Effects of doping on structural, physical, and chemical properties of multiferroic BiMnO₃ and BiCrO₃

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Effects of isovalent substitutions in the Mn(Cr)- and Bi-sublattices of BiMnO₃ and BiCrO₃ on the magnetic, structural, and chemical properties have been studied. Phase diagrams in the whole compositional range were constructed for BiMn_{1-x}Sc_xO₃, BiMn_{1-x}Cr_xO₃, and Bi_{1-x}R_xMO₃ (R = Y and La, M = Cr and Mn). BiMn_{1-x}Sc_xO₃ and BiMn_{1-x}Cr_xO₃ keep the monoclinic *C2/c* structure at RT for all *x* values; a spin-glass transition was found for *x* ≥ 0.4 in BiMn_{1-x}Sc_xO₃ and at *x* = 0.4 and 0.5 in BiMn_{1-x}Cr_xO₃. Magnetic phase diagrams of BiMn_{1-x}Sc_xO₃ and BiMn_{1-x}Cr_xO₃ are similar to each other for *x* ≤ 0.5. In Bi_{1-x}R_xMO₃, the *Pnma* modification is stabilized very fast with *x*; the *Pnma* phases show antiferromagnetic transitions with weak ferromagnetism.

Key words: Multiferroics, BiMnO₃, BiCrO₃, phase diagrams

1. INTRODUCTION

Multiferroics are an interesting class of materials from viewpoints of application and basic physics.¹ In multiferroic systems, two or all three of (anti)ferroelectricity, (anti)ferromagnetism, and ferroelasticity are observed in the same phase.² BiMnO₃ has been extensively studied as a multiferroic material. Three modifications of BiMnO₃ exist at ambient pressure.³ The so-called phase I modification is stable below 474 K, and its average structure is very well described by the *C2/c* symmetry⁴ even though the local symmetry is lower.^{5,6} Phase I has the orbital order. The phase II modification is stable between 474 and 768 K. Phase II has the same symmetry as that of phase I, however, it is believed that there is no orbital order in phase II.⁴ The orthorhombic (O) modification (space group *Pnma*) is stable above 768 K and up to the decomposition temperature. BiCrO₃ has two modifications: the first one has the phase II structure and the *C2/c* symmetry (stable below 420 K) and the second one has the *Pnma* symmetry.⁷

Heterovalent substitutions in the Bi sublattice of BiMnO₃ have been investigated in a number of works.⁸ Transitions with different spin, charge, and orbital orders were found in Bi_{1-x}M_xMnO₃ (M = Ca and Sr). There is very limited information on isovalent substitution effects in BiMnO₃ and BiCrO₃.

In this work, effects of isovalent substitutions in the Mn(Cr)- and Bi-sublattices of BiMnO₃ and BiCrO₃ on the magnetic, structural, and chemical properties will be discussed. Phase diagrams in the whole compositional range were constructed for BiMn_{1-x}Sc_xO₃, BiMn_{1-x}Cr_xO₃, and Bi_{1-x}R_xMO₃ (R = Y and La, M = Cr and Mn).

2. EXPERIMENTAL PART

All the samples were prepared at high pressure of 6 GPa and 1273-1673 K. Magnetic properties were studied by dc and ac susceptibility and specific heat using

MPMS and PPMS Quantum Design instruments. High-temperature phase transitions and thermal stability were studied using differential scanning calorimetry (DSC) and TG/DTA analysis.

3. RESULTS and DISCUSSION

3.1 Substitutions in the Mn(Cr)-sublattice

Compositional dependence of the lattice parameters in the solid solutions BiMn_{1-x}M_xO₃ (M = Al, Sc, Cr, Fe, and Ga) is shown on Figure 1.⁹ The results on these solid solutions show that phase II is stabilized very fast with increasing *x*. It means that the orbital ordered phase I of BiMnO₃ is rather unstable compared, for example, with the stability of orbital order in LaMn_{1-x}Ga_xO₃. During the phase I to phase II transition, the *a* parameter increases, and the *b* and *c* parameters and *β* angle decrease for all the substitutions. The same changes of the lattice parameters were observed during the temperature-driven phase I to phase II transition in BiMnO₃.³ It means that the temperature-driven and composition-driven phase I to phase II transitions have the same nature.

Figure 2a shows the DSC curves of BiMnO₃ and BiMn_{0.95}Ga_{0.05}O₃ with the phase I structure.⁹ The temperature of orbital ordering *T*_{OO} drops by 60 K with substitution of 5 % Ga. Figure 2b shows the magnetic susceptibility curves for the same samples, the ferromagnetic transition temperature *T*_C decreases only by 3 K.⁹ It means that as long as the orbital-ordered phase I is stable, the *T*_C changes a little. However, as soon as the phase II is stabilized, the *T*_C drops significantly (see the data for BiMn_{0.8}Ga_{0.2}O₃ on Figure 2b and also Figure 3). This fact may mean that the orbital order enhances the magnetic interactions and increases the *T*_C.

Figure 3 gives the magnetic phase diagrams of BiMn_{1-x}Sc_xO₃ and BiMn_{1-x}Cr_xO₃ where the solid solutions exist in the whole compositional range.^{10,11} It is interesting that at 0.0 ≤ *x* ≤ 0.5, the phase diagrams are very similar

Fig. 1. Compositional dependence of the lattice parameters in solid solutions $\text{BiMn}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Al}, \text{Sc}, \text{Cr}, \text{Fe},$ and Ga) with the $C2/c$ symmetry.^{9,10} Note that the a parameter for $\text{M} = \text{Sc}$ with $x \geq 0.05$ is given using the right-hand axis.

to each other independent of the non-magnetic or magnetic substitution in the Mn-sublattice. With increasing x , we observed the decrease of the T_C , and the appearance of a re-entrant spin-glass (RSG) state at rather low temperatures. At $x = 0.4$ and 0.5 , a classical spin-glass (SG) transition was found (Figure 4). For $x \geq 0.6$, the phase diagrams are, of course, different because BiScO_3 is non-magnetic and BiCrO_3 is an antiferromagnet (with weak ferromagnetism due to spin canting).⁷ Note that the RSG lines on the phase diagrams can be determined only with the ac susceptibilities because no anomalies were detected on the dc susceptibilities,^{10,11} and the real nature of the SG lines can also be determined with the ac susceptibility.

Fig. 2. (a) DSC curves of BiMnO_3 and $\text{BiMn}_{0.95}\text{Ga}_{0.05}\text{O}_3$ with the phase I structure in the vicinity of the orbital ordering temperature T_{OO} .⁹ (b) Magnetic susceptibilities (measured at 100 Oe in the ZFC and FC modes) of BiMnO_3 , $\text{BiMn}_{0.95}\text{Ga}_{0.05}\text{O}_3$, and $\text{BiMn}_{0.8}\text{Ga}_{0.2}\text{O}_3$.⁹

3.2 Substitutions in the Bi-sublattice

Solid solutions $\text{Bi}_{1-x}\text{La}_x\text{MnO}_3$ have been studied in a number of works.¹² Our results showed that $\text{Bi}_{0.95}\text{La}_{0.05}\text{MnO}_3$ contained a mixture of phase I (with $T_C \sim 100$ K) and phase II (with $T_C \sim 85$ K). $\text{Bi}_{0.9}\text{La}_{0.1}\text{MnO}_3$ contained a majority of phase II and traces of phase I. Because phases I and II are both ferromagnetic the presence of these phases can be easily detected by magnetic susceptibility measurements (Figure 5). $\text{Bi}_{0.8}\text{La}_{0.2}\text{MnO}_3$ had a majority of the O-phase (with $T_N = 80$ K) and traces of phase II. Because the O-phase has a ferromagnetic component its presence can also be easily detected by magnetic measurements (Figure 5). The T_N of O-phases increases with increasing x in $\text{Bi}_{1-x}\text{La}_x\text{MnO}_3$. Unfortunately, the T_{OO} of $\text{Bi}_{1-x}\text{La}_x\text{MnO}_3$ cannot be determined because on heating in air, $\text{Bi}_{1-x}\text{La}_x\text{MnO}_3$ changes the oxygen content and, therefore, irreversibly changes the symmetry.

The O-phase is stabilized much faster in solid solutions $\text{Bi}_{1-x}\text{Y}_x\text{MnO}_3$ where the O-phase is already observe at $x = 0.1$. It means that the smaller the substituting ion the faster the O-phase appears. The T_N of O-phases decreases with increasing x in $\text{Bi}_{1-x}\text{Y}_x\text{MnO}_3$ because $T_N = 40$ K in the O-phase of YMnO_3 .

In $\text{Bi}_{1-x}\text{La}_x\text{CrO}_3$ at $x = 0.05$, we found a new modification having an orthorhombic symmetry and a superstructure of $\sqrt{2}a_p \times 4a_p \times 2\sqrt{2}a_p$, where a_p is the parameter of the cubic perovskite subcell. Actually this superstructure is closely related to the phase II structure with the $C2/c$ symmetry as discussed for thin films of BiScO_3 .¹³ As a results, magnetic properties of

Fig. 3. Low-temperature (magnetic) phase diagrams of $\text{BiMn}_{1-x}\text{Sc}_x\text{O}_3$ and $\text{BiMn}_{1-x}\text{Cr}_x\text{O}_3$.^{10,11} Vertical dash lines show two-phase regions where phases I and II coexist. PM: paramagnetic, FM: ferromagnetic with the Curie temperature T_C , FCG: ferromagnetic cluster glass, RSG: re-entrant spin glass, SG: spin-glass with the freezing temperature T_f , AF: antiferromagnetic with the Neel temperature T_N .

Fig. 5. dc magnetic susceptibilities (measured at 100 Oe in the ZFC and FC modes) of $\text{Bi}_{0.95}\text{La}_{0.05}\text{MnO}_3$ (containing phases I and II), $\text{Bi}_{0.9}\text{La}_{0.1}\text{MnO}_3$ (containing phase II and traces of phase I), $\text{Bi}_{0.8}\text{La}_{0.2}\text{MnO}_3$ (containing O-phase and traces of phase II), and $\text{Bi}_{0.5}\text{La}_{0.5}\text{MnO}_3$ (containing O-phase). Note that the T_N of the O-phase increases with increasing the La content; the O-phase has a ferromagnetic component due to spin canting.

Fig. 4. Frequency dependence of the real (χ') and imaginary (χ'') parts of the ac susceptibilities of $\text{BiMn}_{0.5}\text{Sc}_{0.5}\text{O}_3$ measured on cooling at $H_{ac} = 5$ Oe and $H_{dc} = 0$ Oe. Inset shows the fit to the Vogel-Fulcher law (the fitting parameters are $E_a/k_B = 64.8(9)$ K and $T_0 = 15.31(4)$ K).¹¹

$\text{Bi}_{0.95}\text{La}_{0.05}\text{CrO}_3$ ($T_N = 120$ K) are very similar with those of BiCrO_3 . $\text{Bi}_{0.8}\text{La}_{0.2}\text{CrO}_3$ has the O-phase as a majority phase, and $\text{Bi}_{0.7}\text{La}_{0.3}\text{CrO}_3$ ($T_N = 190$ K) contained only the O-phase.

$\text{Bi}_{0.95}\text{Y}_{0.05}\text{CrO}_3$ has the O-phase as a majority phase and traces of monoclinic phase II, and $\text{Bi}_{0.9}\text{Y}_{0.1}\text{CrO}_3$ ($T_N = 155$ K) contained only the O-phase. All the O-phases are antiferromagnetic with weak ferromagnetism due to spin canting. The results on the substitution in the Bi-sublattice of BiCrO_3 are similar with those of BiMnO_3 in a sense that the substituting ions with smaller ionic radii stabilize the O-phase faster (that is, at smaller x values).

As a conclusion, Figure 6 gives schematic comparison of the phase diagrams of $\text{Bi}_{1-x}\text{La}_x\text{MnO}_3$ and $\text{BiMn}_{1-x}\text{Sc}_x\text{O}_3$. One general feature on these diagrams is a very narrow stability range of the monoclinic phase I with orbital order. In $\text{BiMn}_{1-x}\text{Sc}_x\text{O}_3$, phase I is replaced by phase II with increasing x . In $\text{Bi}_{1-x}\text{La}_x\text{MnO}_3$ with $x \geq 0.2$, the O-phase is stable. Structural analysis at room temperature showed that the O-phases of $\text{Bi}_{1-x}\text{La}_x\text{MnO}_3$ have the orbital order (that is, two long Mn-O bond lengths and two short Mn-O bond lengths) similar to the orbital order of LaMnO_3 . As already mentioned, the compositional dependence of T_{OO} in $\text{Bi}_{1-x}\text{La}_x\text{MnO}_3$ could not be studied because of the change of the oxygen content on heating in air. However, an interesting question is the existence of orbital order in the O-phase of undoped BiMnO_3 above 768 K.

Fig. 6. Schematic comparison of the phase diagrams of $\text{Bi}_{1-x}\text{La}_x\text{MnO}_3$ and $\text{BiMn}_{1-x}\text{Sc}_x\text{O}_3$. The general feature is a very narrow stability range of the monoclinic phase I. The grey part on the left means that the T_{OO} could not be determined because of the change of the oxygen content. T_{STR} means the structural phase transition from the monoclinic to orthorhombic modification.

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