Local distortions in multiferroic BiMnO₃ as a function of doping

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Abstract

The structure of doped BiMnO₃ was studied using synchrotron x-ray powder diffraction. The dopants included isostructural magnetic and non-magnetic ions in the magnetic Mn sublattice (BiMnₓ₋ₓMₓO₃ with M = Cr, Fe and Ga), isostructural ions in the Bi sublattice (Bi₀.₈La₀.₂MnO₃) and isostructural self-dopants (Bi₀.₉₅MnO₂.₉₂₅). The results indicate that at low doping levels, the orbitally ordered structure (C2/c(I)) of BiMnO₃ persists with strong Jahn–Teller distortions of two MnI₂O₆ and MnII₂O₆ octahedra (e.g. in BiMn₀.₉₅Ga₀.₀₅O₃ and BiMn₀.₉₅MnO₂.₉₂₅); the distortion parameters of the MnI₂O₆ and MnII₂O₆ octahedra are noticeably smaller in BiMn₀.₉₅Ga₀.₀₅O₃ and BiMn₀.₉₅MnO₂.₉₂₅ than in BiMnO₃. At higher doping levels, the orbitally disordered structure (C2/c(II)) of BiMnO₃ is realized with almost identical Mn–O bond lengths for one of the MnI₂O₆ or MnII₂O₆ octahedra (e.g. in BiMn₀.₈₅Cr₀.₁₅O₃ and BiMn₀.₈₅Fe₀.₁₅O₃). BiMn₀.₈₅Fe₀.₁₅O₃ shows some anomalies in the distortion of the MnI₂O₆ octahedra and in the magnetic properties. Rather strong Jahn–Teller distortions were found for both the MnI₂O₆ and MnII₂O₆ octahedra in Bi₀.₈La₀.₂MnO₃. The MnI₂O₆ and MnII₂O₆ octahedra were compressed along one direction in Bi₀.₈La₀.₂MnO₃ whereas the octahedra were elongated in BiMnO₃. Magnetic measurements indicate that Bi₀.₈La₀.₂MnO₃ adopts the orbitally disordered C2/c(II) structure. The orbitally ordered state of BiMnO₃ 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, BiMnO₃, 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 BiMnO₃ (M = transition metal), only BiFeO₃ [4, 5] and BiCoO₃ [8] clearly show polar structures and antiferromagnetic Néel temperatures, Tₙ, above room temperature (RT). The preparation of bulk BiCoO₃ is rather difficult and requires high pressure; therefore, the number of experimental studies of bulk BiCoO₃ is very limited [8, 9]. On the other hand, BiFeO₃ can easily be prepared at ambient pressure and, therefore, has been well characterized. Nevertheless, some BiFeO₃ problems are still unresolved [4].

BiMnO₃ is the second most studied compound within the BiMnO₃ series. There are three modifications of BiMnO₃ at ambient pressure and above RT, with the phase transition temperatures of 474 K (C2/c(I) ⇒ C2/c(II)) and 768 K (C2/c(II) ⇒ Pnma) [10, 11]. The C2/c(II) structure is characterized by a monoclinic angle, β, of about 110.5°, and it has the orbital order. The C2/c(II) structure has a β of 108.5–109.0°. Similar to BiFeO₃, there are still unresolved and puzzling problems concerning BiMnO₃. The magnetic properties of BiMnO₃ are well established, and it is a ferromagnet with a ferromagnetic Curie temperature,
of the possible reasons for the different properties is the dissimilarity of the crystallographic phases of 

\[ \text{BiMnO}_3 \]

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 

\[ \text{BiMnO}_3 \]

tubes were rotated 0°. The pseudo-Voigt function of Toraya was used as a profile function. 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 \( \text{Bi}_2\text{O}_2\text{CO}_3 \) impurity, we refined only a scale factor and the lattice parameters, fixing the structure parameters. The mass percentage of \( \text{Bi}_2\text{O}_2\text{CO}_3 \) was estimated from the refined scale factors as 1%.

In this work, we have characterized the structure of 

\[ \text{BiMnO}_3 \]

with different types of doping: isovalent doping with magnetic and non-magnetic ions in the magnetic 

\[ \text{Mn} \]

sublattice (\( \text{BiMn}_{1-x}\text{M}_x\text{O}_3 \) with \( M = \text{Cr}, \text{Fe} \) and \( \text{Ga} \))

isovalent doping in the \( \text{Bi} \) sublattice (\( \text{Bi}_{0.95}\text{La}_{0.05}\text{MnO}_3 \)) and the so-called self-doping (\( \text{Bi}_{0.95}\text{MnO}_{3.925} \)). The term ‘self-doping’ was often used for non-stoichiometric 

\[ \text{BiMnO}_3 \]

I.e., when the oxidation state of manganese is kept at +3; therefore, we use the term ‘isovalent self-doping’ for \( \text{Bi}_{0.95}\text{MnO}_{3.925} \). We found that the vertically ordered \( \text{C}_2/\text{c}(1) \) phase of 

\[ \text{BiMnO}_3 \]

is very fragile to any type of doping. There are correlations between the distortions of the 

\[ \text{MnO}_6 \]

octahedra and magnetic properties. As long as the vertically ordered phase persists, the ferromagnetic transition temperature remains almost the same.

2. Experimental section

Stoichiometric mixtures of 

\[ \text{Bi}_2\text{O}_3 \]

(99.99%), \( \text{M}_2\text{O}_3 \) (\( M = \text{Cr}, \text{Fe} \) and \( \text{Ga} \); 99.9%) and \( \text{Mn}_2\text{O}_3 \) were placed in Aucapsules and annealed at 6 GPa in a belt-type press at 1443–1453 K (\( M = \text{Cr} \) and \( \text{Ga} \)), \( \text{Bi}_{0.9}\text{La}_{0.1}\text{MnO}_3 \) and \( \text{Bi}_{0.95}\text{MnO}_{3.925} \) and 1333 K (\( M = \text{Fe} \)) 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 \( \text{Bi}_2\text{O}_2\text{CO}_3 \) as an impurity in perovskite phases. Single-phase \( \text{Mn}_2\text{O}_3 \) was prepared from a commercial MnO \( \text{Mn}_2\text{O}_3 \) powder (99.9%) 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 \( \text{BiMn}_{0.95}\text{Ga}_{0.05}\text{O}_3 \)) 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 20 range of 1–75° at 0.01° steps. The structure parameters of \( \text{BiMnO}_3 \) 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 \( \text{Bi}_2\text{O}_2\text{CO}_3 \) impurity, we refined only a scale factor and the lattice parameters, fixing the structure parameters. The mass percentage of \( \text{Bi}_2\text{O}_2\text{CO}_3 \) was estimated from the refined scale factors as 1%.

3. Results and discussion

The final lattice parameters, \( R \) factors, fractional coordinates and \( B \) parameters for \( \text{Bi}_{0.9}\text{La}_{0.1}\text{MnO}_3 \), \( \text{Bi}_{0.95}\text{MnO}_{3.925} \) and \( \text{BiMn}_{1-x}\text{M}_x\text{O}_3 \) with \( M = \text{Cr} \) and \( \text{Fe} \) and \( \text{Ga} \) are listed in tables 1 and 2. Mn–O bond lengths, distortion parameters (\( \Delta \)) of the \( \text{MO}_6 \) 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 \( \text{Bi}_{0.95}\text{Ga}_{0.05}\text{O}_3 \) 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 \( \text{BiMn}_{1-x}\text{M}_x\text{O}_3 \), we assumed random distribution of \( \text{Mn}^{3+} \) and \( \text{M}^{3+} \) ions between the two crystallographically distinct Mn sites of \( \text{BiMnO}_3 \). 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 Mn1 and 2.036 Å for Mn2 [11]), and (ii) under the high-pressure high-temperature synthesis conditions, solid solutions of \( \text{BiMn}_{1-x}\text{M}_x\text{O}_3 \) (\( M = \text{transition metal} \)) should have the \( \text{Pnma} \) (or higher) symmetry with one crystallographic site for \( \text{Mn}^{3+} \) and \( \text{M}^{3+} \) 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 \( \text{Bi}_{0.95}\text{MnO}_{3.925} \) among three oxygen sites because the detection of small oxygen deficiency is very difficult by SXRD.

\[ \text{BiMnO}_3 \]

has strong Jahn–Teller distortions of the \( \text{MnO}_6 \) octahedra in the orbitally ordered \( \text{C}_2/\text{c}(1) \) phase: \( \Delta(\text{MnO}_6) \times 10^4 = 37.2 \) and \( \Delta(\text{MnO}_6) \times 10^4 = 51.3 \) [11]. Long Mn1–O1 and short Mn2–O1 distances and short Mn1–O2 and long Mn2–O2 distances are alternated in the crystal structure of \( \text{BiMnO}_3 \) forming a long-range orbital order. Above the orbital-ordering temperature \( T_{00} = 474 \) K in the \( \text{C}_2/\text{c}(II) \) phase, the octahedral distortions of \( \text{MnO}_6 \) are considerably reduced in \( \text{BiMnO}_3 \) (\( \Delta(\text{MnO}_6) \times 10^4 = 4.5 \) and \( \Delta(\text{MnO}_6) \times 10^4 = 15.4 \)) [11], but this reduction is not so dramatic as that of \( \text{LaMnO}_3 \) above \( T_{00} = 750 \) K (\( \Delta(\text{MnO}_6) \times 10^4 = 0.9 \)) [26].
A small amount of doping at the magnetic Mn sublattice, BiMn$_{0.95}$Ga$_{0.05}$O$_3$, or isovalent self-doping, Bi$_{0.95}$MnO$_2$$_{2.95}$, significantly reduces the octahedral distortion parameters (table 3). Nevertheless, these compounds maintain the orbitally ordered $C2/c$ (I) structure with alternating short/long Mn1–O and long/short Mn2–O distances. $T_C$ remains almost unchanged in BiMn$_{0.95}$Ga$_{0.05}$O$_3$ and Bi$_{0.95}$MnO$_2$$_{2.95}$ because the orbital order persists, and the
Table 3. Mn–O bond lengths (Å) bond valence sums (BVSs), and distortion parameters of MnO₆ (Δ × 10⁴) at different temperatures and ferromagnetic Curie temperatures (T_C) in BiMnO₃, BiMn₀.₉₅Ga₀.₀₅O₃, Bi₀.₈₅La₀.₁₅O₃ (La) and Bi₀.₉₅MnO₂.₉₂₅ (Bi₀.₉₅).

| Sample        | x   | T_C (K) | BVS(Mn1) | BVS(Mn2) | BVS(Mn3) | Δ(MnO₆) |
|---------------|-----|---------|----------|----------|----------|----------|
| Mn₁–O₁        | 0.05| 295     | 1.924    | 2.242    | 1.914    | 51.3     |
| Mn₁–O₂        | 0.05| 550     | 2.121    | 2.234    | 2.092    | 51.3     |
| Mn₁–O₃        | 0.2  | 295     | 2.020    | 2.224    | 1.957    | 51.3     |
| BVs(Mn1)      | 3.05| 295     | 2.80     | 2.142    | 1.976    | 51.3     |
| Mn₂–O₂        | 0.05| 295     | 1.982    | 2.142    | 1.976    | 51.3     |
| Mn₂–O₃        | 0.15| 295     | 2.033    | 2.088    | 1.976    | 51.3     |
| Δ(Mn₂O₆)      | 102 | 99      | 40.9     | 2.036    | 1.944    | 51.3     |

BVS = \sum_{i=1}^{N} v_i, v_i = \exp((R_{\text{av}} - l_i) / B), N (= 6) is the coordination number, B = 0.37, R_{\text{av}}(Mn^{3+}) = 1.76, l_i is a Mn–O bond length [27]; \Delta = (1 / N) \sum_{i=1}^{N} (l_i - l_{\text{av}})^2 / l_{\text{av}}^2 where 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 Bi₂O₃CO₃ impurity (1.1 wt%).
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$_{0.95}$Fe$_{0.05}$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: $\Delta(MnO_6)$ $\times 10^4 = 11.7$ and $\Delta(MnO_6) \times 10^4 = 20.1$. 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.

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