I. INTRODUCTION

One simple example of the geometrically frustrated system is the two-dimensional (2D) triangular lattice antiferromagnets (TLAFs) [1–4]. At zero magnetic field, the ground state of TLAF is known to have a highly degenerate spin structure with three spins oriented 120° relative to each other. With increasing magnetic field, the magnetization process exhibits successive magnetic phase transitions. First, the spin structure evolves into up-up-down (uud) phase where the spins tilted toward the external magnetic field deviating from the 120° ordered phase. Above a certain field, the up-up-down (uud) phase emerges, in which the magnetization is 1/3 of the saturation magnetization $M_{sat}$ in a finite range of temperature. For classical spin systems such as with $S = 5/2$, the thermal fluctuations are known to stabilize the uud phase by a mechanism called order-by-disorder [5]. The existence of the uud phase in the finite range of temperature implies that the thermal fluctuations lift the degeneracy of the ground state. Without the thermal fluctuations, the uud phase would have been stabilized at a single point. In the order-by-disorder mechanism, the fluctuations lower the free energy of the system by selecting the highest entropic state, in which two spins align parallel with the external field direction and the other spin points in the opposite direction. At higher fields, the oblique phase, a canted version of the uud phase, is stabilized. Experimentally, RbFe(MoO$_4$)$_2$ (Fe$^{3+}$, $S = 5/2$) [6, 7] and Rb$_2$Mn(MoO$_4$)$_3$ (Mn$^{2+}$, $S = 5/2$) [8] are typical examples of TLAFs with spin-5/2 that demonstrate the existence of the magnetic plateau at 1/3 $M_{sat}$.

More recently, multiferroicity, where magnetic orders are strongly correlated to the spontaneous electric polarization, has been reported in a few TLAFs. For example, RbFe(MoO$_4$)$_2$ [9–11] and ACrO$_2$ ($S = 3/2$, A = Ag and Cu) [12, 13] have shown multiferroicity in the 120° and the Y phases where the spin chirality is nonzero for a triangular plaquette. In Ba$_3$NiNb$_2$O$_9$ ($S = 1$) [14] and Ba$_3$CoNb$_2$O$_9$ ($S = 1/2$) [15], the multiferroicity was observed not only in the noncollinear spin state but also in the uud and oblique phases. So far, considerable efforts have been made to understand the multiferroicity of various magnetic materials [16–21]. The exchange striction [22–24], the spin current model [25], and the inverse DM mechanism [26] have been successfully used to explain the multiferroicity in some types of materials. Nevertheless, a unified picture for magnetic-controlled ferroelectric materials is still not complete especially for multiferroic TLAFs. Part of the reason is that there are not many TLAFs showing multiferroicity with variations of structures and magnitude of spins and so forth. Considering the few known cases of multiferroic TLAFs, the spin chirality seems to be a key factor for the multiferroicity in TLAFs with large spins while not so much in TLAFs with small spins.

In this paper, we studied another TLAF with spin-5/2, Ba$_3$MnNb$_2$O$_9$, with experimental and theoretical probes and constructed a phase diagram. Various experimental techniques such as dc and ac susceptibility, magnetization, specific heat, neutron powder diffraction (NPD), dielectric constant, and electric polarization were employed, and density functional theory (DFT) calculations were performed. The results suggest that Ba$_3$MnNb$_2$O$_9$ makes a very good example of quasi-2D Heisenberg TLAF with weak easy-axis anisotropy. We also found that Ba$_3$MnNb$_2$O$_9$ is multiferroic in the 120° and the Y phases but not in the collinear spin phases, which are different from its sister compounds Ba$_3$NiNb$_2$O$_9$ and Ba$_3$CoNb$_2$O$_9$.
II. EXPERIMENTAL

Polycrystalline-Ba₃MnNb₂O₉ samples were prepared using solid state reaction method. Stoichiometric mixtures of BaCO₃, MnO, and Nb₂O₅ were ground together and calcined in Ar gas at 1230 °C for 24 hours. The room temperature powder x-ray diffraction (XRD) shows that the equilateral triangular lattice layers are formed by magnetic ions of Mn, and each layer is separated by two nonmagnetic Nb layers in Ba₃MnNb₂O₉, with the space group P-3m1 and lattice parameters a = b = 5.7737 Å and c = 7.0852 Å. This is isostructural with the previous reported TLAFs, Ba₃NiNb₂O₉ [14] and Ba₃CoNb₂O₉ [15].

The dc magnetization was measured using a vibrating sample magnetometer (VSM) at the National High Magnetic Field Laboratory and a commercial SQUID magnetometer (MPMS, Quantum Design). The VSM was calibrated with a standard Ni sphere. The ac susceptibility data were obtained with a homemade ac susceptometer. The neutron powder diffraction (NPD) measurements down to 1.5 K were performed using the HB2A powder diffractometer at the High Flux Isotope Reactor (HFIR), Oak Ridge National Laboratory (ORNL). About 3 g of powder was loaded in a vanadium can with an inner diameter of 12 mm. The diffraction data were collected using the wavelength λ = 2.406 Å and collimation of 12'-open-6', which would provide a better Q resolution at low Q for investigating magnetic structures. Additional measurements down to 0.3 K were carried out on the HB1A triple-axis spectrometer at HFIR employing a 3He insert system. HB1A was operated with a fixed incident neutron energy of 14.6 meV using a double pyrolytic graphite (PG) monochromator system and PG analyzer. A collimation of 40'-40'-40'-80' was used and contamination from higher-order beams was removed using two PG filters placed after each monochromator. The diffraction data were analyzed using the Rietveld refinement program FullProf [27].

For the dielectric constant and electric polarization measurements, a polycrystalline sample was polished into a plate shape with typical dimensions of 4 × 4 × 0.1 mm³ to have a parallel capacitor geometry. The electrical contacts were made by silver epoxy on the two flat surfaces. The capacitance of the sample was measured with an Andeen-Hagerling AH-2700A commercial capacitance bridge, and the dielectric constant was obtained by approximating the sample as an infinite parallel capacitor. The electric polarization was obtained by integrating the pyroelectric current signal (I_p) in the time domain. For I_p measurement, the sample was cooled in the presence of electric field (poling) and/or magnetic field. The detailed procedure of I_p measurement has been published elsewhere [15].

III. RESULTS

A. dc magnetic susceptibility and specific heat

We show the temperature dependence of the dc magnetic susceptibility (χ = M/H) measured at various fields in Fig. 1. The inset of Fig. 1 shows the inverse susceptibility (1/χ) for μBH = 1 T, which is linear in T following the Curie-Weiss law at high temperatures. At low temperatures, χ(T) shows features of magnetic transitions; for example, the 0.1 T data show an upturn (denoted as TN1) and a shoulderlike structure at a lower temperature (denoted as TN2). At higher fields, there is only a broad peak visible for μBH = 1 and 3 T data, while two broad peaks appear for 6.5 T data. Relying on the features observed from the raw data (the first derivative dχ/dT did not give us consistent phase transition features), we assigned TN1 as the temperature of the upturn or the high-T peak and TN2 as low-T peak. TN1 is about 3.5 K at μBH = 0.1 T and increases to 3.8 K at 6.5 T.

Using the Curie-Weiss law, we obtained μ_eff = 5.86 μ_B and Θ_CW = −26 K from the T dependence at high temperatures. The μ_eff agrees well with the theoretical value 5.93 μ_B with an assumption of spin-only S = 5/2 contribution [28]. The negative Weiss constant suggests the transitions at lower temperatures are originated from paramagnetic (PM) to antiferromagnetic ordering. According to the mean field theory, Θ_CW is given as (−zJS(S+1))/3kB, where J is the exchange interaction of the Heisenberg Hamiltonian, J ∑(i,j) S_i · S_j, and z is the number of nearest neighbors. For the S = 5/2 triangular lattice with z = 6, we obtained J/k_B = −2/3Θ_CW = 1.45 K from the χ(T) result.

The specific heat data taken at different fields are shown in Fig. 2. At zero field, two clear peaks are observed at 3.29 and 3.04 K, which survives up to 2 T. At higher fields, only a single peak becomes visible at the measured temperature range. The positions of the first high-T peak at μBH = 0 and 1 T are very similar to TN1's from the χ measurement indicating a long range magnetic ordering at TN1. The low-T peak denoted as TN2 is also close to TN2 from the χ(T, μBH = 0.1 T) data indicating another long range ordering. As the magnetic field increased, TN1 increases initially up to μBH = 6 T and decreased with further increasing field, while TN2 decreases only slightly.

B. Neutron powder diffraction

We performed neutron powder diffraction (NPD) experiments to identify the spin structure at zero field. The pattern measured at 1.5 K was shown in Fig. 3(a). According to
FIG. 2. (Color online) Specific heat divided by temperature as a function of temperature for magnetic fields up to 9 T. At 0, 1, and 2 T, two clear peaks are observed marked as $T_{N1}$ and $T_{N2}$. As the field increases, a single peak at $T_{N1}$ was observed. Data offset by 1 J mol$^{-1}$K$^{-2}$ gradually from the 0 T data.

the refinement, the magnetic Bragg peaks are observed at $Q = (n_1 + 1/3, n_2 + 1/3, n_3)$ ($n_i$: integer). In Fig. 3(e), the difference between the 5 and 1.5 K patterns clearly shows the details of these magnetic Bragg peaks. The refined magnetic structure and the crystal structure of Ba$_3$MnNb$_2$O$_9$ are shown in Figs. 3(b), 3(c), and 3(d). It is a 120° antiferromagnetic ordering in the $ab$ plane with out-of-plane cantings. The canting angles are $\varphi = 8.7(4)^\circ$ and $\psi = 18.7(9)^\circ$, respectively. In addition, it is collinear ferromagnetic spins between the nearest neighbor layers. The refined ordered moment is $4.71(25)$ $\mu_B$ for each Mn$^{2+}$ ion. Figure 3(f) shows the order parameter of $(1/3, 1/3, 0)$ between 0.3 and 5 K. Only one magnetic transition was clearly identified at $T_N$ around 3.3 K within the resolution limit of our experiment. The structural and magnetic parameters obtained by refining the 1.5 K data are listed in Table I. The refinement results of the 0.3 K data (not shown here) do not show significant difference from that obtained at 1.5 K within the resolution limit.

C. dc magnetization and ac susceptibility

Figure 4 shows the field dependence of the dc magnetization $M(H)$ and its derivative $dM/dH$ at 1.5 K. Above 30 T, $M(H)$ increases slowly due to the polycrystallinity of the sample before the saturation with $M_{\text{sat}} \sim 4.9$ $\mu_B$. The saturation value and the overall shape of the magnetization is similar to reported values [29]. $M(H)$ shows weak but notable inflections around 5.5, 9.3, and 12.4 T, which are more clearly seen from $dM/dH$ as a peak-valley-peak structure. The magnetization value at the valley is $\sim 1.7\mu_B$, close to $1/3 M_{\text{sat}}$. The shape of $dM/dH$ is reminiscent of what was observed in other TLAF single crystal [6,8,30] or polycrystal [31] samples reported to have a magnetization plateau. Although the $M(H)$ curve

FIG. 3. (Color online) (a) The neutron powder diffraction (NPD) pattern obtained at 1.5 K. The red solid curve is the best fit from the Rietveld refinement by using FULLPROF. (b) Triangular lattice composed of Mn$^{2+}$ ions and its spin structure at zero field. (c) Unit cell of Ba$_3$MnNb$_2$O$_9$ and spin structure of Mn ions. (d) Crystal structure for Ba$_3$MnNb$_2$O$_9$: the red octahedra represent Mn sites and the green octahedra represent Nb sites. (e) NPD patterns taken at 1.5 and 5 K. (f) Order parameter of $(1/3, 1/3, 0)$ between 0.3 and 5 K.
TABLE I. Structural and magnetic parameters obtained by the Rietveld refinement for the NPD pattern at $T = 1.5$ K.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(1)</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.6617  (13)</td>
</tr>
<tr>
<td>Ba(2)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.5000</td>
</tr>
<tr>
<td>Nb</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.1762  (10)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.5000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.1726  (7)</td>
<td>0.3452  (13)</td>
<td>0.3229  (8)</td>
</tr>
</tbody>
</table>

Space group: $P\overline{3}m1$
Lattice parameters (Å): $a = 5.8036(1)$, $b = 5.8036(1)$, $c = 7.0808(3)$
RF-factor: 5.84
Bragg $R$-factor: 6.91

Here is not as apparent as in those compounds, $dM/dH$ and the $1/3 \ M_{sat}$ magnetization value imply the magnetization plateau in the $uid$ phase. Accordingly, we assigned the peak fields as $\mu_0 H_{c1}$ and $\mu_0 H_{c2}$ as phase boundaries of $Y$-$uid$ and $uid$-oblique phase, respectively. At higher fields, $dM/dH$ decreases rapidly above $\mu_0 H_{c3}$, above which spins enter polarized states due to the external magnetic field. The polycrystallinity of the sample and the easy-axis anisotropy (to be discussed later) are probably the reasons why the magnetization plateau was not clearly observed.

To further study magnetic phase transitions at lower temperatures and at different fields in more detail, ac magnetic susceptibility ($\chi'$) measurements were performed. In Fig. 5(a), we show the temperature dependence of the ac magnetic susceptibility $\chi'(T)$ at 1 and 0.4 T. The overall temperature dependence of $\chi'$ measured at 1 T is similar to dc susceptibility $\chi(T)$ data at the same field, which is expected because $\chi'(T)$ usually resembles $\chi$ for nonglassy systems (as is the case in our work). We therefore assigned the prominent peak temperature of $\chi'$ as $T_{N1}$ (slightly larger than the value obtained from the $\chi$ measurement), which is likely from a transition from PM to an ordered state. At lower temperatures below 1 K, there is another shoulderlike feature whose temperature is assigned as $T_{N3}$, which becomes more prominent for 0.4 T data.

At lower fields, we observed even more features, whose temperatures are assigned as $T_{N1}$, $T_{N2}$, and $T_{N3}$ as shown in Fig. 5(b). We note $T_{N2}$ at zero field is close to the lower $T$ peak of the zero field specific heat data ($T_{N2}$ in Fig. 2) and also to the lower $T$ feature of the $\chi(T)$ at 0.1 T ($T_{N2}$ in Fig. 1), consistent with a long-range magnetic phase transition at $T_{N2}$. Upon cooling, $\chi'(T)$ initially increases rapidly (instead of peak at higher fields) at $T_{N1}$, followed by a shoulder at $T_{N2}$ and a peak at $T_{N2}$. Both theoretical and experimental works have shown that the temperature dependence of magnetic susceptibility can probe phase transitions from PM-$uid$-$Y$ phase in TLAF [8,32,33].

For example, according to a MC simulation result, the rapid increase of $\chi'$ at low fields at $T_{N1}$ is a result of the ferrimagnetic ordering for the $z$-component (out-of-plane) moment while the $xy$-component (in-plane) remains paramagnetic.

At higher fields above 0.3 T, $\chi'$ shows a prominent peak at $T_{N1}$, which is also observed from Rb$_4$Mn(MoO$_4$)$_3$ [8] (note that the phase boundary in their work was defined differently as a peak of $d\chi/dT$). As the field is increased, the shoulder structure at $T_{N2}$ also evolves into a more prominent peak [see Fig. 5(c)] until it becomes too low to be detected. At high...
fields above 10 T, only $T_{N1}$ was observed in the measured temperature range, as it decreases with increasing fields.

The field dependence of the ac susceptibility $\chi'(H)$ measured at three temperatures is shown in Fig. 6. $\chi'(H)$ is sensitive to magnetic phase transitions since it probes $dM/dH$ directly. In Fig. 6, we plot $\Delta\chi'(H,T) = \chi'(H,T) - \chi'(H,T = 5 K)$ to emphasize the field induced phase transitions. All three curves show a similar structure with increasing field; peak-valley-peak structure as seen from $dM/dH$ obtained from the dc magnetization data. The width between the two peaks, the $udu$ phase with magnetization plateau, becomes wider as the temperature increases, which implies that the thermal fluctuations play an important role to stabilize the order-by-disorder driven phase.

**D. Dielectric constant and polarization**

Figure 7 shows the temperature dependence of the dielectric constant $\varepsilon'$ at different fields. At zero field, two features were observed: an abrupt increase of $\varepsilon'$ around $T = 3.4$ K followed by a peak around $T = 3.0$ K, whose temperatures are again similar to those from $\chi(T)$, $\chi'(T)$, $C_p(T)$. Therefore we assigned them as $T_{N1}$ and $T_{N2}$ accordingly. With increasing fields, the two features evolve differently; $T_{N2}$ shifts rapidly to lower temperatures and the peak becomes broader, while $T_{N1}$ increases with fields up to 7 T before starts to decrease at higher fields. There is a shoulderlike anomaly denoted as an asterisk for the data taken between $\mu_0H = 4$ and 8 T, which was not observed from other experimental techniques.

The field dependence of the dielectric constant is shown in Fig. 8. As the field is increased from zero field, a first prominent peak is apparent at each temperature, whose position increases with decreasing temperature. The position and its temperature dependence is similar to those of $\mu_0H_{c1}$ obtained from the $\chi(H)$ and the $M(H)$ measurements. There are also features related to critical fields, $\mu_0H_{c2}$ and $\mu_0H_{c3}$, seen as a much broader peak and a slope change (see the inset of Fig. 8). At lower temperatures, all the features related to the critical fields become weaker implying the importance of thermal fluctuations, and $\mu_0H_{c2}$ and $\mu_0H_{c3}$ become too weak to be identified from the $\varepsilon'(H)$ data.
FIG. 9. (Color online) Temperature dependencies of (a) pyroelectric current and (b) polarization measured with $E = 1100 \text{kV/m}$ at different fields. (c) and (d) show the pyroelectric current and polarization measured under different conditions of electric field poling.

$I_p$ measured at different fields from 0 to 12 T and the resulting $P$ is shown in Fig. 9(b). The $I_p$ shows a peak at similar temperatures to $T_{N2}$. With increasing field, it shifts to lower temperatures while becoming weaker and broader. The $I_p$ completely disappears above 5 T in the measured temperature range. Accordingly, the $P$ shows the maximum of polarization of $3.45 \text{µC/cm}^2$ at zero field and decreases with increasing field and eventually suppressed above 5 T. We note here that there is no feature of $I_p$ at the phase boundary of either PM-$uud$ or PM-oblique phases at all measured fields, therefore no polarization in the $uud$ and the oblique phase. As seen from Figs. 9(c) and 9(d), $I_p$ and $P$ were observed only in the presence of the electric field poling, and the directions of $I_p$ and $P$ can be reversed poling in the opposite direction. We also found that the presence or absence of magnetic field during cooling didn’t make any difference. The spontaneous and reversible polarization confirms the ferroelectricity concomitant with the magnetic phase transition, hence multiferroelectricity.

E. DFT calculation

To help the understanding of experimental observations, a density functional theory (DFT) calculation was performed using the Vienna $ab\ initio$ simulation package (VASP) [34,35]. An in-plane enlarged supercell consisting of three chemical units of $\text{Ba}_3\text{MnNb}_2\text{O}_9$ with experimental structures was used in the following calculations [36]. The projector augmented wave (PAW) potentials were adopted [37,38], the plane-wave cutoff energy was 500 eV, and a $5 \times 5 \times 6$ Monkhorst-Pack $k$-point mesh centered at the $\Gamma$ point was used. The electronic correlation was treated using the generalized gradient approximation (GGA) plus Hubbard $U$ [39,40]. The effective Hubbard parameter $U_{\text{eff}} = U - J = 3 \text{eV}$ was applied to the 3$d$ electrons of Mn ion. To account for noncollinear spin orders, the spin-orbit coupling is enabled in all following calculations.

FIG. 10. (Color online) Density functional theory (DFT) energy as a function of tilting spin angle, rotating from the in-plane $120^\circ$ structure to the complete out-of-plane $uud$ structure. The energy of $120^\circ$ structure is the reference point. $\theta$ is defined as the angle between spins and the $ab$-plane. Two of the three spins tilt up, while the last one tilts down.

The magnetic ground phase is checked by comparing the energies of various magnetic patterns. In our DFT calculation, the in-plane $120^\circ$ structure is lower than the out-of-plane $uud$ one for $\sim 1.7 \text{meV/\text{per Mn}}$. Within the Wigner-Seitz sphere defined in the PAW potential, the local magnetic moment of Mn is about $4.4 \mu_B$ in both these two phases, implying the high-spin state, in agreement with the experimental observation.

Furthermore, to test the canting ground state observed in the above neutron study, the spin directions of Mn’s are rotated from the in-plane $120^\circ$ structure to the out-of-plane $uud$, characterized by a tilting angle from the original spin plane. The energy difference is shown in Fig. 10 as a function of tilting angle. The global tendency is that the energy difference increases with the tilting angle. However, in a small tilting angle range (e.g. $<5^\circ$), the energy is almost degenerate.

FIG. 11. (Color online) Density of states (DOS) of the $120^\circ$ structure. (a) Total DOS. (b) Atomic-resolved DOS.
with the 120° structure one. The energy fluctuation in this region is beyond our DFT precision. Hence, according to our calculation, the ground state is the in-plane 120° structure, with or without a small out-of-plane tilting angle. Such a theoretical result agrees with the experimental observation qualitatively.

According to the density of states (DOS), the 120° structure state is insulating, with a small band gap of 0.2 eV, as shown in Fig. 11(a). The atomic-projected DOS (PDOS) [Fig. 11(b)] shows that the topmost valence bands are mostly from Mn’s 3d orbitals (the eg doublets), while the lowest conducting bands are from Nb’s 4d orbitals (the t2g triplets), in agreement with the expected valences: Mn2+ and Nb5+. Therefore, here Nb ions are not directly involved in the magnetism.

IV. DISCUSSION

A magnetic field versus low temperature phase diagram was constructed by combining the data from Sec. III as shown in Fig. 12. Some phase boundaries are not apparent throughout the various experimental techniques and there are uncertainties (large error bars) in determining the phase boundaries. For example, the dielectric constant anomalies denoted as asterisks (large error bars) show the topmost valence bands are mostly from Mn’s 3d orbitals (the eg doublets), while the lowest conducting bands are from Nb’s 4d orbitals (the t2g triplets), in agreement with the expected valences: Mn2+ and Nb5+. Therefore, here Nb ions are not directly involved in the magnetism.

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compound. Whether the difference is related to either classical or quantum spins can be a subject for future studies.

V. CONCLUSIONS

In conclusion, our detailed studies on Ba₃MnNb₂O₉ show that it is a quasi 2D spin-5/2 TLAF with weak easy-axis anisotropy. With increasing magnetic field, successive magnetic phase transitions are observed. The overall behaviors of the magnetic phase diagram are consistent with the theoretical prediction of a Heisenberg TLAF. Moreover, multiferroicity is observed in its low field phase with nonzero spin chirality. Therefore, Ba₃MnNb₂O₉ provides another unique example of TLAFs with classical spins showing successive magnetic phase transitions and multiferroicity.

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