contained sample was about 2 μm, which was smaller than that without BLT-doping. It may be due to the existence of Li^+ which was speculated to segregate at grain boundary. As a consequence of the segregation of Li^+, the concentration of oxygen vacancies, which was important for the transfer of mass and energy between reactants during sintering, on grain boundaries declined, thus inhibiting the grain growth indirectly. Therefore, the BLT-contained ceramics possessed smaller grain size.

The ρ_{RT} of the sintered ceramic samples is illustrated in Table 1. It is seen that the ρ_{RT} varied distinctly with the BLT and Nb_2O_5 content. With 0.1 mol% Nb_2O_5 doped, BT ceramic possessed the lowest ρ_{RT}. However, with the increasing addition of BLT, the ρ_{RT} of $(1-x)$BT–xBLT–0.001Nb_2O_5 ceramics raised sharply from 265 Ω cm ($x=0.01$) to 10^6 Ω cm ($x=0.03$). The defects compensating mechanisms from electronic compensation to cation vacancies compensation could clarify these results [12]. While the concentration of Nb was low, the semiconducting behavior was explained by the following equation:

$$Nb_2O_5 \rightarrow 2Nb_{Ti}^{\bullet} + 4O_O + \frac{1}{2}O_2 + 2e \qquad (1)$$

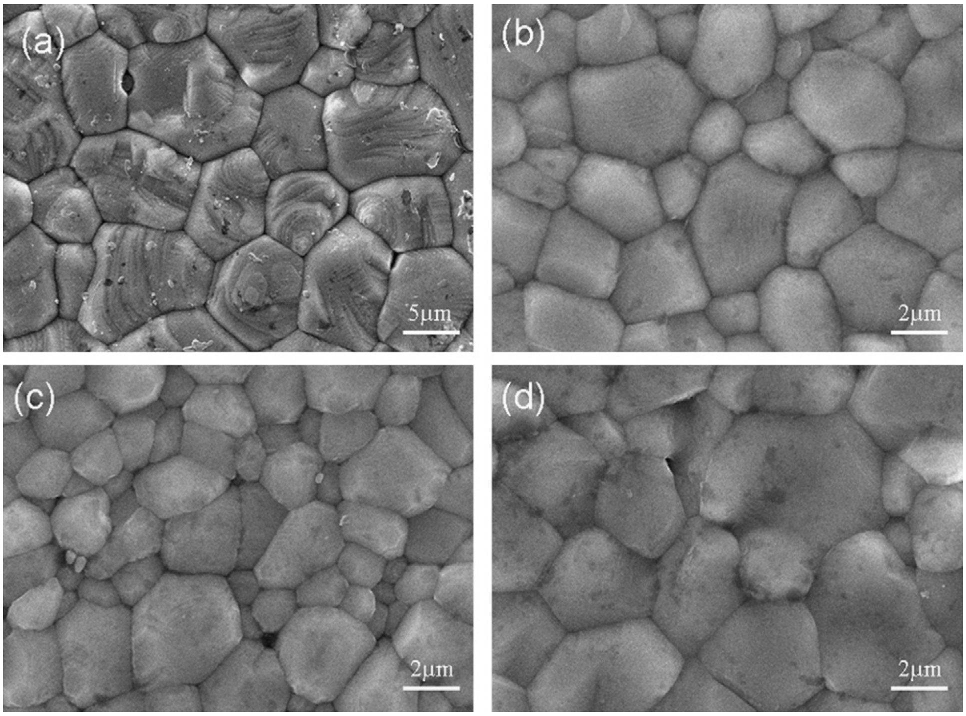

Fig. 2. SEM micrographs of the as-sintered surface of $(1-x)$BT–xBLT–0.001Nb_2O_5 ceramics sintered in air at 1260 °C for 2 h: (a) $x=0$; (b) $x=0.01$; (c) $x=0.02$; (d) $x=0.03$.

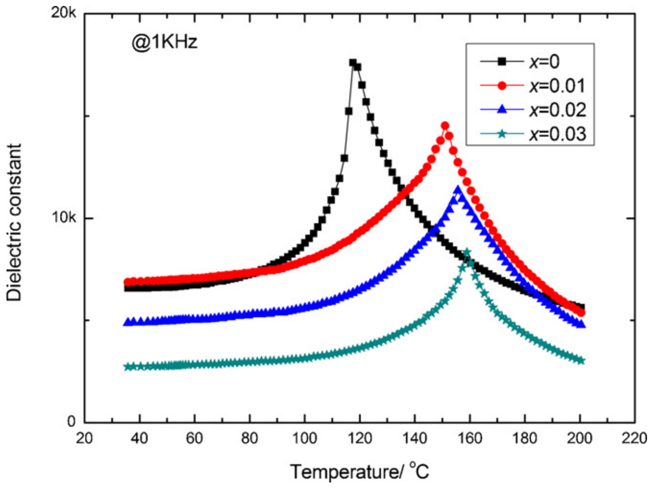

Fig. 3. Temperature dependence of permittivity of $(1-x)$BT–xBLT–0.001Nb_2O_5 ceramics sintered in air at 1260 °C for 2 h.

As the Nb content increased, Ti vacancy model represented possible mode of compensation for the donor:

$$2Nb_2O_5 \rightarrow 2Nb_{Ti}^{\bullet} + V_{Ti}^{''''} + 10O_o \qquad (2)$$

Table 1 also shows that the ρ_{RT} of sample 0.99BT–0.01BLT–0.001Nb_2O_5 possessed minimum ρ_{RT}. It is due to the Bi^{3+} ion as a donor occupied the Ba^{2+} site to generate more electron carries when the BLT content was low. But when the BLT content increased, more Li^+ ion segregated at grain boundary and caused the ρ_{RT} to rise sharply.

The dielectric properties at 1 KHz as a function of temperature for the $(1-x)$BT–xBLT–0.001Nb_2O_5 ceramics sintered in air at 1260 °C for 2 h are illustrated in Fig. 3. The curve of dielectric constant (ε) shows a peak at about 150 °C with the addition of BLT, which was about 30 °C higher than the BT–0.001Nb_2O_5 ceramics. As well known, the peak position of ε-temperature curve corresponded to the *Tc*, and did not depend on the measurement frequency. The result indicated that *Tc* value of BT–BLT ceramics was relatively higher than that (120 °C) of BT. It was attributed to the Bi^{3+}, which entered Ba-site and *Tc* can increase with only Bi incorporation [13]. Because no report verified that Li^+ occupied A-site of perovskite ABO_3 structure, the effect of Li^+ on the *Tc* was not clear and not discussed in this study.

The temperature dependence of resistivity of $(1-x)$BT–xBLT–0.001Nb_2O_5 $(0 \le x \le 0.03)$ ceramics sintered in air at 1260 °C for 2 h is shown in Fig. 4. All samples possessed good PTC effect and marked resistivity jump $(\rho_{max}/\rho_{min} > 10^3)$ near the Curie temperature. With only Nb-doped BT sample revealed a markedly abrupt increase in resistivity at 120 °C. However, with a little addition of BLT, the samples showed a significant resistivity jump of three orders of magnitudes at about 150 °C. It was indicated that the *Tc* was evidently affected by a small amount of BLT. The results were also coincided with the curve of permittivity-temperature dependence.

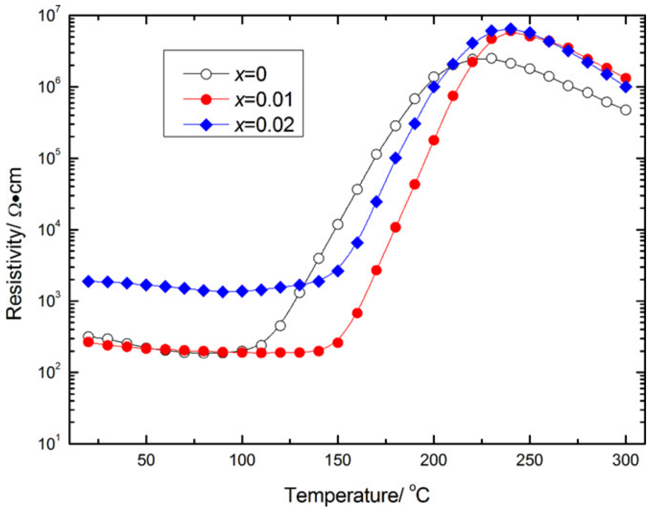

Fig. 4. Temperature dependence of resistivity of $(1-x)$BT–xBLT–0.001 Nb_2O_5 ceramics sintered in air at 1260 °C for 2 h.

4. Conclusions

Nb-doped BT–BLT lead-free PTCR ceramics were prepared by solid-state reaction method. The *Tc* was enhanced to ~150 °C by introducing a small amount of BLT and ρ_{RT} decreased to ~10^2 Ω cm with a little addition of Nb_2O_5. The optimum composition of 0.99BT–0.01BLT–0.001Nb_2O_5 sintered at 1260 °C for 2 h in air possessed the lowest ρ_{RT} of 265 Ω cm, a high resistivity jump of four orders of magnitude, and *Tc* of ~150 °C.

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