Room-temperature ferroelectric polarization in multiferroic BiMnO$_3$

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Abstract

Single-phase multiferroic BiMnO$_3$ ceramic was synthesized via high-pressure and high-temperature solid-state reaction. Microstructure modification accompanied by emergence of superlattice due to electron-beam irradiation was observed wherein by means of electron diffraction (ED) combined with high-resolution transmission electron microscopy (HRTEM). It was clearly evidenced that the well-established C2 monoclinic substructure (I) of BiMnO$_3$ is metastable and prone to transform into a new pseudo-cubic superstructure (I*) with larger unit cell and higher symmetry. Magnetic characterization manifesting a unique ferromagnetic phase transition at 103 K has corroborated our speculation that as-prepared BiMnO$_3$ ceramic is free of polymorphism at room temperature. Weak ferromagnetism characterized by a well-saturated ferromagnetic hysteresis loop was manifested in the bulk BMO with Curie temperature $T_C \sim 105$ K. Modestly saturated ferroelectric hysteresis loops were observed at room temperature. In light of comprehensive evaluation, we can conclude the synthetic BiMnO$_3$ ceramic displays ferromagnetic and ferroelectric ordering simultaneously, i.e. ferroelectromagnetism below its ferromagnetic Curie temperature $T_M \sim 105$ K.

1. Introduction

Magnetoelectric multiferroic [1], sometimes termed ferroelectromagnet [2], with simultaneous ferroelectric and magnetic ordering has gained resurgence of research interest in the very recent years, because of the potential applications in the next-generation multifunctional electronic devices and fascinating physics. From the viewpoint of potential for device applications, two novel classes of memory elements can be expected due to the intrinsic magnetoelectric (ME) and magnetodielectric (MD) [3] or magnetocapacitance (MC) [4] effects in ferroelectromagnet. The former strategy is related to the substantial coupling and mutual control of electric polarization and magnetization. The latter strategy is associated with the alteration of dielectric permittivity or capacitance as a function of applied magnetic field. Tremendous potential applications including the emerging field of multiple state memory elements, spintronics, sensors, actuators and transducers have been envisaged in such a promising candidate, complementing purely ferroelectric and magnetic devices. From the viewpoint of fundamental physics, ferroelectromagnets are rare in nature, given that ferroelectricity and ferromagnetism are potentially exclusive and hard to compromise at least in oxides with d-electron metals [5]. An additional structural driving force must be present to engender the concurrence of ferroelectricity and ferromagnetism in a single-phase compound. Stereochemistry of electron lone pairs has proven to fulfill this kind of coexistence in the time-hornered multiferroic perovskite BiFeO$_3$. The same mechanism has been elaborated by first-principles computation in multiferroic BiMnO$_3$, exhibiting ferromagnetic super-exchange interactions in sharp contrast with antiferromagnetic BiFeO$_3$. In this presentation, we report the high-pressure synthesis and characterization of candidate multiferroic BiMnO$_3$. 

2. Experimental

The bulk BiMnO$_3$ ceramic was synthesized via high-pressure and high-temperature solid state reaction as
reported in our previous publication [6]. Selected area electron diffraction (SAED) patterns and high-resolution electron microscopy (HREM) images were collected with a Philips Tecnai F20 electron microscope equipped with a field emission gun operating at accelerating voltage of 200 kV. Magnetization measurement was carried out in a commercial MagLab System (Oxford Instruments, U.K. 2000). $P–E$ hysteresis loops were accomplished on TF ANALYZER 2000 ferroelectric tester at a fixed frequency of 1000 Hz.

3. Results and discussions

Room-temperature ferroelectric $P–E$ hysteresis loops measured at different electric field cycles were plotted in Fig. 1. Modestly saturated polarization was detected in the full range of applied electric fields. The spontaneous polarization $P_s$, remnant polarization $P_r$ and coercive field $E_c$ of the BiMnO$_3$ ceramic are 0.11, 0.06 $\mu$C/cm$^2$, and 0.5 kV/cm, respectively. These values are significantly lower than those reported by Santos et al. [7].

Magnetization as a function of temperature was performed at an applied magnetic field of 0.1 T after field cooling. As can been seen in Fig. 2, as-prepared BiMnO$_3$ ceramic is ferromagnetic, signaled by a sharp increase of magnetization below 105 K. The inset illustrates the ferromagnetic hysteresis loop measured at 5 K. The saturated magnetic moment is 3.14 $\mu_B$, which is comparable with the refined magnetic moment of 3.2 $\mu_B$ by neutron powder diffraction, but considerably smaller than the fully spin aligned value of 4 $\mu_B$ for high spin $3d^4$ Mn$^{3+}$. The significant reduction of spin contribution to magnetic moment may be attributed to somewhat spin canting induced by 6s$^2$ lone pairs of Bi$^{3+}$. Remnant magnetization $M_r$ and coercive field $H_c$ are 0.34 $\mu_B$/Mn and 0.02 T, respectively, suggestive of soft ferromagnetic behavior. It is noteworthy that the $M_r$ is far larger than that of antiferromagnetic counterpart BiFeO$_3$ (0.05 $\mu_B$/Fe) and BiCrO$_3$ (0.02 $\mu_B$/Cr) as a result of ferromagnetic arrangement of spins in BiMnO$_3$.

To shed further light on the origin of multiferroism in BiMnO$_3$, precise characterization of microstructure becomes indispensable. BiMnO$_3$ was primitively assigned to be a pseudo-triclinic perovskite without any superstructure lines being ascertained, and later refined to be a monoclinic (C2) superstructure (hereinafter denoted as I) by means of electron and neutron powder diffraction. In the light of electron diffraction (ED), both Chiba et al. and Montanari et al. have suggested the existence of room-temperature polymorphism in BiMnO$_3$ independent of the preparative conditions. They ascribed the polymorphism to be an intrinsic feature of BiMnO$_3$ quenched from high-pressure and high-temperature conditions. We performed electron diffraction (ED) combined with in situ high-resolution transmission electron microscopy (HRTEM) imaging of
selected BiMnO$_3$ single grains [8]. As shown in Fig. 3, the transition from $I$ to $I^*$ is not synchronous in different regions. As can be seen in the bottom left corner, the new superstructure $I^*$ with well-defined periodic modulation streaks has been well developed from C2 monoclinic structure $I$ after considerable exposure time to electron-beam irradiation. On prolonging the irradiation time, the new phase $I^*$ encroaches upon its adjacent virgin region of primitive phase $I$, as shown in the top right corner. The solid arrows indicate the aggression direction from $I^*$ to $I$.

This serendipitous observation indicates that the as-prepared BiMnO$_3$ ceramic is metastable at ambient pressure and easily transformed to a new polymorph under the irradiation of electron beam.

4. Conclusion

Coexistence of ferroelectricity and ferromagnetism in candidate magnetoelectric multiferroic BiMnO$_3$ below the ferromagnetic Curie temperature was unraveled. Super-lattice induced by electron-beam irradiation in as-synthesized BiMnO$_3$ was observed by ED combined with HREM.

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References