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Temperature stability, structural evolution and dielectric properties of $BaTiO_3$–$Bi(Mg_{2/3}Ta_{1/3})O_3$ perovskite ceramics

Dandan Ma, Xiuli Chen*, Guisheng Huang, Jie Chen, Huanfu Zhou*, Liang Fang

Ministry-province Jointly-constructed Cultivation Base for State Key Laboratory of Processing for Non-ferrous Metal and Featured Materials, Guangxi Zhuang Autonomous Region, Key Laboratory of New Processing Technology for Nonferrous Metals and Materials, Ministry of Education, School of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, China

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Abstract

Lead-free $(1-x)BaTiO_3-xBi(Mg_{2/3}Ta_{1/3})O_3$ [$(1-x)$BT$-x$BMT, $0 \le x \le 0.1$] perovskite solid solutions were synthesized via the conventional solid state reaction technique. Raman spectra and XRD analysis demonstrate that a systematically structural evolution from a tetragonal to pseudo-cubic phase occurred near $0.01 < x < 0.03$. A phenomenon from a normal ferroelectric behavior to diffusive and dispersive relaxor-like characteristic was also observed. As BMT content further increases ($0.06 \le x \le 0.1$), the temperature stability of permittivity was markedly improved ($\Delta\varepsilon/\varepsilon_{30}$ °C $\le \pm 15\%$), high relative permittivity ($\sim$1000–2000) and low loss ($\le 2\%$) were obtained over a wide temperature range from 30 °C to 150 °C at 1 kHz. Moreover, when $x=0.08$ and 0.1, $\Delta\varepsilon/\varepsilon_{30}$ °C was $\le \pm 10\%$. These results indicate that $(1-x)$BT$-x$BMT ceramics could be suitable for thermally stable dielectric applications.

Keywords: D. $BaTiO_3$; Phase structure; Dielectric temperature stability

1. Introduction

Multilayer ceramic capacitors (MLCC) are one of the most important electronic components at the surface mounting of electronic circuits, military equipments and automation industries [1]. At room temperature (RT), dielectrics must possess high permittivity (> 1000) for MLCC applications [2]. Barium titanate ($BaTiO_3$, BT) has been reported as a satisfactory perovskite compound for MLCC applications because of its outstanding dielectric properties [3]. Nevertheless, BT ceramics have three phase transitions at about 125 °C, 0 °C, and −90 °C, leading to three dielectric anomalies, which restricts the applications of BT in the electronic information manufacturing industry [4]. To solve the above mentioned problem, a number of $BaTiO_3$–based solid solutions [5–14] have been researched owing to their high relative permittivity and good temperature-stability, especially for the addition of Bi-based [general formula-$Bi(Me)O_3$] perovskite materials to $BaTiO_3$, such as $BaTiO_3$–$Bi(Mg_{0.5}Zr_{0.5})O_3$ [6,7], $BaTiO_3$–$Bi(Zn_{0.5}Zr_{0.5})O_3$ [15], $BaTiO_3$–$Bi(Li_{1/3}Ti_{i2/3})O_3$ [16], $BaTiO_3$–$BiScO_3$ [17,18], and $BaTiO_3$–$Bi(Mg_{0.5}Ti_{0.5})O_3$ [19,20]. These ceramics show a common phenomenon that the curves of dielectric constant as a function of temperature (ε–T) flatten gradually with increasing the $Bi(Me)O_3$ content, which is highly attractive for MLCC applications.

Recently, Wang et al. [21] investigated that $BaTiO_3$–$Bi(Mg_{2/3}Nb_{1/3})O_3$ ceramics displayed a potential application in MLCC. In our previous work [22], $BaTiO_3$–$Bi(Mg_{2/3}Nb_{1/3})O_3$ solid solutions showed good dielectric temperature stability over a wide temperature range from 20 to 240 °C for thermal stability device applications. Based on the above analysis, the substitution of A-site by Bi^{+3} and/or B-site by (Mg^{+2} and Nb^{+5}) can tailor the dielectric properties of BT. Considering the identical valence and similar ionic radius of Nb^{5+} and Ta^{5+}, we could anticipate that $Bi(Mg_{2/3}Ta_{1/3})O_3$ would improve the temperature stability of the $BaTiO_3$ ceramic. In

*Corresponding author. Tel./fax: +86 773 5896436.
**Corresponding author.
E-mail addresses: cxlnwpu@163.com (X. Chen), zhouhuanfu@163.com (H. Zhou).

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the present work, temperature stability, structural evolution and dielectric properties of $(1-x)BaTiO_3$–$xBi(Mg_{2/3}Ta_{1/3})O_3$ $(0 \le x \le 0.1)$ ceramics were investigated. Furthermore, the structure-property relationship of ceramics was also discussed.

2. Experimental

Polycrystalline ceramic samples of $(1-x)$BT–xBMT $(0 \le x \le 0.1)$ solid solutions were prepared via the conventional solid state reaction technique. Carbonates and oxides were the main raw powders, including $BaCO_3$ (99%, Guo-Yao Co. Ltd., Shanghai, China), TiO_2 (99.99%, Guo-Yao Co. Ltd., Shanghai, China), Bi_2O_3 (99%, Guo-Yao Co. Ltd., Shanghai, China), MgO (98.5%, Guo-Yao Co. Ltd., Shanghai, China) and Ta_2O_5 (99.99%, Guo-Yao Co. Ltd., Shanghai, China). Stoichiometric proportions of BT and BMT were mixed in alcohol medium using zirconia balls for 4 h. The slurries were dried and then calcined at 1100 and 800 °C for 4 h, respectively. Subsequently, $(1-x)$BT–xBMT $(0 \le x \le 0.1)$ powders were weighed and milled in alcohol medium using zirconia balls for 4 h. The resultant powders were mixed with 5 wt% of polyvinyl alcohol and pressed into pellets with 12 mm in diameter and 2 mm in thickness by uniaxial pressing at 200 MPa, at room temperature. The pellets were embedded with calcined powders of the same composition to minimize alkaline elements volatilization and sintered at different temperatures, depending on the added content of BMT, ranging from 1290 to 1410 °C for 2 h in air.

X-ray diffraction (XRD) patterns were recorded at room temperature using an X-ray diffractometer (X'Pert PRO) with CuK_α radiation ($\lambda = 0.15406$ nm) operated at 40 kV and 40 mA with a step size of 0.02°. The phase analysis for the XRD data was performed with PanAlytical software (X'Pert Highscore Plus). Raman spectroscopy was carried out on a Thermo Fisher Scientific DXR using a 10 mW laser with a wavelength of 532 nm. The microstructural observation of the samples was performed using a scanning electron microscopy (Model JSM6380-LV SEM, JEOL, Tokyo, Japan). Silver electrodes were coated on both sides of the pellets, and then fired at 650 °C for 30 min. Dielectric properties were measured with an applied voltage of 500 mV over 100 Hz–1 MHz from room temperature to 500 °C using a precision impedance analyzer (Model 4294A, Hewlett-Packard Co., Palo Alto, CA) at a heating rate of 3 °C/min.

3. Results and discussion

Fig. 1(a) shows the room temperature X-ray diffraction (XRD) patterns of $(1-x)$BT–xBMT samples. All samples display the symmetry related to a single perovskite phase (JCPDS: #75-0460) and no additional diffraction peaks of impurity or secondary phases were observed in the XRD patterns, which indicates that $Bi(Mg_{2/3}Ta_{1/3})O_3$ has fully diffused into the lattice of $BaTiO_3$ and formed a solid solution. The enlarged XRD patterns of the samples in the range of 2θ from 44° to 46° clearly demonstrate that a pseudo-cubic phase appeared and increased gradually with increasing BMT content. The merging of (002)/(200) diffraction peaks into a single (200) peak occurred near the compositions of $0.01 < x < 0.03$,

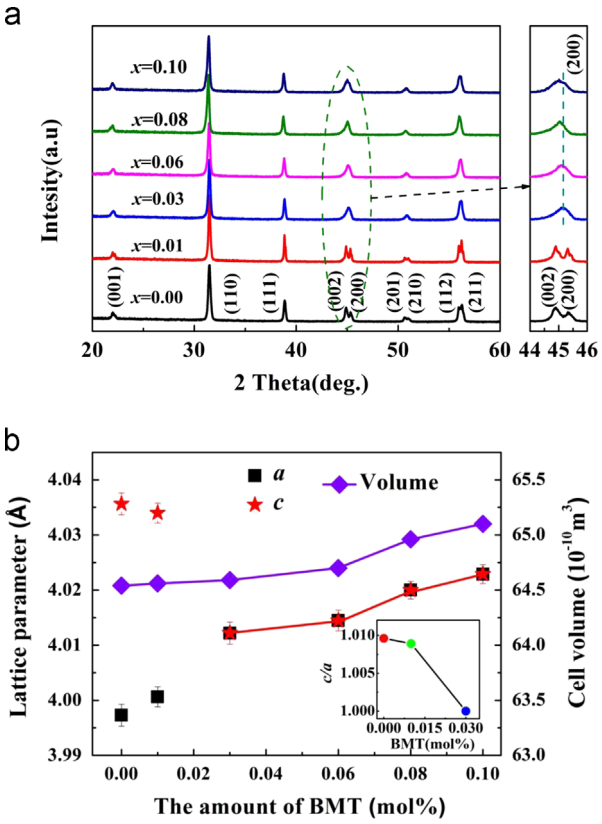

Fig. 1. (a) X-ray diffraction patterns of $(1-x)$BT–xBMT $(0.00 \le x \le 0.10)$ ceramics, the enlarged photograph is the XRD of Fig. 1(a) in the range of 2θ from 44° to 46°. (b) Lattice parameters of $(1-x)$BT–xBMT ceramics as a function of BMT content. Inset shows the c/a values of $(1-x)$BT–xBMT ceramics as a function of BMT content.

indicating a transformation from tetragonal phase (*P4mm*) to pseudo-cubic symmetry [23,24].

The variation of lattice parameters of $(1-x)$BT–xBMT ceramics as a function of x is demonstrated in Fig. 1(b). As $x \le 0.01$, the parameter a increased and c decreased with increasing x. The parameter a became identical to c with $x \ge 0.03$, and the parameters c and a increased with further increasing x. This variation is consistent with the shift of the (200) reflection toward lower 2θ angles, as shown in Fig. 1(a). The c/a ratio decreased from 1.0096 for $x=0$ to 1.0083 for $x=0.01$, and became equal to 1 at $x \ge 0.03$, as shown in the inset of Fig. 1(b). The unit cell volume of $(1-x)$BT–xBMT $(0 \le x \le 0.1)$ specimens was calculated from the XRD data. It was evidently viewed that the unit cell volume increased almost linearly with the increase of x. The coordination of A-sites in a typical cubic perovskite ABO_3 structure is 12 [25,26]. It is anticipated that the radius of Bi^{3+} (1.03 Å $< r_{Bi}^{3+} < 1.61$ Å) should substitute for Ba^{2+} (1.61 Å) at A site, while Ti^{4+} (0.604 Å) should be replaced by Mg^{2+} (0.72 Å) and Ta^{5+} (0.64 Å) at B-site. The substitution of B-site may be the main influence factor on the BT lattice. The BO_6 octahedra possess the unit cell volume and lead to the dilatation of the crystal unit cell, which is consistent with the XRD analysis that the merged peak of (002) and (200) shifted markedly to lower angles.