



Phase transition, high figure of merit and polar nano-regions in dielectric tunable lanthanum substituted barium titanate



Pengrong Ren, Huiqing Fan*, Xin Wang, Dong Guangzhi

State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China

ARTICLE INFO

Article history:

Received 3 June 2014

Received in revised form 17 July 2014

Accepted 18 July 2014

Available online 7 August 2014

Keywords:

BaTiO₃

Dielectric tunability

Polar nano-regions

ABSTRACT

Ba_{1-x}La_xTi_{1-x/4}O₃ (BLT, $x = 0-0.08$, abbreviated as BLT100x) ceramics were prepared by using a solid state reaction process. Their phase transition, surface morphology, dielectric properties, tunability and ferroelectric behaviors were examined. Substitution of La at A-site in BaTiO₃ leads to a downward shift of Curie temperature and diffused cubic-tetragonal (C-T) phase transition. BLT6 exhibits a high tunability (35.4 at 20 kV/cm), a low dielectric loss (0.002) and a high figure of merit (177 at 20 kV/cm) at 10 kHz and room temperature. The nonlinear dielectric behavior under the applied electric field is well described by the multipolarization model. And the temperature dependence of ferroelectric hysteresis loops proves that the field induced phase transition is restrained by substitution of La in BaTiO₃, whereas polar nano-regions (PNRs) which are an extrinsic polarization contribution are present in BLT and play an important role to the high dielectric tunability of BLT.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The latest development of next-generation radar and microwave communication devices have required tunable dielectric materials which make use of the variation of dielectric permittivity of polar dielectrics under dc electric fields [1,2]. The required dielectric properties usually include as follows: low dielectric permittivity, low loss and high dielectric tunability. Traditionally (Ba, Sr)TiO₃ [3], Ba(Ti, Zr)O₃ [4] and (Pb, Sr)TiO₃ [5] have been extensively studied. And Ba_{0.6}Sr_{0.4}TiO₃ film has been considered as one of the most promising materials for frequency agile microwave devices [6,7]. However, high dielectric permittivity and relatively high dielectric loss have limited its applications. This is because high dielectric permittivity is not favorable for device impedance matching, which leads to less efficient power transfer in the device; and high dielectric loss attenuates the microwave signal and thus results in inferior device performances [8]. Consequently, it has been expected to develop new materials to meet the requirements of tunable applications. For BaTiO₃-based materials, their properties are usually tailored through different dopants, either the donor or acceptor, depending on the valence of doping elements [9]. Donor doped BaTiO₃ associated with electron compensation usually degrades its insulating properties, which is not favorable to the tunable applications. The incorporation of accep-

tors into the BaTiO₃ has the effect of fixing the charged oxygen vacancies through ionic compensation and suppresses the generation of electron. In this case, acceptors act as traps for conduction electrons, as described in Eq. (1),



leading to the increase in insulating resistance near the room temperature. However, acceptor-doped BaTiO₃ containing oxygen vacancies are found to exhibit poor insulating resistance at high temperatures and high electrical fields. And various models have been set up to explain this phenomenon, for example, grain boundary model [10], reduction model [11,12] and the de-mixing model [13,14].

Lanthanum is an interesting element. It has a fixed 3+ oxidation state and La³⁺ (1.15 Å) is exclusively incorporated at the Ba²⁺ (1.35 Å) site, as its size is incompatible with that of Ti⁴⁺ (0.68 Å), which has been commonly recognized [15]. However, the compensation mechanism of charge balance has been a matter of debate for a long time. Undoped BaTiO₃ is a good insulator with a high energy gap $E_g = 3.5$ eV [16]. When Ba²⁺ is replaced by low amounts (<0.5 at.%) of La³⁺, it can lead to an initial decrease in resistivity of BaTiO₃ and the samples exhibit n-type semiconductivity; however, when the concentration of La³⁺ increases, the samples return to be insulating [16].

Although the defect chemistry of La-doped BaTiO₃ has been studied a lot [17–20], its applications are only limited to positive temperature coefficient of resistivity (PTCR) characteristics [21].

* Corresponding author.

E-mail address: hqfan3@163.com (H. Fan).

Much less publications reported aspects concerning the dielectric and tunability behaviors of La-doped BaTiO₃. A. Ianculescu [22] studied tunability properties of lightly La-doped BaTiO₃ (Ba_{1-x}La_xTi_{1-x/4}O₃, 0.005 ≤ x ≤ 0.025), which are in a ferroelectric phase at room temperature. In the present paper dielectric tunability of La-doped BaTiO₃ (Ba_{1-x}La_xTi_{1-x/4}O₃, labelled as BLT) are investigated in a compositional range of 0 ≤ x ≤ 0.08, corresponding BLT from ferroelectric, ferroelectric–paraelectric crossover to paraelectric state at room temperature. It is found that large tunability is obtained when samples are in the ferroelectric–paraelectric crossover region. Meanwhile, the observed dielectric nonlinear dielectric permittivity under high applied electric field is described by using a multipolar mechanism model and the reason for the high tunability in this ferroelectric–paraelectric crossover region is explored.

2. Experimental procedures

2.1. Materials preparation

Ba_{1-x}La_xTi_{1-x/4}O₃ (x = 0, 0.02, 0.04, 0.05, 0.06, 0.08, labelled as BT, BLT2, BLT4, BLT5, BLT6 and BLT8, respectively) ceramics were prepared by solid state reaction using BaCO₃ (Sinopharm 99.5%), La₂O₃ (Sinopharm 99.99%) and TiO₂ (Sinopharm 99.9%), which were dried prior to weighing at 180, 900 and 900 °C, respectively. Samples were mixed with acetone manually in a mortar and pestle, dried and fired in Pt crucibles, initially decarbonated at 1000 °C for 6 h, and then heated at 1100 °C for 6 h to reaction. Pellets were prepared by uniaxial pressing, heated in air at 1250 °C for 6 h and cooled slowly inside the furnace.

2.2. Characterization and measurement

The present phases were analysed by X-ray powder diffraction (XRD; D/Max2550VB+/PC, Rigaku, Tokyo, Japan) using Cu Kα1 radiation with linear position-sensitive detector. Lattice parameters were determined by least-squares refinement for reflections in the range 20° < 2θ < 80°, using the software MDI Jade version 5.0 and an external Si standard. Raman spectra were measured on pellets at 100–1000 cm⁻¹ by Raman Microscope (inVia, Renishaw, London, UK). The spectral excitation was provided by an Ar⁺ laser, using the 514.5 nm line and with proper power density on the sample surface. Microstructures such as grain size distribution and morphology were determined using a scanning electron microscope (JEOL-6700F, Japan Electron Co., Tokyo, Japan) equipped with an Oxford Link ISIS (Oxford Instruments Ltd., Oxfordshire, UK) Energy Dispersive X-ray Spectroscopy (EDS) detector.

The sintered pellets were polished to a final thickness of 0.5 mm for dielectric characterization. Silver electrodes with appropriate configurations were coated on both polished surfaces and fired at 550 °C for 30 min to form a metal–insulator–metal (MIM) capacitor for electrical test. Weak-field dielectric response at a signal level of 500 mV/mm was measured by using a precision impedance analyzer (4294A, Agilent, Santa Clara, CA, USA) associated with temperature controller (TP94, Linkam, Surrey, UK) over a temperature range of -80 ~ 200 °C at a heating rate of 2 °C/min. The dielectric tunability properties were measured at 30 °C using an automatic component analyzer (TH2818, Tonghui, Changzhou, China) at 10 kHz. A blocking circuit was adopted to protect the analyzer from applied bias voltages. External bias field was applied in steps of 1 kV cm⁻¹. The dependence of the electric polarization and the mechanical strain on an external electric field was measured at 10 Hz using a ferroelectric test unit analyzer (TF-2000, AixACCT, Aachen, Germany).

3. Results and discussion

3.1. Phase structure and surface morphology

XRD patterns of the BLT ceramics sintered at 1250 °C are shown in Fig. 1. From Fig. 1(a), it can be seen that all the compositions are pure phase. Fig. 1(b) shows the enlarged region of (002)/(200). For BLT2 and BLT4, the (002)/(200) diffractions peaks clearly split, indicating that BLT2 and BLT4 are tetragonal phase at room temperature. However, for BLT5, BLT6 and BLT8, the (002)/(200) diffractions peaks merge to one peak, which suggests that they are cubic phase at room temperature. Lattice parameters of the samples are shown in Table 1 a initially increases but c decreases with the increase of La concentration. When the La contents are above 5 mol%, all the samples are cubic phase, and c decreases with La

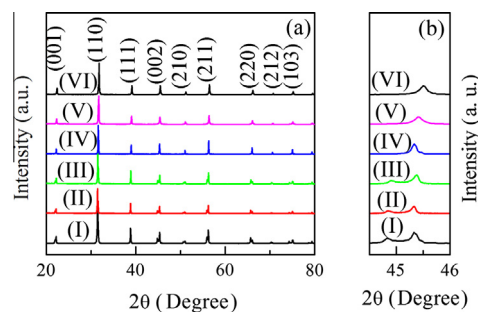


Fig. 1. (a) XRD patterns of (I) BT, (II) BLT2, (III) BLT4, (IV) BLT5, (V) BLT6 and (VI) BLT8 sintered at 1250 °C; (b) The enlarged region of (002)/(200) peak.

contents increasing. For all the samples, volumes of unit cell monotonically decrease. On the one side, the radius of 12-coordinate La³⁺ is 1.15 Å, which is smaller than that of 12-coordinate Ba²⁺ (1.35 Å) [15]. On the other side, as shown in the Eq. (2):



when Ba²⁺ is substituted by La³⁺, Ti vacancies are created for charge balance. Therefore, both these two reasons lead to the contraction of the unit cell volumes.

Raman spectra of the BLT ceramics from 100 to 1000 cm⁻¹ at room temperature are shown in Fig. 2. For BaTiO₃, the tetragonal phase is usually characterized by sharp bands at 306 cm⁻¹ and asymmetric broader bands at ~264, 515 and 720 cm⁻¹. These latter three bands are also present but much broader and more symmetrical in the cubic paraelectric phase. They relate to the disorder of Ti displacements in the octahedral [23–25]. We can see from Fig. 2 that the peaks at 307 cm⁻¹ are clear for spectra of BLT2 and BLT4, while are absent for other samples. These results further indicate that BLT2 and BLT4 are tetragonal, but BLT5, BLT6 and BLT8 are cubic at room temperature. In the region of reciprocal wavelength, an A_{1g} octahedral breathing mode is Raman inactive for simple perovskites since the mode is symmetrical and does not result in a change in polarization. However, for complex perovskites and solid solutions with two or more B-site species, the A_{1g} becomes Raman active since the presence of dissimilar ions in the center of the octahedra creates asymmetry in the breathing like mode [26]. It is particularly intense and narrow for ordered complex perovskites but appears as a broad peak in disordered perovskite solid solutions [27]. In Fig. 2, there is a peak at 839 cm⁻¹ and as La contents increase, the A_{1g} mode increases in intensity, which are probably due to that mixed Ti⁴⁺ and V_{Ti}^{IV} are present on the B-site and induce an asymmetric breathing mode in the volume fraction of octahedral.

Fig. 3(a–e) illustrate SEM images of the BLT ceramics sintered at 1250 °C. After sintered at 1250 °C all the samples have a dense microstructure and the grain sizes increase with the La contents increasing. As shown in Fig. 3(f), the average grain size increases from ~0.94 μm for BLT2 to ~1.62 μm for BLT8. The relative densities of each sample are listed in Table 1. All the La-doped samples have high density (>95%). The measured compositions of BLT by EDS are close to the cation ratio in Ba_{1-x}La_xTi_{1-x/4}O₃ within instrument resolution and standard deviations (see Table 2).

3.2. Temperature dependence of dielectric permittivity and loss

Fig. 4 shows temperature dependence of dielectric permittivity (ε') and dielectric loss (tan δ) at various frequencies over -80 ~ 200 °C for BLT ceramics sintered at 1250 °C. As can be seen, substitution of La in BaTiO₃ leads to a downward shift of Curie temperature and the permittivity at the Curie temperature increases with the contents of La increasing. For all the compositions, Curie

Download English Version:

<https://daneshyari.com/en/article/8000844>

Download Persian Version:

<https://daneshyari.com/article/8000844>

[Daneshyari.com](https://daneshyari.com)