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Investigation on ferromagnetic and ferroelectric properties of (La, K)-doped $BiFeO_3$–$BaTiO_3$ solid solution

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Abstract

Multiferroic materials of $BiFeO_3$–$BaTiO_3$ solid solution have been fabricated in order to improve ferromagnetic and ferroelectric properties. The effects of La (1 mol%) and K (varied from 0.5–5 mol%) doped $0.75BiFeO_3$–$0.25BaTiO_3$ on phase formation, ferromagnetic and ferroelectric properties have been investigated and discussed. The rhombohedral perovskite phase of specimens was characterized by XRD technique. Fracture morphology reveals the grain growth characteristics with increasing K content. (La, K)-doped $0.75BiFeO_3$–$0.25BaTiO_3$ with La = 1 mol% and K = 3 mol% exhibits the highest remnant polarization and remnant magnetization.

Keywords: Ferroelectric properties; Magnetic properties; Multiferroic

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1. Introduction

$BiFeO_3$-based compounds have received considerable attention and have been studied extensively, because they exhibit both ferroelectric and ferromagnetic characteristics; thus they provide the possibility of applications in devices such as nonvolatile memory, sensors, waveguides, modulators, switches, phase invertors, rectifiers, etc. [1–4]. Bulk $BiFeO_3$ ceramic possesses a ferroelectric Curie temperature (T_C) of 1103 K (830 °C) and an antiferromagnet Néel temperature (T_N) of 643 K (370 °C) [3]. However, bulk $BiFeO_3$ ceramic has some disadvantages such as it is difficult to prepare pure single phase $BiFeO_3$, and $BiFeO_3$-based materials have a 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, thus creating oxygen vacancies for charge compensation. These problems have prevented the material's practical applications as piezoelectric or magnetoelectric functional components [3].

Processing $BiFeO_3$ with other perovskite structured materials, such as $BaTiO_3$ (BT) and $PbTiO_3$, would prevent the formation of secondary phases [5–7] and enhance the electrical resistivity. In addition, Ti substitution at the Fe sites can increase the magnetization of the novel compounds [7]. Prior research, S.O. Leontsev and R.E. Eitel have been prepared on Mn-doped $(1-x)BiFeO_3$–$xBaTiO_3$, it was found that ceramics with 25 mol% BT showed the highest value of dielectric and ferroelectric properties. It is expected that with continuous processing improvements and composition modification, the $0.75BiFeO_3$–$0.25BaTiO_3$ (0.75BF–0.25BT) system will form the basis of an important family of high-performance lead free piezoelectric ceramics [8].

Although the perovskite structure of these solid solutions has been found to be stable at room temperature, their ferromagnetism is still weak. To improve the ferroelectric and ferromagnetic properties, (La, K)-doped

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$0.75BiFeO_3$–$0.25BaTiO_3$ ceramics, with fixed La of 1 mol% and varied K of 0.5, 1.0, 3.0 and 5.0 mol% will be investigated and discussed, of which no report has been found to date.

2. Experimental

Multiferroic materials of (La, K)-doped $0.75BiFeO_3$–$0.25BaTiO_3$ were prepared by a solid state mechanical milling technique. The effects of La (Fixed 1 mol%) and K (varied from 0.5–5 mol%) addition on ferroelectric and ferromagnetic properties of $0.75BiFeO_3$–$0.25BaTiO_3$ have also been investigated and discussed. Stoichiometric mixtures of starting reagent-grade oxides of $BaCO_3$ (98.5%), Bi_2O_3 (99.9%), K_2CO_3, (99.9%), Fe_2O_3 (99.9%) La_2O_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 cover alumina crucible at a temperature of 900 °C for 6 h [8]. 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. Following binder burnout 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). 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 fixed measuring frequency of 50 Hz) and Vibrating Sample Magnetometer (VSM), respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of (La, K)-doped $0.75BiFeO_3$–$0.25BaTiO_3$ ceramics with fixed La-doped of 1 mol% and varied K-doped of 0.5, 1.0, 3.0 and 5.0 mol%, prepared by a solid-state reaction. The ceramics were sintered at 1025 °C for 2 h with a heating/cooling rate of 5 °C/min. XRD patterns clearly present the perovskite structure without traces of secondary phase for all compositions. As reported earlier, the BF–xBT system with $x < 33$ mol% is expected to have rhombohedrally-distorted perovskite structure [8]. For the samples in this present study, no characteristic splitting associated with (1 1 0) could be seen in the XRD patterns, possibly due to a small rhombohedral distortion [8]. However, all observed diffraction lines of (La, K)-doped BF–BT compounds suggest the presence of the rhombohedral-rich phase with increasing K content of up to 5 mol%, as sharpening of (0 1 0), (0 2 0) and (2 1 1) peaks is noticed.

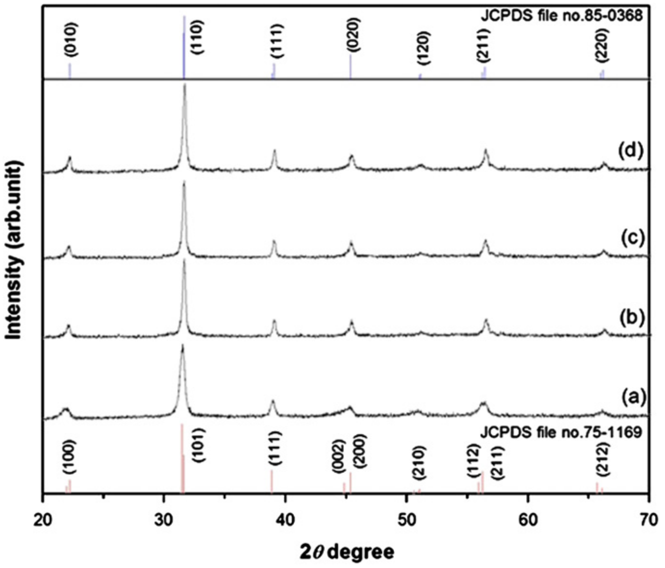

Fig. 1. XRD patterns of (La, K)-doped $0.75BiFeO_3$–$0.25BaTiO_3$ ceramics with fixed La of 1 mol% and varied K of (a) 0.5, (b) 1.0, (c) 3.0 and (d) 5.0 mol% K content. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2 shows the fracture morphology of (La, K)-doped $0.75BiFeO_3$–$0.25BaTiO_3$ ceramics, with fixed La of 1 mol% and varied K of 0.5, 1.0, 3.0 and 5.0 mol%, characterized by scanning electron microscopy (SEM) technique. The SEM micrographs clearly elucidate the grain growth characteristics with increasing K content. The observation could be caused by the La and K doping in the crystal structure are affected on the movement of grain boundaries of the specimens. A similar behavior is observed in other K-doped $LiNbO_3$ systems [9].

The polarization-electric field (P–E) hysteresis loops of (La, K)-doped $0.75BiFeO_3$–$0.25BaTiO_3$ ceramics, with fixed La of 1 mol% and varied K of 0.5, 1.0, 3.0 and 5.0 mol%, measured at 10 kV/cm are presented in Fig. 3. It is seen that remnant polarization (P_r) and coercive field (E_c) slightly increase with increasing K content. The decrease in the remnant polarization at K-doped for 5.0 mol% could be caused by rhombohedral-rich phase in this composition [10]. It is of great interest to observe that the ferroelectric properties of $0.75BiFeO_3$–$0.25BaTiO_3$ ceramics can be controlled by addition of La and K. An enhancement of ferroelectric properties is probably due to Ba, La and K ions replacing Bi ions in the perovskite unit cell, releasing the dislocation of the Fe ion in the [1 1 1] direction. This dislocation originated from Bi to O orbital hybridization [8], resulting in the emergence of the Cm phase and breaking the toroidal order of the $BiFeO_3$ structure ($R3c$). In fact, the hybridization of Ti–O orbitals supports the dislocation of the Ti ion in the [1 0 0] direction [8].

Fig. 4 shows the M–H hysteresis loops of (La, K)-doped $0.75BiFeO_3$–$0.25BaTiO_3$ ceramics with fixed La and varied K. In some of these doped materials, slim hysteresis loops are observed in the ceramics with 0.5 mol% K content. As the K content increases from 0.5 to 3 mol%, the remnant magnetization (M_r) increases and reaches a maximum value of $M_r \approx 0.6$ emu/g at 3 mol%. Upon further increasing the K content from 3 mol% to 5 mol%, M_r decreases. Nevertheless, the coercive field (H_c) is seen to decrease with increasing K content, the lowest H_c is also seen at 3.0 mol% ($H_c \approx 1.5$ kOe). Usual