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Room temperature multiferroic properties of Ni-doped Aurivillus phase $Bi_5Ti_3FeO_{15}$

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Abstract

Single-phase Aurivillius $Bi_5Ti_3Fe_{0.5}Ni_{0.5}O_{15}$ (BTFN) ceramics were synthesized by the solid-state reaction method. The substitution of Ni for half Fe ions does not introduce magnetic impurity phase but increases magnetic moment more than two orders. The ferroelectric and magnetic Curie temperatures are determined to be 1100 K and 726 K. The room-temperature multiferroic behavior of the BTFN ceramics were demonstrated by the ferroelectric ($2P_r$=8.5 μC/cm^2, $2E_c$=74 kV/cm) and ferromagnetic ($2M_r$=27.86 m emu/g, $2H_c$=553 Oe) measurements. The ferromagnetism can be ascribed to the aggregation of magnetic ions at the inner octahedra by Ni doping and the spin canting of magnetic-ion-based sublattices via the Dzyaloshinskii-Moriya interaction. The present work suggests the possibility of doped $Bi_5Ti_3FeO_{15}$ as a potential room-temperature multiferroic.

Keywords: Aurivillius phase; $Bi_5Ti_3FeO_{15}$; Multiferroic

1. Introduction

Multiferroic materials exhibiting ferroelectric and magnetic orders simultaneously have attracted a lot of interest in recent years due to their special phenomena and potential applications in multifunctional devices [1,2]. At present, the coexistence of the two orders in most single-phase (SP) multiferroic materials always occurs at low temperature, and the large difference between the magnetic and ferroelectric transition temperature is clearly one of the obstacles to the exploitation of multiferroics in real applications at room temperature (RT). Thus, the search for SP multiferroic materials exhibiting multiferroic properties above RT is going on. So far, one of the most frequently investigated SP multiferroic material is $BiFeO_3$, offering ferroelectric order and spin order at relatively high temperature (T_c ~ 830 °C, T_N ~ 370 °C) [3–5]. But the $BiFeO_3$ suffers from large leakage current and its antiferromagnetic nature, and this will degenerate its electric and coupling properties [6].

Recently, the layered bismuth compounds with structures related to Aurivillius phase have been reconsidered as one of the candidates in SP multiferroics because of their potential magnetoelectric coupling behaviors [7]. $Bi_5Ti_3FeO_{15}$ (BTF) is such a compound and a four-layered perovskite unit of $(Bi_3Ti_3FeO_{13})^{2-}$ sandwiched by two $(Bi_2O_2)^{2+}$ layers along the *c* axis was considered as its structure. The $(Bi_2O_2)^{2+}$ layers play key roles as both space–charge compensation and insulation, which are expected to reduce the leakage current [8]. The ferroelectric Curie point was reported to be about 1023 K corresponding to a structural transition from the $A2_1am$ to the $I4/mmm$ [9]. However, BTF is antiferromagnetic with T_N of 80 K [10]. Consequently, the ferromagnetism of BTF at RT is still very weak. Many efforts have been made to improve it. Usually, element doping is a good choice to improve the performance of materials. Co is the most usually reported magnetic element substituted for Fe in BTF. Mao et al. reported three orders of magnitude increase of remnant

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magnetization in $Bi_5Ti_3Fe_{0.5}Co_{0.5}O_{15}$ ceramic [11], while they could not rule out the possible presence of small amount $CoFe_2O_4$ which might also contribute to the tremendous improvement of the magnetic properties of Co-doped BTF [12]. Wang et al. observed the enhancement of the magnetization in La and Co co-substituted BTF ceramics [13]. We have also reported the large magnetic response was observed through co-substitutions of Co for Fe and Nd for Bi in BTF [14]. Except Fe and Co elements, Ni is also a ferromagnetic element. To our knowledge, the report on Ni substitution in BTF system is still lack. In this paper, we investigated the enhanced multiferroic properties of $Bi_5Ti_3Fe_{0.5}Ni_{0.5}O_{15}$ (BTFN) ceramics prepared by the conventional solid state reaction.

2. Experimental procedure

BTFN ceramics were prepared by the conventional solid state reaction method [15,16]. Bi_2O_3 (99.999%), Fe_2O_3 (99.9%), Ni_2O_3 (99.9%), and TiO_2 (99%) were used as starting materials. An excess of 8% Bi was added to compensate for the volatilization of Bi_2O_3 in the sintering process. The raw materials were mixed by ball milling with agate and ethanol for 4 h, followed by calcining at 600 °C. The presintered powders were milled again, and then pressed into pellets with a diameter of 10 mm and a thickness of 0.5 mm. The discs were sintered at 900 °C for 2 h in air and then furnace cooled to RT. For electrical measurement, the discs were lapped and polished to about 0.2 mm thick. Silver was pasted on both surfaces as electrodes.

The crystal structure was examined by a Bruker D8 ADVANCE X-ray diffractometer (XRD) with Cu K_α radiation. The differential scanning calorimetry (DSC) analysis was performed on a Netzsch STA 449C thermal analysis system. The cross-sectional microstructure was characterized by a scanning electron microscope (SEM) (JEOL, JSM6510LV). The ferroelectric properties were measured using a precision workstation ferroelectric tester system (Radiant Technologies) at RT. A vibrating sample magnetometer (VSM) was used to measure RT magnetic hysteresis loops and the high temperature M–T curve. For M–T measurement, the sample was in the thermal insulation system.

3. Results and discussion

Fig. 1 shows the θ–2θ XRD pattern of BTFN. The Aurivillius structure containing four perovskite layers is identified by indexing all the diffraction peaks on the basis of an orthorhombic cell (Joint Committee for Powder Diffraction Standard (JCPDS) No. 38-1257). It is seen that no impurity phases are detected, indicating the formation of SP BTFN. And the (119) peak has the highest intensity which indicates that the sample is randomly-oriented. The inset of Fig. 1 is the DSC curve of BTFN sample. Only one endothermic peak was detected on heating, indicating a phase transition, which is coincident with earlier reports [9], even Li et al. observed two phase transitions occurred in BTF during heating [17]. The onset temperature of

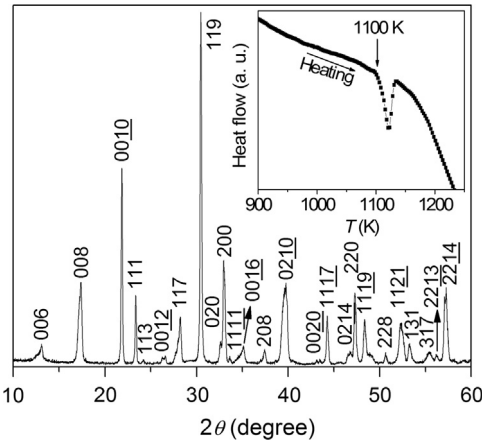

Fig. 1. X-ray θ–2θ diffraction pattern of BTFN ceramic. The inset shows the DSC curve.

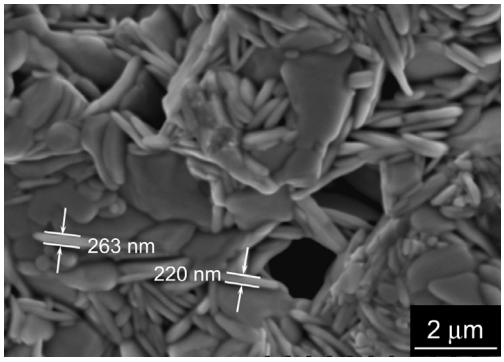

Fig. 2. Cross-sectional SEM micrograph of BTFN ceramic.

the peak for BTFN is 1100 K, slightly higher than the reported 1023 K for BTF [9].

Fig. 2 shows SEM image taken from fresh fracture surface of BTFN sample. The grain of the sample is formed in the shape of thin platelets, which is typical for Aurivillius bismuth layered compounds due to the preferential growth of the *ab* crystalline plain. The random arrangement of the grains is consistent with the random orientation of the sample indicated by Fig. 1. The thickness of the platelike grains varies from 200 to 300 nm. Also, prominently, apart from closely piled grains, there are some micropores, indicating a low density. This lower density is believed to be a result of the formation of the platelike grains [18].

The polarization versus electric field (P–E) loop of the BTFN ceramic capacitor is shown in Fig. 3. Even though the applied electric field is not enough to saturate the loop, the loop still reflects clear ferroelectricity in the sample. The measured remnant polarization $2P_r$ and coercive field $2E_c$ values are about 8.5 $\mu C/cm^2$ and 74 kV/cm respectively at a maximum applied electric field of 100 kV/cm, which is larger than that of the BTF at the same maximum field [12,19]. It has been demonstrated that the higher ferroelectric transition temperature (T_c) leads to the larger ferroelectric polarization [20]. And the T_c of Aurivillius compounds is inversely proportional to the tolerance factor t [21], which can be estimated by the

following formula:

$$t = (r_A + r_O)/\sqrt{2}(r_B + r_O) \quad (1)$$

where r_A, r_B, and r_O are ionic radii of an *A*-site cation, a *B*-site cation, and an oxygen ion, respectively. For BTFN and BTF samples, r_A is 0.093 nm for Bi^{3+}, r_B is 0.0559 nm for Ti^{4+}, 0.055 nm for Fe^{3+} or 0.056 nm for Ni^{3+}, and r_O is 0.14 nm for O^{2-} [22]. Since the ionic radius of Ni^{3+} is slightly larger than that of Fe^{3+}, the Ni substitute is expected to decrease the tolerance factor *t*, and hence the T_c of the sample should increase. In fact, the T_c of the BTFN is 1100 K as shown in the inset of Fig. 1, and the T_c of the BTF is 1028 K [12]. Therefore, according to the above, it is reasonable that the $2P_r$ value of BTFN is larger than that of the BTF at the same maximum field. The inset of Fig. 3 is *dc* leakage current characteristic of BTFN ceramic capacitor. It can be seen that the leakage current density is $\sim 10^{-5}$ A/cm^2 under an electric field of 56 kV/cm. This leakage current density is higher than those (10^{-7}–10^{-6} A/cm^2) of BTF and Co-doped BTF thin films under the same electric field deposited on (111) Pt/Ti/SiO_2/Si/ substrates [23,24]. As is reported, suitable electrodes can effectively decrease the leakage current density [25]. Silver was pasted on both surfaces of the BTFN ceramic as electrodes, as the above mentioned. Although the electrical conductivity of silver is better than that of platinum, platinum is inert than silver and platinum is not easy to be oxidized. Therefore, platinum is better than silver as electrodes. Moreover, compared with thin films, ceramics are bulk materials and more defects would exist in ceramics rather than in thin films. The above two factors combined would lead to higher leakage current density of the BTFN ceramic capacitor. In addition, the lower density indicated by Fig. 2 might also contribute to the higher leakage current density. In order to decrease the leakage current density and increase the squareness of *P*–*E* loop, decreasing the sample defects such as micropores through preparing grain-oriented ceramics and modifying electrodes are all necessary.

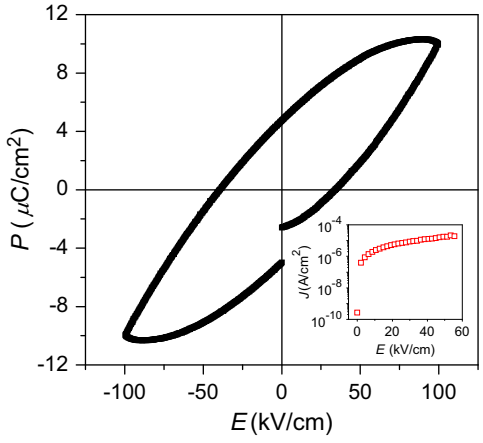

Fig. 3. RT *P*–*E* hysteresis loop of BTFN ceramic capacitor. The inset is *dc* leakage current characteristic of BTFN ceramic capacitor.

Fig. 4(a) shows the high temperature *M*–*T* curve for the BTFN ceramic at a magnetic field of 1 kOe. The plot indicates that the sample shows a spontaneous magnetic moment, indicating a ferromagnetic nature. Compared with typical ferromagnetic materials, the intensity of magnetic signal in BTFN is relatively weak, which leads to the low signal-to-noise ratio of the magnetization data. However, the magnetic Curie temperature of the BTFN sample could still be approximately determined to be around 726 K, defined as the temperature corresponding to the peak of d*M*/d*T* shown in Fig. 4(b). Fig. 4(c) is the magnetization hysteresis loop for BTFN sample measured at RT. The typical *S*-type ferromagnetic hysteresis (although nonsaturating) is observed with $2M_r \approx 27.86$ m emu/g and $2H_c \approx 553$ Oe at a magnetic field of 8 kOe. The $2M_r$ is about two orders magnitude larger than the reported 122 μ emu/g for BTF prepared by the same method [19], indicating that Ni doping improves magnetic response greatly. We could explain the improvement from the following factors. It is reported that the filled or partially filled *d*-orbitals of transition metal ions could easily hybridize with the O 2*p* orbitals [26] and this hybridization could lead to high symmetrical octahedra or similar bond length between magnetic ion and oxygen ions at the opposite direction [27]. As can be seen from the schematic illustration of BTF crystal structure

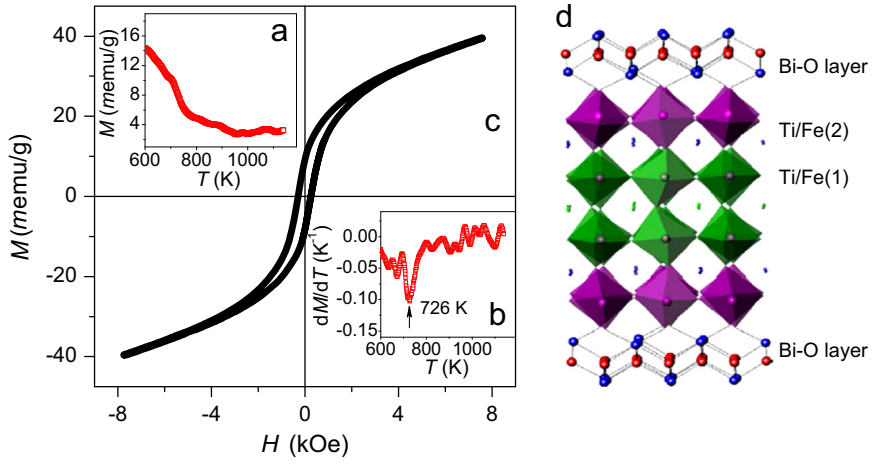

Fig. 4. (a) High temperature *M*–*T* curve for the BTFN ceramic at a magnetic field of 1 kOe; (b) The temperature dependence of d*M*/d*T*; (c) The magnetic hysteresis loop at RT (d) Schematic illustration of BTF crystal structure.

shown in Fig. 4 (d), Fe ions can occupy two non-equivalent positions between two Bi-O layers. One is at the center of the "inner" Ti/Fe(1)O_6 octahedra, the other is at the center of "outer" Ti/Fe(2)O_6 octahedra, and the occupancy of Fe ions in BTF is random with Ti ions although the outer octahedra are considerably more distorted than the inner octahedra [28]. Zulhadjri et al. considered that in Mn-doped four-layer Aurivillius $Pb_{1-x}Bi_{4+x}Ti_{4-x}Mn_xO_{15}$, transition metal Mn ions mainly resided in the inner TiO_6 octahedra with lower distortion because of the high symmetry of Mn octahedra which is induced by the hybridization between filled or partially filled *d*-orbitals of Mn ions and the O 2*p* orbitals [27]. Therefore, it might be inferred that Ni ions substituted for randomly distributed Fe ions are inclined to occupy the center of the inner octahedra in BTFN. As a result, more magnetic ions would aggregate at the inner octahedra, namely, chance of adjacently appearing Fe-O and Ni-O octahedra will be big and it could be expected that a more direct M–O–M, where M represents magnetic ions, rather than M–O–Ti–O–M interactions would take place. Furthermore, taking into account of the different radius of Fe^{3+} and Ni^{3+} ions, the BTFN would have a more distorted crystal structure compared to BTF and thus induced tilting of MO_6 octahedra. The tilting of MO_6 octahedra would give rise to a canted spin structure, and this canted spin state would favor the existence of weak ferromagnetic phase via the antisymmetric Dzyaloshinskii–Moriya interaction [29,30]. All the above may contribute to the improved magnetic response. Here, it should be mentioned that the above discussion is preliminary and more work is needed to understand the mechanism of improved magnetic response.

4. Conclusion

In summary, $Bi_5Ti_3Fe_{0.5}Ni_{0.5}O_{15}$ ceramics were synthesized by the conventional solid-state reaction method. The microstructure, ferroelectric, and magnetic properties were investigated. The X-ray diffraction pattern demonstrated that the sample shows a SP Aurivillius structure containing four perovskite layers. The ferroelectric and magnetic Curie temperatures are determined to be 1100 K and 726 K, respectively. The BTFN exhibits defined ferroelectric hysteresis loop with the remanent polarization ($2P_r$) of 8.5 μC/cm^2 and the coercive field ($2E_c$) of 74 kV/cm under an electric field of 100 kV/cm. Vibrating sample magnetometer measurements of the BTFN ceramic clearly demonstrated ferromagnetic behavior, with the remanent magnetization ($2M_r$) of 27.86 m emu/g under a magnetic field of 8 kOe at RT. The origin the ferromagnetism was discussed. The present work suggests the possibility of doped $Bi_5Ti_3FeO_{15}$ as a potential room-temperature multiferroic.

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