Unusual enhancement of multiferroicity in YMn$_{2-x}$Ti$_x$O$_5$ due to ferroelectrically active TiO$_6$ oxygen octahedral units


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Multiferroic manganites have recently been attracting special attention, but searching for multiferroics with high ordering temperature and large ferroelectric (FE) polarization $P$ remains challenging. Although major efforts are being devoted to the RMn$_2$O$_5$ family, multiferroics with $R=Y$, Bi, and Tb-Ho, family RMn$_2$O$_5$ ($R=Y$, Bi, and La-Lu) have been addressed too with sizable coupling between the magnetic and FE order parameters, as revealed by recent magnetocapacitance measurements.

The RMn$_2$O$_5$ compounds mainly crystallize in orthorhombic space group $Pbam$ at room temperature. The RMn$_2$O$_5$ family can be simply written as $R$ 3 $\overline{4}$ $m$ $m$ $m$ with the octahedra. Obviously, the two structural blocks (pyramid Mn$_3$O$_5$ bipyramids. The edge sharing linked octahedra form ribbons along the $c$-axis, which is connected on the $ab$ plane by the edge sharing bi-pyramids that are corner-connected to the octahedra. Although the two structural blocks (pyramid Mn-O units and octahedral Mn-O units) stack alternatively and constitute different stacking sequences along the three orthogonal axes, making a number of degrees of freedom for structural distortions and magnetic interactions, as well as triggering a set of magnetic transitions upon cooling from high temperature ($T$). At $T>T_N=45$ K, the antiferromagnetic (AFM) Neel point, paramagnetic/paraelectric phase is favored but this phase is replaced then by an AFM order of incommensurate $x$- and $z$-components below $T_N$. For some RMn$_2$O$_5$ ($R=$ Tb, Ho, and Dy), the FE and commensurate (wave vector $k_c$) AFM phase appears at several degrees below $T_N$.

In contrast, YMn$_2$O$_5$ is unique in terms of some specific behaviors. The reported $T_N$ is $\sim 45$ K, below which the two-dimensionally modulated incommensurate Mn spin order is developed. Below the FE phase ensuing at $T_c$, a reversal of the FE polarization $P$ at $T=T_{c1}<T_{c2}$ is identified, indicating a transition of this FE phase into another low-$T$ FE phase with incommensurate AFM order. This effect is attributed to the difference in the antiparallel spin alignment between two neighboring Mn$^{3+}$-Mn$^{3+}$, Mn$^{4+}$-Mn$^{4+}$, Mn$^{3+}$-Mn$^{3+}$-Mn$^{4+}$ chains along the $a$-axis. Because of the exchange striction, this phase difference leads to the net ionic displacement between the neighboring Mn$^{3+}$-Mn$^{4+}$ chains. Recent experiments also detected a small deviation of the Mn spins from the $ab$ plane, forming a non-collinear (spiral) modulation along the $c$-axis.

Even though the physical significance of the above-mentioned mechanisms is appreciated, the as-generated polarization for YMn$_2$O$_5$ is small and the ferromagnetism if any is weak. To our knowledge, modulating the Mn$^{3+}$-Mn$^{3+}$-Mn$^{4+}$-Mn$^{3+}$-Mn$^{3+}$-Mn$^{4+}$ spin-chains by nonmagnetic substitution may break the spin order and is usually believed to damage the multiferroicity.

Surely, such an approach must rely on structural perturbations as small as possible. This is the main motivation for the present work. Furthermore, it is known that Ti$^{4+}$O$_6$ octahedron is ferroelectrically active, as shown in titanates such as BaTiO$_3$ and PbTiO$_3$, and the local Ti$^{4+}$O$_6$ octahedral network may contribute to the polarization. No test of this scheme for multiferroic RMn$_2$O$_5$ has been performed although improvement of multiferroic properties using nonmagnetic substitution for magnetic ions was once reported earlier. We shall investigate the effect of Ti$^{4+}$ substitution of Mn$^{4+}$ to induce the Ti$^{4+}$O$_6$ octahedra in YMn$_2$O$_5$. The measured data do show a significant impact of the Ti$^{4+}$ substitution on the magnetism and FE polarization.

The polycrystalline YMn$_{2-x}$Ti$_x$O$_5$ (YMTO) samples were prepared by solid-state sintering using Y$_2$O$_3$, Mn$_2$O$_3$, and TiO$_2$ as starting materials. The powder was pre-sintered in flowing oxygen ambient at 1100 C for 24 h. Then, the pellets were sintered again in flowing oxygen ambient at 1350 C under 4.0 bar oxygen pressure for 36 h. The samples were characterized by X-ray diffraction (XRD) and the species valence states were checked using X-ray photoemission spectroscopy (XPS) by an Al K$\alpha$ source.

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Subsequently, these samples were shaped into pellets of ~0.4 mm in thickness, and the Au top electrodes with area of 7.0 mm² were deposited. For multiferroicity characterization, magnetization $M$ as a function of $T$ and magnetic field $H$ was measured using the Quantum Design superconducting quantum interferometer devices (SQUIDs) and dielectric constant $\varepsilon$ was measured using HP4294A impedance analyzer over a broad range of frequency, connected with the Quantum Design physical property measurement systems (PPMSs), where the specific heat ($C_p$) measurements were implemented too. The polarization $P$ was probed using two different methods. One is the pyroelectric current method with the Keithley 6514 electrometer, combined with the PPMS. The reliability of this pyroelectric current was demonstrated in earlier works. The method is the so-called PUND (positive-up-negative-down pulses) technique, which is used to probe the FE polarization and details of the measuring procedure were reported in literature.

Fig. 1 presents the 0-2θ XRD spectra of several samples. All these samples show the single-phase crystallinity and each spectrum can be indexed with the $Pbam$ space group. In an effort to resolve the delicate structural difference between these samples, the structural refinements of the data by means of the General Structure Analysis System (GSAS) program were carried out, in which the isotropic thermal parameters ($U_{iso}$) for Y/Mn and the anisotropic thermal parameter ($U_{aniso}$) for oxygen were used. The refined results are shown in Figs. 1(a)–1(d), with inserted Rietveld reliability parameters $R_{wp}$ and $R_p$. The as-evaluated room temperature lattice constants ($a$, $b$, and $c$), selected bond lengths, and bond angles are listed in Table I. It is seen that the Ti substitution results in slight lattice expansion. The data of bond lengths and angles suggest that the MnO$_5$ tetragonal pyramids are distorted by the Ti substitution. While lattice distortion behaviors may be relevant to the difference between the Mn and Ti ions in terms of electronic structure and magnetism. In the data refinement, no substitution of Mn$^{3+}$ by Ti$^{4+}$ is considered since such a substitution needs excess oxygen interstitials due to the charge non-neutrality. However, YMn$_2$O$_5$ free of oxygen vacancies cannot be synthesized unless the sintering is done in oxygen ambient, suggesting that excess oxygen interstitials in YMn$_2$O$_5$ are unstable.

Subsequently, we probe the valence state of Ti ions to confirm the above assumption. Due to the very low substitution levels, the collected XPS signals from Ti ions are unfortunately very weak. No reliable data can be obtained for samples with $x < 0.03$ considering the XPS uncertainty as high as ~2%. We employed the high-precision probing mode to collect the data on Ti 2p$_{1/2}$ and 2p$_{3/2}$ core energy levels for sample $x = 0.04$, and the data are plotted in Fig. 2(a). It is clearly shown that only Ti$^{4+}$ signals can be collected and those signals from the Ti$^{3+}$ ions, if any, are submerged in the background noises. Therefore, it is safe to claim that the Ti ions in the samples are in the Ti$^{4+}$ valence state. In addition, we come to check the Ti$^{3+}$-substitution of Mn$^{4+}$ instead of Mn$^{3+}$. The XPS data on the Mn 2p core energy levels are plotted in Figs. 2(b)–2(e). By carefully fitting the Mn 2p$_{3/2}$ and 2p$_{1/2}$ peaks by an imposition of the Mn$^{3+}$ and Mn$^{4+}$ contributions, a rough evaluation of the Mn$^{4+}$/Mn$^{3+}$ atomic ratio is acceptable although such a fitting may not allow high accuracy (with error bars of ~±3%).

Therefore, we pay our attention to the multiferroic behaviors. First, the measured $M$-$T$ data under the zero-field cooled (ZFC) and field cooling (FC) conditions (measuring field $H = 100$ Oe) for several samples are plotted in Figs. 3(a)–3(d), respectively. The $M$-$H$ hysteresis loops for these samples measured at $T = 2$ K are given in inset Figs. 3(e)–3(h). Here, it is found that the small magnetic moments measured under the FC mode (Fig. 3(a)) were observed for pure YMn$_2$O$_5$ sample, which was surprising at the first glance, since the pure YMn$_2$O$_5$ is of AFM order. The $M$-$H$ hysteresis

![FIG. 1. Measured XRD 0-2θ spectra for four samples and corresponding Rietveld refinement results. The refinement reliability parameters $R_{wp}$ and $R_p$ are inserted.](image-url)

| TABLE I. Evaluated lattice parameters and bond lengths/bond angles. |
|---|---|---|---|---|
| $x$ | 0.00 | 0.02 | 0.03 | 0.04 |
| $a$ (Å) | 7.29798(5) | 7.30202(5) | 7.31145(8) | 7.31594(9) |
| $b$ (Å) | 8.48779(7) | 8.49189(7) | 8.50010(6) | 8.50623(8) |
| $c$ (Å) | 5.67879(6) | 5.68326(6) | 5.69041(5) | 5.69709(8) |
| Mn$_{2}$-O$_5$($\times2$) (Å) | 2.044(16) | 2.067(16) | 2.081(26) | 2.090(23) |
| Mn$_{2}$-O$_4$($\times2$) (Å) | 1.806(9) | 1.962(11) | 1.958(13) | 1.970(13) |
| Mn$_{2}$-O$_3$-Mn$_{2}$ ($\times2$) (Å) | 2.187(10) | 1.864(11) | 1.902(16) | 1.944(16) |
| Mn$_{2}$-O$_2$-Mn$_{2}$ ($\times2$) (Å) | 1.812(11) | 1.863(13) | 1.889(18) | 1.904(19) |
| Mn$_{2}$-O$_2$ (Å) | 1.910(8) | 1.876(10) | 1.893(13) | 1.913(14) |
| Mn$_{2}$-Ti$_{1}$ (Å) | 2.809(19) | 2.782(26) | 2.798(26) | 2.790(27) |
| Mn$_{2}$-Ti$_{1}$-Ti$_{1}$ ($\times2$) (Å) | 2.908(26) | 2.907(27) | 2.906(28) | 2.907(27) |
| Mn$_{2}$-O$_4$-Mn$_{2}$ ($\times2$) (Å) | 1.812(11) | 1.863(13) | 1.889(18) | 1.904(19) |
| Mn$_{2}$-O$_2$-Mn$_{2}$ ($\times2$) (Å) | 1.812(11) | 1.863(13) | 1.889(18) | 1.904(19) |
| Ti$_{1}$-O$_2$-Ti$_{1}$ (Å) | 2.809(19) | 2.782(26) | 2.798(26) | 2.790(27) |
| Mn$_{2}$-Ti$_{1}$-Ti$_{1}$ ($\times2$) (Å) | 2.908(26) | 2.907(27) | 2.906(28) | 2.907(27) |
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shown in Fig. 3(e) also generates a small loop. This anomalous behavior was checked to be true by a set of samples sintered at various temperatures. The weak ferromagnetism is probably from the weak spin-canting on the grain boundaries and/or domain walls as well as due to existence of small spin glass clusters. Similar effects were observed in quite a few of multiferroic compounds with AFM ground state.19,23

The measured $M$ has a broad transition at $T_N \approx 50$ K from the paramagnetic state to the AFM state with a weak spin-canting induced moment. This transition point seems to be several degrees higher than earlier reported value $T_N \approx 45$ K. The Ti$^{4+}$ substitution remarkably enhances the magnetic moment, in particular, at $x = 0.03$, although the $M$-enhancement is still weak if the spin-canting induced initial net moment is excluded. The measured $M$-$H$ loops confirm this effect, and the remnant moment for sample $x = 0.03$ is $\sim 0.3 \mu_B$/f.u. with a coercivity of $\sim 2$ kOe. As $x > 0.03$, one observes gradual decay of $M$.

In the lattice level, the origin of the weak ferromagnetism induced by the Ti substitution seems to be complicated and may be linked to the Mn$^{3+}$-Mn$^{4+}$ super-exchange FM interactions.24 The substitution may disturb the Mn$^{3+}$-Mn$^{3+}$-Mn$^{3+}$-Mn$^{4+}$ AFM chains, suppressing the super-exchange AFM interactions between the Mn$^{3+}$-Mn$^{3+}$ spin pairs. The excess Mn$^{3+}$ ions in the substituted samples benefit to the enhancement of $M$, although the over AFM order can be substantially maintained. It is understandable that over-substitution of Ti will eventually damage the magnetic order.

For the ferroelectricity, we use both the pyroelectric current technique and the PUND method to probe the $P$. For a clear comparison, the measured $\epsilon$ and $P$ as a function of $T$ for samples $x = 0.0$ and $x = 0.03$ are plotted in Figs. 4(a) and 4(b), respectively, where the $P$ was measured using the pyroelectric current technique. The measured specific heat data ($C_p/T$) as a function of $T$ for the two samples are given in Fig. 4(c) for better identification. First, for $x = 0.0$, the two dielectric anomalies at $T_{c1} \approx 42$ K and $T_{c2} \approx 20$ K are consistent with earlier report. The anomalies in the $C_p/T$-$T$ curves coincide with the dielectric anomalies within the measurement uncertainties. The higher-$T$ anomaly is slightly lower but roughly consistent with $T_N$, and the lower-$T$ anomaly indicates the reversal of $P$ at $T_{c2}$. In addition, sample $x = 0.03$ has a lower $T_{c1}$ and higher $T_{c2}$ for several degrees. Third, polarization $P$ ensues at $2-3$ K below $T_{c1}$, and the Ti-substitution significantly enhances the $P$. The measured $P$ at $T \approx 2$ K is $\sim 21.15 \mu C/m^2$ for $x = 0$ and $\sim 77 \mu C/m^2$ for $x = 0.03$, while the measured $P$ is $20.0 \mu C/m^2$ at
$T \sim 23$ K for $x = 0$ and 140.0 $\mu$C/m$^2$ at 28 K for $x = 0.03$. The slightly lower ensuing point for the $P$ ($\sim 40$ K for $x = 0$ and $\sim 38$ K for $x = 0.03$) than $T_{c1}$ for the dielectric anomaly and $T_N$ for the AFM ordering was also observed earlier.\textsuperscript{7,10}

Regarding the $T$-dependence of the $C_p/T$, slightly different from the data for single crystals,\textsuperscript{29} the polycrystalline samples here show one broad $\lambda$-anomaly and one step-like anomaly at $T \sim 42$ K and $\sim 20$ K, respectively, corresponding to $T_{c1}$ and $T_{c2}$. The broadening of the two anomalies is obviously due to the polycrystalline nature. The estimated entropy change at $T \sim T_{c2}$ is roughly the same for both samples. Several examples of the $P(x, H)$ dependences are shown in Figs. 5(a) and 5(b). It is seen that the Ti-substitution at a proper level ($x = 0.03$) does enhance the $P$. However, no remarkable response of $P$ against $H < 9 T$ was observed, although the measured $P$ becomes smaller under higher $H$. One may argue that the magnetic field available to us is insufficient for inducing a significant response, which may be the reason for rare reports available on $P(H)$ in YMn$_2$O$_5$, and similar fact was reported in BiMn$_2$O$_5$.\textsuperscript{28–30}

We show the PUND method measured $P-E$ loops for sample $x = 0.03$ in Figs. 5(c) and 5(d) at $T = 12$ K. It is seen that the saturated $P$ is available under $E = 30$ kV/cm. The saturated $P$ and coercive field ($E_c$) at 12 K are $\sim 175$ $\mu$C/m$^2$ and 14 kV/cm, respectively. With increasing $T$, both $P$ and $E_c$ tend to decrease, in the similar tendency as the data obtained by the pyroelectric current method. However, it is noted that the quality of the evaluated $P-E$ hysteresis deserves for further improvement. In fact, the observed remnant polarization ($\sim 130$ $\mu$C/m$^2$ at $T \sim 12$ K) is somehow larger than that evaluated from the pyroelectric current method ($\sim 80$ $\mu$C/m$^2$ at $T \sim 12$ K). This remarkable difference may be attributed to two reasons. One is the difference in the poling field used for the two methods. It seems that the poling field for the pyroelectric current scheme is 10 kV/cm, much lower than that used for the leakage current method, noting that a poling field higher than 5 kV/cm at $T > 60$ K may lead to failure of the electrometer operation. Therefore, the measured $P$ by the pyroelectric current method may be smaller than the true remnant polarization. The other reasons, in spite of less important, may be the error induced by subtracting the $dc$ leakage current from the total leakage current including the polarization switching current. Therefore, the real remnant polarization should be a value slightly lower than $\sim 130$ $\mu$C/m$^2$.

To this stage, the underlying mechanism for the Ti-substitution induced effects as revealed in the present work remains unclear to the authors. We can present a very preliminary discussion on the possible reasons and additional investigation is needed. First, it is certain that the Ti-substitution induces some minor changes in structure, which will disturb and modulate the exchange striction mechanism associated with the Mn$^{3+}$-Mn$^{4+}$-Mn$^{3+}$-Mn$^{4+}$ AFM chains,\textsuperscript{31} while a tiny substitution as low as 3% does not suppresses the AFM order substantially. Second, the substitution results in the lattice expansion and induces distorted TiO$_6$ octahedra, which may benefit to the polarization enhancement. One may infer that the distorted TiO$_6$ octahedral are ferroelectrically active, and this activity contributes to the polarization enhancement. Similar effect was argued recently in Cr-doped Ho$_2$Ti$_2$O$_7$.\textsuperscript{32} This mechanism may work although it is not dominant since the doping level is low.

Surely, we may include other effects induced by the Ti-substitution and consequent lattice distortion, such as the enhanced titling of MnO$_6$ toward the central oxygen\textsuperscript{33} and the enhanced interchain dipole interaction,\textsuperscript{32} both of which are believed to benefit to the ferroelectricity enhancement.

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\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{(a) Measured $P(T)$ data for samples $x = 0$, 0.02, 0.03, and 0.04 under $H = 0$. (b) Measured $P(T)$ data under various $H$ for sample $x = 0.03$. (c) Measured $I-E$ loop for sample $x = 0.03$ at $T = 12$ K. (d) Evaluated $P-E$ hysteresis for sample $x = 0.03$ at $T = 12$ K, 16 K, and 20 K by the PUND method, respectively.}
\end{figure}

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