Materials Research Bulletin 94 (2017) 174–182

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Correlation between microstructural evolutions and electrical/mechanical behaviors in Nb/Ce co-doped $Pb(Zr_{0.52}Ti_{0.48})O_3$ ceramics at different sintering temperatures

Yu Chen[a,b,1], Shaoxiong Xie[c,1], Qingyuan Wang[a,c,*], Lei Fu[d,*], Rui Nie[b], Jianguo Zhu[b]

[a] School of Mechanical Engineering, Chengdu University, Chengdu 610106, China, China
[b] College of Materials Science and Engineering, Sichuan University, Chengdu 610065, China
[c] School of Architecture and Environment, Sichuan University, Chengdu 610065, China
[d] School of Mechanical Engineering, Sichuan University of Science & Engineering, Zigong 643000, China

ARTICLE INFO

Article history:
Received 19 January 2017
Received in revised form 17 May 2017
Accepted 23 May 2017
Available online 4 June 2017

Keyword:
PZT ceramics
Sintering temperature
Grain size
Electrical properties
Mechanical behaviors

ABSTRACT

For Nb/Ce co-doped $Pb(Zr_{0.52}Ti_{0.48})O_3$ ceramics $\{Pb(Zr_{0.52}Ti_{0.48})_{0.95}Nb_{0.05}O_3 + 0.2\ wt.\%CeO_2\}$ sintered between 1150 °C and 1250 °C, with increasing sintering temperatures, a gradual lattice distortion associated with an increased grain size are identified. Electrical test reveals that the ceramics exhibit a diffused phase transition, and the intensity of permittivity peaks increase with increase in sintering temperatures. The samples sintered at higher temperatures present a stronger piezoelectric property because of a larger grain size. While the mechanical test demonstrates that the samples sintered at lower temperatures exhibited a higher hardness because of a smaller grain size. Both the second crack and crack deflection are observed in the sample sintered at 1200 °C. The domain switching caused by a compression load contributes to the nonlinear ferroelastic deformation of ceramics. At last, the sample sintered at 1125 °C gains some good properties such as: $T_c = 312$ °C; $d_{33} = 443$ pC/N; $K_{IC} = 0.66\ MPa\ m^{1/2}$ and $\sigma_c = 430$ MPa.

1. Introduction

Since lead zirconate titanate $Pb(Zr_xTi_{1-x})O_3$(PZT) with a typical perovskite structure was identified as a strong ferroelectric [1], various PZT-based materials have been widely used as sensitive elements for electromechanical devices [2–5] because of their good dielectric, ferroelectric and piezoelectric properties. Especially, a special PZT system with a Zr/Ti ratio of 52/48 was considered around the morphotropic phase boundary (MPB), possessing some better electromechanical properties such as a higher d_{33} and k_p, etc. Thus $Pb(Zr_{52}Ti_{48})O_3$ has been studied extensively in recent years. In the meantime, many efforts are aimed at optimizing their electromechanical properties for further improving the practicability of PZT, such as the co-doping technique by combining donor ions (like Nb^{5+}, Ta^{5+} and W^{6+}, etc) and oxide additive (like CeO_2, Cr_2O_3 and MnO_2, etc.) [6–8]. Here, Nb/Ce co-doped $Pb(Zr_{0.52}Ti_{0.48})O_3$ceramics have not been reported yet, which are expected to achieve some excellent electromechanical properties as deduced from some reports about the doping effect of Nb_2O_5 and CeO_2 on ceramics [9,10]. Moreover, more researches revealed that the sintering process dominates the grain growth of ceramics, which determines their microstructural characteristics and then influences their electrical properties [11–13].

On the other hand, it is well known that the premature failure of ceramic materials due to the brittle fracture limits their wide applications. However, as a sensitive material both for the stress and electricity, the mechanical properties of piezoceramics are usually ignored by us, which tends to be instead by their intuitionistic electrical properties. In fact, in some special applications, such as high-frequency ultrasonic transducers and bending actuators [14,15], some lattice defects like ionic vacancies and interstitial atoms, or structural defects like flaws, pores and impurities existing in piezoceramics can trigger the dielectric breakdown even functional failure of electrical devices.

In this paper, Nb/Ce co-doped $Pb(Zr_{0.52}Ti_{0.48})O_3$ ceramics were prepared by a conventional ceramic process. We observed the

* Corresponding author at: School of Mechanical Engineering, Chengdu University, Chengdu 610106, China.
E-mail addresses: wangqy@scu.edu.cn (Q. Wang), kunmingfulei@126.com (L. Fu).
[1] These authors contributed equally to this work and should be considered co-first authors.

http://dx.doi.org/10.1016/j.materresbull.2017.05.045
0025-5408/

microstructural evolution of ceramics with the sintering temperature, investigated the regulation of electrical behaviors contributed by the ionic substitution, also examined their mechanical behaviors subjected to different stress loads. This work could help us to pierce the correlation between microstructural evolution and electrical/mechanical behaviors in piezoceramics.

2. Experiment

Nb/Ce co-doped $Pb(Zr_{0.52}Ti_{0.48})O_3$ ceramics with a chemical formula of $Pb(Zr_{0.52}Ti_{0.48})_{0.95}Nb_{0.05}O_3$ + 0.2 wt.%CeO_2(PZT-NC), were fabricated by two steps according to a conventional ceramic process. Firstly, reagent-grade oxide powders: PbO (99%), TiO_2 (99%) and Nb_2O_5 (99%) were weighed in stoichiometric amounts and ball milled together for 12 h using ethanolas as medium and zirconia as grinding balls. After drying, the homogeneous mixtures were calcined at 860 °C for 2 h to obtain the compound of Pb $(Zr_{0.52}Ti_{0.48})_{0.95}Nb_{0.05}O_3$. Secondly, 0.2 wt.% of CeO_2 (99%) as additive were added into the calcined powders, and then milled with them again in the same condition. After drying, the homogeneous mixtures were granulated with polyvinyl alcohol (PVA). The powders obtained were compacted into a disk with a diameter of 10 mm and a thickness of 1 mm. After PVA was burned out at 550 °C for 2 h, these disks were sintered at 1150–1250 °C for 2 h in a sealed alumina crucible for getting PZT-NC ceramics.

On the structural characterization of PZT-NC ceramics, the relative density was calculated as the ratio between the apparent density which was measured by the Archimedes method and the theoretical density which was obtained from crystallographic structures. The crystallographic structure was determined by an X-ray diffractometer (DX2700, Dandong, China) using Cu-Kα radiation (λ = 1.5418 Å) at room temperature. The structural morphology was observed by using a scanning electron microscopy (JSM-610LV, JEOL, Japan). The average grain size was obtained by the linear intercept method based on SEM images.

To evaluate the mechanical properties of PZT-NC ceramics, the sintered samples should be polished firstly. The hardness was gained by a Vickers diamond indenter (AKASHI, AVK-A, Japan) at a load of 9.8 N, and the fracture toughness was determined by the indentation fracture (IF) technique with combining Vickers diamond indenter and scanning electron microscopy. The compression strength of the samplewith a cylindrical shape (Φ10 mm × h10 mm) was measured by the uniaxial compression loading on a universal testing machine (INSTRON, 8501, UK), and the loading mode was in the displacement control at a stoke rate of 0.5 mm/min. To evaluate the electrical properties of PZT-NC ceramics, the sintered samples were fired with silver paste at 700 °C for 10 min as electrodes, and then poled in a silicon oil bath at room temperature under 3–5 kV/mm for 30 min. The dielectric constant (ε_r) and loss (tan δ) as a function of temperature were recorded using an LCR analyzer (HP4980A, Agilent, USA). The piezoelectric constant (d_{33}) was obtained by using a quasi-static d_{33} meter (ZJ-3A, IACAS, China).

3. Result and discussion

XRD patterns of PZT-NC ceramics sintered at different temperatures are shown in Fig. 1. The diffraction peaks marked by rhombs match with the standard diffraction data in JCPDS card #33-0784, thus confirming the corresponding phase as $Pb(Zr_{0.52}Ti_{0.48})O_3$ with the coexistence of rhombohedral phase (R) and tetragonal (T) phase. This result suggests that Nb_2O_5 and CeO_2 were successfully diffused into the crystal lattice of PZT, forming a solid solution with the matrix. The substitution of Nb^{5+} and Ce^{4+} for Ti^{4+} at the B-site of perovskite structure was achieved due to their similar ionic radius [16,17]. However, there is second phase found in the samples

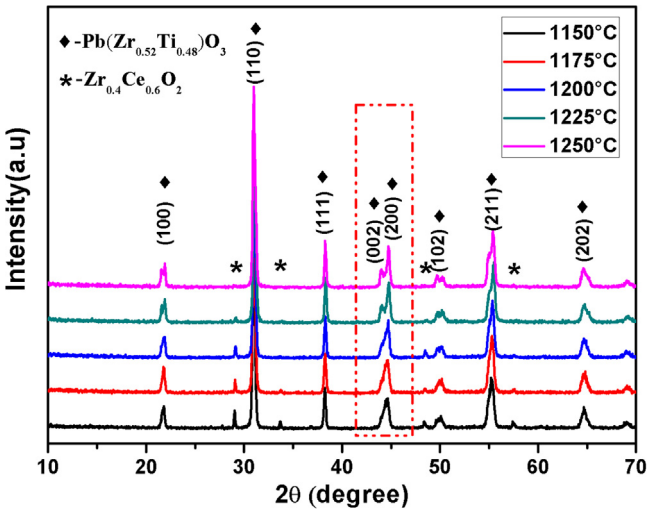

Fig. 1. XRD patterns of PZT-NC ceramics sintered at different temperatures.

sintered below 1225 °C, which could be detected as $Zr_{0.4}Ce_{0.6}O_2$ by checking those diffraction peaks marked by asterisk according to JCPDS card #38-1439. This impurity was probably formed by the reaction between the residual Ceric oxide which did not diffuse into the crystal lattice and the zirconium element which were segregated from the chemical composition in the sintering process of ceramics at low temperatures. But $Zr_{0.4}Ce_{0.6}O_2$ disappeared in the two samples sintered at 1225 °C and 1150 °C, which implies that a higher sintering temperature tends to promote the substitution of Ce^{4+} for Ti^{4+} by supplying a stronger driving force for atomic diffusion, and the appearance of emergent liquid phase at high temperatures may also hinder the formation of secondary phase by improving the thermal stability of sintering system [13,18]. Moreover, for these two samples sintered at higher temperatures, an obvious split between $(200)_T$ and $(002)_T$ reflection peaks near the 2θ angle of 45° could be also observed, a higher peak ratio of $(002)_T/(200)_T$ indicates a higher content of tetragonal phase in samples [19], which is contributed by the inner stresses relieving induced by the enlarged grain size [5]. Here, an higher sintering temperature leads to more stress relaxation in ferroelectric ceramics, which tends to provide an easier ferroelectric-paraelectric phase transformation and a better grain growth for them.

Fig. 2 describes the cell parameters of PZT-NC ceramics as a function of their sintering temperatures. It can be seen that lattice constants a (b) decreases while c increases with the increase of sintering temperature in the rough, which indicates that the change of sintering temperature has caused some lattice distortion of PZT-NC. Corresponding to the variation in lattice constants, cell volume (v) shows an analogous downtrend like a and b with the increase of sintering temperature, while the axial ratio c/a derived from the lattice parameters of tetragonal ferroelectric phase keeps a similar uptrend with c, showing that the distortion of the tetragonal unit cell from the basic perovskite cell was larger at higher sintering temperatures. Here, the increase of c/a value could be attributed to microscopic compositional fluctuations caused by different sintering temperatures, which cannot provide the solid solution with a truly atomic homogeneity, and by the different inner stresses existing in ceramic grains, which determined the coexistence of two ferroelectric phases [20]. Moreover, the increase of c/a value seems to agree with the increase of tetragonal phase content for PZT-NC ceramics too.

Further, SEM images focusing on the natural surfaces of PZT-NC ceramics sintered at different temperatures are exhibited in Fig. 3.