

Influences of dopants on BiFeO₃–PbTiO₃ ferroelectric ceramics

Ruzhong Zuo^{a,*}, Yang Wu^a, Jian Fu^a, Shi Su^a, Longtu Li^b

^a Institute of Electro Ceramics & Devices, School of Materials Science and Engineering, Hefei University of Technology, Tunxi Road 193, Hefei, Anhui Province 230009, China

^b State Key Lab of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:

Received 11 May 2008

Received in revised form 9 July 2008

Accepted 27 July 2008

Keywords:

Ceramics
Dielectrics
Ferroelectrics
Conductivity

ABSTRACT

This work dealt with effects of various dopants on sintering, structures and complex impedance characteristic of a BiFeO₃–PbTiO₃ (BF–PT) composition. It was found that the addition of 1 mol% Ta⁵⁺, Nb⁵⁺ or La³⁺ has a clear effect on the crystal structure, unlike V⁵⁺, Li⁺ or Zn²⁺, facilitating a dense strong ceramic of BF–0.32PT composition without a particular heating or cooling processing. Moreover, the Ta⁵⁺- or Nb⁵⁺-doped samples own relatively improved electrical resistance with different conductive mechanisms, and fine grain morphology, compared to the La³⁺-doped counterparts. The results demonstrate that Ta⁵⁺ and Nb⁵⁺ could be good dopants for improving BF–PT compositions to achieve the future application.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Solid solutions of bismuth based perovskite compositions (BiScO₃ (BS), BiFeO₃ (BF), BiInO₃, and so on) and PbTiO₃ (PT) exhibit high Curie points (T_c) near a morphotropic phase boundary (MPB), having potential to be utilized in high-temperature piezoelectric applications [1–5]. The T_c of those MPB compositions demonstrates a linear relationship with the tolerance factor of bismuth-based perovskites [6]. Among them, BS–PT solid solutions achieved more attention, as they own relatively high T_c and modest piezoelectric properties, being suitable for some of the applications. However, these applications could be quite-limited due to a large cost of scandium oxides. By comparison, BF–PT systems are relatively cheap, own even higher T_c , and exhibit good ferroelectric behavior. Unfortunately, several studies have reported that a large extrinsic conductivity of these materials rendered measurement of the ferroelectric loops extremely difficult, and even made the accurate location of the Curie temperature impossible only by dielectric measurements [7]. In addition, the poling treatment becomes extremely difficult as well, making them difficult to become good piezoelectric materials.

The MPB BF–PT compositions at tetragonal side show high tetragonality, making the sintered bodies crack during cooling due to high internal stresses or during domain switching under a high dc field. Moreover, BF–0.32PT is a composition near the MPB where the superior dielectric and piezoelectric properties can be achieved

[8,9]. As known, a piezoelectric composition with a high tetragonality tends to have a large coercive field. Therefore, both high conductivity and large tetragonality make the MPB BF–PT compositions difficult for applications. These problems were alleviated by doping a small amount of La₂O₃ or Ga₂O₃, accompanied by a great reduction in T_c [8,9]. Therefore, how to achieve a combination of high resistivity, enhanced mechanical properties and desirable T_c values becomes a key issue for BF–PT high temperature piezoelectric compositions. In this work, a couple of dopants with different valences, which could occupy A-site or B-site in a perovskite structure according to their own ionic sizes, were employed to explore effects on the crystalline structures, microstructure and impedance characteristics of 0.68BF–0.32PT ceramics.

2. Experimental

Samples with a composition of 0.68BiFeO₃–0.32PbTiO₃ were prepared by a mixed oxide processing route. High purity oxides, Bi₂O₃ (99.5%), Fe₂O₃ (99.3%), PbO (99.9%) and TiO₂ (99.7%) were weighed out in stoichiometric amounts and ball-milled for 12 h using 3 mm yttria-stabilized zirconia milling media with distilled water. The slurry was dried and reacted in a lidded alumina crucible at 820 °C for 2 h. Reacted powders were mixed with 1 mol% of various dopants, such as Ta⁵⁺, Nb⁵⁺, La³⁺, V⁵⁺, Zn²⁺ and Li⁺ and further ground in a planetary ball mill for 24 h. The dopants were added in the form of oxides and carbonates (Ta₂O₅ (99.5%), Nb₂O₅ (99.5%), La₂O₃ (99.3%), V₂O₅ (99.7%), ZnO (99.5%), Li₂CO₃ (99.9%)). After drying, disk samples were compacted in a stainless steel die under 50 MPa.

Specimens covered with double crucibles were sintered in air in the temperature range of 950–1100 °C at a heating rate of 5 °C min^{−1}, and then cooled at a rate of 1 °C min^{−1} till 900 °C, and then 5 °C min^{−1} to room temperature. Simultaneously, samples were buried with the powder of the same composition to prevent the reaction with alumina substrate and to reduce the volatilization of PbO and Bi₂O₃.

The microstructure was observed by scanning electron microscopy (SEM, JEOL6301F, Tokyo, Japan). Powder X-ray diffraction (XRD, Rigaku, Tokyo, Japan) patterns of crushed pellets using Cu K α radiation were recorded in the 2θ range of

* Corresponding author. Tel.: +86 551 2905285.

E-mail address: piezolab@hfut.edu.cn (R. Zuo).

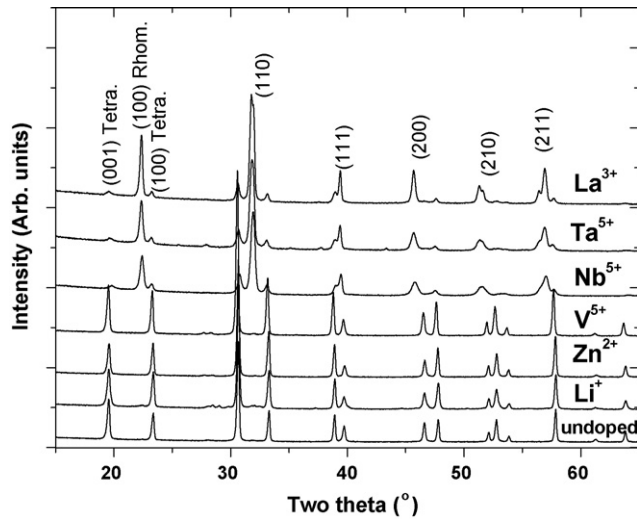


Fig. 1. X-ray diffraction patterns of BF-0.32PT ferroelectric compositions with 1 mol% dopants as indicated.

15–65°. Silver paste was fired on two major surfaces of each specimen as electrodes after a careful polishing process. Dielectric properties were measured as a function of temperature and frequency by means of an LCR meter (HP 4284A, Hewlett-Packard, Palo Alto, CA) and a temperature-controlling box where a sample was put close to the tip of a thermocouple. All samples for AC impedance measurements have similar dimensions.

3. Results and discussion

Fig. 1 shows the crystalline structures of BF-0.32PT ferroelectric compositions doped with 1 mol% dopants. It can be seen that undoped samples own typical tetragonal symmetry. It means that this composition lies at tetragonal side close to a MPB between rhombohedral and tetragonal phases. Its tetragonality amounts to 1.17, as calculated from the split (2 0 0) peaks. By comparison, it can be found that the doping of Li^+ , Zn^{2+} and V^{5+} does not induce any change in the crystalline symmetry of BF-0.32PT compositions. On

the one hand, the addition of 1 mol% V^{5+} seems to cause a little expansion of perovskite unit cells, considering that the diffraction peaks slightly shift to low angles. On the other hand, the tetragonality seems to slightly increase due to a small amount of dopants. On the contrary, the doping of La^{3+} , Ta^{5+} and Nb^{5+} causes a clear change from pure tetragonal symmetry to the coexistence of two phases (rhombohedral and tetragonal). The appearance of rhombohedral phases is expected to facilitate the preparation processing, due to a reduced internal stress on cooling. It can be seen that V^{5+} shows different effects from Ta^{5+} and Nb^{5+} , although three of them lie in the same group. Moreover, V^{5+} often has different roles from Ta^{5+} and Nb^{5+} , for instance, in Li^- , K^- or Na^- -based complex oxides. This may be due to the difference in ionic sizes and electronic structures.

Due to a large tetragonality, samples-doped with Li^+ , Zn^{2+} or V^{5+} crack into powders during the period of cooling to room temperature. It is difficult to achieve dense samples of those compositions. The undoped samples look complete but probably contain large internal stresses. Therefore, only the microstructure of samples undoped and doped with La^{3+} , Nb^{5+} and Ta^{5+} was shown in Fig. 2. It can be seen that the grain size changes obviously after doping. The undoped samples approximately have a grain size of $7\ \mu\text{m}$. It slightly increases when the sample is doped with 1 mol% La^{3+} . However, the microstructure gets fine in the samples-doped with Nb^{5+} and Ta^{5+} . The corresponding grain size drops to $\sim 2\ \mu\text{m}$. The change in grain size after doping seems to correlate with the formation of atomic defects. The iso-valent replacement of La^{3+} for Bi^{3+} seems to have little effect on the microstructure, considering that La^{3+} and Bi^{3+} have the same valences and closer ionic sizes. On the contrary, the A-site cation vacancies were generated due to the substitution of Ta^{5+} or Nb^{5+} for Ti^{4+} or Sc^{3+} . The cation vacancies tend to inhibit the grain growth to a certain degree by pinning the boundary movement. Ta^{5+} and Nb^{5+} appear to have similar effects on BF-PT ceramics, probably based on the same valences and ionic sizes.

Fig. 3 shows the AC impedance characteristic of the Nb^{5+} - and La^{5+} -doped BF-0.32PT ceramics. Ta^{5+} has the same effect as Nb^{5+} and thus its result is not included. Moreover, the undoped BF-0.32PT ceramics tend to crack into the powder during re-heating for the measurement of dielectric properties owing to a

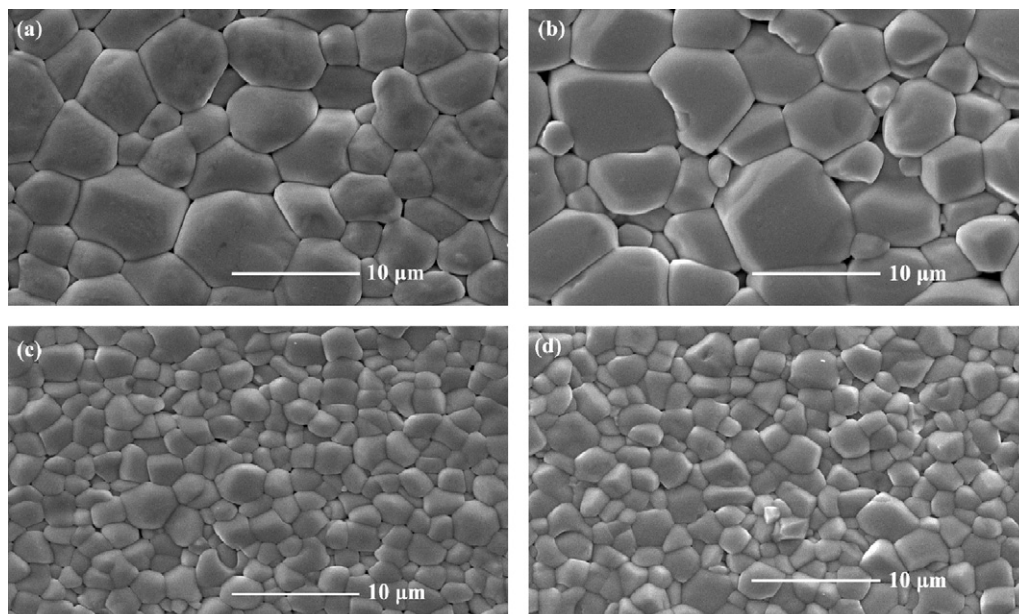


Fig. 2. Grain morphology of (a) undoped BF-0.32PT and ones-doped with 1 mol% (b) La^{3+} , (c) Ta^{5+} and (d) Nb^{5+} . All samples were sintered at 1060 °C.

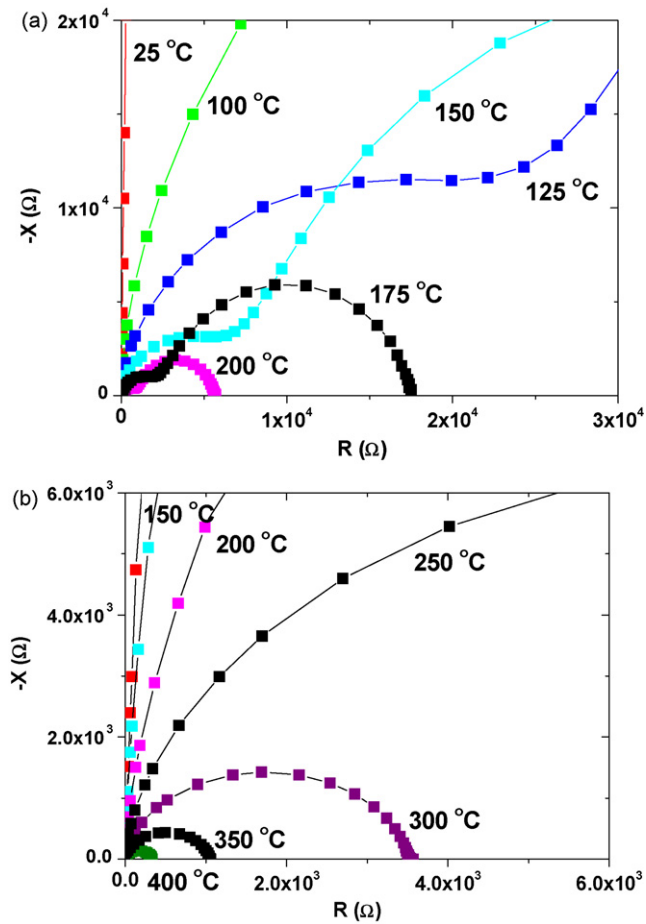


Fig. 3. Complex impedance spectra of 1 mol% (a) La^{3+} and (b) Nb^{5+} -doped BF-0.32PT samples.

large internal stress formed during previous sintering. It is thus impossible to get the data for them. It can be seen from Fig. 3 that the La^{3+} - and Nb^{5+} -doped samples exhibit extremely different complex impedances. For the La^{3+} -doped BF-0.32PT samples, two semicircles are easily resolved: one at high frequencies due to the contribution of grains to the electrical resistivity and the other due to the contribution of grain boundaries. By comparison, the Nb^{5+} -doped BF-0.32PT samples solely exhibit a conductivity feature of grains, and the resistivity of grain boundary phases was significantly increased, such that only a well-formed arc is observed. Since the complex impedance reaches zero when the measuring signal frequency f tends to ∞ , the bulk materials can be defined in the equivalent circuit composed by a grain resistance R_g and a grain capacitance C_g . Therefore, the conductive mechanism of BF-0.32PT-doped with La^{3+} and Nb^{5+} is different. The doping of 1 mol% Nb^{5+} has improved the resistivity of grain boundary. In contrast to the La^{3+} -doped BF-0.32PT ceramics, the Nb^{5+} -doped counterpart will be expected to have improved insulation performance. Actually, the addition of La^{3+} may also improve the insulation if we compare with undoped BF-PT ceramics. Cheng et al. reported that the substitution of La^{3+} for Bi^{3+} made BF-PT solid solutions insulating and soft [8–10]. As known, the high conductivity of BF-PT systems has hindered their applications in the field of ferroelectric and piezoelectric ceramics. The same results were obtained from the Ta^{5+} -doped samples. Therefore, Nb^{5+} and Ta^{5+} could be useful dopants for decreasing the conductivity of BF-PT compositions, other than that the preparation processing was facilitated as well.

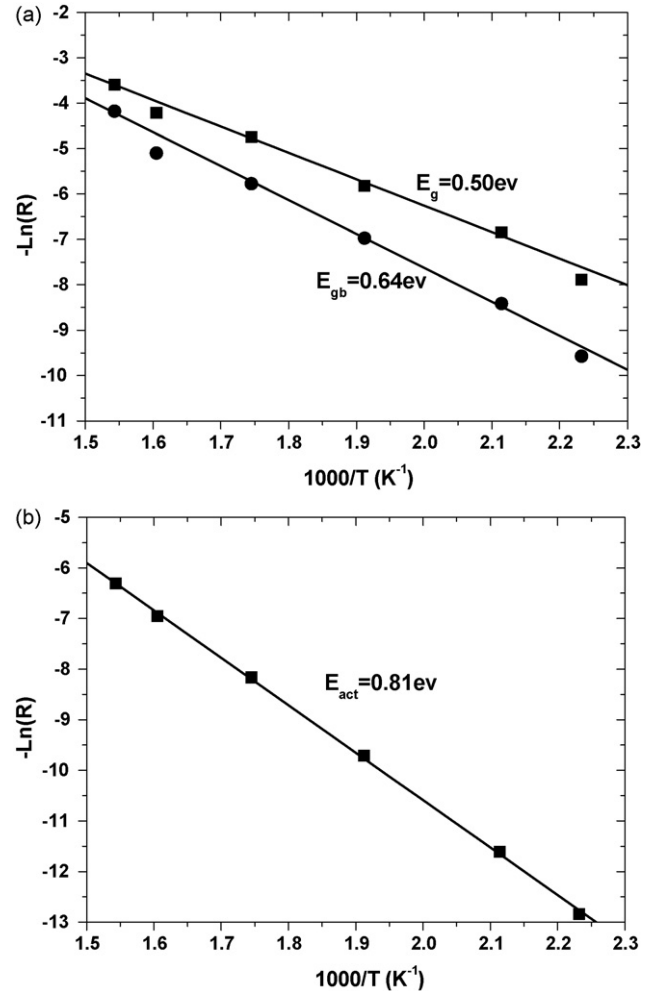


Fig. 4. Arrhenius plots for AC impedance characteristics of 1 mol% (a) La^{3+} , and (b) Nb^{5+} -doped BF-0.32PT samples by least-squares linear fitting.

According to Fig. 3, the Arrhenius dependence of $\ln(R)$ vs. $1/T$ is shown in Fig. 4. These curves are well fitted by straight lines, indicating that the conductive processes are thermally excited. For the La^{3+} -doped BF-0.32PT samples, the activation energies E of R_g and R_{gb} were calculated to be ~ 0.50 and ~ 0.64 eV, respectively, in terms of the slopes of fitted straight lines. Both grains and boundaries show similar conductive processes from the activation energies. However, different values were obtained in the Nb^{5+} -doped samples. Only grain conductivity was observed, with an energy value of ~ 0.81 eV for R_g . The increased E value indicates the improvement of resistivity. The obtained E values demonstrate that the response of ionic vacancies to signal frequency at different temperatures is responsible for doped BF-PT ceramics, rather than oxygen vacancies which usually own an E value of ~ 1.0 eV [11]. These ionic vacancies may be produced during sintering, for example, the volatilization of bismuth or lead oxides, or due to the replacement of Nb^{5+} for Ti^{4+} or Sc^{3+} .

4. Conclusions

BF-0.32PT ferroelectric ceramics-doped with various dopants were prepared by a solid-state route. Effects of dopants on various physical and electrical properties of BF-0.32PT compositions were demonstrated. The crystal structures change from pure tetragonal symmetry to a mixture of rhombohedral and tetragonal phases due

to the addition of La^{3+} , Ta^{5+} or Nb^{5+} . This makes manufacturing of a dense ceramic with BF–PT compositions possible without controlling heating and cooling processing. The results of AC impedance measurements demonstrate that the addition of Ta^{5+} and Nb^{5+} leads to an improved conductivity characteristic and an inhibited grain growth.

Acknowledgements

This work was financially supported by HFUT RenCai Foundation (No. 103-035006), a special Program for Excellence Selection (No. 103-035034) and an open fund of State Key Laboratory of New Ceramics and Fine Processing.

References

- [1] V.V.S.S. Sai Sunder, A. Halliyal, A.M. Unarji, *J. Mater. Res.* 10 (1995) 1301.
- [2] D.I. Woodward, I.M. Reaney, R.E. Eitel, C.A. Randall, *J. Appl. Phys.* 94 (2003) 3313.
- [3] T.P. Comyn, S.P. McBride, A.J. Bell, *Mater. Lett.* 58 (2004) 3844.
- [4] R. Duan, R.S. Speyer, E. Alberta, T.R. Shrout, *J. Mater. Res.* 19 (2004) 2185.
- [5] S.Z. Zhang, R.E. Eitel, C.A. Randall, T.R. Shrout, *Appl. Phys. Lett.* 86 (2005) 262904.
- [6] R.E. Eitel, C.A. Randall, T.R. Shrout, P.W. Rehrig, W. Hackenberger, S.E. Park, *Jpn. J. Appl. Phys.* 40 (2001) 5999.
- [7] M.M. Kumar, V.R. Palkar, K. Srinivas, S.V. Suryanarayana, *Appl. Phys. Lett.* 76 (2000) 2764.
- [8] J.R. Cheng, R. Eitel, L.E. Cross, *J. Am. Ceram. Soc.* 86 (2003) 2111.
- [9] J.R. Cheng, N. Li, L.E. Cross, *J. Appl. Phys.* 94 (2003) 5153.
- [10] J.R. Cheng, S.W. Yu, J.G. Chen, Z.Y. Meng, L.E. Cross, *Appl. Phys. Lett.* 89 (2006) 122911.
- [11] N.H. Chan, R.K. Sharma, D.M. Smyth, *J. Am. Ceram. Soc.* 65 (1987) 167.