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$Bi_3Mn_3O_{11}$: A New $KSbO_3$-Type Random Ferrimagnet with High T_C

Alexei A. Belik* and Eiji Takayama-Muromachi

International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Received May 25, 2009; E-mail: Alexei.Belik@nims.go.jp

ABO_3 compounds crystallize in a number of structure types including perovskite, pyroxene, corundum, ilmenite (ordered corundum), hexagonal manganites, bixbyite, rare earth sesquioxide structures (C, B, and A types), $PbReO_3$, $KSbO_3$, $AlFeO_3$, and others.[1] Some of these families have a tremendous number of representatives, for example, perovskites, while others have just a few; for example, only $GaFeO_3$ is isostructural with $AlFeO_3$.[2] In addition to a large number of cation variations, perovskite-type compounds can adopt oxygen and cation deficiency $ABO_{3-\delta}$ and $A_{1-x}B_{1-y}O_3$. These variable parameters (δ, x, and y) and ordering of vacancies create many possibilities.[3] Applications of perovskites range in use from catalysts or sensors to superconductors, ferromagnetic, or ferroelectric materials. There is continuous interest in some families of ABO_3 compounds (e.g., perovskite, pyroxene, hexagonal manganites), although some families were almost "forgotten". The revival of multiferroic materials[4] brings new interest, for example, to $GaFeO_3$ and $AlFeO_3$.[5]

The $KSbO_3$-type family is one of the "forgotten" families probably because no interesting physical properties have been reported so far. However, from a structural point of view, this family is interesting because it can adopt three interpenetrating networks[6] with the composition changing from ABO_3 ($KSbO_3$ and $KIrO_3$)[7] to $ABO_{3.667}$ ($Bi_3GaSb_2O_{11}$, $Bi_3AlSb_2O_{11}$, $Bi_2NaSb_3O_{11}$, $Bi_3Ru_3O_{11}$, and $La_3Ru_3O_{11}$).[8−11] $Pb_6Re_6O_{19}$ with intermediate oxygen content was also reported.[12] In this work, we prepared another member of the $KSbO_3$-type family, namely $Bi_3Mn_3O_{11}$, using a high-pressure technique. $Bi_3Mn_3O_{11}$ was found to be a ferrimagnet with a rather high transition temperature of 150 K despite the fact that Mn^{3+} (or Mn^{4+}) and Mn^{5+} ions are statistically distributed in one crystallographic site.

$Bi_3Mn_3O_{11}$ was prepared from stoichiometric mixtures of Bi_2O_3 (99.9999%), MnO_2 (99.997%), and $Bi_2O_{4.20}$ (99%). The phase purity and oxygen content of MnO_2 were confirmed by X-ray powder diffraction and thermogravimetric analysis (TGA). The oxygen content of commercial product "Bi_2O_5" was found to be $Bi_2O_{4.20}$ by TGA. The synthesis was performed in a belt-type high pressure apparatus at 6 GPa and 1600 K for 40 min in Pt capsules. Synchrotron X-ray powder diffraction (SXRD) data were collected on a large Debye−Scherrer camera at the BL02B2[13] beamline of SPring-8 from 100 to 740 K (λ = 0.423 28 Å). Diffraction data were analyzed by the Rietveld method with RIETAN-2000.[14] Temperature- and field-dependent magnetization was measured on a SQUID magnetometer (Quantum Design, MPMS) between 2 and 400 K under both zero-field-cooled (ZFC) and field-cooled (FC; on cooling) conditions.

$Bi_3Mn_3O_{11}$ was found to be isostructural with $Bi_3GaSb_2O_{11}$ and $Bi_3Ru_3O_{11}$, and we used fractional coordinates of $Bi_3GaSb_2O_{11}$ as initial ones in the refinement of the crystal structure of $Bi_3Mn_3O_{11}$.[8] The Bi1 atom was found to be disordered in $Bi_3Mn_3O_{11}$ similar to $Bi_3GaSb_2O_{11}$.[8] Final fractional coordinates, thermal parameters (B), lattice parameters, and R factors at RT are listed in Table 1, and selected bond lengths in the Supporting Information (SI). Figure 1 displays observed, calculated, and difference SXRD patterns at RT. The inset of Figure 1 shows the connections between MnO_6 octahedra. There are dimer units formed by the edge-shared (through O2) octahedra; these dimers are connected by corners (O3) into a three-dimensional structure.

Table 1. Structure Parameters of $Bi_3Mn_3O_{11}$ at RT[a]

site		x	y	z	B (Å^2)
Bi1	24*h*	0.4067(2)	0.379 69(10)	= *y*	0.89(3)
Bi2	4*b*	0	0	0	0.829(14)
Mn	12*g*	0.4061(2)	0.75	0.25	0.22(3)
O1	8*e*	0.1467(5)	= *x*	= *x*	0.8(2)
O2	12*f*	0.6190(8)	0.25	0.25	0.71(16)
O3	24*h*	0.5902(6)	0.2476(5)	0.5420(8)	0.54(14)

[a] Note: Space group is $Pn\bar{3}$ (No. 201) at origin choice 2, Z = 4, a = 9.16336(11) Å, and V = 769.421(16) Å^3. R factors were R_{wp} = 2.84%, R_p = 1.83%, R_B = 2.04%, and R_F = 1.42%. The occupation factor g = $^1/_3$ for Bi1, and g = 1 for other sites.

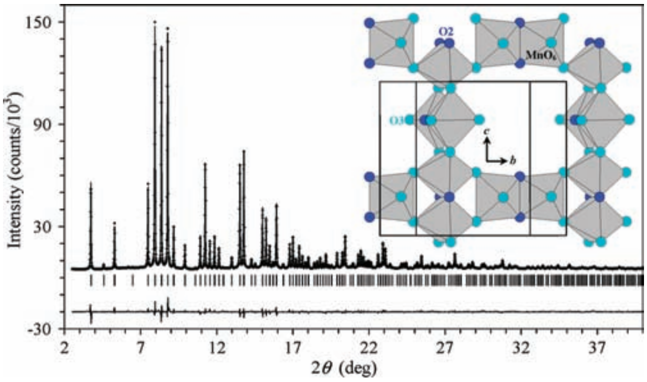

Figure 1. Portions of observed (crosses), calculated (solid line), and difference SXRD patterns for $Bi_3Mn_3O_{11}$ at 293 K. Bragg reflections are indicated by tick marks. Inset shows connections between MnO_6 octahedra in $Bi_3Mn_3O_{11}$ (one layer in the *bc* plane is shown; the view is slightly tilted along the *a* axis).

Figure 2a shows χ vs T and χ^{-1} vs T curves between 2 and 400 K. A sharp increase of magnetic susceptibilities was observed below T_C = 150 K indicating a ferromagnetic-like transition. However, the transition was rather smeared as it can be seen from broad peaks on the d(χT)/dT vs T and *ac* susceptibility curves (see SI) probably because of the structural disorder. The large difference was observed between the ZFC and FC curves below ~30 K at 100 Oe and 20 K at 1 kOe. This behavior resembles a glassy transition. *ac*-Susceptibility measurements confirmed glassy behavior: we found strong frequency dependence and no *ac*-field dependence near 30 K. On the other hand, we found no frequency dependence near 150 K but observed *ac*-field dependence on the imaginary part due to interactions of the *ac*-field with domain structures. The FC χ^{-1}

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vs T curve (at 100 Oe) was fit by the simple Curie−Weiss equation between 300 and 400 K. The effective magnetic moment was calculated to be 6.27 μ_B per formula unit (f.u.), and the Curie−Weiss temperature is 222 K.

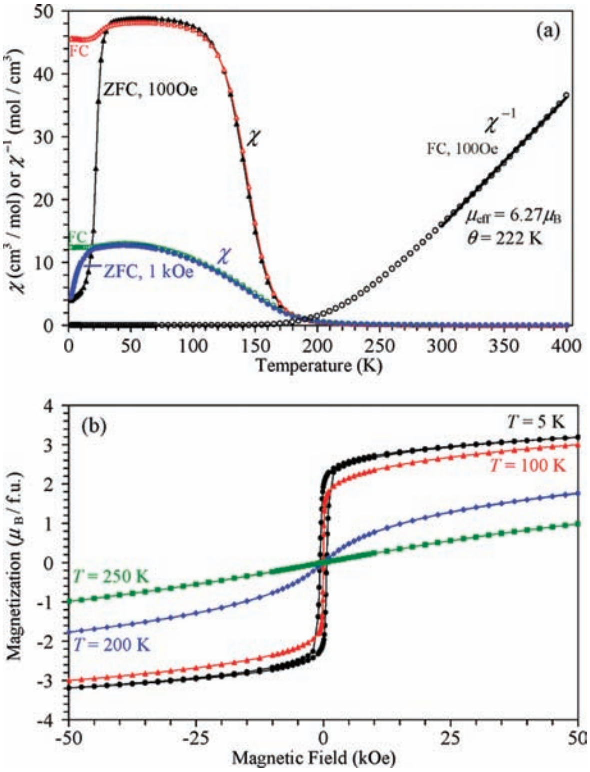

Figure 2. (a) Temperature dependence of magnetic susceptibilities (χ) of $Bi_3Mn_3O_{11}$ measured at 100 Oe and 1 kOe under ZFC and FC conditions between 2 and 400 K. The FC χ^{-1} vs T curve (100 Oe) is also shown with the fitting results. (b) Isothermal magnetization curves at 5, 100, 200, and 250 K between −50 and 50 kOe.

The oxidation states in $Bi_3Mn_3O_{11}$ can be written as $Bi_3Mn^{3+}Mn^{5+}{}_2O_{11}$ (μ_{eff}(calc) = 6.33 μ_B) or $Bi_3Mn^{4+}{}_2Mn^{5+}O_{11}$ (μ_{eff}(calc) = 6.16 μ_B). Therefore, it is rather difficult to determine the real ones. Using the analogy with $Bi_3Ga^{3+}Sb^{5+}{}_2O_{11}$ we can assume that the oxidation states should be $Bi_3Mn^{3+}Mn^{5+}{}_2O_{11}$. However, this question needs further study. In any case, Mn^{5+} ions should present, and Mn^{5+} is very rare in oxides. We should emphasize that, with the synthesis conditions used, we could not prepare a pyrochlore phase with Mn^{4+} ($Bi_2Mn^{4+}{}_2O_7$). $Bi_3Mn_3O_{11-\delta}$ (not $Bi_2Mn_2O_7$) was formed as an impurity during the course of studies on oxygen nonstoichiometric perovskites $BiMnO_{3+\delta}$ (see SI).[15]

Figure 3b gives the isothermal magnetization curves. The magnetization reaches 3.19 μ_B per f.u. at 5 K and 50 kOe. Because the full magnetization should be 8 μ_B per f.u., these data indicate that $Bi_3Mn_3O_{11}$ behaves as a ferrimagnet. At 5 K, the coercive field (H_c) was ~650 Oe (showing that it is a soft ferrimagnet), and the remnant magnetization (M_r) was ~1.92 μ_B. There is only one crystallographic Mn site. It means that Mn^{3+} and Mn^{5+} ions are distributed statistically. Noncompensated magnetic moments may appear due to antiferromagnetic interactions between Mn^{3+} (d^4) and Mn^{5+} (d^2) ions and due to ferromagnetic interactions between adjacent Mn^{3+} ions (for example, ferromagnetism is realized in $BiMn^{3+}O_3$).[16] We note that there is a noticeable deviation of the inverse magnetic susceptibilities from the linear Curie−Weiss behavior far above 150 K. This fact may indicate that magnetic correlations take place at higher temperatures; however, a long-range magnetic transition takes place only at 150 K due to disordering.

The TGA and *in situ* high-temperature SXRD data showed that $Bi_3Mn_3O_{11}$ gradually loses oxygen on heating forming several intermediate phases with the same structure (e.g., $Bi_3Mn_3O_{10.45}$ at 740−770 K) (see SI). Oxygen vacancies are formed at the O1 site, which is not involved in the Mn coordination and the construction of the main framework. Magnetic properties strongly depend on the oxygen content (T_C increases to 210 K and saturation magnetization decreases to 1.7 μ_B at 5 K and 50 kOe for $Bi_3Mn_3O_{11}$ heated up to 740 K (see SI)). Above 900 K, $Bi_3Mn_3O_{11}$ decomposes to $Bi_2Mn_4O_{9+\delta}$ and $Bi_{25}MnO_{39+\delta}$.

The Bi−Mn−O system has a number of interesting compounds including multiferroic perovskites $BiMnO_{3\pm\delta}$ and $(BiMn_3)Mn_4O_{12}$.[15−18] It was shown that their magnetic properties strongly depend on the oxygen content.[15,18] Unusual magnetic properties were recently found in bismuth−manganese oxynitrate $Bi_3Mn_4O_{12}(NO_3)$.[19] In our work, we found another compound in the Bi−Mn−O system. We hope that the discovery of interesting magnetic and chemical properties in $Bi_3Mn_3O_{11}$ will revive interest in the $KSbO_3$ family of compounds, which is rather adaptive considering the cation variations and oxygen content.

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Supporting Information Available: SXRD patterns and structural parameters at different temperatures, TGA/DSC results, EPMA, *ac* susceptibilities, specific heat, differential magnetization, structural figures. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Giaquinta, D. M.; zur Loye, H.-C. *Chem. Mater.* **1994**, *6*, 365.
(2) Bouree, F.; Baudour, J. L.; Elbadraoui, E.; Musso, J.; Laurent, C.; Rousset, A. *Acta Crystallogr., Sect. B* **1996**, *52*, 217.
(3) Antipov, E. V.; Abakumov, A. M.; Istomin, S. Y. *Inorg. Chem.* **2008**, *47*, 8543.
(4) (a) Fiebig, M. *J. Phys. D: Appl. Phys.* **2005**, *38*, R123. (b) Hill, N. A. *J. Phys. Chem. B* **2000**, *104*, 6694.
(5) Jung, J. H.; Matsubara, M.; Arima, T.; He, J. P.; Kaneko, Y.; Tokura, Y. *Phys. Rev. Lett.* **2004**, *93*, 037403.
(6) Sleight, A. W.; Bouchard, R. J. *Inorg. Chem.* **1973**, *12*, 2314.
(7) Hoppe, R.; Claes, K. *J. Less-Common Metals* **1975**, *43*, 129.
(8) Ismunandar; Kennedy, B. J.; Hunter, B. A. *Solid State Commun.* **1998**, *108*, 649.
(9) Champarnaud-Mesjard, J. C.; Frit, B.; Aftati, A.; El Farissi, M. *Eur. J. Solid State Inorg. Chem.* **1995**, *32*, 495.
(10) (a) Facer, G. R.; Elcombe, M. M.; Kennedy, B. J. *Aust. J. Chem.* **1993**, *46*, 1897. (b) Abraham, F.; Thomas, D. *Bull. Soc. Chim. Fr.* **1975**, 25.
(11) (a) Cotton, F. A.; Rice, C. E. *J. Solid State Chem.* **1978**, *25*, 137. (b) Abraham, F.; Trehoux, J.; Thomas, D. *Mater. Res. Bull.* **1978**, *13*, 805.
(12) Abakumov, A. M.; Shpanchenko, R. V.; Antipov, E. V. *Z. Anorg. Allg. Chem.* **1998**, *624*, 750.
(13) Nishibori, E.; Takata, M.; Kato, K.; Sakata, M.; Kubota, Y.; Aoyagi, S.; Kuroiwa, Y.; Yamakata, M.; Ikeda, N. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2001**, *467−468*, 1045.
(14) Izumi, F.; Ikeda, T. *Mater. Sci. Forum* **2000**, *321−324*, 198.
(15) Belik, A. A.; Kolodiazhnyi, T.; Kosuda, K.; Takayama-Muromachi, E. *J. Mater. Chem.* **2009**, *19*, 1593.
(16) Kimura, T.; Kawamoto, S.; Yamada, I.; Azuma, M.; Takano, M.; Tokura, Y. *Phys. Rev. B* **2003**, *67*, 180401(R).
(17) Imamura, N.; Karppinen, M.; Motohashi, T.; Fu, D.; Itoh, M.; Yamauchi, H. *J. Am. Chem. Soc.* **2008**, *130*, 14948.
(18) Imamura, N.; Karppinen, M.; Yamauchi, H. *Chem. Mater.* **2009**, *21*, 2179.
(19) Smirnova, O.; Azuma, M.; Kumada, N.; Kusano, Y.; Matsuda, M.; Shimakawa, Y.; Takei, T.; Yonesaki, Y.; Kinomura, N. *J. Am. Chem. Soc.* **2009**, *131*, 8313.

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