Materials Letters 76 (2012) 222–225

Contents lists available at SciVerse ScienceDirect

Materials Letters

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

Study of electrical and dielectric properties of Y_2O_3 doped $Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$ ceramics

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ARTICLE INFO

Article history:
Received 1 February 2012
Accepted 22 February 2012
Available online 3 March 2012

Keywords:
$BaTiO_3$ ceramics
Ferroelectric
Dielectric
Impedance
Perovskites

ABSTRACT

Y_2O_3-doped $Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$ ceramics were prepared by a conventional mixed oxide method. The XRD results showed that the phase compositions of all samples were pure tetragonal phases and the tetragonality *c/a* of the perovskite lattice varied with the Y_2O_3 and NBT contents. In order to study the electrical properties of $(1\text{-}y)Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3\text{-}yY_2O_3$ ceramics, we used the Cole–Cole plot, that is, the graphic of Y' versus Y''. The results showed that a single semicircular arc appeared and its radii of curvature firstly decreased and then increased with the increase of NBT and Y_2O_3 contents. In addition, the relative permittivity and dielectric loss versus frequency were characterized in the frequency range of 100 Hz–2 MHz. It can be found that relative permittivity and dielectric loss regularly changed with the increase of Y_2O_3 and NBT contents.

1. Introduction

Barium titanate ($BaTiO_3$) is a ferroelectric compound with the perovskite-type structure and an important material for dielectric application [1]. $BaTiO_3$ ceramics exhibit an excellent positive temperature coefficient of resistivity (PTCR) effect and many attentions have been paid for improvement such as rising the Curie temperature (*Tc*) and reducing the room temperature resistivity. Generally, the elevation of the *Tc* is easily achieved by substituting Pb^{2+} for Ba^{2+}. However, lead-free PTCR ceramics (such as $BaTiO_3\text{-}Na_{0.5}Bi_{0.5}TiO_3$(BT-NBT)) are expected to replace lead-contained PTCR materials due to the growing concern with environmental protection [2].

Although NBT, which is a complex perovskite-type ferroelectric, has a relatively high Curie temperature (320 °C), its solid solubility in $BaTiO_3$ is very low. Generally, the resistivity of $BaTiO_3$ ceramics will be more than $10^4 \Omega \cdot cm$ when the NBT content exceeds 3.0 mol% [3]. Therefore, donor doping (Nb^{5+}, La^{3+}, Y^{3+} etc.) is needed so as to achieve semiconducting ceramics [4–8]. In our previous research, we have studied the influences of NBT and Nb_2O_5 on PTCR behaviors of barium titanate ceramics [9]. However, the introduction of donor and NBT may have effects not only on PTCR behaviors of barium titanate ceramics, but also on electrical and dielectric properties.

In this paper, we studied the effects of the Y_2O_3 and NBT contents on the electrical and dielectric properties of barium titanate ceramics. The phase compositions of $(1\text{-}y)Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3\text{-}yY_2O_3$ ceramics were studied by X-ray diffraction and the lattice parameters were also calculated.

2. Experimental

$BaCO_3$ and TiO_2 powders with a purity of 99.99% were thoroughly mixed according to the formula of $BaTiO_3$ and calcined at 1220 °C for 2 h so as to obtain a pure $BaTiO_3$ phase. Na_2CO_3, Bi_2O_3 and TiO_2 powders with a purity of 99.99% at a molar ratio of Bi:Na:Ti = 1:1:4 were weighted and mixed well, then the mixture was calcined at 900 °C for 2 h so as to obtain a pure NBT phase.

According to the nominal composition $(1\text{-}y)Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3\text{-}yY_2O_3$, Y_2O_3 powders with a purity of 99.99%,the synthesized NBT and $BaTiO_3$ powders were mixed in distilled water using a zirconia ball mill in polyethylene pot for 6 h. Meanwhile, in order to improve the densification and reduce the sintering temperature of ceramic samples, 0.06 mol% SiO_2 and 0.18 mol% TiO_2 powders were added simultaneously. After drying and granulating with polyvinyl alcohol (PVA, 3 wt.%), the well-mixed powders were pressed into a disk (Φ 10×1.5 mm) at 120 MPa and sintered at different temperatures in air for 2 h.

X-ray diffraction (XRD) patterns were obtained using an automated diffractometer (D/max-2200PC, RIGAKU, Japan) with Cu $K\alpha_1$ radiation. Subsequently, the In–Ga paste was applied to both surfaces of the sintered samples as the electrode. The relative permittivity and dielectric loss versus frequency were obtained by using Agilent E4980A from 100 Hz to 2 MHz. In addition, the complex impedance spectroscopy was characterized by using Agilent 4192A from 100 Hz to 13 MHz at the oscillation voltage of 0.005 V_{rms}.

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doi:10.1016/j.matlet.2012.02.105

3. Results and discussion

3.1. Phase characterization

Fig. 1 shows the XRD patterns of (1-y)$Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$-$yY_2O_3$ ceramics sintered at 1380 °C. It can be found that there was no secondary phase emerged from XRD results. All the peaks of sintered samples were similar to that of pure $BaTiO_3$, indicating that the samples consisted of a single perovskite phase.

From Fig. 1, it can be seen that the phase of (1-y)$Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$-$yY_2O_3$ ceramics were tetragonal phase and the (200) peaks and (002) peaks were split into two peaks. This phenomenon must be related to the substitution of Y^{3+} (90 pm), Bi^{3+} (103 pm) and Na^{+} (102 pm) to Ba^{2+} (135 pm), which led to a decrease in the volume of unit cell. However, when the content of Y^{3+} exceeded 0.3 mol%, Y^{3+} (90 pm) might replace Ti^{4+} (60.5 pm), which led to an increase in the volume of unit cell. In order to demonstrate it, the lattice parameters of ceramic samples were calculated and listed in Table 1.

3.2. Dielectric properties

Fig. 2(a) shows the relative permittivity and dielectric loss versus frequency for $0.999Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$-$0.001Y_2O_3$ ceramics. It can be seen that the relative permittivity and dielectric loss firstly increased and then decreased with the increase of NBT content, especially at low frequency range (<10^4 Hz). When the NBT content is 1 mol%, the relative permittivity reached the maximum value. However, the dielectric loss had the minimum value when the NBT content is 0.25 mol%. This phenomenon could be explained by the interfacial polarization. $Na_{0.5}Bi_{0.5}TiO_3$ would be accumulated at the grain boundaries and impeded the transfer of free charge, which resulted in accumulation of charges or ions in intergranular areas and formation of interfacial polarization. However, the spontaneous polarization would be weakened with the further increase of $Na_{0.5}Bi_{0.5}TiO_3$ content because it could restrain the grain growth. And the grain size of $BaTiO_3$ ceramics had a great influence on the relative permittivity [10]. In addition, the relative permittivity and dielectric loss rapidly decreased with the increase of frequency. Generally, a higher value of the relative permittivity at low frequency is due to the appearance of all types of polarizations (i.e., electronic, ionic, dipolar, interfacial, etc.) in the samples at room temperature [11,12]. Since only electronic polarizations are dominated at the higher frequency (i.e., other type of polarization vanished), the value of relative permittivity decreases with the increase of frequency. At the same time, the dielectric loss is much higher at low frequency, which is similar to the relative permittivity.

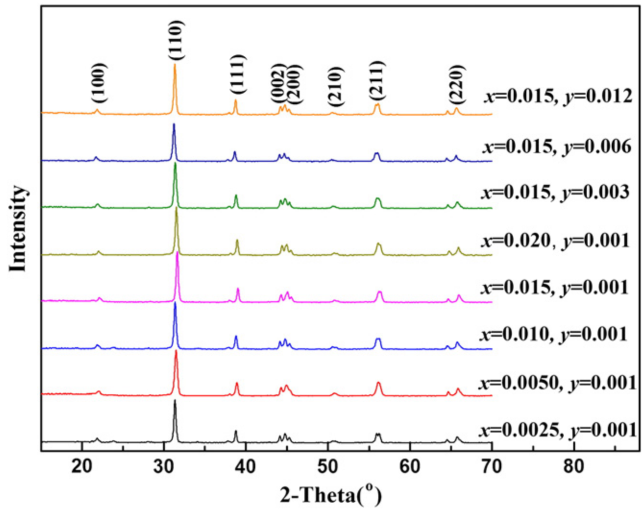

Fig. 1. XRD patterns of (1-y) $Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$-$yY_2O_3$ ceramics sintered at 1380 °C.

Table 1
Lattice parameters for (1-y) $Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$-$yY_2O_3$ ceramics.

Composition	a(Å)	c(Å)	a^2c(Å^3)
$x=0.0025$, $y=0.001$	3.9946	4.0676	64.9077
$x=0.0050$, $y=0.001$	3.9984	4.0538	64.8100
$x=0.010$, $y=0.001$	3.9883	4.0690	64.7264
$x=0.015$, $y=0.001$	3.9933	4.0334	64.3206
$x=0.020$, $y=0.001$	3.9917	4.0250	64.1359
$x=0.015$, $y=0.003$	3.9869	4.0047	63.6604
$x=0.015$, $y=0.006$	3.9960	4.0710	65.0092
$x=0.015$, $y=0.012$	4.0009	4.0922	65.5048

Fig. 2(b) shows the relative permittivity and dielectric loss versus frequency for (1-y)$Ba_{0.985}(Bi_{0.5}Na_{0.5})_{0.015}TiO_3$-$yY_2O_3$ ceramics. It can be found that the relative permittivity and dielectric loss firstly decreased and then increased with the increase of Y_2O_3 content. When the Y_2O_3 content is 0.6 mol%, the relative permittivity reached the minimum value. This phenomenon might be related to the variation of polarization. When the content of Y_2O_3 was lower, the electron and ion displacement polarization would be weakened, as well as the spontaneous polarization. This was because Y^{3+} replaced Ba^{2+} and Ti^{4+}. As the content of Y_2O_3 increased, Y_2O_3 were accumulated at the grain boundaries and formation of interfacial polarization. In addition, the relative permittivity and dielectric loss rapidly decreased with the increase of frequency, which was explained as above.

3.3. Electrical properties

The electrical behaviors of the samples were characterized in the frequency range from 100 Hz to 2 MHz using the ac technique of complex impedance spectroscopy. This technique enables us to separate the real and imaginary components of the electrical parameters. At the same time, it is an important method to separate the impedance of grains, grain boundaries and electrodes because they have different relaxation times, which resulted in separate semicircles in complex impedance spectroscopy. The electrical properties of a sample obtained using complex impedance spectroscopy are often presented by the following forms: impedance (Z), admittance (Y), permittivity (ε) or electrical modulus (M) [13]. In this study, the electrical properties of ceramic samples were studied by means of admittance.

$$Y^* = Y' - iY'' = j\omega\varepsilon_0\varepsilon^* \tag{1}$$

where $\omega = 2\pi f$ is the angular frequency.

In order to study the electrical properties of (1-y)$Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$-$yY_2O_3$ ceramics, we used the Cole–Cole plot, that is, the graphic of Y' versus Y'', as shown in Fig. 3. It showed that the electrical process occurring in (1-y)$Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$- yY_2O_3 ceramics had a single relaxation process and a single semicircular arc appeared in the Cole–Cole plot. This phenomenon can explain that the resistivity of grain boundaries is far more than that of grains due to their large resistance and capacitance compared to those of grains [14]. In addition, the radii of curvature firstly decreased and then increased with the increase of NBT and Y_2O_3 contents. This was because Bi^{3+} and Y^{3+} would replace Ba^{2+} when the contents of NBT and Y_2O_3 were lower. However, NBT and Y_2O_3 would be accumulated at the grain boundaries and impeded the