Synthesis and characterization of multiferroic BiMn$_7$O$_{12}$

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We report on the high pressure synthesis of BiMn$_7$O$_{12}$, a manganite displaying a "quadruple perovskite" structure. Structural characterization of single crystal samples shows a distorted and asymmetrical coordination around the Bi atom, due to presence of the 6s$^2$ lone pair, resulting in non-centrosymmetric space group Im, leading to a permanent electrical dipole moment and ferroelectric properties. On the other hand, magnetic characterization reveals antiferromagnetic transitions, in agreement with the isostructural compounds, thus evidencing two intrinsic properties that make BiMn$_7$O$_{12}$ a promising multiferroic material.

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Multiferroics are defined as materials that simultaneously exhibit more than one ferroic order parameter among ferromagnetism, ferroelectricity and ferroelasticity. Although there are a lot of compounds presenting magnetic or ferroelectric order, the constrains required for their coexistence are so severe that only an extremely limited number of multiferroic materials exists. Besides scientific interest in their physical properties, multiferroics have potential for technological applications as actuators, switches, magnetic field sensors or new types of electronic memory devices. However, at present, only magnetoelectric composites, realized by combining magnetostrictive and piezoelectric materials, are ready for technological applications. Typical multiferroics belong to the group of the perovskite transition metal oxides, and include rare-earth manganites and ferrites (TbMn$_2$O$_4$, HoMn$_2$O$_5$, LuFe$_2$O$_4$), bismuth-based compound BiFeO$_3$ non-oxides (BaNiF$_2$) and spined chalcogenides (ZnCr$_2$Se$_2$). In usual perovskite-based materials, the ferroelectric distortion occurs due to the displacement of B-site cation (for example, Ti in BaTiO$_3$) with respect to the oxygen octahedral coordination. One possible mechanism for the coexistence of ferroelectricity and magnetism, is the presence in the A-site of an atom carrying a non-bonding pair of electrons in an outer shell (lone pair), whose stereochemical effect may be at the origin of ferroelectricity, while partially filled d orbitals on the B site should be responsible for the magnetic behavior. Examples include BiFeO$_3$ and PbVO$_3$. In these materials, the 6s$^2$ lone-pair on the A-site cation (Bi$^{3+}$, Pb$^{2+}$) causes the Bi/Pb 6p (empty) orbital to come closer in energy to the O 2p orbitals. This leads to the hybridization between the Bi/Pb 6p and O 2p orbitals and drives the off-centering of the cation towards the neighboring anion resulting in ferroelectricity. BiMn$_7$O$_{12}$ is a metastable material, belonging to the family of "quadruple-perovskite" manganites, with general formula AA$'_3$B$_4$O$_{12}$,$^{11,12,13}$ derived by the doubling of the conventional ABO$_3$ manganites axes. The complex and highly distorted structure is based on a 3D network of corner-sharing MnO$_6$ tilted octahedra, centred on the B site; it can only be accommodated under high pressure by the presence of a Jahn-Teller atom (Mn$^{3+}$ or Cu$^{2+}$) on the A' site, displaying an uncommon square planar coordination due to large distortion of the standard dodecahedral coordination, typical of the A site. Since the occupation of the A site determines the properties of the compounds, the motivation of this work is the synthesis of the Bi-substitute member and to correlate the structural distortion induced by the Bi$^{3+}$ lone pair to the electronic properties, in particular searching for multiferroic properties.

BiMn$_7$O$_{12}$ was synthesized by solid state reaction in high pressure/high temperature (HP/HT) conditions. Stoichiometric mixture of Mn$_2$O$_3$ (Ventron 98%) and Bi$_2$O$_3$ (Merck 99%) was used as reagent. They were mixed,
TABLE I: Atomic coordinates and parameters for BiMn$_7$O$_{12}$. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor. Anisotropic displacement parameters: $U_{ij} = \exp(-2\pi^2(U_{11}h^2(a^*)^2 + ... + 2U_{12}hk(a^*)(b^*) + ...))$.

| Atom | x     | y     | z     | $U_{eq}$ | $U_{11}$ | $U_{12}$ | $U_{13}$ | $U_{22}$ | $U_{23}$ | $U_{33}$ |
|------|-------|-------|-------|----------|----------|----------|----------|----------|----------|----------|
| Bi   | 0.0284(6) | 0 | 0.0173(6) | 0.0255(3) | 0.0247(8) | 0.0307(3) | 0.0210(5) | 0 | -0.0028(4) | 0 |
| Mn1  | 0.0030(30) | 0 | 0.4551(3) | 0.0166(6) | 0.0066(15) | 0.0185(10) | 0.0066(16) | 0 | -0.0041(10) | 0 |
| Mn2  | 0.4997(4)  | 0 | 0.5019(4) | 0.0102(6) | 0.0142(15) | 0.0101(9) | 0.0069(13) | 0 | -0.0041(11) | 0 |
| Mn3  | 0.4955(2)  | 0 | -0.0022(4) | 0.0161(6) | 0.0034(14) | 0.0082(9) | 0.0185(14) | 0 | -0.0049(10) | 0 |

| Mn4  | 0.2542(3) | 0.7419(3) | 0.2540(3) | 0.0080(10) | 0.0076(6) | 0.0093(8) | -0.0020(7) | -0.0031(7) | -0.0030(8) |
| Mn5  | 0.2476(2) | 0.7493(17) | 0.0067(5) | 0.0066(12) | 0.0084(6) | 0.0049(10) | -0.0016(5) | -0.0046(7) | 0.0006(6) |
| O1   | 0.3366(19) | 0.1827(18) | 0.015(2) | 0.006(5) | 0.023(5) | 0.015(6) | 0 | -0.0074(7) | 0 |
| O2   | 0.1916(19) | 0.6755(19) | 0.017(2) | 0.010(6) | 0.023(5) | 0.017(6) | 0 | -0.0074(7) | 0 |
| O3   | 0.1742(18) | 0.3031(18) | 0.004(5) | 0.029(6) | 0.017(6) | 0 | -0.0011(4) | 0 |
| O4   | 0.825(2)  | 0.3094(19) | 0.020(3) | 0.012(6) | 0.029(6) | 0.017(6) | 0 | -0.0105(5) | 0 |
| O5   | 0.4910(16) | 0.8086(13) | 0.0196(19) | 0.0164(4) | 0.028(4) | 0.0154(5) | -0.0145(4) | -0.0155(5) | -0.0086(6) |
| O6   | 0.3081(15) | 0.8259(10) | -0.0105(14) | 0.0192(15) | 0.0194(4) | 0.0164(4) | 0.023(4) | 0.0013(3) | -0.0093(3) |
| O7   | 0.0167(14) | 0.6830(13) | 0.1765(15) | 0.0094(4) | 0.031(4) | 0.0194(4) | -0.0103(4) | -0.0063(6) | -0.0104(3) |
| O8   | 0.6796(15) | 0.1800(10) | 0.0112(13) | 0.0162(15) | 0.0174(4) | 0.0154(5) | 0.016(4) | 0.0003(3) | -0.0083(3) |

TABLE II: Interatomic distances (Å).

| Atoms | Distance | Atoms | Distance |
|-------|----------|-------|----------|
| Bi-O1 | 2.392(14) | Mn3-O6 | 2x1.910(10) |
| Bi-O6 | 2x2.481(9) | Mn3-O8 | 2x1.923(10) |
| Bi-O7 | 2x2.631(10) | Mn4-O7 | 1.920(12) |
| Bi-O4 | 2.706(13) | Mn4-O5 | 1.922(13) |
| Bi-O2 | 2.872(15) | Mn4-O1 | 1.969(6) |
| Bi-O1 | 2.874(14) | Mn4-O3 | 2.035(5) |
| Bi-O8 | 2x2.945(11) | Mn4-O8 | 2.076(11) |
| Mn3-O6 | 2.130(11) | Mn5-O8 | 1.897(10) |
| Mn5-O8 | 1.907(14) | Mn5-O1 | 1.987(10) |
| Mn5-O6 | 1.916(16) | Mn5-O2 | 1.961(11) |
| Mn5-O3 | 1.943(16) | Mn5-O2 | 1.969(6) |
| Mn5-O2 | 1.956(13) | Mn6-O2 | 1.986(6) |
| Mn5-O4 | 2x1.887(11) | Mn6-O5 | 2.087(12) |
| Mn6-O7 | 2x1.925(10) | Mn6-O7 | 2.163(11) |

The crystal structure of BiMn$_7$O$_{12}$ at RT was determined by single crystal X-ray diffraction. Intensity data were collected by using MoK$_{\alpha}$ data in the range 3.79 $\leq \theta \leq 28.83^\circ$ on a Bruker AXS Smart diffractometer, equipped with a CCD area-detector. The structure is monoclinic, with lattice parameters $a = 7.5351(15)$, $b = 7.3840(15)$, $c = 7.5178(15)$ Å and $\beta = 91.225(3)^\circ$. The cell volume is $V = 418.19(15)$ Å$^3$, consistent with 2 formula units per cell. In analogy with other monoclinic AMn$_7$O$_{12}$ compounds, the structure was initially refined with SHELX97 in the centrosymmetric space group I2/m, using anisotropic atomic displacements parameters (a.d.p.’s) for all the atoms. The refinement converged to $R_1 = 0.0535$, $wR_2 = 0.1413$ and g.o.f = 1.101 for 562 data and 59 parameters. In spite of the fact that these final agreement indices can be considered satisfactory, when the sole numeric values are considered, a careful inspection of the refined parameters points out a very unusual trend of the a.d.p.’s showing, in particular for the oxygen atoms, not only very high values but also an anomalous elongation in a common direction of the ac plane (Fig.1), that indicates static disorder. Therefore the possibility of an artifact induced by forcing an acentric structure in a centric symmetry was taken into account and the structure was further refined in the noncentrosymmetric I2 and Im space groups. While the results obtained in I2 are comparable to those of the centrosymmetric model, the ones produced in Im are characterized by a significant improvement in terms of agreement indices ($R_1 = 0.0391$, $wR_2 = 0.0928$ and g.o.f = 1.113 for 1082 data and 103 parameters) and a.d.p.’s. The latter is clearly evidenced in Fig.1, that shows a comparison of the ORTEP plots of the crystal structure of BiMn$_7$O$_{12}$ refined in both Im and I2/m, in which the a.d.p.’s are represented by ellipsoids drawn at the 50% probability level. Atomic parameters, refined in the acentric space group Im, and relevant bond distances are shown in Table II and III respectively. Charge distribution analysis, performed with CHARDIS, indicates a 3+ oxidation state for all the Mn atoms. The decrease of symmetry from the centrosymmetric space group I2/m, typical of other monoclinic A$^{3+}$Mn$_7$O$_{12}$ compounds, to Im in BiMn$_7$O$_{12}$ is mainly determined by the steric hindrance of the 6$s^2$ lone pair of the Bi$^{3+}$ ion. This typically produces a quite distorted coordination around the Bi atom, with the strongest bonds lying on the same side in order
to accommodate the lone pair on the opposite one. Structural data suggest that the Bi atom moves out from the center of the icosahedral oxygen coordination determining an asymmetrical coordination. An electrical polarization of 7.33 $\mu$C/cm$^2$ at RT, generated by the displacement of all the Bi atoms in a common direction, can be computed by a simple model as dipole moment for volume unit, suggesting the existence of ferroelectricity in BiMn$_7$O$_{12}$. A similar value was reported for the simple perowskite BiFeO$_3$, where a spontaneous polarization of 6.1 $\mu$C/cm$^2$ was measured at 77 K on bulk samples. This hypothesis is further supported by TEM investigations, performed on a Philips TECNAI F20 transmission electron microscope operating at 200 KV, which show the presence of twinning domains extending on a few tens of nanometers, evidenced in Fig. 2a and Fig. 2b by sharp contrast variations. The domains orientation is consistent with the inversion of the polar axis, namely the shift of the Bi ions in opposite directions.

The magnetic properties of BiMn$_7$O$_{12}$ have been studied using a SQUID magnetometer. The measurements were carried out on polycrystalline samples because the single crystals yielded a too weak signal, approaching the instrumental sensitivity. The Zero Field Cooled (ZFC) and Field Cooled (FC) DC magnetization curves in applied magnetic field $H = 10$ Oe are reported in Fig. 3 (upper panel), where a sharp transition to antiferromagnetic regime at $T_c \approx 50$ K can be seen. The antiferromagnetic nature of the ordered phase is more clear looking at the inverse susceptibility shown in Fig. 3 (lower panel), where one can also estimate the Curie-Weiss temperature $\theta \approx 206$ K. The anomaly at $T$...
A. Prodi, E. Gilioli, A. Gauzzi, F. Licci, M. Marezio, F. Bolzoni, E. Gilioli, Q. Huang, A. Santoro, and J.W. Lynn, Nature Materials 3, 48 (2004).

Detailed structural characterization carried out by single crystal X-ray diffraction yields the definition of a non-centrosymmetric space group (Im) never observed before in this class of compounds. This feature is originated by the stereochemical effect induced by the presence of the 6s² lone pair of the Bi³⁺ ions, that induces an asymmetrical coordination of the oxygen neighbors, leading to a permanent electrical dipole moment. Magnetic characterization points out, in agreement with isostructural compounds, the presence of antiferromagnetic transitions at 50 and 26 K should correspond to the ordering of the B and A’ sites respectively. The coexistence of the two ferroic orders makes of BiMn₇O₁₂ a new promising multiferroic material.

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J. Wang, J.B. Neaton, H. Zheng, V. Nagarajan, S.B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D.G. Schlom, U.V. Waghmare, N.A. Spaldin, K.M. Rabe, M. Wuttig, and R. Ramesh, Science 299, 1719 (2003).

C. Ederer and N.A. Spaldin, Phys. Rev. B 74, 024102 (2006).

T. Rudolf, Ch. Kant, F. Mayr, J. Hemberger, V. Tsurkan, and A. Loidl, Phys. Rev. B 75, 054210 (2007).

H.D. Megaw, Acta Cryst. 5, 739 (1952).

D.J. Singh, Phys. Rev. B 73, 094102 (2006).

A. Prodi, E. Gilioli, A. Gauzzi, F. Licci, M. Marezio, F. Bolzoni, Q. Huang, A. Santoro, and J.W. Lynn, Nature Materials 3, 48 (2004).

A. Prodi, F. Licci, R. Cabassi, F. Bolzoni, E. Gilioli, Q. Huang, A. Santoro, J.W. Lynn, M. Affronte, A. Gauzzi and M. Marezio, to be published.

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1. H. Schmid, Ferroelectrics 162, 317 (1994).
2. Ce-Wen Nan, M.I. Bichurin, Shuxiang Dong, D. Viehland, and G. Srinivasan, J. Appl. Phys. 103, 031101 (2008).
3. T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Nature 426, 55 (2003).
4. G.R. Blake, L.C. Chapon, P.G. Radaelli, S. Park, N. Hur, S-W. Cheong, and J. Rodriguez-Carvajal, Phys. Rev. B 71, 214402 (2005).
5. N. Ikeda, H. Ohsumi, K. Ohwada, K. Ishii, T. Inami, K. Kakurai, Y. Murakami, K. Yoshii, S. Mori, Y. Horibe, and H. Kitô, Nature 436, 1136 (2005).
6. J. Wang, J.B. Neaton, H. Zheng, V. Nagarajan, S.B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D.G. Schlom, U.V. Waghmare, N.A. Spaldin, K.M. Rabe, M. Wuttig, and R. Ramesh, Science 299, 1719 (2003).
7. C. Ederer and N.A. Spaldin, Phys. Rev. B 74, 024102 (2006).
8. T. Rudolf, Ch. Kant, F. Mayr, J. Hemberger, V. Tsurkan, and A. Loidl, Phys. Rev. B 75, 054210 (2007).
9. H.D. Megaw, Acta Cryst. 5, 739 (1952).
10. D.J. Singh, Phys. Rev. B 73, 094102 (2006).
11. A. Prodi, E. Gilioli, A. Gauzzi, F. Licci, M. Marezio, F. Bolzoni, Q. Huang, A. Santoro, and J.W. Lynn, Nature Materials 3, 48 (2004).
12. A. Prodi, F. Licci, R. Cabassi, F. Bolzoni, E. Gilioli, Q. Huang, A. Santoro, J.W. Lynn, M. Affronte, A. Gauzzi and M. Marezio, to be published.