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Letter

Room-temperature ferromagnetism in nitrogen-doped $BaTiO_3$

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HIGHLIGHTS

- The nitrogen-doped $BaTiO_3$ has been synthesized by the standard solid-state reaction method.
- The nitrogen-doped $BaTiO_3$ is ferromagnetism.
- The origin of the magnetism is associated with the presence of nitrogen.

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ABSTRACT

The nitrogen-doped $BaTiO_3$ with a tetragonal phase has been synthesized in the NH_3 (67%)/Ar atmosphere by the standard solid-state reaction method. A weak ferromagnetic behavior with a remanent magnetization of about 5.89×10^{-5} emu/g is observed at 300 K. The origin of the magnetism is associated with the presence of nitrogen. These results may have implications for further studies on multiferroics.

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1. Introduction

Multiferroics, defined as those multifunctional materials in which two or more kinds of fundamental ferroicities coexist, have received considerable interest in recent years due to their basic physics and potential applications in information storages, spintronics, magnetoelectronic devices, etc. [1–8]. Unfortunately, multiferroics are rare since the transition metal d electrons, which are essential for the magnetism, reducing the tendency for the off-center ferroelectric distortion [9]. Much research in magnetic ferroelectrics has been focused on the Bi-containing perovskites such as $BiFeO_3$ or $BiMnO_3$ and the hexagonal rare earth manganites LnMnO$_3$ (with Ln = Ho, Er, Tm, Yb, Lu, or Y) [10–14]. However, these multiferroic materials are not very fascinating for the applications in the short time because they show either small net spontaneous magnetization or small electric polarization at room temperature [15]. The unexpected room temperature ferromagnetism was also found in the two types of non-magnetic systems in the absence of magnetic ion dopants, which is referred as the d^0 magnetism since the magnetism is not induced by the partially filled d orbitals. One is the undoped binary oxides, such as CaO, TiO_2, ZnO, and SnO_2 [16–20]. The other is the binary oxides doped with 2p light elements, such as C- or N-doped ZnO, SrO, MgO, and TiO_2 [21–25]. Recently, Hu and co-workers have found room temperature multiferroics in the conventional ferroelectric $(K_{0.5}Na_{0.5})NbO_3$ nanocrystalline films with the cation vacancy [26]. Waghmare and co-workers have shown that multiferroic properties in the intermediate size nanocrystalline $BaTiO_3$ through a combination of the experiments and first-principles simulations [27]. However, no experimental studies are performed on the magnetic properties of the nitrogen-doped perovskite $BaTiO_3$. Therefore, it is of interest to investigate the effect of the nitrogen-doping in the prototypical perovskite ferroelectrics and explore the possibility of the magnetism in these conventional ferroelectrics. In this paper, we present our studies on the $BaTiO_3$ doped with nitrogen and show that the nitrogen-doped $BaTiO_3$ is a room-temperature ferromagnetic material.

2. Experimental details

In this paper, the $BaTiO_3$ ceramic was synthesized by the standard solid-state reaction. Stoichiometric precursor powders of the $BaCO_3$ (99%, Guoyao, China) and

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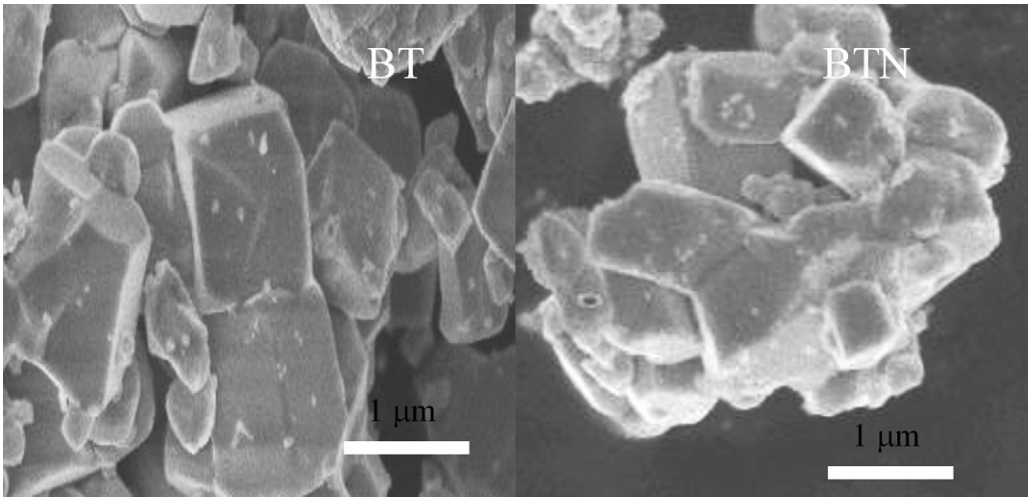

Fig. 1. SEM images of the pure $BaTiO_3$ (left) and nitrogen-doped $BaTiO_3$ (right) ceramics.

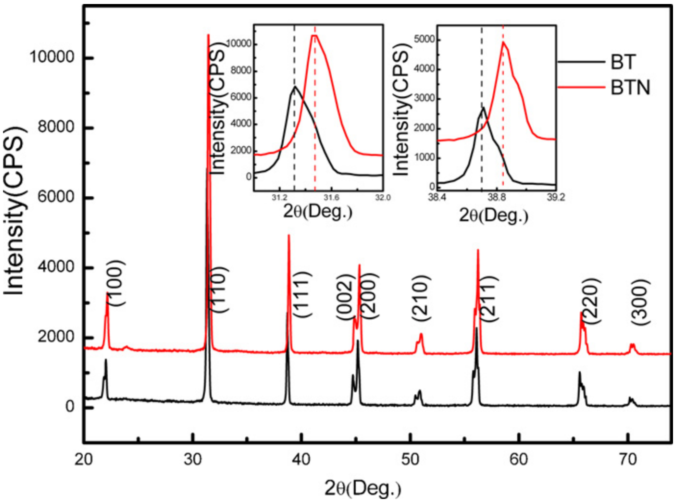

Fig. 2. XRD patterns of the pure $BaTiO_3$ and nitrogen-doped $BaTiO_3$ ceramics. The inset shows the (1 1 0), (1 1 1) peaks of the pure $BaTiO_3$ and nitrogen-doped $BaTiO_3$ ceramics.

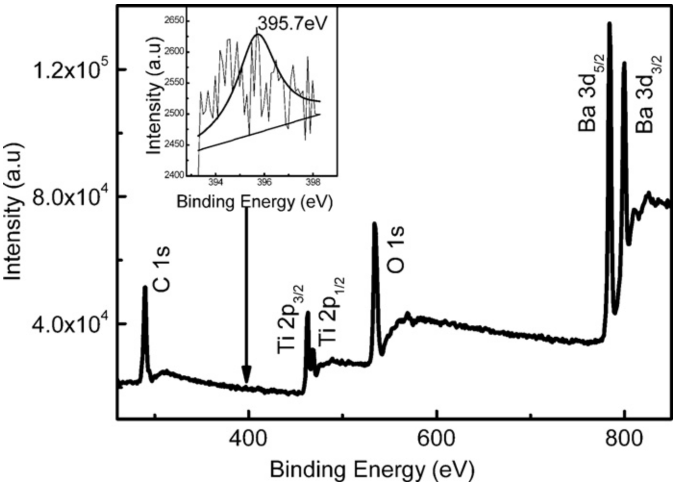

Fig. 3. XPS spectrums of the nitrogen-doped $BaTiO_3$ ceramics. The inset corresponds to the N 1s peak. The value of 248.6 eV for the C 1s line is used of an internal standard.

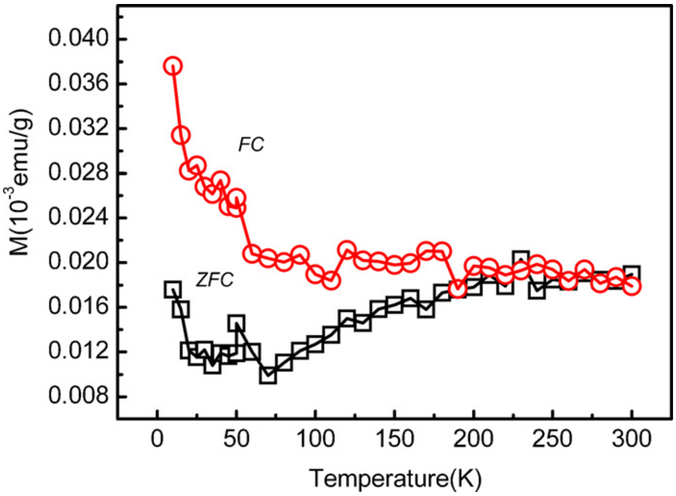

Fig. 4. The temperature dependence of magnetization curves (ZFC) and (FC) of the nitrogen-doped $BaTiO_3$ ceramic.

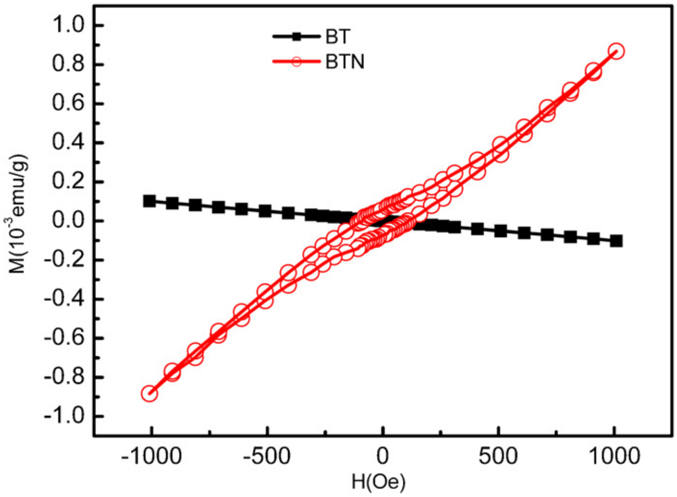

Fig. 5. The hysteresis loops of the pure $BaTiO_3$ and nitrogen-doped $BaTiO_3$ ceramics at 300 K.

TiO_2 (99%, Dengfeng, Tianjin) were mixed, and then sintered in the air at 1200 °C for 12 h (denoted as BT). After the grinding, the powder was sintered in the NH_3 (67%)/Ar atmosphere at 600 °C for 4 h (denoted as BTN) [28]. The ceramic was characterized by X-ray diffraction (*XRD*), X-ray photoelectron spectroscopy (*XPS*) and scanning electron microscopy (SEM, JSM-6700) for their crystal structures, chemical valence states and morphology, respectively. The magnetization as a function of the field and the temperature was measured by the superconducting quantum interference device (*SQUID*) magnetometry.

3. Results and discussion

Fig. 1 shows the SEM images of the BT and BTN samples. The SEM images of the both samples show the grain size of ~0.8 μm. The microstructures of BTN and BT ceramics are shown in Fig. 2. Both XRD patterns show a polycrystalline perovskite structure without any impurity phases, indicating that BTN forms a single-phase solid solution. At room temperature, the microstructures of pure BT and BTN ceramics are determined to form a tetragonal phase, with the lattice parameters $a = 4.0044$ Å & $c = 4.0483$ Å and $a = 3.9967$ Å & $c = 4.0358$ Å. The inset image shows the detailed XRD patterns of the BTN and BT (1 1 0) reflection. The XPS was employed to decide the chemical valence states, as shown in Fig. 3. All the indexed peaks are ascribed to N, O, Ba, C and Ti elements and no other ions can be detected in the BTN sample. As seen in the inset of Fig. 3, there is only one peak located at about 395.7 eV, which correspond to Ti–N bond [29,30]. This result means that the N ions have substituted the O atoms of the $BaTiO_3$ (without nitrogen clusters).

The zero-field-cooled (*ZFC*) and field-cooled (*FC*) magnetization curves of the BTN sample in the temperature range from 10 to 300 K at a magnetic field of 50 Oe are plotted in Fig. 4. The curves manifest that the BTN exhibits a Curie temperature of about 300 K. The *ZFC–FC* curves are conversed into one flat curve at the temperature of about 50 K, indicating the absence of the superparamagnetism. This rules out the possibility of the nitrogen clusters being the origin of the observed ferromagnetism in our BTN sample, which is consistent with the XPS results above. Fig. 5 depicts the magnetic hysteresis loops of the BT and BTN at 300 K. The BTN sample shows a clear hysteresis loop with its saturated magnetization (*Ms*) of about 5.89×10^{-5} emu/g. The coercivity is in the order of 92 Oe. It is worthwhile to highlight that no ferromagnetism can be detected in the BT sample, implying the observed ferromagnetism is associated with the presence of nitrogen.

4. Conclusions

In summary, the nitrogen-doped $BaTiO_3$ ceramic has a tetragonal phase at room temperature and the ferromagnetic Curie temperature of about 300 K. We demonstrated that nitrogen-doped $BaTiO_3$ is ferromagnetic at room temperature.

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