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Local distortions in multiferroic BiMnO$_3$ as a function of doping

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Abstract

The structure of doped BiMnO$_3$ was studied using synchrotron x-ray powder diffraction. The dopants included isovalent magnetic and non-magnetic ions in the magnetic Mn sublattice (BiMn$_{1-x}$M$_x$O$_3$ with $M =$ Cr, Fe and Ga), isovalent ions in the Bi sublattice (Bi$_{0.9}$La$_{0.1}$MnO$_3$) and isovalent self-dopants (Bi$_{0.95}$MnO$_{2.925}$). The results indicate that at low doping levels, the orbitally ordered structure (C2/c(I)) of BiMnO$_3$ persists with strong Jahn–Teller distortions of two Mn1O$_6$ and Mn2O$_6$ octahedra (e.g. in BiMn$_{0.95}$Ga$_{0.05}$O$_3$ and Bi$_{0.95}$MnO$_{2.925}$): the distortion parameters of the Mn1O$_6$ and Mn2O$_6$ octahedra are noticeably smaller in BiMn$_{0.95}$Ga$_{0.05}$O$_3$ and Bi$_{0.95}$MnO$_{2.925}$ than in BiMnO$_3$. At higher doping levels, the orbitally disordered structure (C2/c(II)) of BiMnO$_3$ is realized with almost identical Mn–O bond lengths for one of the Mn1O$_6$ or Mn2O$_6$ octahedra (e.g. in BiMn$_{0.85}$Cr$_{0.15}$O$_3$ and BiMn$_{0.85}$Fe$_{0.15}$O$_3$). BiMn$_{0.85}$Fe$_{0.15}$O$_3$ shows some anomalies in the distortion of the MnO$_6$ octahedra and in the magnetic properties. Rather strong Jahn–Teller distortions were found for both the Mn1O$_6$ and Mn2O$_6$ octahedra in Bi$_{0.9}$La$_{0.1}$MnO$_3$. The Mn1O$_6$ and Mn2O$_6$ octahedra were compressed along one direction in Bi$_{0.9}$La$_{0.1}$MnO$_3$ whereas the octahedra were elongated in BiMnO$_3$. Magnetic measurements indicate that Bi$_{0.9}$La$_{0.1}$MnO$_3$ adopts the orbitally disordered C2/c(II) structure. The orbitally ordered state of BiMnO$_3$ was found to be very fragile to any type of doping. However, as long as the orbitally ordered phase persists, the ferromagnetic transition temperature remains almost the same.

Keywords: multiferroic, BiMnO$_3$, crystal structure, Jahn–Teller distortion

1. Introduction

Bi-containing perovskites have attracted much attention as lead-free ferroelectric and multiferroic materials [1–6]. Multiferroic materials have at least two properties among (anti)ferroelectricity, (anti)ferromagnetism and ferroelasticity [3]. Multiferroics have experienced revived interest and a return to the forefront of materials science research because of the advances in the preparation and characterization techniques [7]. Among the very simple compositions of BiMO$_3$ ($M =$ transition metal), only BiFeO$_3$ [4, 5] and BiCoO$_3$ [8] clearly show polar structures and antiferromagnetic Néel temperatures, $T_N$, above room temperature (RT). The preparation of bulk BiCoO$_3$ is rather difficult and requires high pressure; therefore, the number of experimental studies of bulk BiCoO$_3$ is very limited [8, 9]. On the other hand, BiFeO$_3$ can easily be prepared at ambient pressure and, therefore, has been well characterized. Nevertheless, some BiFeO$_3$ problems are still unresolved [4].

BiMnO$_3$ is the second most studied compound within the BiMO$_3$ series. There are three modifications of BiMnO$_3$ at ambient pressure and above RT, with the phase transition temperatures of 474 K (C2/c(I) $\Rightarrow$ C2/c(II)) and 768 K (C2/c(II) $\Rightarrow$ Pnma) [10, 11]. The C2/c(II) structure is characterized by a monoclinic angle, $\beta$, of about 110.5°, and it has the orbital order. The C2/c(II) structure has a $\beta$ of 108.5–109.0°. Similar to BiFeO$_3$, there are still unresolved and puzzling problems concerning BiMnO$_3$. The magnetic properties of BiMnO$_3$ are well established, and it is a ferromagnet with a ferromagnetic Curie temperature,
shows observed, calculated, and difference loops. Thin-film samples demonstrate ferroelectric hysteresis loops usually have different magnetic properties (reduced $T_c$ and strongly reduced saturated magnetization) from those of the bulk stoichiometric BiMnO$_3$ [15–19]. One of the possible reasons for the different properties is the dissimilar composition. Therefore, detailed characterizations of non-stoichiometric and doped bulk samples are rather important for understanding the multiferroic properties of BiMnO$_3$.

In this work, we have characterized the structure of BiMnO$_3$ with different types of doping: isovalent doping with magnetic and non-magnetic ions in the magnetic Mn sublattice (BiMn$_{1-x}$M$_x$O$_3$ with $M$ = Cr, Fe and Ga), isovalent doping in the Bi sublattice (Bi$_{0.95}$La$_{0.05}$O$_3$) and the so-called self-doping (Bi$_{0.95}$MnO$_{2.925}$). The term ‘self-doping’ was often used for non-stoichiometric La$_{1-x}$MnO$_3$ [20, 21]. In all our cases, the oxidation state of manganese is kept at +3; therefore, we use the term ‘isovalent self-doping’ for Bi$_{0.95}$MnO$_{2.925}$. We found that the orbitally ordered C2/c(1) phase of BiMnO$_3$ is very fragile to any type of doping. There are correlations between the distortions of the Mn$_6$ octahedra and magnetic properties. As long as the orbitally ordered phase persists, the ferromagnetic transition temperature remains almost the same.

2. Experimental section

Stoichiometric mixtures of Bi$_2$O$_3$ (99.99%), M$_2$O$_3$ ($M$ = Cr, Fe and Ga; 99.9%) and Mn$_2$O$_3$ were placed in Au capsules and annealed at 6 GPa in a belt-type press at 1443–1453 K ($M$ = Cr and Ga, Bi$_{0.95}$La$_{0.05}$O$_3$ and Bi$_{0.95}$MnO$_{2.925}$) and 1333 K ($M$ = Fe) for 60–70 min [22]. Then, the samples were quenched to RT, and the pressure was slowly released. The resultant samples were black powders. X-ray powder diffraction (XRD) showed that some samples contained a small amount of Bi$_2$O$_3$CO$_3$ as an impurity in perovskite phases. Single-phase Mn$_2$O$_3$ was prepared from a commercial MnO$_2$ powder (99.99%) by heating in air at 923 K for 24 h.

Magnetic susceptibilities ($\chi$) were measured with a SQUID magnetometer (Quantum Design, MPMS) between 2 and 400 K in an applied field of 100 Oe under zero-field-cooling (ZFC) and field-cooling (FC; on cooling) conditions.

Synchrotron x-ray powder diffraction (SXRD) patterns for the structure refinement were collected at RT (also at 470 K for BiMn$_{0.95}$Ga$_{0.05}$O$_3$) on a large Debye–Scherrer camera at the BL02B2 beam line of SPring-8 [23]. Incident beams from a bending magnet were monochromatized to $\lambda = 0.4227$ Å. The samples were packed in glass capillary tubes with an inner diameter of 0.2 mm, and the tubes were rotated during the measurements. The SXRD data were collected in the 2θ range of 1–75° at 0.01° steps. The structure parameters of BiMnO$_3$ at RT and 550 K [11] were used as the initial values in the Rietveld refinements using RIETAN-2000 software [24]. The pseudo-Voigt function of Toraya was used as a profile function [25]. The background was represented by a composite background function, i.e. 11th-order Legendre polynomial. Isotropic atomic displacement parameters, $B$, with the isotropic Debye–Waller factor represented as exp$((-B \sin^2 \theta)/\lambda^2)$ were assigned to all the sites. For the Bi$_2$O$_2$CO$_3$ impurity, we refined only a scale factor and the lattice parameters, fixing the structure parameters. The mass percentage of Bi$_2$O$_2$CO$_3$ was estimated from the refined scale factors as 1%. The presence of Bi$_2$O$_2$CO$_3$ can be explained by a physical adsorption of CO$_2$ on Bi$_2$O$_3$ or by diffusion of carbon from carbon heaters through cracks in the Au capsules during the synthesis.

3. Results and discussion

The final lattice parameters, $R$ factors, fractional coordinates and $B$ parameters for Bi$_{0.95}$La$_{0.05}$O$_3$, Bi$_{0.95}$MnO$_{2.925}$ and BiMn$_{1-x}M_x$O$_3$ with $M$ = Cr, Fe and Ga are listed in tables 1 and 2. Mn–O bond lengths, distortion parameters (A) of the MnO$_6$ octahedra [26], bond-valence sums for Mn/M sites [27], and the ferromagnetic transition temperatures $T_c$ are given in table 3. Figure 1 shows observed, calculated, and difference SXRD patterns of BiMn$_{0.95}$Ga$_{0.05}$O$_3$ as an example. $T_c$ is defined by the peak position on the FC $d\chi/dT$ versus $T$ curves (figure 2).

In the structure analyses of BiMn$_{1-x}M_x$O$_3$, we assumed random distribution of Mn$^{3+}$ and $M^{3+}$ ions between the two crystallographically distinct Mn sites of BiMnO$_3$. The two reasons for this assumption are (i) these two sites have a very similar size (the average bond lengths are 2.030 Å for Mn$_1$ and 2.036 Å for Mn$_2$ [11]), and (ii) under the high-pressure high-temperature synthesis conditions, solid solutions of BiMn$_{1-x}M_x$O$_3$ ($M$ = transition metal) should have the $Pnma$ (or higher) symmetry with one crystallographic site for Mn$^{3+}$ and $M^{3+}$ and, therefore, a random distribution of these ions. This random distribution should remain after the quenching and pressure release at RT. We also assumed the random distribution of oxygen vacancies in Bi$_{0.95}$MnO$_{2.925}$ among three oxygen sites because the detection of small oxygen deficiency is very difficult by SXRD.

BiMnO$_3$ has strong Jahn–Teller distortions of the Mn$_6$ octahedra in the orbitally ordered C2/c(I) phase: $\Delta$(MnO$_6$)$_x \times 10^3 = 37.2$ and $\Delta$(MnO$_2$)$_y \times 10^3 = 51.3$ [11]. Long Mn$_1$–O$1$ and short Mn$_2$–O$1$ distances and short Mn$_1$–O$2$ and long Mn$_2$–O$_2$ distances are alternated in the crystal structure of BiMnO$_3$ forming a long-range orbital order. Above the orbital-ordering temperature $T_{OO}$ = 474 K in the C2/c(II) phase, the octahedral distortions of MnO$_6$ are considerably reduced in BiMnO$_3$ ($\Delta$(MnO$_6$)$_x \times 10^3 = 4.5$ and $\Delta$(MnO$_2$)$_y \times 10^3 = 15.4$) [11], but this reduction is not so dramatic as that of LaMnO$_3$ above $T_{OO} = 750$ K ($\Delta$(MnO$_6$)$_x \times 10^4 = 0.9$) [26].
A small amount of doping at the magnetic Mn sublattice, BiMn$_{0.9}$Ga$_{0.1}$O$_3$, or isovalent self-doping, Bi$_{0.95}$Mn$_{0.05}$O$_2$, significantly reduces the octahedral distortion parameters (Table 3). Nevertheless, these compounds maintain the orbitally ordered C2/c(I) structure with alternating short/long Mn1–O and long/short Mn2–O distances. $T_C$ remains almost unchanged in BiMn$_{0.95}$Ga$_{0.05}$O$_3$ and Bi$_{1.05}$Mn$_{0.95}$O$_2$ because the orbital order persists, and the
BiMn0.95Ga0.05O3

Table 3. Mn–O bond lengths (Å) bond valence sums (BVSs), and distortion parameters of MnO6 (Δ × 103) at different temperatures and ferromagnetic Curie temperatures (Tc) in BiMnO3, BiMn1−xMxO3, Bi0.95La0.05MnO3 (La) and Bi0.95MnO2.925 (Bi0.95).

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (K)</th>
<th>M = Ga</th>
<th>M = Ga</th>
<th>M = Cr</th>
<th>M = Fe</th>
<th>La</th>
<th>Bi0.95</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>0.05</td>
<td>0.20</td>
<td>0.15</td>
<td>0.15</td>
<td>295</td>
</tr>
<tr>
<td>Mn1–O1</td>
<td>295</td>
<td>550</td>
<td>295</td>
<td>470</td>
<td>295</td>
<td>295</td>
<td>295</td>
</tr>
<tr>
<td>Mn1–O2</td>
<td>1.906</td>
<td>2.011</td>
<td>1.924</td>
<td>2.018</td>
<td>2.040</td>
<td>2.052</td>
<td>2.119</td>
</tr>
<tr>
<td>Mn1–O3</td>
<td>1.986</td>
<td>2.112</td>
<td>2.020</td>
<td>2.090</td>
<td>1.982</td>
<td>2.033</td>
<td>2.002</td>
</tr>
<tr>
<td>BVS(Mn1)</td>
<td>3.05</td>
<td>2.75</td>
<td>3.03</td>
<td>2.81</td>
<td>3.00</td>
<td>2.80</td>
<td>2.81</td>
</tr>
<tr>
<td>Δ(Mn1–O0)</td>
<td>37.2</td>
<td>4.5</td>
<td>15.8</td>
<td>2.8</td>
<td>1.6</td>
<td>0.1</td>
<td>6.7</td>
</tr>
<tr>
<td>Mn2–O1</td>
<td>1.924</td>
<td>2.024</td>
<td>1.955</td>
<td>2.042</td>
<td>1.960</td>
<td>1.978</td>
<td>2.008</td>
</tr>
<tr>
<td>Mn2–O2</td>
<td>2.242</td>
<td>2.106</td>
<td>2.234</td>
<td>2.115</td>
<td>2.142</td>
<td>2.088</td>
<td>2.036</td>
</tr>
<tr>
<td>Mn2–O3</td>
<td>1.941</td>
<td>1.913</td>
<td>1.957</td>
<td>1.925</td>
<td>1.987</td>
<td>1.964</td>
<td>1.994</td>
</tr>
<tr>
<td>BVS(Mn2)</td>
<td>3.05</td>
<td>3.09</td>
<td>2.91</td>
<td>2.98</td>
<td>2.96</td>
<td>3.04</td>
<td>3.04</td>
</tr>
<tr>
<td>Δ(Mn2–O0)</td>
<td>51.3</td>
<td>15.4</td>
<td>40.9</td>
<td>14.9</td>
<td>15.6</td>
<td>7.7</td>
<td>0.8</td>
</tr>
<tr>
<td>Tc (K)</td>
<td>102</td>
<td>99</td>
<td>70</td>
<td>76</td>
<td>98</td>
<td>78</td>
<td>103</td>
</tr>
</tbody>
</table>

BVS = \sum_{i=1}^{N} v_i, v_i = \exp((R_0 - l_i)/B), N (= 6) is the coordination number, B = 0.37, R0(Mn8+) = 1.76, l_i is a Mn–O bond length [27]; Δ = \left(1/N\right)\sum_{i=1}^{N}(l_i - \bar{l}_\text{av})^2 where \bar{l}_\text{av} = (1/N)\sum_{i=1}^{N}l_i is the average Mn–O distance [26].

Figure 1. Parts of observed (crosses), calculated (solid line) and difference patterns resulting from the Rietveld analysis of the synchrotron x-ray powder diffraction data of BiMn0.95Ga0.05O3 at 295 K. Bragg reflections are indicated by tick marks. The lower tick marks correspond to the reflections from the Bi2O2CO3 impurity (1.1 wt%).

Orbital order is considered to enhance the ferromagnetic interactions [28]. Bi1−xMnO3−1.5x, with x = 0.05 corresponds to the maximum level of isovalent self-doping when the C2/c(I) structure still persists. At larger x, other perovskite-type phases appear in large amounts. Self-doped La1−xMnO3−1.5x containing only Mn3+ ions can be prepared up to x = 0.12 at ambient pressure [29]. Therefore, the stability range of isovalent self-doping is noticeably smaller in Bi1−xMnO3−1.5x than in La1−xMnO3−1.5x. It was reported that the magnetic transition temperature and orbital-ordering temperature are very similar in La0.98MnO2.92 and LaMnO3 [29]. The Tc values are also close for Bi0.95MnO2.95 (103 K) and BiMnO3 (102 K); however, the T200 values are different: 474 K in BiMnO3 and 425 K in Bi0.95MnO2.925. Heterovalent self-doping of BiMnO3 (e.g. Bi1−yMn1+yO3 with the appearance of Mn4+) suppresses the orbitally ordered phase much faster, already at y = 0.01 [30].

Larger amounts of doping at the magnetic Mn sublattice, e.g. BiMn0.8Ga0.2O3, stabilizes the orbitally disordered C2/c(II) phase. The distortion of Mn1O6 in BiMn0.8Ga0.2O3 (\(\Delta \times 10^3 = 1.6\)), BiMn0.95Cr0.05O3 (\(\Delta \times 10^3 = 0.1\)), BiMn0.9Al0.1O3 (\(\Delta \times 10^3 = 1.4\)) [31] and BiMn0.8Sc0.2O3 (\(\Delta \times 10^3 = 0.5\)) [32] and the distortion of Mn2O6 in BiMn0.85Fe0.15O3 (\(\Delta \times 10^3 = 0.8\)) are almost negligible and comparable to the Mn6O6 distortion in LaMnO3 above \(T_{OO} (\Delta \times 10^4 = 0.9)\) [26]. Therefore, the long-range orbital ordering should be disturbed even though a small distortion of the second MnO6 octahedron.

\[ \lambda = 0.4227 \text{ Å} \]

BiMn0.95Ga0.05O3

\[ T = 295 \text{ K} \]
remains. Because the orbital-ordering mechanism for the $T_C$ enhancement is absent, $T_C$ is reduced by about 25–30 K in BiMn$_{0.8}$Ga$_{0.2}$O$_3$ and BiMn$_{0.85}$Cr$_{0.15}$O$_3$. $T_C$ is also smaller for BiMn$_{0.85}$Fe$_{0.15}$O$_3$ (98 K) than for the orbitally ordered BiMn$_{0.85}$Fe$_{0.15}$O$_3$ (110 K) [17]. In this case, the presence of Fe$^{3+}$ with strong antiferromagnetic coupling is probably responsible for the larger $T_C$ in BiMn$_{0.85}$Fe$_{0.15}$O$_3$, which is comparable to that of BiMnO$_3$.

The magnetic Mn sublattice remains undisturbed in Bi$_{0.9}$La$_{0.1}$MnO$_3$, and the orbital order is expected to be similar to that of BiMnO$_3$. Octahedral distortions in Bi$_{0.9}$La$_{0.1}$MnO$_3$ are indeed rather large: $\Delta(\text{MnO}_6) \times 10^4 = 11.7$ and $\Delta(\text{MnO}_6) \times 10^4 = 20.1$. However, the lattice parameters ($\beta \approx 108.9^\circ$) and $T_C (= 78$ K) of Bi$_{0.9}$La$_{0.1}$MnO$_3$ suggest that it has the orbitally disordered C2/c(II) structure. The detailed analysis of Mn–O bond lengths allows resolving this controversy. The MnO$_6$ octahedra are elongated along one axis in BiMnO$_3$; they have two long Mn–O distances and four short Mn–O distances, which is typical for the Jahn–Teller ions. Bi$_{0.9}$La$_{0.1}$MnO$_3$ has two short Mn–O distances and four longer Mn–O distances, and the MnO$_6$ octahedra are compressed along one axis. Therefore, the octahedral distortions in Bi$_{0.9}$La$_{0.1}$MnO$_3$ are different from those of BiMnO$_3$ and BiMn$_{1-x}$M$_x$O$_3$ in both orbitally ordered and orbitally disordered states. The presence of Bi$^{3+}$ ions with a lone electron pair should be crucial for the stabilization of a highly distorted monoclinic C2/c(I) structure of BiMnO$_3$ with the orbital order. The introduction of La$^{3+}$ ions without lone electron pairs suppresses the unique C2/c(I) structure and stabilizes the C2/c(II) structure. However, a larger amount of La$^{3+}$ ions (Bi$_{0.8}$La$_{0.2}$MnO$_3$) or smaller Y$^{3+}$ ions (Bi$_{0.8}$Y$_{0.2}$MnO$_3$) stabilize the Pnma structure observed in LaMnO$_3$ (structural results are not shown here). Bi$_{0.8}$La$_{0.2}$MnO$_3$ and Bi$_{0.8}$Y$_{0.2}$MnO$_3$ have the orbital ordering pattern as in LaMnO$_3$; in other words, the orbital order in these compounds is restored compared with that of Bi$_{0.9}$La$_{0.1}$MnO$_3$. Oxygen-stoichiometric solid solutions of Bi$_{1-x}$La$_x$MnO$_3$ with $x \geq 0.5$, which can be prepared at ambient pressure, also have the same orbital and magnetic orders as that of LaMnO$_3$ [33, 34].

4. Conclusions

We have investigated the crystal structures of BiMnO$_3$ with different types of doping and traced the effects of doping on local distortions of the MnO$_6$ octahedra and the stability of the orbital order. The orbitally ordered state of BiMnO$_3$ was found to be very fragile to any type of (isovalent) doping. As long as the orbitally ordered phase persists, the ferromagnetic transition temperature remains almost the same.

Acknowledgments

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