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Effects of oxygen content on the electric and magnetic properties of $BiFeO_3$ compound

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ABSTRACT

Multiferroic $BiFeO_\delta$ (δ=2.67, 2.95 and 3.02) compound of various oxygen contents (δ) have been prepared by gel sol method. The influence of oxygen contents on the structure, electric and magnetic properties of $BiFeO_3$ compound has been investigated. X-ray diffraction (XRD) measurements indicate that all the samples of $BiFeO_\delta$ have the same crystal structure regardless of oxygen content. The SEM micrograph reveals microstructures comprising of grains with various sizes from 200 nm to 1 μm. XPS study confirms the coexistence of Fe^{3+} and Fe^{2+} ions in $BiFeO_\delta$ compound. The $M(H)$ curves exhibit weak ferromagnetic behavior with unsaturated magnetization at room temperature, independent of the oxygen content. The $M(T)$ curves of suggest anti-ferromagnetic behavior with Neel temperature of ~370 °C for $BiFeO_{2.95}$ and $BiFeO_{3.02}$ samples and paramagnetic behavior of $BiFeO_{2.67}$ sample from RT up to 500 °C. The experimental results show that the antiferromagnetic ordering is strongly correlated with the oxygen content and is almost entirely suppressed in $BiFeO_\delta$ with δ=2.67. The effect of oxygen vacancies is to weaken the magnetic ordering rather than to enhance it as previously suggested in the literature.

1. Introduction

As a promising multiferroic material, $BiFeO_3$ compound has shown great potential for applications on high-density ferroelectric random access memories (FeRAMs) due to their large remanent polarization ($Pr \geq 60\ \mu C/cm^2$) at room temperature [1,2]. It is well known that the leakage current characteristics are very critical in FeRAMs applications of ferroelectric film due to its direct relation to power consumption and long-term reliability of the storage element. Unfortunately, $BiFeO_3$ thin film suffers from high leakage currents as the results of the existence of Fe^{2+} and oxygen vacancies hindering its applications in memory devices [3–6]. Experimental results have suggested that defects and impurity energy levels in the band gap can lead to high leakage current [7]. In particular, oxygen vacancies (V_O), rather than Fe^{2+} ions, have been approved to be the main cause of high leakage current in $BiFeO_3$ films [8–11]. The physical properties of $BiFeO_3$ are strongly modified by the presence of various kinds of defects. The oxygen vacancy (V_O) is one of the most important kinds [12].

Since V_O is almost unavoidable in the preparation of $BiFeO_3$ samples, both qualitative and quantitative studies on the V_O are of great importance. The experiment and theoretical calculation have suggested that oxygen content in $BiFeO_3$ not only affects the leakage performance but also influences the magnetization of $BiFeO_3$ films [10–19]. Theoretically, Ju et al. investigated the effect of V_O on the electronic structure and linear optical response of multiferroic $BiFeO_3$ using First-principles method [12]. Ederer and Spaldin studied effect of V_O on the ferroelectric properties of $BiFeO_3$ using density functional theory and predicted that the impact of oxygen vacancy in $BiFeO_3$ on the ferromagnetic properties was not large [13]. But some researchers argued that the Fe^{2+} ions are aligned oppositely to those of the Fe^{3+} ions in $BiFeO_3$ thin film, leading to a net magnetic moment with the presence of oxygen vacancies [19]. Experimentally, efforts have been made to reduce V_O using different deposition oxygen pressure, post-annealing the $BiFeO_3$ in oxygen atmosphere, doping $BiFeO_3$ with higher valence ions, and implanting $BiFeO_3$ by oxygen ions [14,16]. The effect of oxygen vacancies on the leakage mechanism and the leakage current density were investigated by Yang [16]. The influences of deposition oxygen pressure on the ferroelectric properties of $BiFeO_3$ films have been demonstrated [16,17]. Yuan et al. explored the mechanism of formation of V_O by investigating the relationship between V_O and oxygen pressure during cooling [18].

Although the influence of oxygen vacancies on the electric and magnetic properties of $BiFeO_3$ compound has been studied extensively, the exact role of oxygen vacancy is not entirely clear due to the lack of solid experimental data. In this work, multiferroic

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$BiFeO_\delta$ compound of various oxygen contents were prepared by gel–sol method. Particularly, we focus on the study of the effect of oxygen content on the magnetization properties of $BiFeO_3$. We show that the effect of oxygen vacancy in $BiFeO_3$ is to break the antiferromagnetic order rather than to enhance the ferromagnetic properties of the compound.

2. Experimental procedure

The $BiFeO_\delta$ (δ=2.67, 2.95 and 3.02) compound were prepared by the sol–gel method. The $BiFeO_3$ precursor solutions were prepared using bismuth nitrate [$Bi(NO_3)_3 \cdot 5H_2O$] and iron nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] as starting materials. First, iron nitrate and bismuth nitrate (with 5% excess bismuth to compensate the Bi loss during firing) were mixed and dissolved in 2-methoxyethanol by stirring for 30 min at room temperature. Then the acetic anhydride was added to dehydrate under constant stirring. Finally, the concentrations of the solutions were adjusted to 0.3 mol/L by adding 2-methoxyethanol. The resulting mixture was stirred vigorously at room temperature for 24 h to obtain the sol. The precursor solution was dried at 80 °C for about 1 week and the resulting powder was grounded and calcined at 400 °C and 650 °C for 2 h and 1 h, respectively. The obtained powders were milled again, and then pressed into 1 mm-thick pellets of 13 mm in diameter, which were subsequently sintered at 810 °C for 30 min. Finally $BiFeO_\delta$ samples with varied oxygen content were obtained by annealing samples at 650 °C in air, in oxygen flow and in a vacuum of better than 10^{-3} Pa, respectively. For electrical property measurement, the samples were carefully polished before the addiction of conductive silver pastes on both surfaces to form metal-insulator-metal capacitors. To remove organic compounds of silver paste, the samples coated silver paste were again annealed at 300 °C for 1 h in air, in oxygen flow and in a vacuum of better than 10^{-3} Pa, respectively.

The crystalline structure of the $BiFeO_\delta$ samples was characterized by x-ray diffraction (XRD) using a diffractometer with Cu Ka1 radiation (Brock, German). The oxygen content of $BiFeO_\delta$ (δ=2.67, 2.95 and 3.02) compound was determined with a X-ray fluorescence spectrometer (ZSX Primus II, Japan). The morphology of $BiFeO_3$ was observed with scanning electric microscopy (ZEISS -German). The DC J–E curves were measured using a Multiferroic Ferroelectric Test System (Multiferroic-3, USA). The coexistence of $Fe^{3+/2+}$ ions in $BiFeO_\delta$ samples was investigated with X-ray photoelectron spectroscopy (XPS. Axis.Ultra. UK). The magnetic property of $BiFeO_\delta$ was measured with Versa Lab (Quantum Design USA).

3. Results and discussion

3.1. Structural analysis

Fig.1 shows the XRD patterns of the $BiFeO_\delta$ ceramic samples (δ=2.67, 2.95 and 3.02) prepared by annealing in different atmosphere. It can be seen that the three samples are all single-phase with a rhombohedral distorted perovskite structure of the space group R3c. The lattice structure of $BiFeO_3$ remains essentially the same after annealing in different atmosphere.

Fig. 2 shows the scanning electron microscopy (SEM) images of $BiFeO_\delta$ specimen. The SEM micrograph reveals microstructure comprising of grains of varying sizes with well-denned boundaries, indicating polycrystalline nature of the material. For all the samples, the average grain size varies from 200 nm to 1 μm, which agreed with that reported for bulk $BiFeO_3$ prepared using gel–sol method [20,21]. The grains of $BiFeO_{2.67}$ and $BiFeO_{2.95}$ samples are rendered as a cuboid shape, while more uniform grains of $BiFeO_{3.02}$ sample appear cube shaped. Obviously the grain growth of $BiFeO_\delta$ is influenced by different annealing atmosphere.

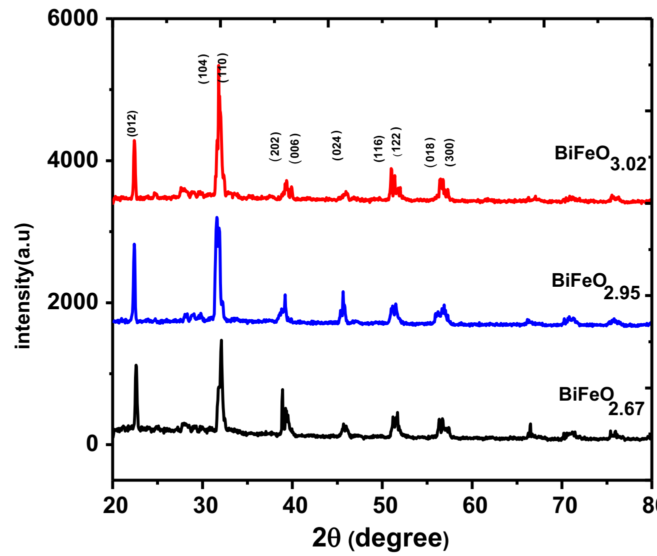

Fig. 1. XRD patterns for $BiFeO_\delta$ samples (δ=2.67, 2.95 and 3.02).

3.2. Electric properties

In order to study the effects of oxygen content on the electrical properties of $BiFeO_3$ sample, the current density (J) of $BiFeO_\delta$ (δ=2.67, 2.95 and 3.02) was measured as a function of applied electrical field (E) and the results are shown in Fig. 3. It can be seen that $\lg J$ increases linearly with $\lg E$ below a critical voltage. Namely [22,23]:

$$\lg J = a \lg E + b \quad (1)$$

with constant "a" the slope and "b" the logarithm of electric current (J) when electric field (E) equals 1 V/cm. Table 1 shows the least squares fitting parameters for the data shown in Fig. 3. For the oxygen-deficient sample $BiFeO_{2.67}$, the value of slope is 1.70, rather than 1 as can be expected from Ohm's Law. For oxygen-rich samples $BiFeO_{2.95}$ and $BiFO_{3.04}$, the slope of the curve is 0.99 and 1.05 respectively, approximately consistent with Ohm's law.

This discrepancy may be an indication that the charge density in $BiFeO_\delta$ is made of a small amount of space charges as well as free charges. The space charge limited current density (J) that flows under an applied electric field (E) is given by the Mott and Gurney square law [15,23], according to which the corresponding slope for the $\lg J$–$\lg E$ plot is 2 for space charge limited current density. With both free charges and space charges present, it is not surprising that a slope between 1 and 2 would be expected.

A large number of oxygen vacancies are formed in $BiFeO_{2.67}$ samples because $BiFeO_3$ sample annealed in the vacuum leads to reduced oxygen consent. The oxygen vacancy with an effective positive charge can capture electrons and these electrons can no longer take part in conducting, resulting in the formation of the space charges. The slope of electric current ($\lg J$) vs electric field ($\lg E$) curves for $BiFeO_{2.67}$ sample is 1.70 rather than 2 as predicted by the Mott and Gurney Square Law [15,23]. This experimental result provides strong evidence that space charge limited current dominates the transport behavior of this oxygen-deficient sample.

It can be seen from Table 1, the value of b is larger for oxygen-rich samples, which implies that the current density of $BiFeO_\delta$ increases with oxygen content at relatively low electric field (E=1 V/cm). At sufficiently high electric field, the captured charges