Ceramics International 42 (2016) 10833–10837

Contents lists available at ScienceDirect

Ceramics International

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

Influence of Nb_2O_5 addition on dielectric properties and diffuse phase transition behavior of $BaZr_{0.2}Ti_{0.8}O_3$ ceramics

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ARTICLE INFO

Article history:
Received 25 February 2016
Received in revised form
25 March 2016
Accepted 28 March 2016
Available online 29 March 2016

Keywords:
C. Dielectric properties
$Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics
Diffuse phase transition

ABSTRACT

Nb_2O_5 doped $Ba(Zr_{0.2}Ti_{0.8})O_3$ (short as BZT20) ceramics were prepared by a mixed-oxide method using a high-energy planetary ball mill and the influence of Nb_2O_5 addition on microstructure, dielectric properties and diffuse phase transition behavior of BZT20 ceramics were investigated. It was demonstrated that Nb^{5+}entered the B-site of BZT20 ceramic and substituted for Ti^{4+}, which caused the expansion and distortion of crystal lattice. BZT20 ceramics doped with 0.2 mol% Nb_2O_5 showed excellent dielectric property and lower diffusivity with ε_m=37,823 and γ=1.49. We supposed that the increase of dielectric constant and decrease of diffuseness parameter with increasing Nb_2O_5 content were caused by lattice disorder and unbalancing of cations induced by the substitution of Ti^{4+} by Nb^{5+} in the B sites of BZT20 ceramics. The Curie temperature decreased with the increase of Nb_2O_5 content, which can be attributed to enlarged distortion energy of the Nb doped BZT20 structure. Besides, grain size effect on the dielectric property and diffuse phase transition behavior of Nb_2O_5 doped BZT20 ceramics was also investigated.

1. Introduction

Diffuse phase transition (DPT) is one of the most interested characteristic in ferroelectric physics [1]. The typical feature of DPT is the relaxor behavior happened in ferroelectric phase transition, mostly in perovskite structure materials, especially in lead-based compounds (PMN, PSN, PLZT, etc.) with more than one type of ions occupying the equivalent six-coordinated crystallographic sites [2–5]. However, the intrinsic properties of volatility and toxicity in these lead-based ceramics have restricted their application in environmental friendly devices (such as dielectrics for capacitors, actuators, etc.). In recent years, most researchers focus on developing lead-free ceramics with DPT behavior [6–8].

Lead-free solid solutions of $BaTiO_3$ and $BaZrO_3$ ($Ba(Zr_xTi_{1-x})O_3$, abbreviated as BZT) is one of the most important compositions for dielectrics in multilayer ceramic capacitors which is found to show DPT behavior [9,10]. The permittivity of BZT ceramic is increased more by the addition of zirconium due to the higher chemical stability of Zr ion than Ti ion [11,12]. The DPT of BZT ceramics is caused by a broadening of the permittivity maximum in the temperature range, which is stimulated by the increase of zirconium amount. As the zirconium content increases to 20%, only one phase transition exists. Below this content, the rhombohedral phase is stable; above the content, the cubic phase is stable [13]. As the ratio of Zr is up to 25%, BZT appears strong relaxor property, and the Curie temperature shifts to lower temperature [9].

Nb_2O_5 doped ceramics, such as Nb_2O_5 doped PZT [14–16] and BNKT [17], have been investigated by many researchers. Chu et al. reported that Nb_2O_5 enabled a good sintering process, promoted domain wall motion and enhanced the densification and dielectric properties of $Pb_{1-0.5x}(Zr_{0.52}Ti_{0.48})_{1-x}Nb_xO_3$ ceramics[14]. Tănăsoiu et al. found that Nb^{5+} in $PbZr_{0.51}(Nb_3Li)_xTi_{0.49-x}O_3$ ceramics is helpful to improve the dielectric and piezoelectric properties [16]. Kumar et al. investigated the effect of Nb_2O_5 doping on the properties of $Bi_{0.5}(Na_{0.5}K_{0.5})_{0.5}TiO_3$ ceramic, the results showed that 0.4 wt% Nb_2O_5 doping exhibited higher P_r and R_{sq} values and also showed relaxor behaviors with DPT [17]. However, the effect of Nb_2O_5 on the DPT behavior and dielectric properties of BZT ceramics has been seldom reported.

In this work, Nb_2O_5 doped BZT20 ceramics were prepared by solid-state method. The influence of Nb_2O_5 contents ranging from 0.1 to 0.4 mol% on the microstructure and dielectric properties BZT20 ceramics were examined and discussed. Moreover, the relationship between DPT behavior and the contents of Nb_2O_5 have been investigated.

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http://dx.doi.org/10.1016/j.ceramint.2016.03.212
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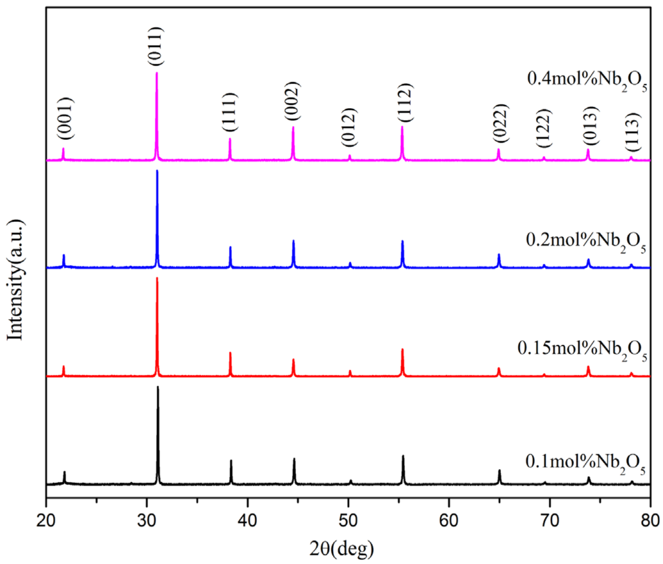

Fig. 1. XRD patterns of Nb_2O_5 doped BZT20 ceramics sintered at 1270 °C.

2. Experimental procedures

BZT20+*x*mol% Nb_2O_5 ceramics with x=0.1, 0.15, 0.2, and 0.4 were fabricated by solid-state reaction using a high-energy planetary ball mill. The raw materials of AR grade $BaCO_3$ (99%), TiO_2 (99%) and ZrO_2 (99%) powders were weighted at appropriate proportion. Powdered oxides in stoichiometry were homogeneously ball milled in deionized water for 6 h using ZrO_2 balls as milling media. The homogeneous mixtures were dried and calcined at 1100 °C for 4 h, and then the pre-synthesized BZT20 powders and Nb_2O_5 (99%) powder were mixed according to the formula and re-milled for 12 h. The powers were subsequently mixed thoroughly with 0.5 wt% polyvinyl alcohol (PVA) organic binder solution to granulate and compacted into disk samples with a diameter of ~10 mm and a thickness of ~1.0 mm. After burning out PVA at 600 °C in the electric furnace, pellets of Nb_2O_5-doped BZT20 were sintered at 1270 °C for 4 h. Then the silver pastes were fired at 800 °C for both sides of these samples as electrodes for electrical measurements.

The crystalline structures of the sintered samples were identified by Powder X-ray diffraction (XRD), using a diffractometer (D8-Focus; Bruker AXS GmbH, Karlsruhe, German) with Cu Kα radiation over a 2θ angle from 20° to 80°. The morphologies of the sintered samples were performed and analyzed with field emission scanning electron microscopy (FE-SEM, S-4800; Hitachi, Ltd., Tokyo, Japan). The temperature dependence of dielectric permittivity was measured with a capacitance meter (HP4278A; Hewlett-Packard, SantaClara, California, USA.) in conjunction with a temperature chamber (GZ-ESPEC) over a temperature range of −50 to 145 °C at 1 kHz.

3. Results and discussion

Fig. 1 plots the XRD patterns of BZT20+*x*mol% Nb_2O_5 ceramics with x=0.1, 0.15, 0.2, and 0.4. From the XRD patterns, it can be seen that all samples exhibited pure perovskite phase with no impurity phase, which suggested that the Nb ion can be dissolved in BZT20 to form a homogenous solid solution.

Fig. 2 illustrates the SEM micrographs of BZT20 ceramics with different Nb_2O_5 contents. The grain sizes of specimens doped with 0.1–0.2 mol% Nb_2O_5 are continually increased with the increasing amount of Nb_2O_5 addition. However, the SEM micrograph in Fig. 2 (d) shows that further increasing the amount of Nb_2O_5 to 0.4 mol% gives rise to the decrease of grain size. In $Ba(Zr_xTi_{1-x})O_3$ solid solution, Ba^{2+} occupies site A of perovskite structure, while

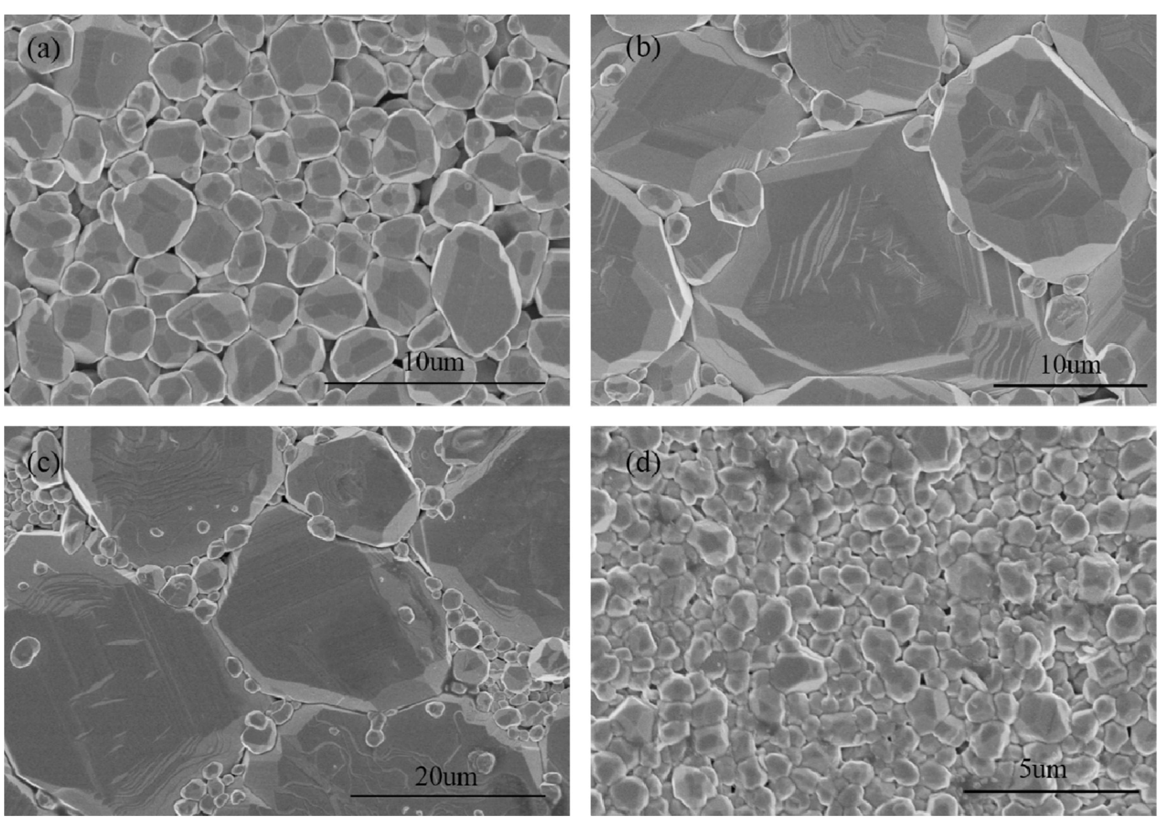

Fig. 2. SEM patterns of the Nb_2O_5 doped BZT20 ceramics. (a) x=0.1 mol% (b) x=0.15 mol% (c) x=0.2 mol% and (d) x=0.40 mol%.