Pressure-induced ferroelectricity and enhancement of Mn-Mn exchange striction in GdMn2O5


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I. INTRODUCTION

Multiferroics in which ferroelectric (FE) and magnetic order coexist have attracted much attention in recent years because of their novel physical phenomena and potential application.1,2 The type-II multiferroics, in which ferroelectricity is induced by magnetic order, usually show large coupling among magnetism (spin), ferroelectricity (charge), and structure (lattice). In fact, giant magnetoelastic (ME) (i.e., magnetic-field-induced change of FE polarization) and/or converse ME (i.e., electric-field-induced change of magnetization) effects have been observed in numerous type-II multiferroics, such as hexaferrites Ba0.52Sr2.48Co2Fe24O41,3 R3MnO3 (R = rare-earth),4 and CoCr2O4.5 Therefore, multiferroic materials provide a playground to study a strong interaction among the three degrees of freedom, i.e., spin, charge, and lattice.

Among several mechanisms that lead to the type-II multiferroics, the symmetric spin exchange interaction, i.e., the so-called exchange-striction mechanism, has usually exhibited large spin-lattice coupling and hence relatively large spin-induced FE polarization.6,7 Orthorhombic RMn2O5 (R = Bi, Y, and rare-earth) family is subject to such a mechanism, in which ferroelectricity arises from the exchange striction with a zigzag chain of Mn4+-Mn3+-Mn3+Mn4+ along the a-axis.8,9 A typical crystallographic and magnetic structure for RMn2O5 with R = Gd is shown in Fig. 1. The family of multiferroic RMn2O5 undergoes a common series of phase transitions as follows: a first phase transition from high-temperature (T) paramagnetic and paraelectric (PM-PE) to high-T incommensurate (HT-IC) antiferromagnetic (AFM) and paraelectric phase (termed as HT-IC-PE) appears at $T_{N1} \approx 40–44$ K, and a second transition into a commensurate (CM) AFM and FE phase (termed as CM-FE) occurs at $T_{N2} \approx 33–39$ K. Upon further temperature being lowered into $T_{N3} \approx 13–20$ K, RMn2O5 except R = Gd and Bi shows a transition into another low-T incommensurate AFM and FE (i.e., LT-IC-PE) state.8–10 As expected from the origin of exchange-striction mechanism, large spin-lattice coupling has been indeed found in RMn2O5.11

It is well known that external pressure is an efficient way to control lattice and thus structure of a material.12 It is hence expected that pressure can effectively tune magnetic and FE properties in numerous multiferroics via spin-lattice-charge coupling. Many recent studies have indeed shown that external pressure is a useful and unique tool to tune the multiferroic and ME properties.13 For example, uniaxial pressure could control the magnetic order and ferroelectricity in a multiferroic Ba2CoGe2O7.14 Giant spin-driven FE polarization (up to $\sim 10,000 \mu C/m^2$) was also observed under high pressure in RMnO3 (R = Tb, Dy, Gd).15,16 In RMn2O5 (R = Y, Ho, Tb, Dy), a pressure-induced incommensurate to commensurate FE phase transition was observed at low temperatures, accompanied by large enhancement of FE polarization.17,18

As one of the multiferroic RMn2O5 compounds, GdMn2O5 exhibits unique magnetic, FE and ME behaviors as compared to other RMn2O5 compounds. All the rare-earth RMn2O5 compounds except GdMn2O5 show IC-FE phase at low temperature.8–10 Moreover, GdMn2O5 shows the largest FE polarization ($\sim 3600 \mu C/m^2$) and magnetic-field-tuned polarization ($\sim 5000 \mu C/m^2$) among the RMn2O5 compounds. These properties are superior to most of the other multiferroics exhibiting FE polarization driven by spin order.19 The giant tuning capability of the FE polarization is likely to be associated with the Gd–Mn exchange striction. All these
results suggest a unique role of Gd$^{3+}$ ions with non-degenerate 4f orbitals (4f$^7$) on the physical properties of Gd-based oxides.

In the present work, we report the multiferroic and ME properties of GdMn$_2$O$_5$ crystals under hydrostatic pressure up to 1.73 GPa. Under the high pressure condition, we found greatly enhanced FE polarization and a new FE phase between $T_{N2}$ and $T_{N1}$ in GdMn$_2$O$_5$. This observation constitutes another unique multiferroic behavior of GdMn$_2$O$_5$ under high pressure that is distinguished from that of other RMn$_2$O$_5$.

II. EXPERIMENTAL DETAILS

GdMn$_2$O$_5$ single crystals were grown using the flux method as reported previously. The crystals were then polished to about 0.2 mm in thickness along the $b$-axis in the orthorhombic structure, and the silver epoxy was applied on both sides of the plate-like crystals as electrical contacts. Pyroelectric/ME currents and dielectric constant were measured by using an electrometer (Keithley 617) and a capacitance bridge (AH2550A) at a frequency of 1 kHz, respectively. In the pyroelectric current measurement, the sample was first cooled down from 50 K to 2 K under a poling electric field $E_p \sim 9$ kV/cm applied along the $b$-axis and the magnetic field $H$ applied along the $a$-axis. After shorting the circuit for a reasonably long duration at 2 K, the current was measured in the warming process without biased electric field. In the ME current measurements, the sample was first cooled from 50 K to a fixed temperature under $E_p \sim 9$ kV/cm, which is hereinafter referred to as the ME poling, and then ME current was collected by sweeping $H$ after removing electric field. Electric polarization $P$ was obtained by integrating the pyroelectric/ME currents with respect to time. Dielectric constant was also measured under warming process. Hydrostatic pressure was applied up to 1.73 GPa by a piston-type cylinder cell made of BeCu/MP35N hybrid walls. The pressure cell was loaded into the chamber of physical property measurement system (PPMS$^\text{TM}$, Quantum Design), which can provide magnetic field and controlled temperature. Daphne 7373 liquid was used as a pressure transmitting medium. Applied pressure inside the cell was estimated in situ by the measurements of the superconducting transition temperature of high purity lead that is located just next to the sample. The magnetization measurements were carried out by using a vibrating sample magnetometer (VSM) in the PPMS$^\text{TM}$.

III. RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of FE polarization $P_b$ along the $b$-axis under different pressures in zero magnetic field. It is observed that the onset of $P_b$ under the ambient pressure appears around $T_{N2} \sim 34$ K, being consistent with previous reports. With temperature lowering to $T_{N3} \sim 15$ K, $P_b$ shows another step-like increase. Two interesting features are found in the pressure-induced enhancement of FE polarization. As found in the lower inset of Fig. 2, $P_b$ at 2 K, except a small decrease in the beginning, overall increases to a maximum value at $p \sim 1.3$ GPa, and then decreases again at higher pressures. This non-monotonous $P_b$ vs $p$ behavior implies different responses of the Gd–Mn and Mn–Mn interactions under pressure as will be discussed below. The second feature is that an additional small step-like increase of $P_b$ appears at $T_X \sim 36$–38 K when $p > 0.88$ GPa, as shown in Fig. 2 and its upper inset. This immediately points to a possibility of
pressure-induced new FE phase. The onset temperature $T_X$ of this new phase as well as the polarization was further increased with pressure.

We discuss below the above two key features in GdMn$_2$O$_5$. Related to the first one, we need to consider the behavior of three magnetic interactions, i.e., Mn–Mn, Gd–Mn, and Gd–Gd interactions, under pressure. Figs. 3(a) and 3(b) show the pyroelectric current, FE polarization, and dielectric constant along $b$ axis at different $H$ in GdMn$_2$O$_5$. It is known that GdMn$_2$O$_5$ undergoes first an incommensurate, long-range AFM ordering with a propagation vector $\mathbf{k}$ $\approx$ (0.49, 0, 0.18) due to the Mn–Mn interaction at $T_{N1}$ $\approx$ 42 K, as characterized by the abnormal increase of dielectric constant (see Fig. 3(b)). Upon being cooled below $T_{N2}$ $\approx$ 34 K, Mn$^{3+}$/Mn$^{4+}$ ions order in a commensurate AFM state with $\mathbf{k}$ $=$ (1/2, 0, 0), and the resulting effective magnetic field from Mn-sublattice acts on the Gd sites, leading to a weak Gd–Mn interaction. This interaction is associated with the small peak in the $M$–$T$ curve (Fig. 3(c)) and the dielectric constant (Fig. 3(b)), and the onset of $P_b$ (Fig. 3(a)). The broad peak in the $M$–$T$ curve at around $T_{N3}$ $\approx$ 15 K can be ascribed to the long-range AFM ordering of Gd spins. This Gd ordering temperature ($\approx$ 15 K) is the highest one among all the rare-earth ordering in the R$_2$Mn$_2$O$_5$ family, implying a strong Gd–Gd magnetic interaction.

Figure 4 shows the isothermal magnetization vs $H$ curves ($M$–$H$) along the $a$-axis at various temperatures. The large hysteresis at a high-$H$ region ($\approx$ 5–7 T) in the $M$–$H$ curves can be attributed to a rotation of the Gd spins since the field needed to reverse the Mn spins is much higher, e.g., above 15 T in BiMn$_2$O$_5$. As shown in Fig. 3, a dielectric constant peak at $T_{N3}$ is induced at a field of 8 T while the pyroelectric current peak near $T_{N3}$ is also largely enhanced. These results can be explained as follows. The Gd spins tend to orient antiparallel to the Mn spins at zero field just below $T_{N2}$ because of the weak Gd–Mn interaction; however, when a large enough $H$ is applied, say, $H$ = 8 T, the Gd spins rotate to the direction of $H$, and the polarization induced by the Gd–Mn interaction is suppressed. With temperature decreasing further at $H$ = 8 T, the Gd–Mn and Gd–Gd interactions become stronger and stronger and finally overcome the strength of the interaction between Gd/Mn and external $H$. Subsequently, the Gd spins reorient and order antiferromagnetically below $T_{N3}$, accompanied by the appearance of large additional FE polarization and a dielectric peak (see Figs. 3(a) and 3(b)).

The ferroelectricity in the R$_2$Mn$_2$O$_5$ family is believed to originate from the symmetric exchange-striction mechanism.
of the two $R$–Mn and Mn–Mn interactions. A total FE polarization in $H=0$T can be then written as $P_{\text{total}}=P_{\text{MnMn}}+P_{\text{GdMn}}$, where $P_{\text{MnMn}}$ is the polarization contribution from the Mn–Mn exchange striction and $P_{\text{GdMn}}$ from the Gd–Mn exchange striction. The latter term $P_{\text{GdMn}}$ at $T_{N2}<T<T_{N2}$ seems to be suppressed by a field of $H=8$T as discussed above, which approximately indicates that $P_{\text{GdMn}}\approx 0$ and $P_{\text{total}}\approx P_{\text{MnMn}}$ at $H=8$T.

To better understand the pressure-dependent FE polarization behavior in GdMn$_2$O$_5$ (Fig. 2), the $P_b$-$T$ curves at $H=8$T were also measured at different pressures. Figure 5 presents the FE polarization $P(H=8$T) (i.e., $P_{\text{MnMn}}$) as a function of pressure at a selected temperature of $T=25$K. If we assume that the $P_{\text{MnMn}}$ term does not change too much at $0\leq H\leq 8$T, i.e., $P_{\text{MnMn}}(0$T)$\approx P_{\text{MnMn}}(8$T), then the $P(0$T)$-P(8$T)$ can be roughly considered as $P_{\text{GdMn}}$ term at zero field. Based on the reasoning, $(P(0$T)$-P(8$T))\approx P_{\text{GdMn}}(0$T) data can be obtained as a function of pressure, as plotted in Fig. 5. It is clearly observed that $P_{\text{MnMn}}$ shows monotonous increase with increasing pressure and begins to saturate around $p=1.3$GPa, while $P_{\text{GdMn}}$ decreases overall with increasing pressure. As a combined result of such pressure-dependent variations of $P_{\text{MnMn}}$ and $P_{\text{GdMn}}$, $P_{\text{total}}$ at $25$K seems to show a rather slight increase below $0.9$GPa, a fast increase starting from $\sim 0.9$GPa, and saturation around $p=1.3$GPa. The pressure-induced variation of $P_b$ at $2$K (the lower inset of Fig. 2) seems to show qualitatively similar behavior; it slightly increases at low pressure regions, followed by a steep increase around $0.9$GPa until it shows saturation around $1.3$GPa.

It should be pointed out that the FE polarization $P_{\text{MnMn}}$ under pressure in YMn$_2$O$_5$ of the same RMn$_2$O$_5$ family with non-magnetic Y$^{3+}$ at $R$ site does not show such monotonous enhancement like that in GdMn$_2$O$_5$. Because of a lack of information about crystallography and magnetism under high pressure, we cannot confirm the proposed origin of the pressure-enhanced $P_{\text{MnMn}}$ in GdMn$_2$O$_5$ and the different pressure-dependent behavior of $P_{\text{MnMn}}$ in GdMn$_2$O$_5$ and YMn$_2$O$_5$. However, the differences in bond length and bond angle of Mn–O–Mn due to different ionic sizes of Gd$^{3+}$ (1.053 A) and Y$^{3+}$ (1.019 A) might be one possible factor to result in such different pressure effects. In the exchange striction model for ferroelectricity with up-up-down-down (↑↑↓↓) spin structure, the Hamiltonian with symmetric superexchange interaction $J$ between two magnetic moments $S_i$ and $S_j$ can be expressed as $H_{ex}=J(r_{ij})\theta S_iS_j$, where $r_{ij}$ and $\theta$ denote the bond length and bond angle, respectively. The FE polarization can be effectively affected by applied pressure via changing the $r_{ij}$ and $\theta$ between $S_i$ and $S_j$. Therefore, in the case of GdMn$_2$O$_5$, the shortened $r_{ij}$ and varied $\theta$ of Mn–O–Mn induced by pressure may contribute to the monotonous enhancement of $P_{\text{MnMn}}$.

We now discuss the second interesting feature under pressure, i.e., pressure induced new phase. In order to get more information on the new phase, the temperature-dependent dielectric constant $\varepsilon'$ under different pressures was measured and presented in Fig. 6(a). With an increase in the pressure, the peak shown in the dielectric constant near $T_{N2}$ is gradually suppressed and shifts toward lower temperatures. When the applied pressure is higher than $\sim 0.88$GPa, another dielectric peak appears above $T_{N2}$, becomes stronger, and shifts to higher temperature with the increase in the pressure. The temperature $T_X$ of the new dielectric constant peak is the same as the onset of FE polarization due to the new phase, as can be clearly observed in the selected $p=1.73$GPa in Fig. 6(b) and its inset. The simultaneous occurrence of the FE polarization and dielectric

![FIG. 5. Pressure-dependence of FE polarizations at $T=25$K, $P(8$T), $P(0$T)$-P(8$T)$, and $P(0$T), which can approximately represent the polarization contributions due to Mn–Mn interaction ($P_{\text{MnMn}}$), Gd–Mn interactions ($P_{\text{GdMn}}$), and their total sum ($P_{\text{total}}$).](Image)

![FIG. 6. (a) Normalized relative dielectric constant as a function of temperature (i.e., $\varepsilon'(T)/\varepsilon'(50$K)$-T$) at $H=0$T under different pressures; (b) $\varepsilon'(T)/\varepsilon'(50$K)$-T$ and $P_b$-$T$ under pressure $p=1.73$GPa. The inset is the locally magnified image.](Image)
peak demonstrates that the new phase induced by pressure is indeed ferroelectric.

To elucidate the magnetic-field effect on the FE polarization and dielectric constant \( \varepsilon' \) in this new FE phase, the ME effect (\( P-H \)) and the magnetodielectric (MD) effect (i.e., \( \Delta\varepsilon'(H)/\varepsilon'(0)-H \)) were investigated both in the new FE phase (termed as the FE2 phase) and in the CM-FE phase after the ME poling, as shown in Fig. 7. In the CM-FE, a sharp anomaly in the dielectric constant and a drop in the FE polarization were observed in the vicinity of \( \sim 5 \text{T} \) at \( T = 25 \text{K} \) under ambient pressure. As discussed above, the \( P-H \) and \( \Delta\varepsilon'(H)/\varepsilon'(0)-H \) behavior in the CM-FE phase at 25 K can be ascribed to the \( H \)-induced Gd-spin reorientation and suppression of the \( P_{\text{GdMn}} \). On the other hand, in the FE2 phase, an anomaly in \( \Delta\varepsilon'(H)/\varepsilon'(0)-H \) and a minimum in \( P-H \) occurred near \( \sim 5 \text{T} \) at \( T = 35 \text{K} \) under \( p = 1.73 \text{GPa} \). In the FE2 phase, the polarization first decreases with increasing \( H \) and reaches a minimum at \( \sim 5 \text{T} \), then increases again above \( \sim 5 \text{T} \). This indicates that the ferroelectricity in the FE2 phase can be suppressed by \( H \) and that it transforms into the phase with higher electric polarization for \( H > 5 \text{T} \). This implies that the FE2 phase might be noncollinear, incommensurate spin structure at a low field region and becomes a gradually collinear, commensurate phase at a high field region above 5 T. It is well known that a magnetic field usually suppresses the non-collinear spin configuration, and in fact, in \( \text{RMn}_2\text{O}_5 \) (\( R = \text{Y}, \text{Ho}, \text{Dy}, \text{Tb} \)), the magnetic field can induce a transition from the low-temperature, incommensurate magnetic order into the commensurate one.\(^{24}\) The \( H \)-induced transition from a non-collinear incommensurate AFM spin structure into a collinear AFM state was also observed in the well-known \( \text{BiFeO}_3 \).\(^{25,26}\)

Based on the above results, we propose that the ferroelectricity in the FE2 phase in \( \text{GdMn}_2\text{O}_5 \) could be of spin-current origin with a non-collinear, incommensurate magnetic structure, instead of exchange-striction origin, coming from the collinear magnetic structure as that in the CM-FE phase. We notice that most of the compounds in the \( \text{RMn}_2\text{O}_5 \) (\( R = \text{Y}, \text{Tb}, \text{etc.} \)) family show a re-entrance of incommensurate FE (LT-IC-FE) phase at temperatures below CM-FE phase with contracted lattice, implying that the energy of LT-IC-FE spin state is somewhat lower than the CM-FE phase. The lattice compression by applied pressure in \( \text{GdMn}_2\text{O}_5 \) may have similar effect on the magnetic structure transition as compared to the low-temperature induced lattice contraction in \( \text{RMn}_2\text{O}_5 \) (\( R = \text{Y}, \text{Tb}, \text{etc.} \)) compounds. In this sense, a new incommensurate spin state out of CM-FE by applying pressure is possibly energetically favorable in \( \text{GdMn}_2\text{O}_5 \). Therefore, the incommensurate structure in the FE2 phase in \( \text{GdMn}_2\text{O}_5 \) is likely similar to the LT-IC-FE state in other \( \text{RMn}_2\text{O}_5 \) (\( R = \text{Y}, \text{Tb}, \text{etc.} \)) compounds, where the magnetization of the Mn ions in each zigzag chain is modulated along the \( a \) axis and spins in every other chain are rotated slightly toward the \( b \) axis.\(^{8,27}\) It is also important to note that both the FE polarization and the FE transition temperature \( T_X \) in the FE2 phase can be enhanced by the external pressure, as can be seen in the upper inset of Fig. 2. The transition temperature \( T_{\text{IC-PE}} \) of the IC-PE phase was also enhanced with the increasing pressure (see Figs. 6(a) and 8). This pressure-induced stabilization of both FE2 and IC-PE phases implies that these two phases may have similar incommensurate magnetic structure, providing further evidence for the possible non-collinear incommensurate magnetic structure in the new FE phase below \( T_X \). The

**FIG. 7.** (a) and (c) \( P_0-T \) under ambient and 1.30 GPa, respectively; (b) and (d) ME and MD effects at 25 K under ambient pressure and at 35 K under 1.30 GPa, respectively.
test for our proposed scenario needs to await further structural investigations under high pressure.

The pressure-temperature (p–T) phase diagram derived from the dielectric data for GdMn$_2$O$_5$ is shown in Fig. 8. One of the common multiferroic features for the RMn$_2$O$_5$ (R = Y, Bi, and rare-earth) families is to show the same phase-sequence of PM-PE, HT-IC-PE (below $T_{N1}$), and CM-FE (below $T_{N2}$) upon cooling. However, the p–T phase diagram of GdMn$_2$O$_5$ shown in Fig. 8 is very different from those of other RMn$_2$O$_5$ (R = Y, Ho, etc.) compounds.\textsuperscript{17,18} In RMn$_2$O$_5$ (R = Y, Ho, Tb, Dy), the pressure only induces a transition of LT-IC-PE into CM-FE phase at low temperatures and no new phase above $T_{N2}$, while in GdMn$_2$O$_5$ pressure induces a new FE2 phase between CM-FE and IC-PE phases. This difference in the p–T phase diagram may arise from two possible aspects: (1) the ionic size of Gd$^{3+}$ is larger than those of Y$^{3+}$ and Tb$^{3+}$–Tm$^{3+}$, resulting in different R–Mn and Mn–Mn interactions. In fact, the commensurate phase CM-FE in RMn$_2$O$_5$ with rare-earth elements with relatively small ionic radius ($R = Y$, Tb–Tm) can be characterized by a vector $k = [1/2, 0, 1/4]$, whereas the CM-FE phase with larger ionic radius $R$ may show slightly different vector $k$.\textsuperscript{28} For instance, $R = Bi$ shows a $k_z = 1/2$ and $R = Gd$ shows a $k_z = 0.19$.\textsuperscript{19} (2) The Gd$^{3+}$ ions with non-degenerate orbitals with seven 4f valence-electrons may also play a unique role in the spin-lattice coupling and $f$–$d$ spin interaction between Gd and Mn in GdMn$_2$O$_5$, which still awaits further investigation. It is noteworthy that the unique role of Gd$^{3+}$ ions, as compared to other rare-earth ions, has also been observed in many other magnetic materials.\textsuperscript{29,30}

IV. CONCLUSIONS

The multiferroic and ME properties under isotropic pressure up to $p \sim 1.73$ GPa were studied in the GdMn$_2$O$_5$ single crystal. The ferroelectricity was enhanced under low and intermediate pressures. The FE polarization reached a maximum at $p \sim 1.30$ GPa and then decreased at higher pressures, which can be attributed to the combined effect of different pressure-dependent polarizations induced by exchange striction from the Gd–Mn and Mn–Mn interactions. When the external pressure is higher than $\sim 0.88$ GPa, a new FE phase between IC-PE and CM-FE phases in the temperature range of 31 K–38 K was found. The magnetic-field-induced suppression and pressure-induced stabilization indicate a non-collinear incommensurate magnetic structure in this new FE phase. Our results show that the external pressure is a useful and effective tool to explore new multiferroic phases.

Note added in proof. Upon completion of the research and writings, we became aware of a recent publication on the pressure studies of GdMn$_2$O$_5$, which reveals p–T phase diagram similar to ours but with a different proposal for the origin of the pressure induced FE2 phase.\textsuperscript{31}

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