ELSEVIER

Materials Science and Engineering B 117 (2005) 241–245

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Ferroelectric and piezoelectric properties of vanadium-doped $CaBi_4Ti_4O_{15}$ ceramics

Jiangtao Zeng[a,b], Yongxiang Li[a,*], Qunbao Yang[a], Qingrui Yin[a]

[a] The State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China
[b] Postgraduate School of the Chinese Academy of Sciences, Beijing, 100390, PR China

Received 2 November 2004; received in revised form 25 November 2004; accepted 25 November 2004

Abstract

Vanadium-doped $CaBi_4Ti_4O_{15}$ ($CBTV_x$, $x = 0-0.2$) bismuth layered structure ferroelectric (BLSF) ceramics were prepared by the solid-state reaction method. X-ray diffraction pattern showed that single phase of BLSF with $m = 4$ formed when $x \leq 0.1$. The sintering temperature of the $CaBi_4Ti_4O_{15}$ ceramics was lowered by doping of vanadium. The effects of vanadium doping on the dielectric, ferroelectric and piezoelectric properties of $CaBi_4Ti_{4-x}V_x$ ceramics were investigated. V^{5+} dopant slightly increased the Curie temperature, enhanced the remnant polarization and decreased the coercive field of $CBTV_x$ ceramics. V^{5+} dopant decreased the temperature coefficient of dielectric constant and dielectric loss at high temperature. V^{5+}-doped $CaBi_4Ti_4O_{15}$ ceramics have superior piezoelectric properties. As a result, V^{5+}-doped CBT ceramics are a promising candidate for high temperature piezoelectric applications.

Keywords: Bismuth layer structure ferroelectric; $CaBi_4Ti_4O_{15}$; Doping effect; Vanadium; Piezoelectric

1. Introduction

Bismuth layered structure ferroelectrics (BLSFs) have recently attracted a great deal of attention because of their low dielectric constant, high Curie temperature and high resistance to polarization fatigue. They are considered to be a good candidate for high temperature piezoelectric and nonvolatile memory applications. BLSFs compounds can be described by the formula $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, where A denotes mono-, di- or tri-valent ions with a large ionic radius, and B denotes tetra- or penta-valent ions with a small ionic radius. The integer m ranges from 2 to 5 [1,2].

$CaBi_4Ti_4O_{15}$ (CBT) is a very promising candidate for high temperature piezoelectric applications due to its high Curie temperature and high resistivity. However, its low piezoelectric activity needs to be improved further. Many efforts have been made to enhance the piezoelectric constant by incorporate other ions, such as Sr^{2+}, Mn^{2+}, into the A-site or B-site of the crystal lattice. Most of them got better piezoelectricity but decreased the Curie temperature [3–5], for example, d_{33} of $Ca_{0.60}Sr_{0.40}Bi_4Ti_4O_{15}$ ceramics increases from 10 to 14.7 pC/N, but its Curie temperature decrease from 700 to 678 °C. Noguchi and Miyayama [6] and Uchida et al. [7] reported that B-site substitution by V^{5+} could increase the remnant polarization of $Bi_4Ti_3O_{12}$ ferroelectric ceramics, and decrease its high-temperature conductivity. They ascribed the better performance to a decreased in vacancy of oxygen thus significantly reducing the influence of domain pinning. Since the structure of $CaBi_4Ti_4O_{15}$ is similar as that of $Bi_4Ti_3O_{12}$ ferroelectric, the authors anticipated that V^{5+} doping could enhance the ferroelectricity of $CaBi_4Ti_4O_{15}$ ceramics. To the best of the authors knowledge there has been no report on the electrical properties of V^{5+}-doped $CaBi_4Ti_4O_{15}$ ceramic yet. In this paper, the effects of V^{5+} dopant on the dielectric, ferroelectric and piezoelectric properties of CBT are studied.

---

[*] Corresponding author. Tel.: +86 21 52411066; fax: +86 21 52413122.
E-mail address: yxli@mail.sic.ac.cn (Y. Li).

0921-5107/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2004.11.015

2. Experimental

$CaBi_4Ti_{4-x}V_xO_{15}$ ($x = 0-0.2$) ($CBTV_x$) ceramics were prepared by the solid-state reaction method. The starting raw materials were analytical pure degree oxides and carbonate powders: Bi_2O_3, TiO_2, V_2O_5, and $CaCO_3$. Chemical stoichiometric amounts of the starting powders were thoroughly mixed with ethanol in a ball mill for 4 h, dried and calcined at 850 °C for 3 h in an alumina crucible. After calcination, the ground and ball-milled powders were pressed into disks of 15 mm in diameter and about 2 mm in thickness. The pressed samples were finally sintered at temperatures of 1000–1180 °C for 4 h in a sealed alumina crucible. Pt electrodes were sputtered on both sides of the ceramic specimens. The samples were electrical poled in a silicon oil bath at 200 °C under electric field of 8–9 kV/mm.

Bulk densities of the sintered ceramics were measured by the Archimedes method. The crystal phase of $CBTV_x$ ceramics was determined by X-ray diffraction (XRD) analysis (D/max 2550 V) using Cu Kα_1 radiation with a scan speed of 4°/min and a step width of 0.02°. The lattice constants were calculated from the XRD patterns using a CHECKCELL refinement software. The accuracy of 2θ of the X-ray diffractometer is ±0.002°. The ferroelectric hysteresis loops were measured by a TF Analyzer 2000 FE-Module ferroelectric tester. Dielectric constants as a function of temperature were measured with an HP4284A LCR meter at 100 kHz. Piezoelectric constant d_{33} was measured by a quasi-static d_{33} meter (Model ZJ-3A, Institute of Acoustics, Chinese Academic of Sciences).

3. Results and discussion

Undoped CBT ceramics are yellowish, while V^{5+}-doped CBT are red and the color get darken with the increase of V^{5+} dopant. The sintering characteristics of bismuth layer structure $CBTV_x$ ceramics are shown in Fig. 1. Undoped CBT ceramics get the highest density at 1150 °C and its density decreases beyond the temperature. For $CBTV_x$ ceramics, the densification curve was shifted to a lower temperature range, and the samples with higher vanadium content have higher density when sintering at the same temperature. The optimal sintering temperatures become lower with the increase of V^{5+} dopant concentration. The optimal sintering temperature of $CBTV_{0.1}$ ceramic is 150 °C lower than that of CBT ceramic. The low sintering temperature of $CBTV_x$ should be ascribed to the low melting point of V_2O_5 (690 °C). Since bismuth is volatile at high temperature, low sintering temperature is significant to avoid the loss of bismuth during high-temperature sintering.

Fig. 2 shows the X-ray diffraction patterns of $CBTV_x$ ($x = 0$–0.2) ceramics. The XRD peaks were indexed and the crystal structure belongs to the orthorhombic system. The X-ray diffraction analysis indicated that pure single phase of layered perovskite ferroelectrics with $m = 4$ was obtained when $x \leq 0.1$, while further increasing of V^{5+}, an unknown impurity phase emerged. It indicates the solid solution capacity of V^{5+} substitute of Ti^{4+} is about 0.1 mol.%. The comparison of the ionic radii reveals that V^{5+} is 11% smaller than Ti^{4+}. The low solid solution capacity results from smaller radii size and higher valence of V^{5+}.

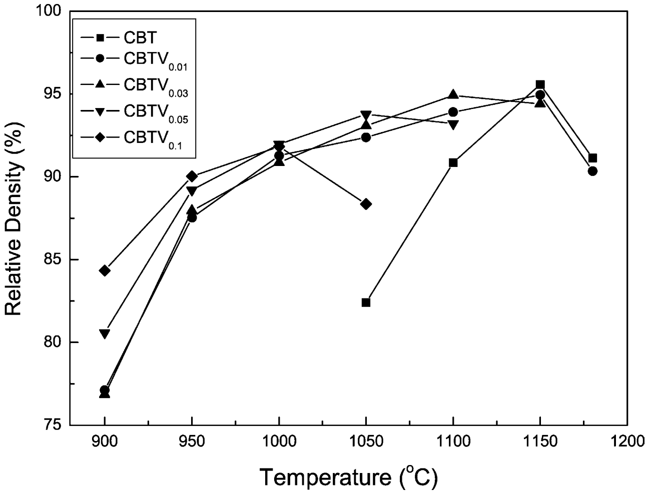

Fig. 1. Sintering characteristics of $CBTV_x$ ceramics.

Fig. 3 is the lattice constants of $CBTV_x$ samples as a function of vanadium content. The lattice constants of *a* and *b* axes decrease in the range of 0–0.05. In the range of 0.05–0.1, the lattice constant of *b* axis nearly keeps constant, while the lattice of *a* axis increases. As a result, it is considered that the anisotropies of *a* and *b* axes decrease when $x = 0.1$. Because the ferroelectric and piezoelectric properties BLSFs are strongly affected by the anisotropies of *a* and *b* axes, it can be expected that increasing V^{5+} dopant to 0.1 mol.% will lead to decrease of the ferroelectricity.

Fig. 4 shows the temperature dependence of the dielectric constant of the $CBTV_x$ ceramics. It can be seen that the maximum value of ε decreases upon vanadium-doping. Fig. 5 shows the Curie temperature as a function of V^{5+} dopant. With doping of V^{5+} the Curie temperature of $CBTV_x$ ceramics increases slightly within $x = 0.05$, however, when x is beyond 0.1 mol.%, the T_c decreases.

The variation of T_c with vanadium doping can be explained by tolerance factor and cation vacancy. The tolerance factor for the perovskite structure is given by $t = (r_A + r_o)/\sqrt{2}(r_B + r_o)$ where r_A, r_B and r_o are ionic radii of an A-site cation, a B-site cation, and an oxygen ion, respectively. The tolerance factor of $CaBi_4Ti_4O_{15}$ is 0.957. Since V^{5+} has smaller ionic radius than Ti^{4+}, incorporation V^{5+} into B-site will increase the tolerance factor of CBT. The Curie temperature of BLSFs decreases as tolerance factor increases [8], thus V^{5+} doping will decrease the Curie temperature of $CBTV_x$ ceramics. On the other hand, V^{5+} has higher valence than Ti^{4+}, the substitution of V^{5+} for Ti^{4+} introduces cation vacancy in A-site to meet the requirement of charge neutrality. The cation vacancies at A-site could lead to an enhancement