Ceramics International 44 (2018) 8057–8063

Contents lists available at ScienceDirect

Ceramics International

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

Tailored electrical properties in ternary $BiScO_3$-$PbTiO_3$ ceramics by composition modification

Zhuang Liu[a], Chunlin Zhao[a], Ruishi Xie[b], Jiagang Wu[a,*]

[a] Department of Materials Science, Sichuan University, 610064 Chengdu, PR China
[b] Analytical and Testing Center, Southwest University of Science and Technology, Mianyang 621010, PR China

ARTICLE INFO

Keywords:
$BiScO_3$-$PbTiO_3$
Ternary system
Phase coexistence
Electrical properties
Composition Modification

ABSTRACT

Ternary $0.99(0.36BiScO_3$-$0.64PbTiO_3)$-$0.01Bi(M_1M_2)_{0.5}O_3$ (BS-PT-BM_1M_2) ceramics were prepared by the solid-state reaction method, where M_1 and M_2 respectively stand for bivalent and quadrivalent elements (M_1 = Sn, Pb, Ni, Sr, Ba, Ca, Cu, Mg and Mn, M_2 = Hf, Sn, Zr, Si, Ce and Mn). Effects of different elements on their structure and electrical properties were studied in detail. It was found that the formation of MPB by optimizing the doped elements can enhance electrical properties (d_{33} = 500 pC/N, ε_r = 2013, tan δ = 0.024 at 100 kHz). Interestingly, different electrical properties can be induced by choosing the doped elements. For example, a high d_{33} can be realized by doping M_1 = Sn, Pb or Sr (M_2 = Ti) as well as M_2 = Hf, Sn or Zr (M_1 = Zn), and the dielectric loss can be suppressed by doping Ce or Mn. In addition, large bipolar strain (S = 0.25–0.46%) as well as high remanent polarization (P_r = 34.7–46.4 μC/cm^2) can be observed for all doped elements, which were superior to pure BS-PT (P_r = 32 μC/cm^2 and S = 0.18%), and high T_C (T_C = 417–443 °C) can be attained in all the ceramics. We believe that the addition of ABO_3-type compounds with optimum elements can enhance electrical properties of BS-PT ceramics.

1. Introduction

It is well known that $xBiScO_3$-$(1$-$x)PbTiO_3$ (BS-PT) ceramics exhibit both high Curie temperature (T_C) of ~ 450 °C and large piezoelectric constant (d_{33}) of ~ 450 pC/N by forming morphotropic phase boundary (MPB) [1,2]. However, some shortcomings still exist in BS-PT ceramics, including high dielectric loss (tan δ = 4% @ 100 kHz) [1–3] and low bipolar strain value (S = 0.18%) [1,4–6]. In the past, some attempts have been employed to overcome these drawbacks. For example, the addition of ABO_3-type compounds can further promote electrical properties of BS-PT ceramics [5,7–12], such as $Ba(Sr,Ti)O_3$, $LiNbO_3$ and $LiSbO_3$. Unfortunately, their T_C values can decrease obviously [8–10,12].

The chemical modification as the third component can strongly affect the electrical properties of BS-PT ceramics. According to the previous reports, different electrical properties can be found in BS-PT-Bi$(C,Ti)_{0.5}O_3$ ceramics (C standing for different bivalent elements) [5,7–14]. For examples, the addition of $Bi(Ni_{0.5}Ti_{0.5})O_3$ can improve the thermal stability of BS-PT ceramics [13], and higher remnant polarization (P_r = 43 μC/cm^2) can be realized by doping $Bi(Mg_{0.5}Ti_{0.5})O_3$ [14]. Therefore, the types of the doped elements can dominate the electrical behavior of BS-PT ceramics. However, effects of $Bi(M_1M_2)_{0.5}O_3$ as the third component on the physical properties of BS-PT ceramics were few systematically studied, and moreover it is necessary to illuminate the relationship between M_1(or M_2) and electrical properties

In this work, we designed the material system of $0.99(0.36BiScO_3$-$0.64PbTiO_3)$ -$0.01Bi(M_1M_2)_{0.5}O_3$ (BS-PT-BM_1M_2), and effects of different bivalent and quadrivalent elements on their structure and electrical properties were investigated. It was found that different modified elements can affect electrical properties of BS-PT ceramics, and the related physical mechanisms were also studied.

2. Experimental section

Ternary $0.99(0.36BiScO_3$-$0.64PbTiO_3)$-$0.01Bi(M_1M_2)_{0.5}O_3$ ceramics [BS-PT-BM_1M_2, M_1 = Sn, Pb, Ni, Sr, Ba, Ca, Cu, Mg and Mn (M_2 = Ti); M_2 = Sn, Pb, Ni, Sr, Ba, Ca, Cu, Mg and Mn (M_1 = Zn)] were fabricated by the conventional solid-state method. Raw materials include Bi_2O_3 (99%), Sc_2O_3 (99.99%), PbO (99%), TiO_2 (98%), ZnO (99.9%), SnO (99%), $SrCO_3$ (99%), NiO (98%), $CaCO_3$ (99.5%), CuO (99%), $BaCO_3$ (99%), MgO (98.5%), $MnSO_4{\cdot}H_2O$ (99%), HfO_2 (98%), SnO_2 (99%), ZrO_2 (99%), SiO_2 (99%), CeO_2 (99.99%) and MnO_2 (99.9%). All raw materials of this work were produced by the Sinopharm Chemical

---

* Corresponding author.
E-mail addresses: msewujg@scu.edu.cn, wujiagang0208@163.com (J. Wu).

https://doi.org/10.1016/j.ceramint.2018.01.247
Received 24 January 2018; Received in revised form 29 January 2018; Accepted 29 January 2018

Reagent Co., Ltd. These powders were weighed according to their chemical compositions with excess 2% Bi_2O_3 to compensate the Bi volatilization under the sintering process [5,6], and were then ball mixed for 24 h with ethanol. All the mixed powders were calcined at 780 °C for 3 h in air, and then the calcined powders incorporating polyvinyl alcohol (PVA) binder were pressed into the disks with ~ 10.0 mm diameter and ~ 6.0 mm thickness. Green pellets were sintered at 500 °C for 3 h in air for burning out the PVA binder, and then the samples were sintered at 1080–1130 °C for 2 h. The sintered samples were pasted silver on both sides and fired at 600 °C for 10 min. All the samples were poled at 120 °C in a silicon oil bath under the direct current (*dc*) field of 6 kV/mm.

The phase structure of the sintered ceramics was identified by X-ray diffraction with a Cu K_α radiation (λ = 1.5406 Å) (XRD, Bruker D8 Advanced XRD, Bruker AXS, Inc., Madison, WI). Surface morphologies were characterized by the field emission-scanning electron microscopy (FE-SEM, JSM7500, Japan). The planar electromechanical coupling factor (k_p) was determined by the resonance-antiresonance method according to the IEEE standards using an impedance analyzer (HP4294A). The temperature dependence of dielectric constant (ε_r-T) was measured by an *LCR* meter (HP4980 Agilent, U.S.A. and TH2816A, China) equipped with a temperature box with 25–470 °C. Polarization versus electric field (*P-E*) hysteresis loops were conducted at 10 Hz using a Radiant Precise Workstation (Riadiant Technologies, Medina NY). Their d_{33} was characterized by a Belincourt meter (ZJ-3A, China). The strain versus electric field (*S-E*) curves were measured using a strain instrument (aixACCT TF Analyzer 1000, Germany).

3. Results and discussions

In this part, effects of different doped elements on phase structure were identified by XRD patterns, as shown in Fig. 1. All the ceramics have a pure perovskite phase except for the addition of Mn^{2+} and Ce^{4+}, confirming that most of the elements can diffuse into BS-PT. It was previously reported that the valence states of Mn and Ce can be easily changed with temperature fluctuation and then lead to the coexistence of different valences [15], which is mainly responsible for the impure phases. According to the previous reports, pure 0.36BS-0.64PT ceramics possess the MPB of rhombohedral-tetragonal (R-T) phase coexistence [1,2]. The phase structure of this work remained unchanged by introducing the types of doped elements, and the R-T phase boundary can be found in all the samples [16,17].

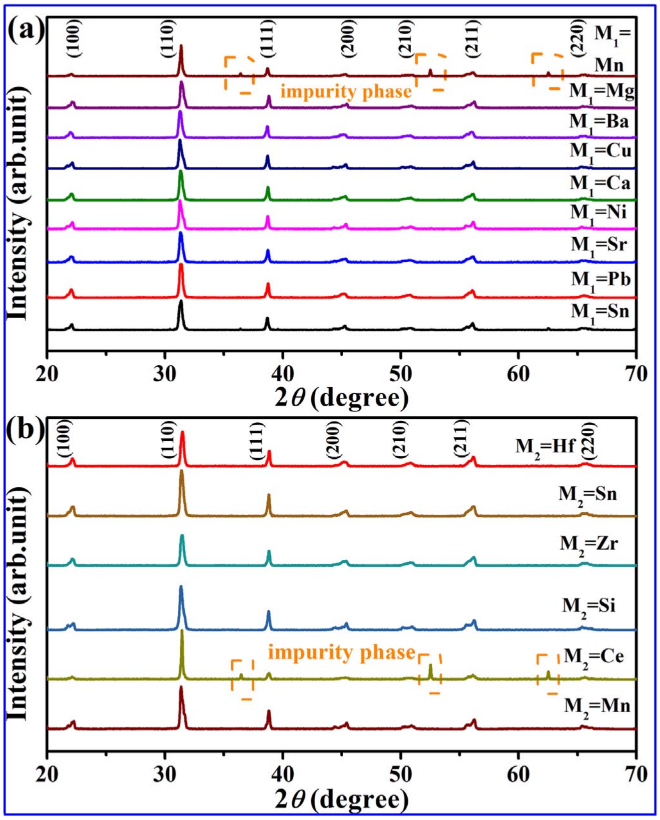

Fig. 1. XRD patterns (2θ = 20–70°) of the ceramics with (a) different bivalent and (b) different quadrivalent elements.

Fig. 2 showed the SEM images of the surface morphologies of the samples with different bivalent and quadrivalent elements. All the samples have a dense microstructure and uniform grain distribution, and large grains were surrounded by the small ones. However, the grain sizes of all the samples slightly fluctuate, indicating that the grain sizes can be slightly influenced by elements types.

Fig. 3 showed the composition dependence of piezoelectric and dielectric properties of the ceramics. As shown in Fig. 3(a) and (b), bivalent (Sn^{2+}, Pb^{2+} or Sr^{2+}) as well as quadrivalent elements (Hf^{4+}, Sn^{4+} or Zr^{4+}) could promote piezoelectric constant (d_{33} = 490–500 pC/N) with respect to pure BS-PT (d_{33}~450 pC/N). However, the addition of some elements can degrade piezoelectric properties of BS-PT ceramics, such as Mn or Ce (d_{33} = 355–410 pC/N). This result indicates that the formation of MPB can enhance piezoelectricity well, and impure phases can degrade piezoelectric properties. On the one hand, it was previously reported that nanodomains were presented only for the compositions near the MPB, which can contribute to the enhancement of piezoelectricity [18]. On the other hand, both polarization rotation and polarization extension mechanisms became stronger at MPB region, leading to the improvement of piezoelectric behaviors [19]. In addition, similar phenomenon was also found in the composition dependence of k_p values [Fig. 3(a) and (b)]. Fig. 3(c) and (d) showed the composition dependence of dielectric properties of the ceramics. It was found that bivalent (Sr^{2+}, Ni^{2+} or Ca^{2+}) as well as quadrivalent elements (Hf^{4+} or Sn^{4+}) can enhance dielectric constant (ε_r = 2013–2054) as compared with pure BS-PT (ε_r = 1825). Interestingly, one can find from Fig. 3(d) that the addition of Ce or Mn could reduce dielectric loss (tan δ = 2.4–2.6%) with respect to pure BS-PT (tan δ = 4%). Previously, it was reported that the addition of Mn can produce oxygen vacancies in the BO_6 octahedron resulting from the multivalent states. In addition, oxygen vacancies can diffuse into domain boundaries, leading to the decreased overall energy, resulting in the pinning of 180° domain motion. Finally, dielectric loss can be reduced due to the hindrance of domain movements [6,7]. As shown in Fig. 3(b) and (d), the addition of Ce could also decrease dielectric loss, and however piezoelectric constant (d_{33} = 410 pC/N) and dielectric constant (ε_r = 1830) were slightly reduced, as compared with Mn modification (d_{33} = 300 pC/N and ε_r = 1504). Therefore, the physical mechanism of the decreased dielectric loss for Ce may be the same as that of Mn, which is due to the intrinsic tendency of valence transition between Ce^{3+} and Ce^{4+}. As a result, the addition of Mn or Ce could decrease dielectric loss effectively, and furthermore Ce can hinder the decreased piezoelectric constant significantly.

The temperature dependence of dielectric constant of the ceramics was shown in Fig. 4(a) and (c), measured at f = 100 kHz. The curves of T_C *vs.* the elements types were exhibited in Fig. 4(b) and (d). It was found from Fig. 4(a) and (c) that the peaks for dielectric constant appeared with increasing temperatures, revealing the ferroelectric-paraelectric phase transition. All the ceramics have high T_C (417–443 °C), and especially high T_C of 441–443 °C can be found for the addition of bivalent elements (Ba^{2+} and Mg^{2+}) as well as quadrivalent elements (Hf^{4+}), which is comparable to that (T_C = 450 °C) of BS-PT ceramics. As a result, the ceramics with Hf^{4+} possessed both large d_{33} (d_{33}=500 pC/N) and high T_C (T_C = 443 °C).

Fig. 5 showed the composition dependence of d_{33} and T_C of the ceramics. As shown in Fig. 5(a) and (b), most of the samples possessed both large d_{33} (> 400 pC/N) and high T_C (> 415 °C), even up to 500