

Temperature-induced magnetization reversal in $\text{BiFe}_{0.5}\text{Mn}_{0.5}\text{O}_3$ synthesized at high pressure

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$\text{BiFe}_{0.5}\text{Mn}_{0.5}\text{O}_3$ could be stabilized in the perovskite structure by preparing it under high pressure and temperature. It has an orthorhombic structure with a possible ordered arrangement of Fe and Mn double rows and shows a magnetic ordering at high temperature (270 K). Low-temperature isothermal magnetization measurements indicate the ground state to be antiferromagnetic with a spin canting. Surprisingly, it exhibits magnetization reversal at low applied fields below a compensation temperature, T^* . Below T^* , the sign of the magnetization can be switched between negative and positive value reversibly by increasing and decreasing the field. Magnetization reversal in this oxide seems to result from a competition between single-ion magnetocrystalline anisotropy and antisymmetric Dzyaloshinsky-Moriya interactions.

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Magnetization reversal or negative magnetization in magnetic materials has been well known for more than five decades.^{1–10} Negative magnetization implies that the magnetic moments are aligned opposite to the applied field which is normally associated with high energy compared to the parallel alignment of magnetic moments. As early as 1948, Néel predicted that certain ferrimagnetic materials such as spinel oxides can exhibit negative magnetization due to different temperature dependence of sublattice magnetizations arising from different molecular fields acting on the magnetic ions in two different crystallographic sites.¹¹ As a result, it is possible that the magnetizations of different sublattices cancel each other, rendering the material to exhibit a net zero magnetization at a characteristic temperature called compensation temperature (T^*). Above and below this temperature, magnetization is dominated by one type of sublattice and the sign of the magnetization changes from positive to negative or vice versa. This behavior was experimentally observed in lithium chromium ferrite, Co_2VO_4 and some garnets.^{1–3} Many molecular ferrimagnets which are analogs of prussian-blue show negative magnetization with one or two compensation temperatures depending on the number of magnetic elements mixed at various crystallographic sites.^{7,8} Since then, other classes of materials have been reported to show negative magnetization but the mechanism seems to be different from that suggested for ferrimagnetic systems. Antiferromagnetic orthovanadates, $R\text{VO}_3$ ($R=\text{La, Ce, Nd, Sm, etc.}$) are reported to show negative magnetization even though all the V^{3+} ions occupy only one crystallographic site and thereby do not confirm to Néel's model for ferrite spinels.^{5,6,12–15} Various explanations have been offered for the behavior of rare-earth orthovanadates. For example, in LaVO_3 , it is suggested that the canted spin moment reverses upon crossing the first-order structural transition at 138 K below which the orbital angular moment is maximized.⁶ In YVO_3 , multiple temperature-induced magnetization reversal

is reported, the origin of magnetization reversal being considered to arise from the competition between single-ion magnetic anisotropy and antisymmetric Dzyaloshinsky-Moriya (DM) interaction.^{15,16} In antiferromagnetic chromites, such as GdCrO_3 , $\text{La}_{1-x}\text{Pr}_x\text{CrO}_3$, and $\text{La}_{0.75}\text{Nd}_{0.25}\text{CrO}_3$, negative magnetization is attributed to the polarization of paramagnetic rare-earth moments opposite to the canted Cr^{3+} moments.^{17–19} The ferromagnetic Laves-phase SmAl_2 with the cubic structure shows zero magnetization due to the large orbital magnetic moment of Sm^{3+} ions aligned antiparallel to the spin moment.²⁰ Recently, it has been found that $(\text{La}_{1-x/2}\text{Bi}_{x/2})(\text{Fe}_{0.5}\text{Cr}_{0.5})\text{O}_3$ with different magnetic ions occupying only one crystallographic site, shows negative magnetization at high temperatures.²¹

In this Rapid Communication, we report magnetization reversal in the perovskite $\text{BiFe}_{0.5}\text{Mn}_{0.5}\text{O}_3$ synthesized at high pressure and temperature. The two end members of this oxide system are BiFeO_3 and BiMnO_3 , the former with a rhombohedral structure ($R3c$) is (canted) antiferromagnetic ($T_N=643$ K) whereas the latter with a monoclinic structure is ferromagnetic ($T_C=105$ K) or (canted) antiferromagnetic ($T_N=30$ K) depending on oxygen stoichiometry.^{22–24} $\text{Bi}(\text{Fe}_{0.5}\text{Mn}_{0.5})\text{O}_3$ has the orthorhombic structure but does not show the 1:1 ordering of Mn^{3+} and Fe^{3+} ions characteristic of the double perovskite. The observation of negative magnetization in this compound seems to be due to competing single-ion anisotropy and antisymmetric DM interactions. More importantly, magnetic switching behavior at 175 K demonstrates the potential use of such materials in magnetic memory and related applications.

Polycrystalline samples were prepared at high pressure and high temperature using cubic anvil-type apparatus. The starting materials Bi_2O_3 , Fe_2O_3 , MnO , and MnO_2 were mixed appropriately and loaded in a gold capsule and pressed. The pressed gold capsule was subjected to 5 GPa pressure and heated to 1073 K for 2 h and cooled down to

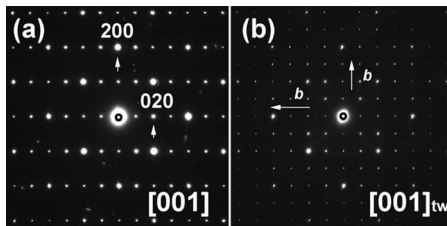


FIG. 1. [001] ED pattern of $\text{BiFe}_{0.5}\text{Mn}_{0.5}\text{O}_3$, (a) untwined and (b) permutation twinned

room temperature and thereafter the pressure was released slowly. The phase purity of the sample was investigated using Bruker D8 Discover diffractometer. Electron transmission microscopy (TEM) has been done by using a Tecnai G2 30 UT microscope operated at 300 kV and having point resolution 0.17 nm. For TEM study, the samples were crushed in n-butanol and deposited on a holey carbon membrane supported by a copper grid. The magnetic properties were studied using a vibrating sample magnetometer in a physical property measurement system, Quantum Design, USA.

Analysis of powder x-ray diffraction (XRPD) pattern of the sample showed that the major phase is a perovskite. Nevertheless, the presence of small amount ($<5\%$) of secondary phase was detected and identified to be one of the oxygen nonstoichiometric phases of BiMnO_3 . It should be mentioned that the samples prepared using Mn_2O_3 as starting material had higher amount of impurity phase. In the perovskite structure, the Fe and Mn ions at the B site can either be disordered or ordered in a rocksalt/layered configuration to form a double perovskite. Mössbauer experiments at room temperature revealed that iron is present in Fe^{3+} state and therefore, manganese also should be present in Mn^{3+} state.

Energy dispersive spectroscopy (EDS) analysis performed on numerous microcrystals of the perovskite shows that the cationic composition does not vary from one crystal to the other and is close to the nominal composition of the sample, i.e., “ $\text{Bi}_{1.09}\text{Fe}_{0.46}\text{Mn}_{0.45}$.” The analysis of the XRPD pattern in the profile matching mode, using FULLPROF program shows that the major phase can be indexed on an orthorhombic cell with the following lattice parameters, $a = 5.562(2)$ Å, $b = 11.191(2)$ Å, and $c = 7.845(2)$ Å. Note that these parameters are closely related to those previously reported for $\text{Bi}_2\text{Mn}_{4/3}\text{Ni}_{2/3}\text{O}_6$ (Ref. 25) and $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ $x=0.2-0.6$.²⁶ The ED study confirms the perovskite subcell and the two lattice parameters $a \approx \sqrt{2}a_p$, $b = 2a_p\sqrt{2}$, as shown from the [001] ED pattern of this phase [Fig. 1(a)]. The corresponding [001] high-resolution transmission electron microscopy image [Fig. 2(a)] suggests that the Mn^{3+} and Fe^{3+} cations are not distributed at random in the structure but may form double zigzag rows [Fig. 2(b)], running along b . Such an arrangement of these cations with same charge may be due to Jahn-Teller distortion associated with Mn^{3+} ions that results in distortion of MnO_6 octahedra which is different from FeO_6 octahedra. Nevertheless, multitwinning phenomena take place in the crystal [Fig. 1(b)] and prevent the c parameter to be established with certainty. In any case, this oxide does not show a 1:1 of Mn^{3+} and Fe^{3+} classically observed in double perovskite. The detailed structural study of

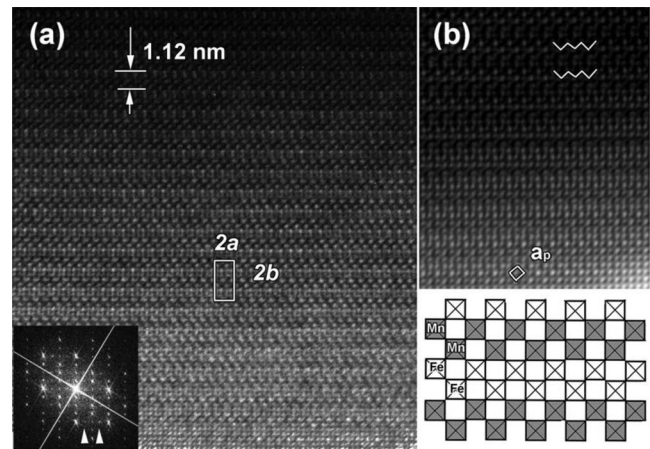


FIG. 2. (a) High-resolution TEM image of $\text{BiFe}_{0.5}\text{Mn}_{0.5}\text{O}_3$ along [001] and corresponding Fourier transform pattern. Note the white arrows which point spots due to twinning. (b) Enlargement of the image: double zigzag rows of bright dots alternate with darker double rows, interpreted as ordering of double rows of MnO_6 and FeO_6 octahedra.

this phase will be the object of a subsequent paper.

Figure 3 shows a plot of magnetization against temperature under field-cooled (FC) conditions at an applied field of ± 50 Oe. It is clearly seen from the bottom inset of this figure that there is a magnetic anomaly at 270 K in both positive and negative applied fields. Considering that the Fe^{3+} and Mn^{3+} ions are one to one ordered, the overall magnetic interaction is antiferromagnetic. If these B-site ions were ordered as rocksalt type, one would expect a ferromagnetic ordering according to the Goodenough-Kanamori rule as, for example, in the case of $\text{La}_2\text{NiMnO}_6$ ($T_C=280$ K).^{27,28} In order to further understand the magnetic ground state, isothermal magnetization $M(H)$ data were recorded at 5 K the result is shown in the inset of the upper panel of Fig. 3. We can see that $M(H)$ data exhibits a large hysteresis loop with a low value of remnant polarization of $0.03 \mu_B/\text{f.u.}$ and a coercive field of 4.3 kOe. Further, the magnetization does

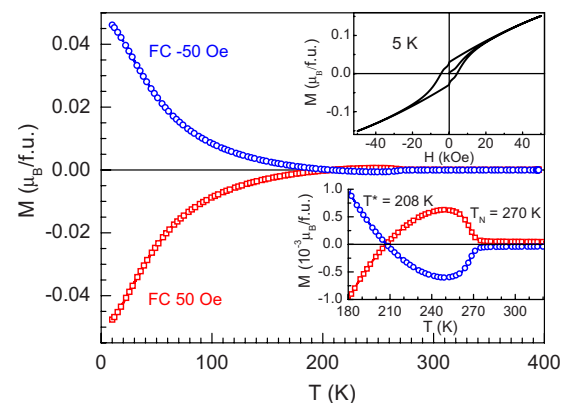


FIG. 3. (Color online) Magnetization as a function of temperature measured at $+50$ Oe and -50 Oe under FC process exhibiting magnetization reversal. Insets show the magnetic ordering temperature (lower panel) and a weak ferromagnetic hysteresis at low temperature (upper panel).

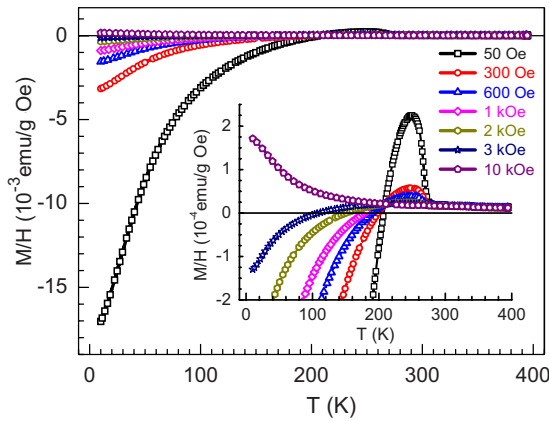


FIG. 4. (Color online) Magnetization versus temperature measured at different magnetic fields showing the decrease in T^* with increasing magnetic field. At 10 kOe, the magnetization switches to positive value.

not saturate even at 50 kOe field and the unsaturated magnetization obtained by extrapolating the linear magnetization to the ordinate is $0.05 \mu_B/\text{f.u.}$ This value is much lower than that expected ($1 \mu_B/\text{f.u.}$) for a collinear antiferromagnetic ordering of Fe^{3+} ($S=5/2$) and Mn^{3+} ions ($S=2$) through the $\text{Fe}^{3+}\text{-O-Mn}^{3+}$ superexchange interactions. Because of the possible ordering of Fe^{3+} and Mn^{3+} ions in the form of double rows, we expect Fe-O-Fe, Mn-O-Mn, and Fe-O-Mn superexchange interactions to be present in this system. Since this compound contains equal proportion of Fe and Mn ions, one would expect a dominant Fe-O-Mn interaction. However, the overall magnetic interaction is antiferromagnetic and the net moment would be zero. The fact that there is small finite moment indicates canting of spin moments. Above the magnetic ordering, the susceptibility could be fitted with the Curie-Weiss law and effective paramagnetic moment obtained from the fit is $4 \mu_B$, which is lower than the expected spin only value of $5.43 \mu_B$. The negative value of paramagnetic Curie-Weiss temperature is consistent with the antiferromagnetic ordering, however, the value ($\theta_p = -105 \text{ K}$) is much lower than the magnetic ordering temperature.

The most noteworthy observation in the case of $\text{BiFe}_{0.5}\text{Mn}_{0.5}\text{O}_3$ is that the sign of magnetization becomes negative below a compensation temperature ($T^* = 208 \text{ K}$) under an applied field of +50 Oe while it is positive under -50 Oe. The two magnetization curves exhibit a mirror like behavior (Fig. 3). This phenomenon is known as temperature-induced magnetization reversal or negative magnetization. With increasing (positive) magnetic field, T^* decreases and the magnetization changes from negative to positive value at high-enough fields as shown in Fig. 4. This suggests that below T^* , the net magnetic moment initially aligned against the applied magnetic field is oriented along the applied direction at high magnetic fields.

To understand the origin of negative magnetization in $\text{BiFe}_{0.5}\text{Mn}_{0.5}\text{O}_3$, first of all, it is essential to know the crystallographic arrangement of magnetic ions. As discussed above, iron and manganese ions are not 1:1 ordered, which is consistent with the antiferromagnetic ground state. These

facts rule out the mechanism proposed by Néel for ferrimagnetic systems involving two different crystallographic sites or three magnetic sublattices. The present compound is similar to recently reported cation disordered perovskite $(\text{La}_{1-x/2}\text{Bi}_{x/2})(\text{Fe}_{0.5}\text{Cr}_{0.5})\text{O}_3$ where the magnetization reversal is explained based on clusters of canted antiferromagnetic $\text{La}_{1-x}\text{Bi}_x\text{FeO}_3$ and $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ which are coupled antiferromagnetically through dipolar interaction.²¹ These clusters with different magnetization vary independently with temperature and thus explain the magnetization reversal. This model may also be not applicable to the present compound because one of the end members, BiFeO_3 is antiferromagnetic ($T_N \sim 640 \text{ K}$) with a rhombohedral structure while the other end member, BiMnO_3 is ferromagnetic ($T_C \sim 105 \text{ K}$) with a highly distorted monoclinic structure. Instead, it appears that the situation is similar to that suggested for YVO_3 and $\text{Y}(\text{Fe},\text{Cr})\text{O}_3$ both possessing orthorhombic ($Pnma$) structure.^{4,15} In these oxides magnetization reversal is explained in terms of competing single-ion magnetic anisotropy and antisymmetric DM interactions.^{29,30} In antiferromagnetic materials having low symmetry, the appearance of weak ferromagnetism is predominantly determined by either single-ion magnetocrystalline anisotropy or DM interactions. In cases where both mechanisms operate, the net moments produced by these mechanisms lie in the same direction.¹⁶ However, it has been suggested that in some cases where the net moment produced by these mechanisms can be oriented in opposite direction and they can have different temperature dependence.^{15,16} Under this situation one can observe negative magnetization under low applied fields.

In the present case, BiFeO_3 is a canted antiferromagnet due to DM interaction.³¹ Substitution of Mn at the Fe site changes the structure from rhombohedral to orthorhombic where the oxygen octahedra are highly distorted which induces or increases the single-ion magnetocrystalline anisotropy. The net moment produced by this mechanism is believed to be oriented opposite to that produced by DM interaction.¹⁶ As we approach the 50% substitution, i.e., $\text{BiFe}_{0.5}\text{Mn}_{0.5}\text{O}_3$, the magnetocrystalline anisotropy dominates and therefore the net moment is aligned opposite to the applied field. As we apply large enough field to overcome the anisotropy, the net moment is switched to the field direction. This is demonstrated clearly by the following isothermal spin-reversal phenomenon.

In order to demonstrate a clear spin-reversal phenomenon, magnetic switching experiments have been performed at a few temperatures below T^* and the results at 175 K are shown in Fig. 5. In this experiment, the sample was first cooled to a particular temperature under 50 Oe field and then the field was increased to 1725 Oe in order to switch the magnetization to an equivalent and a positive value. This process was cycled several times to examine reproducibility of the switching behavior. It is clear from the figure that the magnetization can be switched between a positive and a negative value reversibly by just increasing the field to a nominally large field. In contrast to a ferromagnetic system, where two stable polar states are switched by changing the direction of the applied field, in the present case the polarity can be switched to any value by changing the field in the same direction. It is important to explore whether such a

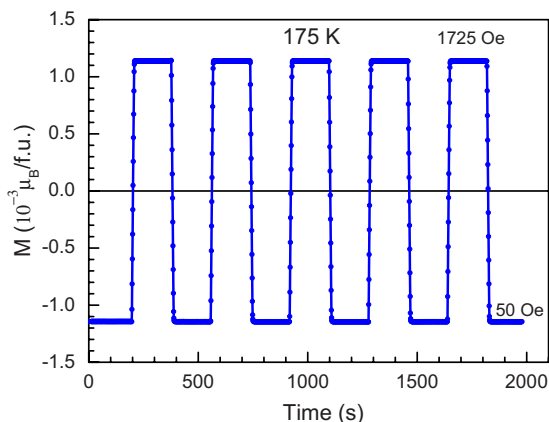


FIG. 5. (Color online) Magnetization versus time showing the reversal of magnetization with change in magnetic fields at 175 K.

phenomenon would be useful in device applications. A similar demonstration of spin reversal has recently been shown in a prussian-blue-type molecular magnet.³²

In order to further support the dominant role of single-ion magnetocrystalline anisotropy, we would like to compare the magnetic properties of a closely related compound $(\text{Bi}_{0.5}\text{La}_{0.5})(\text{Fe}_{0.5}\text{Mn}_{0.5})\text{O}_3$ prepared at ambient pressure by replacing 50% of Bi^{3+} ions by La^{3+} ions in $\text{BiFe}_{0.5}\text{Mn}_{0.5}\text{O}_3$.³³

This compound is also a canted antiferromagnet probably due to DM interaction but does not show negative magnetization or magnetization reversal down to lowest temperature measured. This can be explained on the basis of the crystal structure. Although the structure was reported to be orthorhombic from x-ray diffraction analysis, our recent neutron-diffraction study has shown that this compound $\text{Bi}_{0.5}\text{La}_{0.5}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_3$ has a rhombohedral structure where the oxygen octahedra are relatively less distorted and therefore the effect of single-ion anisotropy is not significant enough to exhibit negative magnetization.

In conclusion, we have shown that $\text{BiFe}_{0.5}\text{Mn}_{0.5}\text{O}_3$, synthesized at high pressure and high temperature, having the orthorhombic structure, exhibits magnetization reversal while changing the temperature and magnetic field. The negative magnetization is explained based on a competition between single-ion magnetic anisotropy and DM interactions. However, a microscopic understanding is necessary to design new materials exhibiting negative magnetization at higher temperatures.

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