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Magnetic and electrical properties of $Bi_{0.8}Ca_{0.2}Fe_{1-x}Mn_xO_3$ $(0 \le x \le 0.5)$

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ABSTRACT

Mn-substituted $Bi_{0.8}Ca_{0.2}FeO_3$ ceramics $Bi_{0.8}Ca_{0.2}Fe_{1-x}Mn_xO_3$ $(0 \le x \le 0.5)$ were synthesized by a solid-state reaction method. Powder X-ray diffraction investigations performed at room temperature show that the crystal structure is rhombohedral for $x \le 0.1$ and orthorhombic for $0.2 \le x \le 0.5$. Compared to the undoped $Bi_{0.8}Ca_{0.2}FeO_3$ compound, enhanced magnetization and electric polarization were observed in the samples with $x \le 0.1$. A further increase in the magnetization with increasing x took place in the samples with $0.2 \le x \le 0.5$. All the Mn-substituted samples studied are basically antiferromagnetic accompanied by the appearance of weak ferromagnetism, which is similar to the $BiFeO_3$ compound. The conductivity of the samples with $x \ge 0.3$, measured between 140 and 380 K, is of the semiconducting type.

1. Introduction

Much attention has been paid to the multiferroic materials that exhibit both magnetic and ferroelectric (FE) properties recently [1–3]. A lot of interesting phenomena can be produced by the coupling between the magnetic and FE degrees of freedom in multiferroics, such as the magnetoelectric (ME) effect, in which the electric polarization can be tuned by applied magnetic field and vice versa [1–3]. Because of these new spectacular properties, multiferroic materials can have many interesting and promising potential applications. However, there are only a few materials exhibiting both ferromagnetic (FM) and FE behaviors. For ABO_3 perovskite compounds, theoretical studies have shown that the mechanisms for magnetism and ferroelectricity are usually mutually exclusive in the same material [4] and empirically there are indeed few multiferroic materials. Among the few multiferroics, Bi-based perovskites are one important class of multiferroics, in which the FM is due to the B-site transitional metal ions and the FE is due to the A-site Bi ions [5]. $BiFeO_3$ is one of the few well-known multiferroics that exhibits both FE order ($T_C = 1100$ K) and G-type antiferromagnetic (AFM) order ($T_N = 643$ K) simultaneously. It possesses a rhombohedrally distorted perovskite structure with space group *R3c* at room temperature (RT) [6]. Due to the canting of the AFM sublattices, $BiFeO_3$ exhibits weak FM even at RT. Meanwhile, a nearly sinusoidal spin structure along $[1\,1\,0]_h$ leads to the cancellation of the macroscopic magnetization and the prohibition for observing the linear ME effect [7]. This spiral spin structure can be suppressed or even destroyed by chemical substitutions [8,9]. Recently, enhancement of magnetization has been reported in $Bi_{1-x}A_xFeO_3$ ($A = Ba^{2+}, La^{3+}, Ca^{2+}, Sr^{2+}$) materials [9–12] and it is thought that the substitution could suppress the incommensurate spin configuration and cause the enhancement of the magnetization. However, the B-site ion doping is a more direct and effective way to affect the magnetic properties in ABO_3 type perovskites while keeping the FE properties similar to the parent compounds [13,14], and enhanced magnetization is indeed observed in the Mn-doped $BiFeO_3$ compound [15,16]. In the present work, we report the effect of Mn-doping at Fe-site on the crystal structure, magnetic and electrical properties of multiferroic $Bi_{0.8}Ca_{0.2}FeO_3$.

2. Experimental

Polycrystalline $Bi_{0.8}Ca_{0.2}Fe_{1-x}Mn_xO_3$ ($x = 0, 0.05, 0.1, 0.2, 0.3, 0.4$ and 0.5) samples were prepared by a conventional solid-state reaction method from high purity Bi_2O_3, Fe_2O_3, MnO_2 and $CaCO_3$. The stoichiometric powders were mixed thoroughly, placed into Al_2O_3 crucibles and then fired in air at 750 °C for 24 h. The resultant powders were ground, pressed into small pellets and sintered at 850 °C for 24 h and finally at 900 °C for another 24 h with intermediate grinding.

The RT X-ray diffraction (XRD) measurements were taken by Philips X'pert PRO X-ray diffractometer with Cu K_α radiation. The structural parameters were obtained

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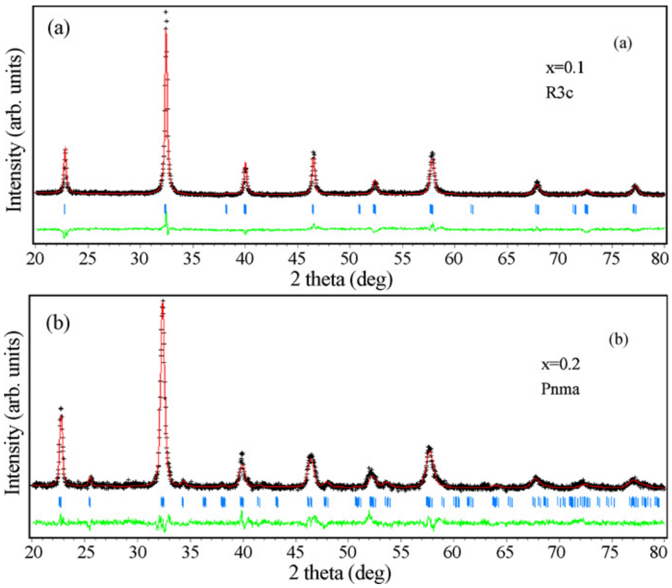

Fig. 1. Powder XRD patterns of the samples $Bi_{0.8}Ca_{0.2}Fe_{1-x}Mn_xO_3$ with $x = 0.1$ (a) and $x = 0.2$ (b) at RT, respectively. Crosses indicate the experimental data and the calculated data is the continuous line overlapping them. The lowest curve shows the difference between experimental and calculated patterns. The vertical bars indicate the expected reflection positions.

by fitting the experimental data of XRD using the standard Rietveld technique. The resistance as a function of temperature was measured by the standard four-probe method from 140 to 380 K. Differential thermal analysis (DTA) was used to determine the FE phase transition temperature (T_C). Dielectric measurements were performed at 25 °C using an LCR meter in the frequency range 100 Hz to 1 MHz. RT FE hysteresis loops were measured by using TF Analyzer 2000 (aixACCT) at a frequency of 1 kHz. The magnetic measurements were carried out with a quantum design superconducting quantum interference device (SQUID) MPMS system.

3. Results and discussion

The RT XRD results show that all $Bi_{0.8}Ca_{0.2}Fe_{1-x}Mn_xO_3$ ($0 \le x \le 0.5$) samples are single phase with no detectable secondary phases. The XRD patterns of the samples with $0 \le x \le 0.1$ can be indexed by a rhombohedral lattice with space group *R*3*c*, which is the same with the compound $BiFeO_3$. While the XRD patterns of the samples with $0.2 \le x \le 0.5$ can be indexed by an orthorhombic lattice with space group *Pnma*. The structural parameters are refined by the standard Rietveld technique [17] and the fitting between the experimental spectra and the calculated values is relatively good based on the consideration of relatively lower R_p (<10%) values. Fig. 1 shows experimental and calculated XRD patterns for the two representative samples with $x = 0.1$ and 0.2, respectively. The structural parameters obtained are plotted versus *x* in Fig. 2. As we can see, for samples with $0 \le x \le 0.1$, with the increase in Mn content there is a decrease in both *a* and *c* parameters of the unit cell. It results in unit cell volume contraction. This is expected since ionic radius of Mn^{4+} (0.53 Å) is slightly smaller than that of Fe^{3+} (0.645 Å). While for samples with $0.2 \le x \le 0.5$, the unit cell volume also contracts with increasing Mn content *x*. This is contrary to the anticipation that there will be only a small structural impact if any, if we expect the ionic ratio to be $Bi_{0.8}Ca_{0.2}Fe^{3+}{}_{0.8-y}Mn^{4+}{}_{0.2}Mn^{3+}{}_yO_3$ ($0 \le y \le 0.3$) with practically identical ionic radius for Mn^{3+} and Fe^{3+} (0.645 Å). This anomaly has also been reported in $Bi_{0.5}Ca_{0.5}Fe_xMn_{1-x}O_3$ ($0 \le x \le 0.6$) systems recently [18].

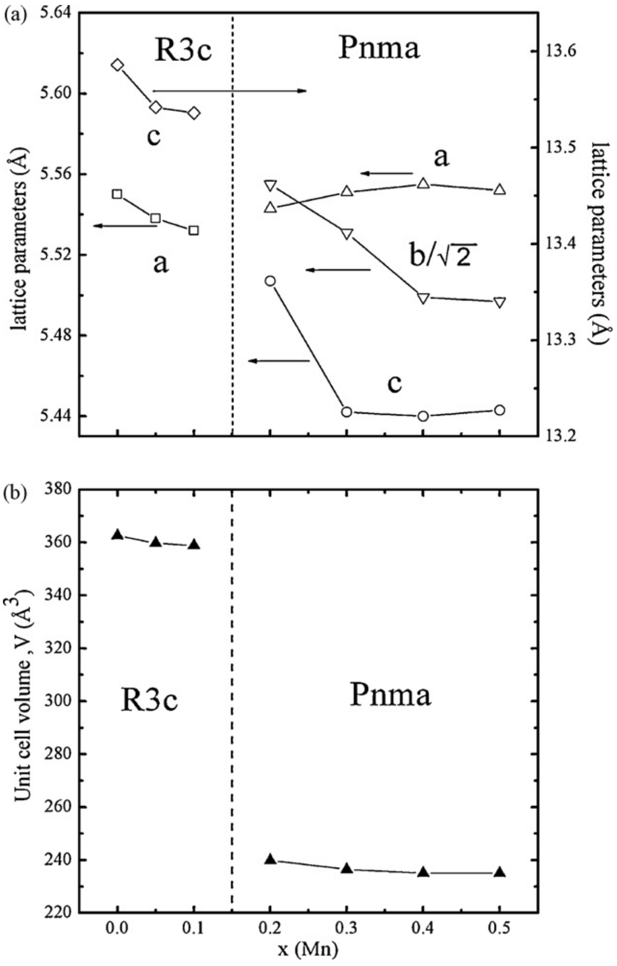

Fig. 2. (a) Mn substitution dependence of the lattice parameters, *a*, $\sqrt{b}$, *c* and (b) unit cell volume, *ν*.

It is reported that $Bi_{0.9}La_{0.1}Fe_{1-x}Mn_xO_3$ ($0 \le x \le 0.5$) compounds possess a rhombohedrally distorted structure and keep FE characteristics similar to $BiFeO_3$ in the whole doping range [15]. Recently $Bi_{1-x}Sr_xFe_{0.8}Mn_{0.2}O_3$ ($0 < x \le 0.2$) ceramics have also been reported to be multiferroic [19]. Similarly, we can also expect that our samples with $x \le 0.1$, which possess noncentrosymmetric rhombohedral structure, keep the FE properties similar to the parent compound $Bi_{0.8}Ca_{0.2}FeO_3$ with the same structure [11]. In order to verify this hypothesis, a DTA study was carried out on the representative sample with $x = 0.1$, which is shown in Fig. 3. A peak in the DTA curve can be observed at around 854 °C, which might be due to the FE transition. Previous reports on the $BiFeO_3$ [20], $Bi_{0.9}La_{0.1}Fe_{1-x}Mn_xO_3$ [15] and $Bi_{1-x}Sr_xFe_{0.8}Mn_{0.2}O_3$ [19] have

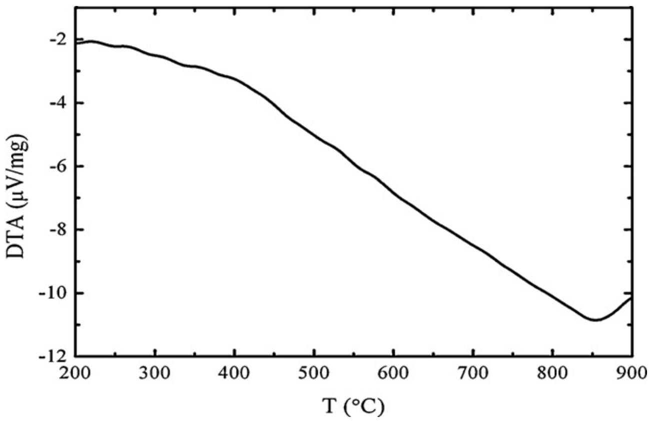

Fig. 3. The DTA curve obtained for the $Bi_{0.8}Ca_{0.2}Fe_{0.9}Mn_{0.1}O_3$ sample indicating presence of ferroelectric transition (T_C) at ~854 °C.