

Ferroelectric and ferromagnetic properties of Mn-doped $0.7\text{BiFeO}_3\text{--}0.3\text{BaTiO}_3$ solid solution

Xiao-Hui Liu ^{*}, Zhuo Xu, Shao-Bo Qu, Xiao-Yong Wei, Jiang-Li Chen

Electronic Materials Research Laboratory, Key Laboratory of the Ministry of the Education, Xi'an Jiaotong University, Xi'an 710049, China

Available online 4 October 2007

Abstract

Binary solid solutions $0.7\text{BiFeO}_3\text{--}0.3\text{BaTiO}_3\text{--}x$ wt.% MnO_2 ($x = 0, 0.2, 0.3$, and 0.5) were prepared by a traditional ceramic process. All ceramic samples show single perovskite phase. The effect of manganese doping on structure, dielectric, ferroelectric and ferromagnetic properties, and resistivity was investigated. Results show that Mn-dopant can improve the sintering ability of the materials when MnO_2 content is below 0.3 wt.%. When MnO_2 content exceeds 0.3 wt.%, the sintering ability is weakened and the phase structure of $0.7\text{BiFeO}_3\text{--}0.3\text{BaTiO}_3$ solid solution changes from rhombohedral into tetragonal phase. With increasing concentration of MnO_2 , the resistivity increases at first and then decreases. Whereas the coercive electric field decreases at first and then increases, the remanent magnetization M_r increases and the coercive magnetic field decreases.

© 2007 Published by Elsevier Ltd and Techna Group S.r.l.

Keywords: Ferroelectricity; Ferromagnetism; $0.7\text{BiFeO}_3\text{--}0.3\text{BaTiO}_3$ solid solution

1. Introduction

Synthesis of ferroelectromagnetic material exhibiting ferromagnetism and ferroelectricity simultaneously has been an interesting subject, not only for possible applications in electronic devices, but also for the fundamental understanding of solid-state physics [1]. Most of single-phase ferroelectromagnetic materials have few applications due to their low Néel temperature or Curie temperature except some materials such as BiFeO_3 . BiFeO_3 and its solid solutions have high Néel temperature and high Curie temperature. However, one of the major problems of earlier BiFeO_3 -based materials is the low resistivity which has prevented practical application of the material as piezoelectric or magnetoelectric functional components. The relatively high conductivity of BiFeO_3 is believed to originate from the reduction of Fe^{3+} species to Fe^{2+} , creating oxygen vacancies for charge compensation [2]. At present, there are two ways used to solve the problem, one is to add perovskites (such as PbTiO_3 , BaTiO_3 , and SrTiO_3) [2–4] into solid solution with BiFeO_3 in order to stabilize a perovskite

structure and enhance the electric insulation resistance, the other is to add some dopants such as gallium [2], neodymium, and tantalum [5,6] to improve properties. Although the perovskite structure of these solid solutions has been shown to be stable, to date the insulation resistance of BiFeO_3 -based materials has not been raised sufficiently, and the ferroelectric and ferromagnetic properties of BiFeO_3 -based solid solutions have not been improved greatly. Since manganese is a magnetic element with multiple valences, the present study is intended to improve properties of BiFeO_3 -based materials by doping manganese, on which few reports have been found to date.

In this work, the focus is on the effect of Mn doping on the structure, dielectric, resistivity, ferroelectric and ferromagnetic properties of $0.7\text{BiFeO}_3\text{--}0.3\text{BaTiO}_3$ solid solution. Possible mechanisms have been discussed.

2. Experimental procedure

$0.7\text{BiFeO}_3\text{--}0.3\text{BaTiO}_3\text{--}x$ wt.% MnO_2 solid solutions were fabricated by conventional solid-state reaction with $x = 0, 0.2, 0.3$, and 0.5 , respectively. The starting materials used were Bi_2O_3 , Fe_2O_3 , BaCO_3 , TiO_2 , and MnO_2 , which all had purities greater than 99%. The oxide powders were mixed in a ball mill for 12 h, using alcohol as media. After drying, the powders

^{*} Corresponding author.

E-mail address: lxhui@mail.xjtu.edu.cn (X.-H. Liu).

were calcined at 810 °C for 2 h in the air, and ball milling for another 12 h. The resultant powders with 5 wt.% polyvinyl alcohol as a binder were pressed as disks in a stainless steel die under a pressure of 400 MPa. After pressing, the disks were 10 mm in diameter and 1.2 mm in thickness, and sintered at 900–1000 °C for 2 h in the air.

The structure and phase evolution of specimens were characterized by X-ray diffraction (XRD) (Rigaku D/MAX-2400, Cu K α radiation). The microstructure of fresh fracture surfaces of sintered pellets was examined by scanning electron microscopy (SEM) (JSM-6360). Dielectric measurements on the poled samples were carried out at 1 MHz, data was collected using a HP4284 Impedance Analyzer interfaced to a computer. The resistivity was tested by HP4339A-HP16339A. Ferroelectric hysteresis loops were tested using TF Analyzer 2000 and magnetic hysteresis loops were measured by LakeShore 7307 vibrating sample magnetometer (VSM).

3. Results and discussion

Fig. 1 shows the XRD patterns for 0.7BiFeO₃–0.3BaTiO₃–*x* wt.% MnO₂ ceramics with *x* = 0, 0.2, 0.3, and 0.5, respectively. All ceramic samples show single perovskite structures. It is believed [3] that the BiFeO₃–BaTiO₃ solid solution structure is rhombohedral with BiFeO₃ above 67 mol%. XRD results also confirm that 0.7BF–0.3BT (*x* = 0) is rhombohedral. However, with 0.5 wt.% MnO₂ content doping, the structure of 0.7BF–0.3BT solid solution has entirely changed to a tetragonal perovskite structure.

Fig. 2 shows SEM images of 0.7BF–0.3BT–*x* wt.% MnO₂ for all different levels of *x*, respectively. All samples were sintered at 970 °C. These images were taken from fresh fracture surfaces. Fig. 2 shows that the grain size increases at first but decreases later with increasing content of Mn. The un-doped sample shows small and inhomogeneous grain size, which results in significant residual porosity. When 0.2 wt.% or 0.3 wt.% MnO₂ content was added, the grain size was increased with high density and the sintering ability of solid solution was improved accordingly. But when the content of MnO₂ is

0.5 wt.%, the grain size decreases, and the sintering ability of the solid solution is deteriorated, as illustrated in Fig. 2(d). The explanation is that when the concentration of MnO₂ is small (below 0.3 wt.%), manganese ions will enter crystal lattices substituting for Fe³⁺ or Ti⁴⁺, which will lead to crystal lattice distortion, and thus improve the sintering ability of the ceramic. But when the concentration of MnO₂ is 0.5 wt.%, which may probably exceed the solubility limit of manganese ions in the solid solution, the sintering ability of the ceramic and the properties of the material are deteriorated accordingly.

Fig. 3 shows the resistivity of the 0.7BF–0.3BT ceramic for different MnO₂ contents. The resistivity increases at first and then decreases with increasing content of MnO₂, which is due to the conversion of MnO₂ into Mn₂O₃ and Mn₃O₄ when at 650 and 980 °C, respectively [7]. All samples were sintered at 960–990 °C, therefore, the manganese ions are mostly in form of Mn³⁺, but there is a reaction between Mn³⁺ and Fe²⁺: $\text{Mn}^{3+} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{Mn}^{2+}$, which can effectively restrain the conversion of Fe³⁺ $\rightarrow$ Fe²⁺, lowering the oxygen vacancy concentration and subsequently lowering the conductivity. Though there are Mn²⁺ and Mn³⁺ ions simultaneously in the solid solution, the amount of these ions is small, and plays little part on the electric conductivity [8]. Hence the resistivity increases evidently when the content of MnO₂ is 0.2 wt.%, namely the resistivity is $\sim 10^{13} \Omega \text{ cm}$, which is the first report of high resistivity in BiFeO₃-based ceramics. But when the content of MnO₂ increases, the oxygen vacancies will increase due to substitution by manganese ions, since there are more Mn²⁺ ions in the vicinity of the Fe³⁺ for the reaction between Mn³⁺ and Fe²⁺. Fe³⁺ ions will be substituted mostly by Mn²⁺ ions, but for substitution by Mn³⁺ ions cannot be excluded. Therefore, when Mn²⁺ ions substitute for Fe³⁺ or Mn³⁺ ions substitute for Ti⁴⁺, oxygen vacancies will be created. Hence when the content of MnO₂ is above 0.2 wt.%, the resistivity decreases due to more oxygen vacancies, as illustrated in Fig. 3.

Fig. 4 shows dielectric constant and loss as a function of temperature for 0.7BF–0.3BT ceramic with different MnO₂ contents. Results show that the Curie temperature increases with increasing content of MnO₂, but the *T_c* value of all the doped samples are lower than that of the un-doped. The *T_c* of BiMnO₃ is known to be 105 K [9], and the magnitude of the melting point can be used to indicate the intensity of the ion bond, the melting points of Mn₃O₄ and TiO₂ are 1564 and 1840 °C, respectively. Hence the intensity of Mn–O bond is lower than that of Ti–O bond. If Mn ions substitute for Ti, this will weaken the stability of ferroelectric state of the solid solution. Therefore, whether Mn ions substitute for Ti or for Fe ions, the Curie temperatures of the doped samples are lower than that of the un-doped. However, with increasing MnO₂ content, the number of Mn ions entering crystal lattices increases, which will produce an interior bias electric field [10], restraining domain movement and making fully poled samples difficult to achieve. Hence the *T_c* will shift towards higher temperature. The dielectric loss of the un-doped sample is higher than those of the doped samples, due to the leakage conductivity of the un-doped sample being larger than those of the doped samples.

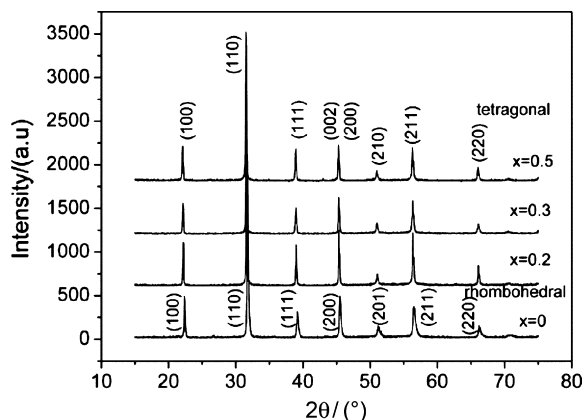


Fig. 1. XRD patterns for 0.7BiFeO₃–0.3BaTiO₃–*x* wt.% MnO₂ solid solution system.

Download English Version:

<https://daneshyari.com/en/article/1463833>

Download Persian Version:

<https://daneshyari.com/article/1463833>

[Daneshyari.com](https://daneshyari.com)