

Indium-Based Perovskites: A New Class of Near-Room-Temperature Multiferroics**

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In multiferroic systems, two or all three of ferroelectricity (or antiferroelectricity), ferromagnetism (or antiferromagnetism), and ferroelasticity are observed in the same phase.^[1–4] These systems may have wide technological applications because they allow control of electric properties by magnetic field and control of magnetic properties by electric field. Applications might include multiple-state memory elements and will allow exploitation of the advantages of both ferroelectric and magnetic random-access memories.^[4–7] Multiferroic materials have been studied in the past, especially in the late 1960s in Japan and the former Soviet Union, but these studies did not attract wide attention, most probably owing to the lack of materials with strong magnetoelectric coupling and high ordering temperatures. Multiferroics has experienced revived interest and has returned to the forefront of materials science research in recent years because of the advent of advanced preparation and characterization techniques.^[1,6]

Being a unique material, perovskite-type BiFeO₃ has received tremendous interest from the viewpoints of fundamental science and applications.^[8–12] BiFeO₃ is a very rare example of a single-phase room-temperature multiferroic material, that is, the magnetism and ferroelectricity exist at room temperature. In BiFeO₃, both the ferroelectric Curie temperature $T_E = 1123$ K and the antiferromagnetic Néel temperature $T_N = 650$ K are well above room temperature. Therefore, BiFeO₃ and its derivatives have become the cornerstones in the research on room-temperature multiferroics.^[12] Also, BiFeO₃ is the only compound among simple

BiMO₃ systems (M = transition metals) that can be prepared at ambient pressure in bulk form. Note that with multiple M ions, materials with only Bi³⁺ ions occupying the A site of ABO₃ perovskites can also be prepared at ambient pressure, for example, Bi₂Mn_{4/3}Ni_{2/3}O₆^[13] and Bi₂Ti_{3/8}Fe_{2/8}Mg_{3/8}O₆.^[14] Moreover, BiFeO₃ shows a very large spontaneous polarization and interesting behaviors at low temperature (spin glass) and high temperature (a number of phase transitions and an insulator–metal transition).^[9–12]

BiFeO₃ crystallizes in the space group *R3c* with $a_H = 5.579$ Å and $c_H = 13.869$ Å (in hexagonal setting) at room temperature and ambient pressure. A number of materials have the same structure as that of BiFeO₃, for example, LiNbO₃,^[15] Bi₂Ti_{3/8}Fe_{2/8}Mg_{3/8}O₆,^[14] and ZnSnO₃ (prepared at 7 GPa).^[16] To our knowledge, none of them has long-range magnetic ordering. The ferroelectric Curie temperature of LiNbO₃ is very high (1430 K), but its very large spontaneous polarization cannot be switched by an external electric field at room temperature. However, LiNbO₃ is a very famous nonlinear optical material.^[15]

Therefore, preparation of new materials displaying spontaneous polarization and magnetism at room temperature is essential for the development of room-temperature multiferroic materials. Herein, we report that In_{1–x}M_xMO₃ ($x = 0.112–0.176$ and M = Fe_{0.5}Mn_{0.5}) has the same structure as multiferroic BiFeO₃ and Néel temperatures near room temperature. In_{1–x}M_xMO₃ presents a new class of perovskite materials (with In³⁺ in the A site of a perovskite ABO₃) that is almost completely unexplored. This class of materials is unique because 1) long-range magnetic ordering survives near room temperature despite significant disordering in the A and B sites, 2) the same transition metals are located in both A and B sites, and 3) a polar distortion is realized without the presence of ions with lone electron pairs.

Figure 1 shows the X-ray powder diffraction (XRD) patterns of In_{0.9}MnO_{2.85}, In_{0.7}MnO_{2.55}, and In_{0.7}Mn_{0.5}Fe_{0.5}O_{2.55} prepared under the same conditions (6 GPa and 1773 K for 30 min). In_{0.9}MnO_{2.85} crystallizes in a hexagonal structure similar to stoichiometric InMnO₃.^[17] However, further decrease of the indium content (In_{1–y}MnO_{3–1.5y} with $y \geq 0.2$) resulted in stabilization of a perovskite-type structure. Perovskite phases were obtained from In_{0.8}MnO_{2.7} to In_{0.5}MnO_{2.25}; these phases have a monoclinically distorted GdFeO₃-type structure (space group *P2₁/n*). The introduction of Fe³⁺ ions into In_{0.7}MnO_{2.55} (or others with $y = 0.2$ and 0.25) stabilized a different perovskite structure with rhombohedral symmetry. Reflection conditions derived from the indexed reflections of In_{0.7}Mn_{0.5}Fe_{0.5}O_{2.55} were $-h + k + l = 3n$ for *hkl* and $h + l = 3n$, $l = 2n$ for *h–hl* (hexagonal axes, obverse

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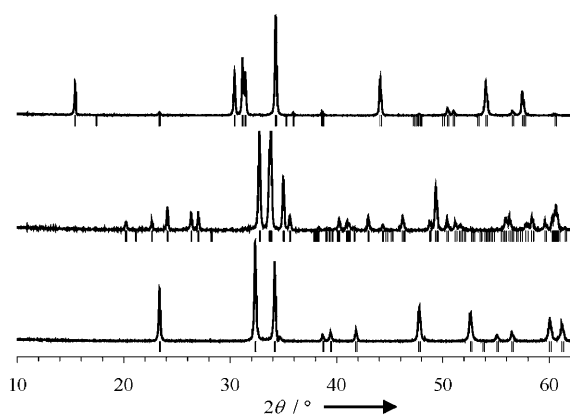


Figure 1. X-ray powder diffraction patterns of $\text{In}_{0.9}\text{Mn}_{0.285}\text{O}_{2.85}$ (space group $P6_3cm$, $a=5.8769(1)$, $c=11.4744(3)$ Å; top), $\text{In}_{0.7}\text{Mn}_{0.255}\text{O}_{2.55}$ (space group $P2_1/n$, $a=5.13333(7)$, $b=5.32401(8)$, $c=7.8645(1)$ Å, $\beta=92.546(1)^\circ$; middle), and $\text{In}_{0.7}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{2.55}$ (space group $R3c$, $a=5.24271(5)$, $c=13.95153(9)$ Å; bottom). The samples were prepared under the same conditions (6 GPa and 1773 K for 30 min). The allowed Bragg reflections for the corresponding space groups are indicated by tick marks. The patterns were obtained at room temperature using $\text{Cu}_{K\alpha}$ radiation.

setting), affording possible space groups $R3c$ (No. 161, non-centrosymmetric) and $R\bar{3}c$ (No. 167, centrosymmetric).

The crystal structure of $\text{In}_{0.7}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{2.55}$ was investigated using synchrotron X-ray powder diffraction (SXRD). We checked different structural models including corundum-type ($R\bar{3}c$), ilmenite-type ($R\bar{3}$), and centrosymmetric perovskite-type ($R3c$). However, all these models gave poor matching between observed and calculated intensities for some reflections. Only the polar perovskite-type model ($R3c$) gave excellent agreement between the observed and calculated SXRD patterns. Furthermore, the structural analysis showed that all of the cation and oxygen sites in $\text{In}_{0.7}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{2.55}$ are fully occupied. Therefore, the crystallographic formula will be $(\text{In}_{1-x}\text{M}_x)\text{MO}_3$ ($x=0.176$; $\text{M}=\text{Fe}_{0.5}\text{Mn}_{0.5}$) with $Z=6$ (where Z is the number of formula units per unit cell). That is, Mn^{3+} and Fe^{3+} ions are statistically distributed in the B site; In^{3+} ions and remaining Mn^{3+} and Fe^{3+} ions are distributed in the A site. Table 1 gives the final lattice parameters, R factors, fractional coordinates, and B parameters. Figure 2a shows the crystal structure of $\text{In}_{0.7}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{2.55}$.

Table 1: Structure parameters of $\text{In}_{0.7}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{2.55}$ at room temperature.

Site	g	x	y	z	B [Å ²]
In	0.8237	0	0	0	0.322(7)
M1	0.1763	0	0	0.0167(3)	0.322(7)
M2	1	0	0	0.21602(4)	0.466(11)
O	1	0.6448(4)	0.0213(3)	0.95106(14)	0.55(3)

Space group $R3c$ (No. 161); $Z=6$; $a=5.24271(5)$, $c=13.95153(9)$ Å, and $V=332.096(5)$ Å³, $R_{\text{wp}}=3.51\%$, $R_p=2.36\%$, $R_B=1.98\%$, and $R_F=0.95\%$. M1, M2 = $\text{Mn}_{0.5}\text{Fe}_{0.5}$. g is the occupation factor, and B is the isotropic thermal parameter. $d(\text{In}-\text{O})=2.038(2)$ Å ($\times 3$) and $2.280(2)$ Å ($\times 3$), $d(\text{M1}-\text{O})=2.118(3)$ Å ($\times 3$) and $2.128(3)$ Å ($\times 3$), $d(\text{M2}-\text{O})=1.999(2)$ Å ($\times 3$) and $2.093(2)$ Å ($\times 3$).

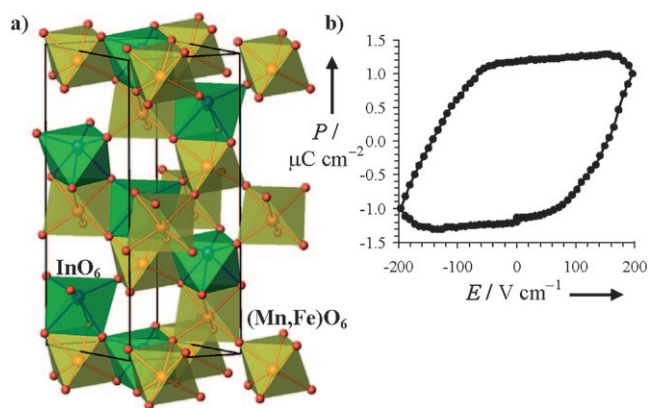


Figure 2. a) Crystal structure of $\text{In}_{0.7}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{2.55}$. The yellow octahedra are $(\text{Mn,Fe})\text{O}_6$, and the green octahedra are InO_6 . Splitting of In^{3+} and $(\text{Mn,Fe})^{3+}$ ions inside InO_6 is shown. b) Polarization (P) versus electric field (E) hysteresis loop in $\text{In}_{0.75}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{2.625}$ at room temperature.

When the vacancy model of the $R3c$ perovskite was used (with $g(\text{In})=0.7$, $g(\text{M})=1$, and $g(\text{O})=0.85$), the fitting of some reflections was not good (including the first 012 reflection), resulting in $R_{\text{wp}}=5.61\%$, $R_p=3.58\%$, $R_B=5.48\%$, and $R_F=1.96\%$ and negative $B(\text{In})$. It is known that the first reflections are the most sensitive to occupation factors. Indeed, the subsequent refinement of occupation factors (together with all B parameters) resulted in $g(\text{In})=0.963(2)$ and $g(\text{O})=1.08(2)$ with fixed $g(\text{M})=1$. Moreover, the experimental density of $6.12(5)$ g cm⁻³ is consistent with $(\text{In}_{1-x}\text{M}_x)\text{MO}_3$ ($x=0.176$, $\rho_{\text{calcd}}=6.23$ g cm⁻³) rather than $\text{In}_{0.7}\text{MO}_{2.55}$ ($\rho_{\text{calcd}}=5.30$ g cm⁻³).

Figure 2b shows the best ferroelectric hysteresis loop obtained for $\text{In}_{0.75}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{2.625}$ at room temperature. The sample still leaks current too easily, and the maximum polarization is $1 \mu\text{C cm}^{-2}$. This value is comparable with the values $2\text{--}6 \mu\text{C cm}^{-2}$ reported for some BiFeO_3 samples.^[9] It took a lot of efforts of different groups before the leakage current in BiFeO_3 was significantly reduced and the intrinsic polarization could be measured. The structural data confirmed that $\text{In}_{0.7}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{2.55}$ is isostructural with BiFeO_3 and should display spontaneous polarization. The ferroelectric Curie temperature of $\text{In}_{0.7}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{2.55}$ is rather high: no phase transitions were detected below 670 K by high-temperature SXRD, differential thermal analysis, and differential scanning calorimetry; above 670 K, $\text{In}_{0.7}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{2.55}$ irreversibly transforms to a corundum-type structure.

Figure 3a shows the inverse magnetic susceptibilities of $\text{In}_{0.75}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{2.625}$ measured at 1 T in the zero-field-cooled (ZFC) and field-cooled (FC) modes. Linear Curie–Weiss behavior was observed above 325 K, and the fitting between 330 and 400 K gave $\mu_{\text{eff}}=5.37 \mu_B$ (versus the calculated value of $5.43 \mu_B$) and a Curie–Weiss temperature of -590 K. Below 325 K, the inverse magnetic susceptibilities decreased, indicating the presence of a weak ferromagnetic component. The isothermal magnetization measurements between 5 and 300 K (Figure 3b) confirmed the existence of weak ferromagnetic properties. The minimum on the χ^{-1} versus T curve near 270 K can be taken as T_N .

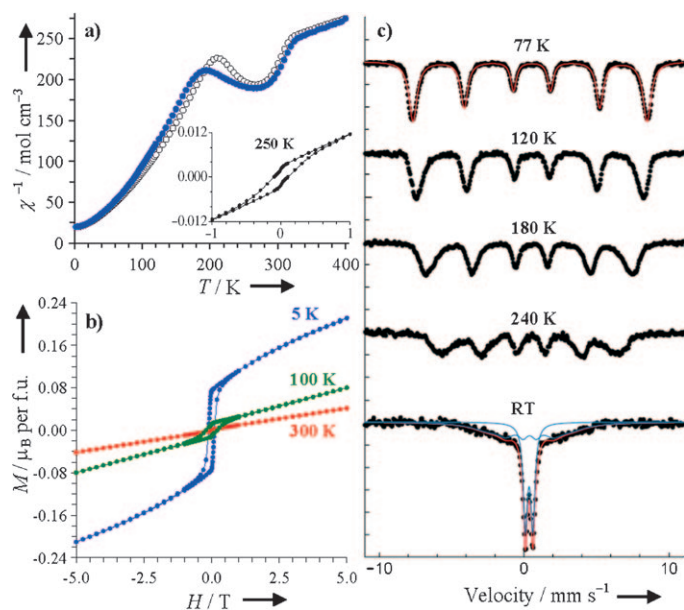


Figure 3. Magnetic properties of $\text{In}_{0.75}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{2.625}$. a) Temperature dependence of the inverse magnetic susceptibilities measured at 1 T under zero-field-cooled (ZFC, empty circles) and field-cooled (FC, filled circles) conditions between 2 and 400 K. The inset gives isothermal magnetization curves (M vs. H) at 250 K between -1 and 1 T. b) Isothermal magnetization curves at 5, 100, and 300 K between -5 and 5 T. c) Mössbauer spectra of $\text{In}_{0.75}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{2.625}$ at different temperatures. The circles are experimental data; the lines are the fits.

To confirm the long-range magnetic ordering in $\text{In}_{0.75}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{2.625}$, we measured ^{57}Fe Mössbauer spectra between 77 K and room temperature (Figure 3c). At room temperature, the Mössbauer spectrum consists of a paramagnetic doublet (about 50% of the area) with an isomer shift of 0.52 mm s^{-1} typical for a high-spin Fe^{3+} ion in an octahedral coordination environment. However, a very broad peak can also be seen at room temperature, arising from the development of long-range magnetic correlations. At 240 K and below, clear splitting to a magnetic sextuplet was observed, thus confirming long-range magnetic ordering. The sextuplet lines are noticeably broadened at 240 K owing to significant structural disorder in $\text{In}_{0.75}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{2.625}$. At 77 K, the isomer shift is 0.49 mm s^{-1} and the hyperfine field is 50.1 T. Mössbauer data confirmed that T_N is between 240 and 290 K.

The existence of long-range magnetic ordering near room temperature in $\text{In}_{0.75}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{2.625}$ is rather unusual, because disordering strongly suppresses magnetic transition temperatures. This fact also suggests that the magnetic transition temperature in $(\text{In}_{1-x}\text{M}_x)\text{MO}_3$ can be increased by different modifications. Using high pressure up to 6 GPa, we could not stabilize perovskite phases in $(\text{In}_{1-x}\text{Fe}_x)\text{FeO}_3$, for which a higher magnetic transition temperature is expected; a higher pressure is probably required. Other unusual features of this type of material are the necessity of the In deficiency to stabilize perovskite-type structures at 6 GPa and the statistical distribution of In^{3+} and $(\text{Mn},\text{Fe})^{3+}$ ions in the A site of a perovskite. There are some other examples in which the same

transition metal is located in the A and B sites, for example $(\text{BiMn}_3)\text{Mn}_4\text{O}_{12}$.^[18] However, that structure displays an ordered arrangement of Bi^{3+} and Mn^{3+} at the A sites.

Many perovskite-type materials that can be prepared only at high pressure in the bulk form can be stabilized as thin films owing to substrate effects, for example, ferroelectric BiAlO_3 ^[19] and ZnSnO_3 ^[20] and multiferroic PbVO_3 .^[21] Therefore, the discovery of a new class of perovskite materials $\text{In}_{1-x}\text{M}_x\text{MO}_3$ that have spontaneous polarization and magnetic transitions near room temperature opens wide possibilities for thin-film research. Understanding the polar structure of $\text{In}_{1-x}\text{M}_x\text{MO}_3$ is important from both theoretical and practical points of view because this class of materials does not require the presence of cations with a lone electron pair such as Bi^{3+} and Pb^{2+} to cause a polar distortion.^[22] However, significant disordering in $\text{In}_{1-x}\text{M}_x\text{MO}_3$ may complicate the theoretical analysis. Since this class of materials has not yet been explored (except for one old synthetic study on InCrO_3 and InRhO_3 perovskites),^[23] there is still room for improvement of the multiferroic properties of $\text{In}_{1-x}\text{M}_x\text{MO}_3$.

Experimental Section

The samples were prepared from stoichiometric mixtures of In_2O_3 (99.99%), Mn_2O_3 (99.99%), and Fe_2O_3 (99.999%) in a belt-type high-pressure apparatus at 6 GPa and 1773 K for 30 min in Pt capsules. After heat treatment the sample was quickly cooled to room temperature, and the pressure was slowly released. XRD data were collected at room temperature on a RIGAKU Ultima III diffractometer using $\text{Cu K}\alpha$ radiation (2θ range 10 – 150° , step width 0.02° , and counting time 2 – 10 s step $^{-1}$). SXRD data were measured at room temperature on a large Debye–Scherrer camera at the BL15XU beam line of Spring-8.^[24] The data were collected between 5° and 60° with a 0.003° interval in 2θ . The incident beam was monochromated at $\lambda = 0.65297 \text{ \AA}$. The sample packed into a Lindemann glass capillary (inner diameter: 0.1 mm) was rotated during the measurement. The Rietveld analysis was performed with RIETAN-2000.^[25] High-temperature SXRD was performed at the BL02B2 beam line of Spring-8. DC magnetic susceptibilities, $\chi = M/H$, were measured on a SQUID magnetometer (Quantum Design, MPMS) between 2 and 400 K in an applied field of 1 T under zero-field-cooled (ZFC) and field-cooled (FC; on cooling) conditions. Isothermal magnetization measurements were performed between -5 and 5 T from 5 to 300 K. ^{57}Fe Mössbauer spectra were measured with transmission geometry using a $^{57}\text{Co}/\text{Rh}$ source. The sample weight for the Mössbauer measurements was about 50 mg, and the sample thickness was about $10 \text{ }\mu\text{m}$. Obtained spectra were calibrated by $\alpha\text{-Fe}$ as a standard and were fitted by a Lorentzian function. For ferroelectric tests, samples fixed to a metal plate by a Ag paste (Aremco Products, 525 bond) were thinned and polished using several grades of alumina slurry to a thickness of about $200 \text{ }\mu\text{m}$. The counter Au electrode of $0.63 \times 10^{-4} \text{ cm}^2$ in area was deposited on the polished surface by a conventional vacuum evaporation technique. The P versus E curves were measured by a ferroelectric tester (Radiant, RT6000).

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