FULL PAPER

Fabrication and magnetization of Ca-doped BiFeO₃–BaTiO₃-tapes by powder in tube methodLi BAO¹, Xiwei QI^{1,†}, Ruibin MEI² and Xiaohui CHEN²¹School of Materials Science and Engineering, Northeastern University, Shenyang, 110819 China²Key Laboratory of Dielectric and Electrolyte Functional Material Hebei Province, Northeastern University at Qinhuangdao, Qinhuangdao, 066004 China

Calcium doped bismuth ferrite (BiFeO₃, BFO)-barium titanate (BaTiO₃, BTO) powders were successfully synthesized by a facile sol–gel route. Subsequently as-synthesized powders were packed within a fugitive silver metal tube and formed into tapes with uniform thickness by means of cold drawing and rolling processes, which is called powder in tube (PIT) method. The influence of calcining temperature on the crystalline structure and characterization of BFO-based tape was also studied. The particle size of tape prepared by PIT method is becoming smaller, indicating PIT method has great effect on refined particle. Furthermore, the remanent magnetization 2Mr and coercive force Hc for the tape are 0.092 emu/g and 281.59 Oe, respectively. The optimized calcining temperature for the tape is 400°C.

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1. Introduction

Multiferroics which exhibit two or more ferroic-properties simultaneously among ferroelectric, ferromagnetic and ferroelastic ordering in one material,^{1)–5)} have been widely noted as multifunctional materials promising for applications in multiple-state memory devices. Calcium doped bismuth ferrite (BiFeO₃, BFO)-based perovskite-type multiferroic compounds have recently been a subject of intensive research, which has driven primarily by their great technological potential of the materials for micro-electronics and spintronics.^{6,7)} BFO is one of the representative single-phase multiferroics with a rhombohedrally distorted perovskite at room temperature, which is known by its exceptionally high transition temperatures (magnetic ordering exists up to $T_N \approx 640$ K and ferroelectric ordering survives up to $T_C \approx 1100$ K^{8,9)}). However, synthesized BFO materials always appear impurity phases such as Bi₂Fe₄O₉ and Bi₂₅FeO₄₀,^{10)–13)} which is ascribed to the volatilization of the Bi³⁺ and the coexistence of Fe³⁺/Fe²⁺.

In order to solve above-mentioned problem, one possible strategy is realized via introducing the doped elements to separately substitute A site, B site and combined AB sites. Another possible strategy is introducing other stable ABO₃ perovskites into a solid solution with BFO helps suppress the formation of secondary phases.^{14),15)} Fortunately, it was considered as a favorable method of the A-

site substitution of rare earth ion for Bi³⁺ ion to decrease the leakage current and improve the properties of BFO.^{3),16)–20)} The A-site doping-induced can suppress the incommensurate spin structure and cause the spontaneous magnetization through weak ferromagnetism.^{21)–23)} In particular, the substitution of smaller Ca²⁺ ions (radius = 0.1 nm) for larger Bi³⁺ ions (radius = 0.103 nm) in BFO are benefit for improving the magnetic properties and reducing the impurity phases. In the literature, Ca doped BFO has been prepared by sol–gel method, exhibiting the better ferroelectric and magnetic properties.^{24),25)} Moreover, BaTiO₃ (BTO) is introduced into BFO to form solid solution, which helps to stabilize the perovskite structure and enhance the performance.²⁶⁾ It should be noted that BFO–BTO binary solid solutions are miscible within the 33% of BTO, in which rhombohedral perovskite structure would exist.²⁷⁾ It is reported that solid solution (1 – x)BFO–xBTO (x = 0.10, 0.15 and 0.30) have been prepared by solid state ceramics route, in which dielectric and magnetic properties are enhanced, and the conductive leakage is decreased.²⁸⁾

Powder in tube (PIT) method is always used to fabricate the super-conductive tapes, in which Ag and super-conductive are integrated into one element. Therefore, PIT is suitable for fabricate monolithic functional elements. So far, there is few report focused on this topic. In this study, the nominal composition of 0.97Bi_{0.9}Ca_{0.1}–FeO₃–0.03BaTiO₃ tapes have been fabricated via PIT method. The phase identification, microstructure and magnetic properties dependence of calcining temperature are investigated.

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2. Experiments

Powders with the nominal composition of $0.97\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_3\text{--}0.03\text{BaTiO}_3$ were synthesized by a novel facile sol–gel method. The bismuth nitrate $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$, ferric nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ and calcium acetate ($\text{C}_4\text{H}_6\text{O}_4 \cdot \text{H}_2\text{O}$), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), barium hydroxide $[\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}]$ and butyl titanate ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$) were used as raw materials. The bismuth nitrate, iron nitrate and calcium acetate were mixed according to stoichiometric analytical reagent grade and then the mixed powders were dissolved into the solution with the ratio of ethylene glycol and ethyl alcohol is 7:3. Subsequently, the mixture was stirred at 60°C for 1 h through magnetic stirrer to form a homogeneous uniform solution. Afterwards, citric acid was added as a chelating agent in 1.2:1 molar ratio with metal ions to the solution. Meanwhile, the barium hydroxide and butyl titanate were mixed by means of the stoichiometric ratio and dissolved into the solution with the same ratio as above solvent (ethylene glycol and ethyl alcohol is 7:3) in another beaker. Then, the hybrid of two type precursor solution constantly was stirred at 60°C for 1.5 h to obtain a uniform sol solution followed by keeping steady state for 2 h. Finally, the sol was dried at 100°C for 12 h to get the xerogel and then the xerogel was calcined at $500\text{--}750^\circ\text{C}$ for 3 h to obtain the final powders (as-prepared powders).

After that, the BCFO–BTO tapes were fabricated by PIT method. The as-prepared powders were sealed within a silver tube and drawn and rolled into tapes subsequently. The detailed processes are demonstrated as following as the as-prepared powders were pressed in die and packed into silver tubes (outer diameter is 8 mm, wall thickness is 0.5 mm and length is 100 mm) in which open sides are sealed by argon arc welding. The sealed tubes were drawn into wires firstly (outer diameter is 1 mm) and then rolled into tapes (thickness is 0.2 mm). A series of dies with different working diameters and the drawing machine were used to carry out drawing experiments at a speed of 10 m/min and an average reduction per pass of 10%. Subsequently, in order to obtain thin tapes two passes rolling were carried out at a rolling speed of 15 m/min through a two roll mill (work roll diameter is 100 mm). After forming, the Ag-sheathed tapes were cut into segments of 5 mm length for heat treatment with the range of temperature $400\text{--}600^\circ\text{C}$ for 1 h.

Finally, the crystalline structure and morphology of BCFO–BTO powders and tapes were characterized by X-ray diffraction (XRD, Smart Lab, Japan) with $\text{CuK}\alpha$ radiation operated at 45 kV and 200 mA in a 2θ range of $20\text{--}70^\circ$ at room temperature and scanning electron microscopy (SEM, Zeiss Supra-55, Germany), respectively. In addition, the magnetic properties of the tapes were carried out using vibrating sample magnetometer (VSM, JDAW-2000C&D, China).

3. Results and discussion

Figure 1 shows the XRD patterns of as-prepared

BCFO–BTO powders calcined at different temperature. It can be clearly observed that there is no second phase in the samples. All the peaks can be indexed, which is in agreement with the JCPDS card No. 72-2112, exhibiting the perovskite BFO with the good crystallization. It should be noted that the intensity of peaks increase with the increase of calcined temperature. Better crystallization can be reached by means of higher calcined temperature. The powders calcined at 500°C , were used for fabricating tapes. Moreover, the average half width of three strongest peaks of the precursor powder is 0.459, and the crystallite size is 19 nm using Scherrer's equation.

The SEM photographs of powders calcined at 500°C are shown in **Fig. 2**. As it can be seen that the shape of the particles are irregular and the particle boundary intervals are inhomogeneous, in which aggregations happen. The composition of powders calcined at 500°C were calculated from the EDX data and shown in **Table 1**. It can be seen that the calculated compositions are close to the nominal composition, which indicates that the composition of the as-prepared powder is closed to the stoichiometric ratios of design significantly.

Figure 3 shows the XRD patterns of fabricated tapes and fabricated tapes calcined at different temperature, respectively. Compared to the precursor powder of the Fig. 1, the half width of diffraction peaks of tape are

Fig. 1. XRD patterns of BCFO–BTO powders calcined at different temperature.

Fig. 2. SEM photographs of powders calcined at 500°C .

becoming wider, indicating the existence nanoparticles fabricated by PIT method. With the increment of calcining temperature, the intensity of diffraction peaks is enhanced, and the second phase of Bi₂Fe₄O₉ is increased gradually. The reason is perhaps that thermal effect of deformation and distortion energy in deformation processes lead to the phase decomposition. The phenomenon is approximately same as the mechanism of deformation induced transformation in metal deformation. The average half width of three strongest peaks of the precursor powder is 0.549, and the crystallite size is 16 nm using Scherrer's equation. Furthermore, it is obviously founded that the second phase mainly focuses on the range of 25 to 32.32°.

The SEM photographs of transverse section of a silver-seathed tape are shown in **Fig. 4**. It is revealed that the

Table 1. Calculated composition from EDX and nominal composition

chemical element	O	Ca	Ti	Fe	Ba	Bi	total
Calculated composition (%)	59.51	1.94	0.33	19.92	0.68	17.62	100.00
Nominal composition (%)	60.00	1.94	0.60	19.40	0.60	17.46	100.00

Fig. 3. XRD patterns of the tape calcined at different temperature.

core was uniform in thickness and free of macro-cracks. The layer of BFO is 184.8 μm. Moreover, the bonding between Ag electrode layer and BFO layer are well bonded.

The SEM photographs of tapes calcined at different temperature were shown in **Fig. 5**, it can be seen that the average size of nanoparticle is approximate 60 nm. It is interested that there wasn't dramatically growth of the nanoparticle with the increase of calcined temperature. Compared with as-prepared powders calcined at 500°C, the size of the tape nanoparticle after drawing and rolling is significantly refined, the nanoparticle combine is closed and the boundaries is clearly.

The M-H hysteresis loops of tapes calcined at different temperature are shown in **Fig. 6**, which had been measured at room temperature to study magnetic properties of the tapes for the magnetic field of 6kOe. It is obviously founded that all the samples exhibits well soft magnetic characteristics, which attributed to the constituent of dopant along with solid solution and the deformation of the drawing and rolling. The particle size of tape prepared by PIT method is becoming smaller, indicating PIT method has great effect on refined particle by means of plastic deformation. Refined particle is beneficial to improve the ceramic properties. With the increase of the calcining temperature, the room temperature magnetization hysteresis loops exhibit the change ferromagnetic behavior for BCFO-BTO nanoparticles. The optimized magnetic property can be obtained for the tapes calcined at 400°C, in

Fig. 4. Micrographs of short transverse cross section of precursor tape.

Fig. 5. SEM photographs of the tape (a) precursor tape (b) 400°C (c) 500°C and (d) 600°C.

Fig. 6. Magnetization hysteresis loops of the tapes.

which the 2Mr (Remanent magnetization) and Hc (Coercive force) are 0.092 emu/g and 281.59Oe, respectively. These may be caused by the following reason. Firstly, with the increase of calcined temperature, the internal stress is released. Furthermore, the second phase gradually increased with the increase of calcined temperature, which can be seen from the Fig. 3. In addition, with the increase of calcined temperature, the density and grain size increase as well as porosity decreases. Therefore, due to the final balance the optimized result can be obtained for the tape calcined at 400°C.

4. Conclusions

The feasibility of using sol-gel to synthesize the BCFO-BTO precursor powders and PIT method to fabricate BCFO-BTO tapes had been demonstrated. The Ca-doped BFO polycrystalline powders and BTO incorporate into this solid solution by a facile sol-gel method is prepared. In order to consolidate and form the precursor powders into tape, the precursor powders were packed into a fugitive silver can, and then drawing and cold rolling into geometrically uniform tapes. XRD and SEM analyses of the powder revealed that the pure BCFO-BTO was successfully synthesized at 500°C. The particle size of tape is smaller than the as-prepared powders significantly. The M-H loops show that the maximum of coercive field and polarization is at the calcining temperature of 400°C.

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References

- 1) M. Sakar, S. Balakumar, P. Saravanan and S. N. Jaisankar, *Mater. Res. Bull.*, **48**, 2878–2885 (2013).

- 2) D. H. Wang, W. C. Goh, M. Ning and C. K. Ong, *Appl. Phys. Lett.*, **88**, 212907 (2006).
- 3) S. K. Singh, C. V. Tomy, T. Era, M. Itoh and H. Ishiwara, *J. Appl. Phys.*, **111**, 120801 (2012).
- 4) J. Schiemer, R. L. Withers, M. A. Carpenter, Y. Liu, J. L. Wang, L. Noren, Q. Li and W. Hutchison, *J. Phys.-Condens. Mat.*, **24**, 125901–125911 (2012).
- 5) I. Coondoo, N. Panwar, A. Tomar, I. Bdkin, A. L. Kholkin, V. S. Puli and R. S. Katiyar, *Thin Solid Films*, **520**, 6493–6498 (2012).
- 6) H. Bea, M. Bibes, S. Cherifi, F. Nolting, B. Warot-Fonrose, S. Fusil, G. Herranz, C. Deranlot, E. Jacquet, K. Bouzehouane and A. Barthelemy, *Appl. Phys. Lett.*, **89**, 242114 (2006).
- 7) L. W. Martin, Y. H. Chu, Q. Zhan, R. Ramesh, S. J. Han, S. X. Wang, M. Warusawithana and D. G. Schlom, *Appl. Phys. Lett.*, **91**, 172513 (2007).
- 8) S. V. Kiselev, R. P. Ozerov and G. S. Zhdanov, *Sov. Phys. Dokl.*, **7**, 742–744 (1963).
- 9) Y. E. Roginskaya, Y. Y. Tomashpol'skii, Y. N. Venetsev, V. M. Petrov and G. S. Zhdanov, *Sov. Phys. JETP*, **23**, 47–51 (1966).
- 10) C. J. Brinker and G. W. Scherer, Gulf Professional Publishing, Oxford, 908 (1990).
- 11) X. K. Chen, Y. J. Wu and J. Zhang, *Sci. China Phys. Mech.*, **55**, 404–408 (2012).
- 12) J. K. Kim, S. S. Kim and W. J. Kim, *Mater. Lett.*, **59**, 4006–4009 (2005).
- 13) Z. W. Chen, Y. F. Li and Y. P. Wu, *J. Mater. Sci.-Mater. El.*, **23**, 1402–1408 (2012).
- 14) A. Halliyal, U. Kumar, R. E. Newnham and L. E. Cross, *Am. Ceram. Soc. Bull.*, **66**, 671–676 (1987).
- 15) T. R. Shrout and A. Halliyal, *Am. Ceram. Soc. Bull.*, **66**, 704–711 (1987).
- 16) D. H. Wang, W. C. Goh, M. Ning and C. K. Ong, *Appl. Phys. Lett.*, **88**, 212907 (2006).
- 17) J. Schiemer, R. L. Withers, M. A. Carpenter, Y. Liu, J. L. Wang, L. Norén, Q. Li and W. Hutchison, *J. Phys.-Condens. Mat.*, **24**, 125901 (2012).
- 18) V. B. Naik and R. Mahendiran, *Solid State Commun.*, **149**, 754–758 (2009).
- 19) H. L. Deng, M. Zhang, Z. Hu, Q. F. Xie, Q. Zhong, J. Z. Wei and H. Yan, *J. Alloy. Compd.*, **582**, 273–276 (2014).
- 20) H. F. Zhou, Z. L. Hou, L. B. Kong, H. B. Jin, M. S. Cao and X. Qi, *Phys. Status Solidi A*, **210**, 809–813 (2013).
- 21) I. E. Dzyaloshinskii, *Sov. Phys. JETP*, **5**, 1259–1262 (1957).
- 22) T. Moriya, *Phys. Rev.*, **120**, 91–98 (1960).
- 23) C. Ederer and N. A. Spaldin, *Phys. Rev. B*, **71**, 401–404 (2005).
- 24) S. Y. Chen, L. Y. Wang, H. C. H. Xuan, Y. X. Zheng, D. H. Wang, J. Wu, Y. W. Du and Z. G. Huang, *J. Alloy. Compd.*, **506**, 537–540 (2010).
- 25) J. Su, N. Zhang, G. L. Song, X. H. Zhou and F. G. Chang, *J. Chin. Ceram. Soc.*, **41**, 1185–1191 (2013).
- 26) O. Serhiy and E. Eitel, *J. Am. Ceram. Soc.*, **92**, 2957–2961 (2009).
- 27) M. Kumar and A. Srinivas, *J. Appl. Phys.*, **87**, 855–862 (2008).
- 28) M. Kumar, S. Shankar, R. K. Kotnala and O. Parkash, *J. Alloy. Compd.*, **577**, 222–227 (2013).