On magnetic properties of BiCrO₃ and BiMnO₃

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Abstract. We investigated magnetic properties of BiCrO₃ having the C₂/c symmetry and Bi₀.₉Y₀.₁CrO₃ having the Pnma symmetry with a = 5.5451(1) Å, b = 7.7185(2) Å, c = 5.3882(1) Å. Bi₀.₉Y₀.₁CrO₃ shows magnetic anomalies at Tₑₙ = 154 K due to an antiferromagnetic transition with weak ferromagnetism and frequency-dependent anomalies near 50 K with very large temperature shifts on both the real and imaginary parts of the ac susceptibilities (43 K at 0.5 Hz and 56 K at 300 Hz on χ''). Based on the results for Bi₀.₉Y₀.₁CrO₃, we could understand some peculiarities in magnetic properties of BiCrO₃. In particular, an orthorhombic modification of BiCrO₃ was found to exist in the monoclinic form. We also discuss magnetic properties of BiMnO₃ that shows more complicated behavior.

1. Introduction

Bi-containing perovskites have attracted much attention during the last decade as multiferroic and lead-free ferroelectric materials because of the presence of the stereochemically-active lone electron pair of a Bi³⁺ ion [1]. In multiferroic systems, two or all three of (anti)ferroelectricity, (anti)ferromagnetism, and ferroelasticity are observed in the same phase [1].

Despite the presence of Bi³⁺ ions in simple BiMO₃ compounds (M = transition metals), only BiFeO₃ (space group R3c) and BiCoO₃ (space group P4mm) definitely have polar structures at room temperature (RT) and ambient pressure (AP) (see Refs in [2]). BiNiO₃ crystallizes in the centrosymmetric space group P-1 (see Refs in [2]). BiCrO₃ and BiMnO₃ have the C₂/c symmetry [2, 3]. Despite of substantial work on BiMO₃, there are still some puzzling and unresolved problems. The structural and magnetic properties of BiFeO₃ are especially interesting [4, 5]. In the case of BiMnO₃ and BiCrO₃, the situation is also not simple. The static magnetic properties (dc magnetization and specific heat) seem to be explained and understood well. While the dynamic magnetic properties show additional anomalies.

In BiCrO₃, four anomalies of magnetic origin were found near 40, 75, 109, and 111 K [6]. The long-range antiferromagnetic order with weak ferromagnetism occurs at Tₑₙ = 109 K. The ac susceptibilities showed that the transition near Tₑₙ is a two-step transition. Additional frequency-independent broad anomalies were observed on the real part of the ac susceptibilities near 75 K. Below 40 K, frequency-dependent anomalies with very large temperature shifts were observed on both the real and imaginary parts of the ac susceptibilities. In BiMnO₃, even more anomalies were found on the imaginary part of the ac susceptibilities, at 5, 15, 84, 99, 104, and 112 K [7, 8].

In this work, we try to understand and explain at least some of the magnetic anomalies in BiCrO₃ and BiMnO₃.

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2. Experimental details
The synthesis of BiCrO$_3$ and BiMnO$_3$ is described in [2, 3]. Single-phase Bi$_{0.9}$Y$_{0.1}$CrO$_3$ was synthesized from a stoichiometric mixture of Bi$_2$O$_3$, Y$_2$O$_3$, and Cr$_2$O$_3$ at 6 GPa and 1550 K for 90 min in an Au capsule. dc magnetic susceptibilities, $\chi = M/H$, were measured on a SQUID magnetometer (Quantum Design, MPMS) between 2 and 300 K in an applied field of 100 Oe under both zero-field-cooled (ZFC) and field-cooled (FC; on cooling) conditions. Frequency dependent ac susceptibility measurements at zero static magnetic field were performed with a Quantum Design MPMS instrument from 250 to 2 K at frequencies ($f$) from 0.5 to 300 Hz and an applied oscillating magnetic field (H$_{ac}$) of 5 Oe.

3. Results and discussion
Figure 1 shows the inverse magnetic susceptibilities (measured at 100 Oe) of two BiCrO$_3$ samples prepared at slightly different conditions. Both samples were single-phase according to X-ray powder diffraction (XRD) data. In addition to the previously reported anomalies [6], we found an anomaly near 165 K on the FC curves. This anomaly can be detected only with a small magnetic field (e.g., 100 Oe), and it is completely suppressed by a large field (e.g., 10 kOe). The thermoremanent magnetization (TRM) curves as a function of temperature for BiCrO$_3$ showed more clearly the anomalies near 165 K (figure 2). The TRM curves were measured at zero magnetic field on heating after cooling the sample from 270 K to 2 K at 1 kOe. The origin of the anomaly at 165 K in BiCrO$_3$ could be understood only after magnetic studies of Bi$_{0.9}$Y$_{0.1}$CrO$_3$ having the $Pnma$ symmetry with $a = 5.5451(1)$ Å, $b = 7.7185(2)$ Å, $c = 5.3882(1)$ Å. Figure 3 shows the real and imaginary parts of the ac susceptibilities of Bi$_{0.9}$Y$_{0.1}$CrO$_3$. This sample shows anomalies at $T_N = 154$ K due to an antiferromagnetic transition with weak ferromagnetism and frequency-dependent anomalies near 50 K with very large temperature shifts on both the real and imaginary parts of the ac susceptibilities (43 K at 0.5 Hz and 56 K at 300 Hz on $\chi''$). YCrO$_3$ has $T_N = 142$ K. That is, $T_N$ decreases in orthorhombic solid solutions Bi$_{1-x}$Y$_x$CrO$_3$ with increasing $x$. Therefore, the anomaly at 165 K in BiCrO$_3$ most probably corresponds to the $T_N$ of the orthorhombic (O-) modification of BiCrO$_3$.

The O-modification of BiCrO$_3$ is stable above 420 K at AP [2, 6]. The O-phase is also formed at the synthesis conditions (that is, at high pressure and high temperature). During the transition from the orthorhombic to monoclinic modification in BiCrO$_3$ [9] or isostructural BiScO$_3$ [10] nanodomains (~10 nm) are formed. The O-modification of BiCrO$_3$ can remain, for example, in the domain boundaries and can be an integral part of the system. The O-modification still remained (by magnetization measurements) after cooling BiCrO$_3$ from 550 K to RT in 40 h at AP. That is, very slow cooling did not eliminate the O-phase. All reflections on XRD and neutron powder diffraction patterns of BiCrO$_3$ can be indexed in space group $C2/c$ (at RT). However, careful Rietveld analysis of XRD data showed that fits of some reflections were not good. Only the introduction of the second orthorhombic $Pnma$ modification greatly improved the fits and $R$ factors. The weight fraction of the $Pnma$ modification ($a = 5.5672(4)$ Å, $b = 7.7416(8)$ Å, $c = 5.4762(3)$ Å) is about 10-15 % in BiCrO$_3$. Therefore, the Rietveld analysis is consistent with the magnetization measurements. The magnetization measurements showed that sample 2 contained a larger amount of the O-modification compared with sample 1 (figures 1 and 2).

The frequency-dependent anomalies in Bi$_{0.9}$Y$_{0.1}$CrO$_3$ near 50 K with very large temperature shifts are much more pronounced than those of BiCrO$_3$ [6]. Therefore, their origin in BiCrO$_3$ seems to come from the presence of the $Pnma$ modification. These data raise another question how to explain such large ‘superparamagnetic-like’ [6] temperature shifts in Bi$_{0.9}$Y$_{0.1}$CrO$_3$. We note that the superparamagnetic-like anomalies in magnetic properties are sometimes explained by a phase separation. It is a possible scenario for orthorhombic Bi$_{0.9}$Y$_{0.1}$CrO$_3$ where domains of the monoclinic phase may emerge and move at low temperatures. In orthorhombic YCrO$_3$, only anomalies at $T_N$ were found on the ac susceptibilities without any anomalies at lower temperatures.

To summarize data on BiCrO$_3$, we believe that magnetic anomalies near 40 K and newly found anomalies near 165 K are originated from the intrinsic presence of the O-modification in the matrix of
the monoclinic modification. The anomalies at $T_N = 109$ K are related to a long-range G-type antiferromagnetic order of the $C2/c$ phase (with weak ferromagnetism and magnetic moments aligned along the $b$ direction [2]). The double-peak structure on the $\chi''$ vs $T$ curves near $T_N$ [6] can probably be explained by small compositional inhomogeneity or a specific phase separation during the transition from the O- to monoclinic modification, but more studies are needed. The anomalies near 75 K are originated from the spin rotation away from the $b$ axis keeping the G-type antiferromagnetic structure [11]. Therefore, almost all the magnetic anomalies in BiCrO$_3$ can be explained.

Here we give some comments on magnetic properties of BiMnO$_3$ [7, 8]. The very weak anomalies at 104 and 112 K that can be clearly detected only on the $\chi''$ vs $T$ curves [8] can be explained by the presence of other perovskite phases [12] (these temperatures are shifted with substitutions: 102 and 107 K in BiMn$_{0.91}$Al$_{0.09}$O$_3$ [13] and 114 and 117 K in BiMn$_{0.98}$Fe$_{0.02}$O$_3$ [14]). However, the increase of the magnetic transition temperature in BiMnO$_3$ was observed only in the case of Fe substitution [15]. It is possible that there is inhomogeneity in the oxygen content of BiMnO$_3$. However, no bulk single-phase examples are known for BiMnO$_{3-\delta}$ where the magnetic transition temperature would increase. The anomalies near 99-100 K in BiMnO$_3$ are well understood and originated from long-range ferromagnetic order (see Refs in [3]).

Two monoclinic modifications of BiMnO$_3$ are known at AP: the so-called phase I with orbital order and phase II stable between 474 and 768 K [3]. Orbital order disappears in phase II [3] or in another interpretation, there is different orbital order in phase II [16, 17]. Phase II can be stabilized by substitutions in BiMn$_{1-x}$M$_x$O$_3$ with M = Al, Sc, Cr, Fe, and Ga and 0.05 $\leq x \leq$ 0.2 [15]. The $T_C$ drops to about 80 K in phase II of BiMn$_{1-x}$M$_x$O$_3$ (except for M = Fe). The magnetic anomalies were observed near 84 K in BiMnO$_3$ [7, 8]. This temperature agrees well with the magnetic transition temperatures of phase II. The additional magnetic anomalies (along with $T_C = 109$ K) were observed near 98 K in BiMn$_{0.98}$Fe$_{0.02}$O$_3$ with the phase I structure [14], and the $T_C$ drops to 98 K in phase II of BiMn$_{0.9}$Fe$_{0.1}$O$_3$ [15]. Therefore, it seems that the $\chi''$ vs $T$ curves of BiMnO$_3$ [7, 8] and BiMn$_{0.98}$Fe$_{0.02}$O$_3$ [14] show the presence of phase II in the main phase I. Several scenarios can explain the appearance of phase II. First, it may appear during the quenching and pressure release after the synthesis similar to the appearance of the O-phase in BiCrO$_3$. Second, it may appear due to compositional (oxygen) inhomogeneity and small non-stoichiometry. Third, the orbital order of phase I may be rather unstable and fluctuate between different states [17]. The effect of the orthorhombic BiMnO$_3$ phase should not be ruled out because $T_N = 80$ K of orthorhombic weakly ferromagnetic Bi$_{0.3}$La$_{0.7}$MnO$_3$ and $T_N = 100$ K of Bi$_{0.5}$La$_{0.5}$MnO$_3$ (but interpolation gives $T_N$ lower than 80 K for a hypothetical orthorhombic BiMnO$_3$). It is obvious that more work will be needed to fully understand the magnetic properties of BiMnO$_3$.

**Figure 1.** Inverse ZFC (open circles) and FC (filled circles) magnetic susceptibilities for two BiCrO$_3$ samples measured with $H = 100$ Oe.

**Figure 2.** TRM curves for two BiCrO$_3$ samples.
Figure 3. Real ($\chi'$) and imaginary ($\chi''$) parts of the ac susceptibilities of orthorhombic Bi$_{0.9}$Y$_{0.1}$CrO$_3$ measured with $H_{ac} = 5$ Oe and at $H_{dc} = 0$ Oe. The curves at three frequencies (2, 25, and 300 Hz) are shown for the clarity.

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