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Ceramics International 39 (2013) S245–S248

CERAMICS INTERNATIONAL

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Ferroelectromagnetic characteristic of Na-doped $0.75BiFeO_3$–$0.25BaTiO_3$ multiferroic ceramics

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Available online 16 October 2012

Abstract

$BiFeO_3$-based materials are expected to have both ferroelectricity and ferromagnetism simultaneously. In this study, effects of Na-doping (0.5, 1.0, 3.0, and 5.0 mol%) on ferromagnetic and ferroelectric properties of $0.75BiFeO_3$–$0.25BaTiO_3$ ceramics which have been fabricated by the solid state reaction technique are studied. The effects of Na-doped $0.75BiFeO_3$–$0.25BaTiO_3$ ceramics on the crystal structure, and magnetic and electrical properties were investigated and discussed. Rhombohedrally distorted $0.75BiFeO_3$–$0.25BaTiO_3$ showed weak ferromagnetic and ferroelectric properties. In addition, ferroelectric and ferromagnetic properties of $0.75BiFeO_3$–$0.25BaTiO_3$ have been controlled by Na doping, and the maximum values of magnetization and polarization were observed at 5.0 mol%.

Keywords: C. Ferroelectric properties; C. Magnetic properties; Multiferroic

1. Introduction

There has been tremendous increase in research interest on multiferroic materials that show simultaneous ferromagnetic and ferroelectric orderings, in the past few years. With the coexistence of ferromagnetic and ferroelectric orderings, magnetization can be induced by an electric field and electrical polarization can be induced by a magnetic field. However, the single-phase materials with both properties could not be widely produced due to their low Néel temperature or Curie temperature. Thus, hardly any practical application of ferroelectricity and ferromagnetism has been reported [1,2].

Bismuth ferrite ($BiFeO_3$) has received considerable attention due to its reported magnetoelectric properties, and potential use in nonvolatile memory applications. It possesses a ferroelectric Curie temperature (T_C) of 1103 K (830 °C) and an antiferromagnetic Néel temperature (T_N) of 643 K (370 °C) [3]. The multifunctional property of $BiFeO_3$ is important and can be applied in sensors, waveguides, modulators, switches, phase invertors, rectifiers, etc. [1–4]. However, the bulk form of $BiFeO_3$ ceramic has some disadvantages: (1) it is difficult to prepare pure single phase $BiFeO_3$, and (2) $BiFeO_3$-based materials have low electrical resistivity. The relatively high conductivity of $BiFeO_3$ is believed to be due to the degradation of Fe^{3+} species to Fe^{2+} species, which creates oxygen vacancies for charge compensation. This has prevented its practical applications as piezoelectric or magnetoelectric functional components [3]. To date, some perovskites such as $BaTiO_3$ (BT) [5–7] have been put into solid solution with $BiFeO_3$ in order to enhance the electrical insulation resistance and stabilize the perovskite structure. Leontsev and Eitel have prepared Mn-doped $(1-x)BiFeO_3$–$xBaTiO_3$. It was found that ceramics with 25 mol% BT showed the highest values of dielectric and ferroelectric properties. It is expected that with continuous improvements in processing and

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http://dx.doi.org/10.1016/j.ceramint.2012.10.070

composition modification, the 0.75BF–0.25BT system will form the basis of an important family of high-performance lead-free piezoelectric ceramics [7].

Although the perovskite structure of these solid solutions has been found to be stable at room temperature, their ferromagnetism is still weak. The present study is intended to improve properties of $BiFeO_3$-based materials in the $0.75BiFeO_3$–$0.25BaTiO_3$ ceramics system with the addition of sodium (Na), of which no report has been found to date.

2. Experimental

The lead-free multiferroic materials with specific composition of $0.75BiFeO_3$–$0.25BaTiO_3$, with addition of 0.5, 1.0, 3.0 and 5.0 mol% of Na, were prepared by a solid state mechanical milling technique. Stoichiometric mixtures of starting reagent-grade oxides of $BaCO_3$ (98.5%), Bi_2O_3 (99.9%), Fe_2O_3 (99.9%), Na_2CO_3 (98.5%) and TiO_2 (anatase-structure) (99.9%) were ball milled in ethanol with yttria-stabilized zirconia balls for 24 h. To achieve phase homogeneity, the powders were calcined in a covered alumina crucible at a temperature of 900 °C for 6 h [7]. The calcined powders were then uniaxially cold-pressed at 2500 psi into disc-shaped pellets with a diameter of 10 mm and a thickness of 1 mm with 3 wt% poly(vinyl alcohol) (PVA) added as a binder. After the burnout of binder at 500 °C, the pellets were sintered at 1025 °C for 2 h with a heating/cooling rate of 5 °C/min. The phase structure of the ceramics was analyzed via X-ray diffraction (XRD; Philips XPert Pro). Density was determined by the Archimedes method. The microstructures of the sintered samples were examined using scanning electron microscopy (SEM; JEOL JSM-840A). The room temperature ferroelectric and ferromagnetic properties were determined using a simple Sawyer-Tower circuit (at a fixed measuring frequency of 50 Hz) and vibrating sample magnetometer (VSM), respectively.

3. Results and discussion

Room temperature XRD patterns of Na-doped $0.75BiFeO_3$–$0.25BaTiO_3$ ceramics for 0.5, 1.0, 3.0 and 5.0 mol% are shown in Fig. 1. The XRD patterns show evidence for the presence of a second phase at 0.5 and 1.0 mol% Na content, probably arising from $Bi_2Fe_4O_9$ and related phases [8,9], and clearly present the perovskite structure without traces of secondary phase at 3.0 and 5.0 mol% Na content. These results clearly showed the significance of Na-doping in controlling the stability of the $0.75BiFeO_3$–$0.25BaTiO_3$ ceramic systems. As reported earlier, the BF–xBT system with $x < 33$ mol% is expected to have rhombohedrally distorted perovskite structure [7]. For the samples in this present study, no characteristic splitting associated with (110) could be seen in the XRD patterns, possibly due to a small rhombohedral distortion [7]. Nevertheless, all observed diffraction lines (reflections)

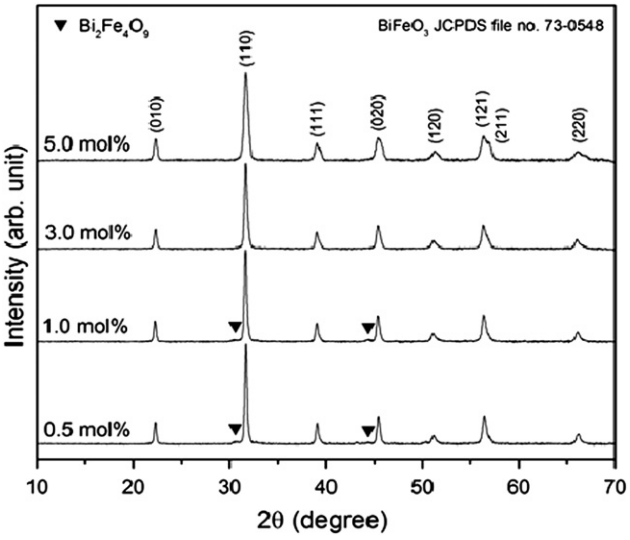

Fig. 1. XRD patterns of Na-doped $0.75BiFeO_3$–$0.25BaTiO_3$ ceramics with 0.5, 1.0, 3.0 and 5.0 mol% Na content.

of Na-doped BF–BT compounds suggest the presence of the tetragonal-rich phase with increasing Na content up to 5 mol%, as broadening of (111), (020) and (121) peaks is noticed. Phase change behavior is reported in other Na-doped $LaMnO_3$ systems [10].

Fig. 2 shows the fracture morphology of Na-doped $0.75BiFeO_3$–$0.25BaTiO_3$ ceramics characterized by scanning electron microscopy (SEM) technique. The SEM micrographs clearly elucidate the grain growth characteristics with increasing Na content up to 3.0 mol% and then decrease at 5.0 mol%. This similar behavior is observed in other Na-doped ZnO systems [11]. Interestingly, the density results (not shown here) can be directly correlated to the microstructure because the high-density value obtained for 3.0 mol% Na-doped $0.75BiFeO_3$–$0.25BaTiO_3$ ceramic is clearly a result of high degrees of grain close packing (Fig. 2(c)), whereas 5.0 mol% Na doping in the ceramic showing many open and closed pores (Fig. 2(d)) has yielded a low-density value.

The polarization–electric field (P–E) hysteresis loops of Na-doped $0.75BiFeO_3$–$0.25BaTiO_3$ ceramics measured at 30 kV/cm are presented in Fig. 3. To assess the effect of Na-doping on ferroelectric characteristics of $0.75BiFeO_3$–$0.25BaTiO_3$ ceramics, the ferroelectric parameters have been extracted from the experimental data. It is seen that remnant polarization (P_r) and coercive field (E_c) slightly increase with increasing Na content. At 5.0 mol% Na content, the result shows an abnormal hysteresis loop, probably due to the presence of oxygen or cation vacancies in this composition that caused many open and closed pores and yielded the low-density, as shown in Fig. 2(d). It is of great interest to observe that the ferroelectric properties of $0.75BiFeO_3$–$0.25BaTiO_3$ ceramics can be controlled by the addition of Na. This result is probably due to Ba and Na ions replacing Bi ions in the perovskite unit cell, releasing the dislocation of the Fe ion in [111] direction,

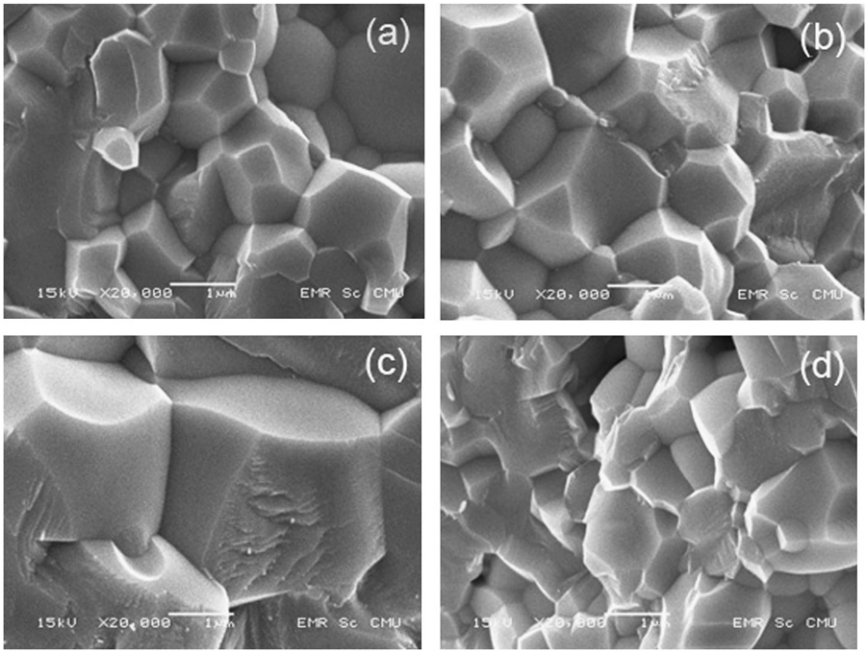

Fig. 2. SEM micrographs of Na-doped 0.75BiFeO–0.25$BaTiO_3$ ceramics with (a) 0.5, (b) 1.0, (c) 3.0 and (d) 5.0 mol% Na content.

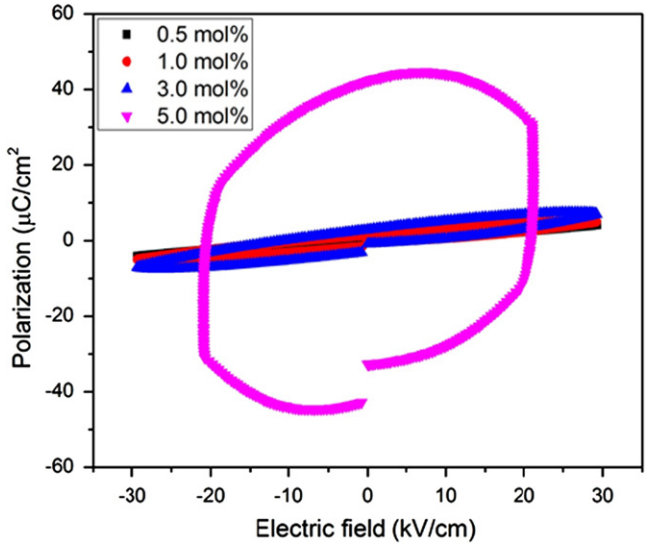

Fig. 3. *P–E* loops of Na-doped 0.75$BiFeO_3$–0.25$BaTiO_3$ ceramics with 0.5, 1.0, 3.0 and 5.0 mol% Na content.

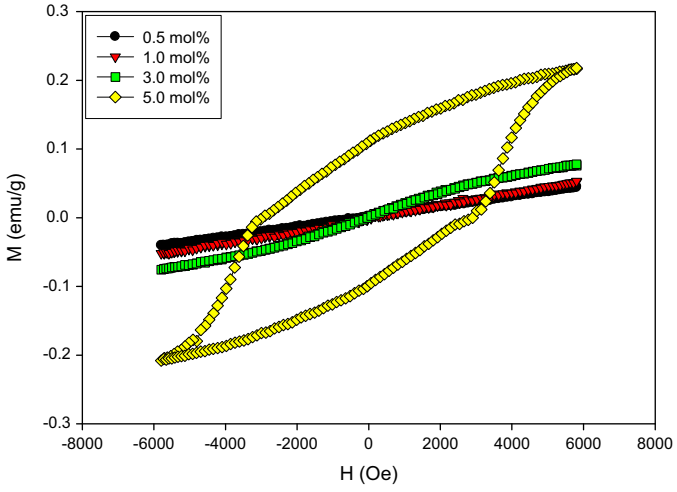

Fig. 4. *M–H* loops of Na-doped 0.75$BiFeO_3$–0.25$BaTiO_3$ ceramics with 0.5, 1.0, 3.0 and 5.0 mol% Na content.

resulting in the emergence of the *Cm* phase and breaking the toroidal order of the $BiFeO_3$ structure (*R3c*) [7].

Fig. 4 shows the *M–H* hysteresis loops of Na-doped $0.75BiFeO_3-0.25BaTiO_3$ ceramics. In some of these doped materials, slim hysteresis loops are observed in 0.5–3.0 mol% samples and abnormality is seen in sample with 5.0 mol% Na doping. The remnant magnetization (M_r) and the coercive field (H_c) are also seen to increase with increasing Na content, and they reach the maximum values at 5.0 mol% ($M_r \approx 0.12$ emu/g, $H_c \approx 2.5$ kOe). This result supports the interpretation of a release of the spin-cyclical arrangement, associated with breaking of its periodicity, once the magnetization was significantly enhanced [7]. However, at 5.0 mol% Na content, the appearance of ferromagnetism in solid solution systems has been attributed to either the canting of the antiferromagnetically ordered spins by a structural distortion [6,7] or the breakdown of the balance between the antiparallel sublattice magnetization of Fe^{3+} due to metal ion substitution with a different valency [1,7].

4. Conclusions

Lead-free and multiferroic Na-doped 0.75$BiFeO_3$–0.25$BaTiO_3$ ceramics (0.5, 1.0, 3.0 and 5.0 mol% Na

content) have been fabricated in order to improve the ferroelectric and ferromagnetic properties. From XRD study, single phase perovskite ceramics are successfully obtained. SEM micrographs indicate the grain growth behavior with increasing Na content for 0.5–3.0 mol%. In addition, ferromagnetic and ferroelectric properties increase with increasing Na content up to 5.0 mol%, with the presence of open and closed pores. More importantly, this study has clearly shown that phase formation behavior, microstructure, ferroelectric and ferromagnetic properties of $0.75BiFeO_3$–$0.25BaTiO_3$ can be controlled by the addition of Na.

Acknowledgments

This work was supported by the Industry/University Cooperative Research Center (I/U CRC) in HDD Component, Faculty of Engineering, Khon Kaen University, and the School of Science, University of Phayao.

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