Polar and Magnetic Mn$_2$FeMO$_6$ (M = Nb, Ta) with LiNbO$_3$-type Structure: High-Pressure Synthesis

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Polar oxides are of much interest in materials science and engineering. Their symmetry-dependent properties, such as ferroelectricity/multiferroics, piezoelectricity, pyroelectricity, and second-order harmonic generation (SHG) effect are important for technological applications.[1] However, polar crystal design and synthesis is challenging, because multiple magnetic interactions of Mn$^{2+}$ and Fe$^{3+}$; however, it adopts a hexagonal centrosymmetric ilmenite (IL) structure. Herein, we present the synthesis of polar LN-type magnetic oxides Mn$_2$FeMO$_6$ (M = Nb, Ta) in the A$_2$BB'O$_6$ family, and investigate their crystal structures, formal oxidation states, magnetic properties, SHG effect, and dielectric properties. Theoretical calculations within the framework of density functional theory (DFT) supplemented with Coulomb interaction, U, were also carried out to provide theoretical verification of the experimental results.

Mn$_2$FeMO$_6$ (M = Nb, Ta) were prepared at 1573 K under 7 GPa in a Walker-type multianvil press (details of the synthesis are presented in the Supporting Information, Section S2). The powder synchrotron X-ray diffraction (SXRD) patterns of the as-prepared Mn$_2$FeMO$_6$ (Figure 1) could be indexed to rhombohedral unit cells (α ≈ 5.27 Å, c ≈ 13.9 Å), and Rietveld refinement quickly showed the LN
structure type. It is important to confirm the polar space group; therefore, convergent-beam electron diffraction (CBED) and selected-area electron diffraction (SAED; Supporting Information, Section S3) were used to determine the presence (R3c) or absence (R3c) of an inversion center. CBED patterns and tilt series of SAED patterns taken from Mn2FeNbO6 are shown at the bottom and top of Figure 2, respectively. These electron-diffraction patterns could be completely indexed with the cell parameters from the XRD refinements. The reflection conditions derived from the patterns are: $hkil: h + k + l = 3n$, $h - k + l = 3n + 2$, and $000l: l = 6n$. The $000l: l = 6n + 3$ reflections that are observed on the [1100] are due to double diffraction, as is confirmed by the appearance of Gjonnes–Moodie lines through these reflections on the corresponding CBED pattern. Some of the [2110] zones show very weak sharp and some show weak diffuse reflections at $000l: l = 6n + 3$ and $h00l: l = 2n + 1$, violating these reflection conditions. This can be due to the presence of local order. The trigonal extinction symbols matching these reflection conditions are $R(200)$— and $R(020)$—. The $[u-u, u-w]$ zones [1100], [2201], and [4401] show as whole pattern symmetry $m$. Within the trigonal point groups, this whole pattern symmetry corresponds to point groups 32 and 3m. Combining the information from CBED and SAED leaves only the space group R3c as a possibility, in agreement with the SXRD results. Further observation of positive SHG effect also confirms the non-centrosymmetric character of the structure of both materials (Supporting Information, Section S5).

Subsequent Rietveld refinements of the SXRD data are given in the Supporting Information, Section S4 (Figure S3a, S3b; Tables S1 and S2). The inset of Figure 1 shows a polyhedral view of the unit cell of Mn2FeMO6 (M = Nb, and Ta) with a typical LN-type structure, where Mn occupies a six coordinated A site and Fe/M are disordered on the six coordinated B site in (Fe/M)O6 octahedra. MnO6 and (Fe/M)O6 groups are arranged to avoid edge-sharing between homonuclear octahedra; the heteronuclear edge-shared octahedra, forming [Mn(Fe/M)]O6 dimers, are arranged to form three-dimensional connectivity by face-sharing between the octahedral layers (Supporting Information, Figure S1). The average (Mn-O) bond lengths are 2.16(1) and 2.22(2) Å for $M = Nb$ and Ta, respectively and are comparable with the average (Mn-O) distance of MnO6 octahedron in Mn2+Ti4+O6 (2.199 Å)[13] and Mn2+Fe3+Si3+O6 (2.173 Å),[9] but longer than those in LaMn3+O6 (2.072 Å)[14] and YMn3+O6 (2.036 Å),[14] which is consistent with the expected formal oxidation state of Mn2+ in Mn2FeMO6. The metal–oxygen distances in the (Fe/M)O6 octahedra are 2.03(6) (M = Nb) and 2.01(2) (M = Ta), comparable to (Fe/M-O) of disordered B site perovskites, such as Sr3Fe3+M3+O6 (1.996 Å for M = Nb[15]) and Pb2Fe3+M3+O6 (1.992 Å for M = Ta[15]), and Pb2Fe3+M3+O6 (2.005 Å for M = Nb[17] and Ta[15]). Thus, the crystal structure analysis indicates a cation formal oxidation state of Mn2+Fe3+M3+O6, which is further confirmed by X-ray absorption near-edge spectroscopy (XANES) studies (Supporting Information, Section S6).

The magnetic properties of Mn2FeMO6 (M = Nb, Ta) show reproducible behavior for samples from different HP batches. Figure 3 shows the evolution of $\chi_{ac}$ versus temper-
ature for Mn₂FeTaO₆ (top) and Mn₂FeNbO₆ (bottom) samples recorded in zero-field cooled (ZFC) and field cooled (FC) modes. A clear difference in the behavior of the Nb and Ta samples is evident. For Mn₂FeTaO₆ (Figure 3 top), $\chi_h$ shows a relatively sharp increase as the oxide is cooled below 200 K, indicating the emergence of magnetic order at this temperature. Below about 80 K, the magnetization starts falling rapidly. Note that this sharp drop is seen in both the ZFC and FC modes, thereby indicating a transition to a strong antiferromagnetic (AFM) state. The Mn₂FeNbO₆ sample, on the other hand, does not exhibit such sharp transitions (Figure 3 bottom). The emergence of magnetic order below 200 K is more gradual here. This is also clearly seen in the $1/\chi_h$ vs $T$ plots (insets of Figure 3), while the paramagnetic region above 200 K in Mn₂FeTaO₆ follows the Curie–Weiss behavior (as evidenced by the linearity of the plot at $T > 200$ K), this is not the case for Mn₂FeNbO₆, where the $1/\chi_h$ plot is not linear even for $T > 200$ K. In fact, the non-linearity extends well up to $T = 300$ K, which indicates the presence of residual magnetic interactions even at RT. Below about 90 K, there is a slight drop in the susceptibility of Mn₂FeNbO₆, both in the ZFC and FC curves, but in this case with a divergence between them, which indicate a transition to an AFM state with magnetic frustrations in the system. The high-temperature inverse susceptibility data for the Mn₂FeTaO₆ sample could be fitted to a Curie–Weiss law, $\chi = \chi_0 / (T - \theta_{CW})$. The fitting allowed us to extract the effective magnetic moment ($\mu_{eff} = 10.07 \mu_B$), which agrees well with the calculated spin only moment per formula unit, $\mu_{sp} = 10.25 \mu_B$; for $\mu_{ip-calc} = 5.92 \mu_B$. The Curie–Weiss constant, obtained from the fitting, $\theta_{CW} = -165$ K consistent with the presence of AFM interactions.

In Figure 4a (top), we show the isothermal $M$ versus $H$ curves of Mn₂FeTaO₆ recorded at various temperatures in the range 5–300 K. The inset of Figure 4a (top) shows an expanded view near the origin. For $T > 200$ K, $M$ versus $H$ is perfectly linear with the curves passing through the origin. These curves correspond to the sample in the paramagnetic region. For $T < 200$ K, a small S-shaped hysteresis loop opens up near the origin. This is probably a manifestation of the emergence of canted ferromagnetism. It is important to note that the $M$ vs $H$ curves show no sign of saturation for an applied magnetic field as high as $H = 5$ T, indicating that the FM interactions are very weak, which is probably due to spin canting. Below the AFM transition at $T \approx 80$ K, this S-shaped hysteresis loop vanishes, indicating a complete transition to the AFM state. The isothermal $M$–$H$ curves of Mn₂FeNbO₆ (Figure 4a (bottom)) reveal a different behavior. The S-shaped hysteresis loop is present in this sample down to the lowest temperature measured ($T = 5$ K), which indicates that FM interactions, again possibly due to spin canting, are present even at low temperatures. Furthermore, even at the highest measured temperature ($T = 300$ K), the $M$–$H$ curve is not perfectly linear (inset of Figure 4a (bottom)), thereby showing that the sample does not reach a pure paramagnetic state even at RT.

The magnetic nature of Mn₂FeMO₆ is further confirmed by Mössbauer spectra (Supporting Information, Section S7). Figure 4b shows the $^{57}$Mössbauer spectra of Mn₂FeNbO₆, where the beginning of the appearance of the sextet at 150 K is observed, which suggests that the sample is at least partially ordered at this temperature. At 92 K the sextet is clearly resolved, consistent with a complete magnetic ordering. The data on Mn₂FeTaO₆ show similar behavior. Thus, we can conclude that the magnetic ordering temperatures in both samples are between 200 and 250 K. The Mössbauer study also provides information about the oxidation state and the positions occupied by Fe cations. Analysis of the data shows that about 92% of iron is trivalent, in good agreement with the XANES results. It also shows the existence of divalent iron (ca. 8%), which is probably due to cation exchange between Mn and Fe in both A and B sites and/or oxygen defects, which cannot be distinguished by X-ray and electron diffraction studies, since the very similar X-ray scattering factors of Mn (Z = 25) and Fe (Z = 26) prevent unambiguous determination of the extent of ordering.

DFT+U calculations[19] (Supporting Information, Section S8) indicate that both compounds have finite polarization owing to the presence of $d^0$ ions Nb⁵⁺ and Ta⁵⁺, while the magnetism arises owing to presence of Mn and Fe. Figure 5 shows the exchange interaction between Mn and Fe to be of AFM nature. The magnetic lattice connecting Mn and Fe atoms consist of triangular arrangements, which renders the AFM interaction frustrated. Such frustration may give rise to non-collinearity of spins. Our non collinear calculations gave rise to solution with canted magnetization axis of Mn and Fe spins and a small uncompensated net moment. The calculated noncollinear arrangement of spins may be checked by further experiments. The nominal $d^0$ valences of Mn and Fe, and $d^0$ valences of Nb and Ta, have also been confirmed through spin-polarized DFT+U calculations, which gave rise to
In conclusion, novel LiNbO₃-type polar magnetic oxides prepared at high pressure have been extended to the perovskite-related multiple B-site A₂BB₆ series (A = Nb, Ta) system. The polar nature of the as-prepared LiNbO₃-type Mn₂FeMO₆ (M = Nb, Ta) is established by powder synchrotron X-ray and electron-diffraction analyses, as well as by second harmonic generation effect, and theoretical calculations. These discoveries are of major significance and open up a new path for novel polar and magnetic materials. The variety of cations and structural versatility of the cation arrangement at both A and B sites in A₂BB₆ oxides, where A is an unusually small cation, including Mg³⁺, Mn²⁺, Zn²⁺, or Sc³⁺, In³⁺, and B is a d⁰ ion, such as Nb⁵⁺, Ta⁵⁺, Mo⁶⁺, W⁶⁺, or Ti⁴⁺. These materials could be polar, and potentially multiferroic, piezoelectric, pyroelectric, and second-order nonlinear optical materials, with important technological applications.

**Experimental Section**

For details of the experiments and calculations, see the Supporting Information. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-425981 and CSD-425982.

**Keywords:** density functional calculations · high-pressure chemistry · LiNbO₃-type structure · Mn₂FeMO₆ · polar magnetic oxides

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**References**


