Magnetic-Structure-Stabilized Polarization in an Above-Room-Temperature Ferrimagnet**

Man-Rong Li, Maria Retuerto, David Walker, Tapati Sarkar, Peter W. Stephens, Swarnakamal Mukherjee, Tanusri Saha Dasgupta, Jason P. Hodges, Mark Croft, Christoph P. Grans, Joachim Hemberger, Javier Sánchez-Benítez, Ashfia Huq, Felix O. Saouma, Joon I. Jang, and Martha Greenblatt*

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SUPPORTING INFORMATION

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1. *Cation Ordering in Corundum Derivatives*

The crystal structure of corundum-type (A₂O₃) oxides consists of hexagonal close packing of the oxygen atoms, where the metal atoms occupy two-thirds of the octahedral sites, the remaining one-third of the octahedral sites are vacant (Fig. S1a).¹-³ Each AO₆ octahedron shares edges with three other AO₆ octahedra to form an intralayer edge-sharing (ES) infinite sheet in the ab plane which is 2/3 occupied and 1/3 vacant. The intralayer ES octahedral sheets are bonded to form a three-dimensional structure via interlayer face-sharing (FS) to form octahedral pairs along the c direction, these pairs corner share with the edge-sharing slabs of alternative layers. The metal atoms near the center of FS octahedral pairs tend to displace away in opposite directions towards the vacant sites in order to reduce the electrostatic repulsions.
Fig. S1 Cation ordering tree in corundum-related phases with (a) $A_2O_3$-type corundum; (b) $ABO_3$-type ilmenite; (c) $ABO_3$-type LiNbO$_3$; (d) $A_2BB'O_6$-type ordered ilmenite, and (e) $A_2BB'O_6$-type Ni$_3$TeO$_6$ crystal structures viewed along the [110] direction. Octahedral color: carmine, AO$_6$; purple, BO$_6$; cyan, B'O$_6$. 
Given the same corundum-type rhombohedral stacking of octahedra, different crystal structures can be derived when the octahedral metal sites are occupied by more than one distinct cation (similar to the double perovskite related $A_2BB'O_6$). Fig. S1 shows the cation ordering tree in corundum-derived systems, including ilmenite (IL), LiNbO$_3$ (LN), ordered IL (OIL), and Ni$_3$TeO$_6$ type structures,$^{2,4,5}$ where the FS octahedral pairs along the $c$ axis are formed by two different cation octahedra. The crystal structures are highly strained: stretched in the $ab$ plane and compressed in the $c$ direction due to the electrostatic repulsions between the cations across the ES and FS octahedral pairs, respectively.

1.1 IL and LN type Structures

The IL and LN structures have two distinct cation-orderings in ABO$_3$. IL adopts a centrosymmetric $R$-$3$ space group, built by alternating ES AO$_6$ and BO$_6$ octahedral layers in the $ab$ plane stacked via FS between unlike A and B cations (Fig. S1b). While in the non-centrosymmetric LN structure ($R3c$), the ES octahedral layers consist of both AO$_6$ and BO$_6$ octahedra to avoid intralayer ES between identical cations (Fig. S1c). The number of reports on related phases increased in the past years, but because of the requirement of relatively high pressures for their preparation, these systems are far less explored than normal ABO$_3$ perovskites.

1.2 Ordered Ilmenite and Ni$_3$TeO$_6$-type Structures

The $A_2BB'O_6$ system is more complex (than IL and LN ABO$_3$), as an additional ordering parameter is introduced into the B-sites. The crystal structure transforms to either OIL or Ni$_3$TeO$_6$ type. Generally, B$^+$ has a higher oxidation state than B; A is typically a monovalent-to-trivalent cation. So far, only a few compounds have been reported in this system: Li$_2$GeTeO$_6$ is
the only phase with OIL structure bearing some B-site cationic disorder, which results in Li2[(Ge0.82Te0.18)B(Te0.82Ge0.18)B′]O6. Several Ni3TeO6-type compounds were reported with A2B′4+2B4+6+O6, A22B3+2B6+O6, A2+2B2+2B′6+O6, A2+2B2+2B′6+O6, and A3+2B2+2B′6+O6 formulae, all of which contain an ion with electronic configuration (n-1)d10 ns0 such as Ge4+, Sb5+, and Te6+. Compared with IL, the OIL (R3) has two crystallographically independent A cations (designated as A1 and A2). The ES layers are formed by either A or B octahedra and the intralayer ordering gives crystallographically unlike neighbors in ES A1O6/A2O6 layers and ES BO6/B′O6 layers (Fig. S1d), respectively. The interlayer FS A1O6/B′O6 and A2O6/BO6 octahedral pairs form A1-B′-A2-B columns parallel to the c axis. As shown in Fig. S1d, the A cations displace away from their FS partner cations (A1-B′; A2-B) toward opposite directions along the c axis; this displacement is largely responsible for the two crystallographically different A-site positions due to the size and charge difference between B and B′ cations. The Ni3TeO6 structure is a close derivate of the LN structure; compared with OIL it has additional intralayer octahedral ordering to avoid ES between like A or B cations, and thus forming alternative stacking of A1O6/BO6 and A2O6/B′O6 octahedral layers in the ab-plane (Fig. S1e).

The cation ordering in corundum derivatives is complex and can be driven by many factors, including the cationic size and charge difference, structural tolerance factor (t), electron configuration, and synthesis condition. The larger the size or charge difference between the cations, the greater is the chance of ordering. The corundum-derived ABO3 and A2BB′O6 systems can be regarded as highly distorted perovskite-related structures with very small tolerance factor (t) values9, due to the unusually small size of A cations. The A-site 12-fold coordination of the ideal perovskite structure transforms to an octahedral 6-fold coordination. These structures are highly distorted and compact, most are metastable at ambient pressure and
often require very high pressure for their synthesis.\textsuperscript{10-12} For example, some IL-type structures transform into LN-polymorphs under higher pressure.\textsuperscript{13,14} Another important effect on the cation ordering is the electronic configuration. For example, Mn\textsubscript{2}FeMO\textsubscript{6} (M = Nb\textsuperscript{5+} and Ta\textsuperscript{5+}, d\textsuperscript{0}) adopt a polar LN structure,\textsuperscript{12} while Mn\textsubscript{2}Fe\textsuperscript{3+}Sb\textsuperscript{5+}O\textsubscript{6} (Sb\textsuperscript{5+}, d\textsuperscript{10}) a non-polar IL structure. We believe the latter behavior is due to the absence of a second-order Jahn-Teller d\textsuperscript{0} cation at the B'-sites, which favors distortion of the octahedra.\textsuperscript{11}

Generally, the cation ordering is affected by the competition and/or combination of several factors for the lowest energy of the system, and the real outcome can be complicated and subtle case by case. For example, both Bi\textsubscript{2}FeCrO\textsubscript{6} and Bi\textsubscript{2}FeTiO\textsubscript{6} were predicted to stabilize in the Ni\textsubscript{3}TeO\textsubscript{6} structure.\textsuperscript{15,16} However, Bi\textsubscript{2}FeCrO\textsubscript{6} prepared under HP crystallizes in the LN structure (R\textsubscript{3c}),\textsuperscript{11} while Bi\textsubscript{2}FeTiO\textsubscript{6} has not been experimentally prepared yet.\textsuperscript{17}

\textbf{2. High Pressure Synthesis and Powder Synchrotron X-ray and Neutron Diffraction Studies}

Polycrystalline Mn\textsubscript{2}FeMoO\textsubscript{6} was prepared from stoichiometric mixtures of MnO (99.999%, Alfa Aesar), Fe (99.999%, Alfa Aesar), Fe\textsubscript{2}O\textsubscript{3} (99.999%, Sigma Aldrich) and MoO\textsubscript{3} (99.998% Alfa Aesar) under high pressure. The oxide mixture was placed in a Pt capsule, pressurized typically over 8-12 hours, and reacted at 1623 K under 8 GPa for 30 minutes in a LaCrO\textsubscript{3} heater inside a MgO crucible in a multi-anvil press,\textsuperscript{18} and then quenched to RT by turning off the voltage supply to the resistance furnace, which reduced the temperature to RT in a few seconds. The pressure is maintained during the temperature quenching and then decompressed in 8-12 hours. Powder synchrotron x-ray diffraction (PSXD) data were recorded on beam line X-16C ($\lambda$ = 0.69991 Å) at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (US). Powder neutron diffraction (PND) data were collected at 10 and 300 K on
~220 mg sample at the POWGEN instrument in the Spallation Neutron Source in the Oak Ridge National Laboratory (US). Diffraction data analysis and Rietveld refinements\textsuperscript{19} were performed with the TOPAS software package\textsuperscript{20} and EXPGUI interface of GSAS programs\textsuperscript{21}. Original powder synchrotron x-ray diffraction (PSXD) data can be indexed to either centrosymmetric $R$-3 or noncentrosymmetric $R3$ cell, corresponding to IL ($R$-3), OIL ($R3$), or Ni$_3$TeO$_6$ ($R3$) type structure. Although the two space groups have the same reflection conditions, Rietveld refinements on PSXD data indicated unambiguously the non-centrosymmetric Ni$_3$TeO$_6$ structure based on the structural model in Ref. 4. More important than the relatively small difference in the refinement statistics ($R_{wp} = 7.72\%$ (OIL), $7.29\%$ (Ni$_3$TeO$_6$), and $8.62\%$ (IL)) was the fact that the IL and OIL structural models yielded unrealistic atomic displacement parameters. The Ni$_3$TeO$_6$-type structure was further reinforced by combined PSXD and PND refinements attributed to the different counting of the electron and neutron scattering ability (electron numbers for PSXD: $Z_{\text{Mn}} = 25$, $Z_{\text{Fe}} = 26$, $Z_{\text{Mo}} = 42$, $Z_{\text{O}} = 8$; neutron scattering lengths for PND: $b_{c,\text{Mn}} = -3.73 \times 10^{-15}$ m; $b_{c,\text{Fe}} = 9.45 \times 10^{-15}$ m, $b_{c,\text{Mo}} = 6.715 \times 10^{-15}$ m; $b_{c,\text{O}} = 5.803 \times 10^{-15}$ m), as totally unacceptable fitting of the 300 K data in IL ($\chi^2 = 21.28$, $R_p/R_{wp} = 10.99/10.50\%$) and OIL ($\chi^2 = 26.17$, $R_p/R_{wp} = 14.75/11.75\%$) models obtained. The final refined plots from Ni$_3$TeO$_6$ structure are presented in Fig. S2 (combined PSXD and PND refinements on 300 K data ($\chi^2 = 1.91$, $R_p/R_{wp} = 7.69/3.04\%$)) and Fig. S3 (PND data at 10 K ($\chi^2 = 2.33$, $R_p/R_{wp} = 3.73/1.99\%$), the fitting and crystallographic parameters are listed in Table S1. Selected interatomic distances and bond angles are listed in Table S2. There are two crystallographically independent Mn atoms (Mn1 and Mn2) occupying the A-sites ($3a$, $(0 0 z)$), and Fe ($3a$, $(0 0 z)$) and Mo ($3a$, $(0 0 0)$) are ordered over the B-sties. The oxygen atoms are driven to two positions ($9h (x, y, z)$) due to the higher degree of cation ordering compared with that of the IL structure.
The anti-site disorder was also refined (constrained to the initial stoichiometry Fe : Mo = 1 : 1), by assuming that some Fe can randomly replace Mo atoms, and vice versa, giving ~7% of Fe/Mo disordering. The octahedral chains in the crystal structure of Mn$_2$FeMoO$_6$ are connected to form infinite octahedral slabs (thickness ~3.4 Å, Fig. S4, left) via corner-sharing between Mn1O$_6$-MoO$_6$ and Mn2O$_6$-FeO$_6$ neighboring chains (Fig. S4, right). The zigzag chains and slab packing leave vacancies right above and below the face-shared octahedral pairs, which favor the stabilization of the structure.

The octahedral distortions (Figures 1b and c) lead to three short and three long metal-oxygen bonds for each metal site (Table S2), with the average $<\text{Mn1-O}>$ and $<\text{Mn2-O}>$ distances of 2.195(3) Å at RT, which are comparable to those of the MnO$_6$ octahedra in the corundum derivatives, Mn$_2^{2+}$FeSbO$_6$ (2.173 Å)$^{10}$ and Mn$_2^{2+}$FeMO$_6$ (M = Nb (2.16 Å) and Ta (2.22 Å))$^{12}$. The $<\text{Fe-O}>$ distance (2.033(4) Å) is also comparable to octahedral $<\text{Fe-O}>$ in similar phases as in Mn$_2^{2+}$Fe$_{3+}$SbO$_6$ (2.006 Å)$^{10}$ and Mn$_2$Fe$_{3+}$MO$_6$ (M = Nb (2.030 Å) and Ta (2.012 Å))$^{12}$, the $<\text{Mo-O}>$ average distance (2.008(2) Å) is larger than in other related ordered double perovskites, e.g., Sr$_2$FeMoO$_6$ where it is 1.947 Å$^{22}$, which indicates a lower oxidation state of Mo in Mn$_2$FeMoO$_6$ compared to the ordered double perovskite where Mo is considered 5+/6+ mixed valent$^{23}$. The crystal structure at 10 K is similar to that at 300 K, but with smaller unit cell and atomic displacement parameters as expected.
**Fig. S2** Experimental, calculated, and difference of (a) PSXD and (b-c) PND patterns of Mn$_2$FeMoO$_6$ at 300 K, corresponding to the combined refinements in Ni$_3$TeO$_6$-type structure. In (b) and (c) PND data are from the low and high D-spacing banks, respectively. The vertical bars (│) show the peak index of vanadium (sample can), and nuclear and magnetic structure, respectively, from top to bottom.
**Fig. S3** Experimental, calculated, and difference of PND patterns of Mn$_2$FeMoO$_6$ at 10 K, corresponding to the refinements in Ni$_3$TeO$_6$-type structure. (a) and (b): PND data from low and high D-spacing banks, respectively. Inset of (b) shows the peak intensity differences of data at 10 and 300 K due to the evolution of the magnetic structure. The vertical bars (│) show the peak index of vanadium (sample can), and nuclear and magnetic structure, respectively, from top to bottom.
Table S1  Atomic parameters and agreement factors after the Rietveld refinements of PND (10 K) and combined PND and PSXD (300 K) data of Mn$_2$FeMoO$_6$ in Ni$_3$TeO$_6$-type structure (rhombohedral, space group of $R\bar{3}$ (No. 146), $Z = 3$).

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<th>Temperature/K</th>
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<td>5.2505(1)</td>
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<td>c/Å</td>
<td>13.8305(2)</td>
<td>13.8355(1)</td>
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<td>$V$/Å$^3$</td>
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**Mn1 (3a, 0 0 $z_p$)**

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<td>$z_p$</td>
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<td>0.2175(2)</td>
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<td>$U_{iso} \times 100$/Å$^2$</td>
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<td>0.99(2)$^i$</td>
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<td>Mag. mom./µ$_B$</td>
<td>+4.0(3)</td>
<td>+1.8(7)</td>
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**Mn2 (3a, 0 0 $z_p$)**

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<td>$z_p$</td>
<td>0.7144(7)</td>
<td>0.7160(2)</td>
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<td>$U_{iso} \times 100$/Å$^2$</td>
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<td>0.99(2)$^i$</td>
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<tr>
<td>Mag. mom./µ$_B$</td>
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<td>-1.8(7)</td>
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**(Fe/Mo)1 (3a, 0 0 $z_p$)**

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<td>Occ.</td>
<td>0.93(1)/0.07(1)</td>
<td>0.93(1)/0.07(1)</td>
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<td>$z_p$</td>
<td>0.4995(8)</td>
<td>0.4949(4)</td>
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<tr>
<td>Mag. mom./µ$_B$</td>
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<td>+1.1(9)</td>
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**(Mo/Fe)2 (3a, 0 0 0)**

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<tr>
<td>Occ.</td>
<td>0.93(1)/0.07(1)</td>
<td>0.93(1)/0.07(1)</td>
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<tr>
<td>$U_{iso} \times 100$/Å$^2$</td>
<td>0.71(2)$^i$</td>
<td>0.99(2)$^i$</td>
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<tr>
<td>Mag. mom./µ$_B$</td>
<td>-1.1(1)</td>
<td>-0.3(9)</td>
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**O1 (9b, $x_p$ $y_p$ $z_p$)**
\[
\begin{array}{lll}
   x_p & 0.0338(12) & 0.0376(1) \\
   y_p & 0.3120(7) & 0.3198(1) \\
   z_p & 0.0996(5) & 0.0976(2) \\
   U_{iso} \times 100/\text{Å}^2 & 0.52(2) & 1.00(2) \\
\end{array}
\]

**O2 (9b, x_p y_p z_p)**

\[
\begin{array}{lll}
   x_p & 0.0410(12) & 0.0417(1) \\
   y_p & 0.7121(12) & 0.7164(1) \\
   z_p & 0.6007(5) & 0.5975(2) \\
   U_{iso} \times 100/\text{Å}^2 & 0.52(2) & 0.98(2) \\
\end{array}
\]

| \(R_p/wR_p\)/% (PND #1) | 2.93/1.68 | 3.14/1.95 |
| \(R_p/wR_p\)/% (PND #2) | 4.19/3.12 | 4.66/3.74 |
| \(R_p/wR_p\)/% (SXRD) | - | 7.84/10.29 |
| \(R_p/wR_p\)/% (Total) | 3.73/1.99 | 7.69/3.04 |
| \(R_{Mag}\) | 2.15 | 5.91 |
| \(\chi^2\) | 2.33 | 1.91 |

\(^1\)\(U_{iso}\) for all cations are constrained to be the same value during refinements of 10 and 300 K data, respectively; \(^2\)\(U_{iso}\) for all oxygen atoms are constrained to be the same value during refinements of 10 and 300 K data, respectively; \(^3\) The moments on Fe and Mo are constrained to be 5.92 : 1.73 according to the expected full spin moments.
Table S2: Selected bond lengths (Å), octahedral distortion parameters (Δ), atomic bond valence sums (BVS), and bond angles (°) of crystal structure of Mn$_2$FeMoO$_6$ at 10 and 300 K, respectively.

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<tr>
<td>Mn1-O1 × 3</td>
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<td>Δ$_{Mn1}$ ($\times 10^{-3}$)</td>
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<td>BVS</td>
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<tr>
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<td>2.18</td>
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<tr>
<td>BVS</td>
<td>2.11</td>
<td>2.08</td>
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</table>
(Fe/Mo)$_1$O$_6$

(Fe/Mo)$_1$-O1 × 3  & 1.961(7) & 1.920(3) \\
-O2 × 3 & 2.146(9) & 2.146(4) \\
<(Fe/Mo)$_1$-O> & 2.054(6) & 2.033(4) \\
Δ(Fe/Mo)$_1$ ($\times 10^{-3}$) & 2.03 & 3.09 \\
BVS & 2.89 & 3.10 \\

(Mo/Fe)$_2$O$_6$

(Mo/Fe)$_2$-O1 × 3  & 2.076(7) & 2.085(2) \\
-O2 × 3 & 1.897(5) & 1.931(2) \\
<(Mo/Fe)$_2$-O> & 1.986(7) & 2.008(2) \\
Δ(Mo/Fe)$_2$ ($\times 10^{-3}$) & 2.03 & 1.47 \\
BVS & 4.85 & 4.56 \\

Selected bond angles (°)

O1-Mn1-O1  & 70.3(3) & 73.6(1) \\
O2-Mn1-O2  & 112.5(3) & 110.9(1) \\
O1-Mn1-O2  & 80.3(3) & 79.9(1)
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<td>116.9(1)</td>
</tr>
<tr>
<td>Mn2-O1-(Fe/Mo)1</td>
<td>115.4(4)</td>
<td>116.1(1)</td>
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<tr>
<td>-(Mo/Fe)2</td>
<td>95.5(3)</td>
<td>96.1(1)</td>
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<td>Mn2-O2-(Fe/Mo)1</td>
<td>84.7(3)</td>
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<tr>
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<td>140.6(4)</td>
<td>141.7(1)</td>
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\[^1\] The octahedral distortion parameter Δ is defined as \( \Delta = 1/6 \sum (d - d_{av})^2/d_{av} \), where \( d \) and \( d_{av} \) denote the individual interatomic distance and the average distance, respectively. \(^{24}\)

In the well-known polar LiNbO\(_3\) \(^{25}\), \( \Delta_{Li} = 1.8 \times 10^{-3} \), \( \Delta_{Nb} = 4.0 \times 10^{-3} \).
**Fig. S4** Octahedral slab (thickness of ~3.4 Å) in the crystal structure of Mn$_2$FeMoO$_6$ viewed along the [-110] (left) and the [110] (right) directions, respectively, to show the octahedral zigzag chains by edge-sharing connection of face-shared octahedral pairs along the c-axis. Mn1O$_6$, blue; Mn2O$_6$, yellow; FeO$_6$, carmine; MoO$_6$, light green; O1, red; O2, deep purple.

3. **Second Harmonic Generation Measurements**

Broadband SHG experiments were conducted at RT on a powder sample$^{26}$. The fundamental beam covering a wide wavelength range ($\lambda = 1100 – 2000$ nm) was produced from an optical parametric oscillator at increments of 100 nm, which was synchronously pumped by an Nd:YAG laser with a pulse width of 30 $\mu$s and a repetition rate of 50 Hz. The input irradiance was about 0.7 GW/cm$^2$ and the SHG signals ($\lambda_{\text{SHG}} = \lambda/2 = 550–1000$ nm) were collected with a
reflection geometry by a fiber-optic bundle, which was coupled to a spectrometer equipped with a charge-couple device camera. Surface-induced SHG as well as SHG signals from other optical components were negligible. The relative SHG signals (Fig. S5) spectrally resolved in a broad wavelength range were precisely calibrated with the known and measured efficiencies of all optical components to produce the wavelength-dependent SHG response.

![Wavelength-dependent SHG spectra of Mn\textsubscript{2}FeMoO\textsubscript{6}](image)

**Fig. S5** Wavelength-dependent SHG spectra of Mn\textsubscript{2}FeMoO\textsubscript{6}

4. X-ray Absorption Near-Edge Spectroscopy

X-ray absorption near-edge spectra (XANES) were collected on the beam line X-19A at Brookhaven NSLS, to confirm the formal oxidation state of the cations. Mn and Fe spectra were collected in both transmission and fluorescence modes with simultaneous standards. The Mo
XANES was collected in fluorescence mode in a He-atmosphere-chamber with standards run in temporal proximity. The main edge features at 3-$d$ transition metal K edges are dominated by 1$s$ to 4$p$ transitions. These features, and the step-continuum onset which lies underneath them, manifest a chemical shift to higher energy with increasing valence. The 4$p$ features can also be split into multiple features by the local atomic coordination/bonding and by final state effects (i.e. admixed $3d$ configurations). The chemical shift of the K edge has been widely used to chronicle the evolution of the transition metal valence state in oxide-based materials.\textsuperscript{12,27-34}

In Fig. S6a-c, the Mn- and Fe-K edges are compared to a series of standard compounds.\textsuperscript{27-29} The nominal proximity of the main edge rise for various formal valence states is indicated by a square in the figures. It is worth noting that the MnO and FeO standards (with edge sharing Mn/Fe-O octahedra) manifest a robust two feature rise and the chemical shift is identified (here) roughly with the inflection point between the two. The less structured steeply rising Mn-K edge of the Mn$_2$FeMoO$_6$ exhibits a chemical shift consistent with MnO, which is the Mn$^{2+}$ standard and are clearly much lower in energy than the Mn$^{3+}$ and Mn$^{4+}$ standards. Thus, the formal oxidation state at the Mn sites in this compounds is consistent with Mn$^{2+}$. Similarly, the chemical shift for the Fe-K edge for Mn$_2$FeMoO$_6$ (Fig. S6b) falls in the formal Fe$^{3+}$ valence range. The Fe K-pre-edge region (7.11-7.12 KeV, Fig. S6c) is shown on an expanded scale. The features in the pre-edge are quadrupole and dipole (through $p$-$d$ hybridization) allowed transitions into final states with 3$d$ character. The onset energy and structure of the pre-edge features are typically coupled to the transition metal valence. The Fe-K pre-edge features of Mn$_2$FeMoO$_6$ occurs at an energy comparable to that of the Fe$^{3+}$ standards and intermediate between those of the Fe$^{2+}$ and Fe$^{4+}$ standards. This provides additional support for the Fe$^{3+}$ state in this material.
Fig. S6 XANES spectra of Mn$_2$FeMoO$_6$. The Mn-K edge spectra (a) along with a series of octahedral O-coordinated Mn compounds with varying formal valences: Mn$^{2+}$O, Mn$^{2+}$FeNbO$_6$, LaMn$^{3+}$O$_3$, and CaMn$^{4+}$O$_3$; the Fe-K edge spectra (b) and its pre-edge region (c) along with a series of octahedral O-coordinated Fe compounds with varying formal valences: Fe$^{2+}$O, LiFe$^{2+}$PO$_4$, LaSrFe$^{3+}$O$_4$, Mn$_2$Fe$^{3+}$NbO$_6$ and SrFe$^{4+}$O$_3$; the Mo-L$_3$ edge (d) compared to reference edges for elemental Mo, the pyrochlore Sm$_2$Mo$_2$O$_7$ (Mo$^{4+}$~4$d^0$), the double perovskite SrMo$_{0.5}$Fe$_{0.5}$O$_3$ (Mo$^{5+}$~4$d^1$) and, the (Mo$^{6+}$~4$d^0$) MoO$_3$ and the quadruple perovskite Sr$_4$Fe$_3$MoO$_{12}$ (Mo$^{6+}$~4$d^0$). Here the formal valence is used ignoring more subtle hybridization/covalency effects.

Fig. S6d shows the Mo L$_3$-edges for Mn$_2$FeMoO$_6$ along with a number of standard spectra. The intense peak features at the L$_3$-edges of 4$d$ transition metals involve dipole allowed 2$p$-core to 4$d$ final-state transitions. These features can provide a probe of the empty 4$d$ state energy distribution, albeit modified by the transition matrix element, core–hole interaction and multiplet
The transition metal $d$-states are split by the octahedral coordination ligand-field into lower energy, $t_{2g}$ (sextet) and a higher energy $e_g$ (quartet) states. In low-$d$-occupancy transition metal ions like Mo$^{5+}$ ($d^1$), the T L$_3$-edges display a robust two peak structure with the lower energy peak (A) involving transitions into empty $t_{2g}$ states; and the high-energy peak (B) involving excitations into empty $e_g$ states. For $d$-hole counts greater than 4, the B-feature intensity reflects the empty $e_g$ states and the intensity of the A-feature scales with the number of $t_{2g}$-holes. Thus the A-feature intensity, relative to that of the B-feature, provides an indicator of the T 4$d$ count/valence state. This trend can be seen in the Mo$^{4+}$/d$^2$, Mo$^{5+}$/d$^1$, and Mo$^{6+}$/d$^0$ standard spectra sequence. The relative A/B feature intensity of the Mn$_2$FeMoO$_6$ spectrum places it in the nominally Mo$^{5+}$/d$^1$ configuration regime. Comparing to the conventionally synthesized perovskite, SrMo$_{0.5}$Fe$_{0.5}$O$_3$, one notes that the $t_{2g}$-$e_g$ ligand field splitting in the Mn$_2$FeMoO$_6$ compound is substantially larger resulting in a larger/better resolved A-B feature splitting. Thus, the formal oxidation states of Mn$^{2+}$Fe$^{3+}$Mo$^{5+}$O$_6$ were manifested. Here, the $d^1$-electron configuration of Mo$^{5+}$ is ascribed to the formation of Ni$_3$TeO$_6$-type structure compared with the Nb$^{5+}$ and Ta$^{5+}$ ($d^0$-electron configuration) analogs, which adopt the polar LN-type structure.

5. Magnetic, Magnetotransport Properties, and Electrical Conductivity Measurements

Magnetization measurements were carried out with a commercial Quantum Design superconducting quantum interference device (SQUID) magnetometer. The susceptibility was measured in zero field cooled (ZFC) and field cooled (FC) conditions under a 0.1 T magnetic field, for temperatures ranging from 5 to 400 K. Isothermal magnetization curves were obtained at $T = 5$-300 K under an applied magnetic field varied from -5 to 5 T. The $dc$ electrical
conductivity properties were measured on the pellet sample with the standard four probe technique in a physical property measurement system (PPMS) from Quantum Design. The magnetotransport properties were measured on the pellet sample with the standard four probe technique in a physical property measurement system (PPMS) from Quantum Design. To avoid the Joule heating effect, measurements were carried out with less than 0.5 μA current. The magnetoresistance is defined as $MR(H) = 100 \times \frac{R(H) - R(0)}{R(0)}$, where R(H) is the resistivity at applied magnetic field H and R(0) is the resistivity without magnetic field. The magnetotransport properties were measured between -9 and 9 T at 100 and 300 K, respectively, showing a maximum negative magnetoresistance about -2% and -2.5% at 9 T at 300 and 100 K, respectively as shown in Fig. S7, thus enhance the multifunctional properties of this material.

Fig. S7 Magnetoresistance measurements results of Mn$_2$FeMoO$_6$ with magnetic field between 0 and 9 T, showing maximum negative magnetoresistance of about -2.5% and -2% at 9 T for 100 and 300 K, respectively.
6. Theoretical Calculations

The theoretical calculations have been performed within the generalized gradient approximation (GGA)\textsuperscript{38} of the exchange-correlation functional with the choice of Perdew-Burke-Ernzerhof (PBE) functional\textsuperscript{39} in a spin polarized scheme. To improve the description of correlation effects in Mn and Fe-d electrons, a DFT+U\textsuperscript{40-42} method within the Dudarev et al.’s approach was used. We have varied the U value between 4-8 eV at Fe and Mn sites and between 1-4 eV at Mo site, with a choice of Hund's coupling constant, $J_H = 0.8$ eV. The variation did not produce significant changes in the result. The calculations were performed in plane wave basis as implemented in Vienna Ab-initio Simulation Package (VASP)\textsuperscript{43}. For these plane wave calculations, we used projector augmented wave (PAW) potentials\textsuperscript{44} and the wave functions were expanded in the plane wave basis with a kinetic energy cutoff of 600 eV. Reciprocal space integrations were carried out with a k mesh of 5 x 5 x 5.

Calculations of electronic and magnetic structure have been carried out using the generalized gradient approximation (GGA) of density functional theory (DFT), supplemented with Hubbard U correction (GGA+U) to take care of strong electron-electron correlation at the transition metal sites, as implemented in plane wave based Vienna Ab-initio Simulation code\textsuperscript{45}. The calculated spin-polarized electronic structure, with chosen U values of 5 eV at the 3$d$ transition metal sites, Mn and Fe, and 2 eV at the 4$d$ transition metal site of Mo, shows Fe and Mn $d$-dominated states to be fully filled in the majority spin channels and empty in the minority spin channel, while Mo $d$ states to be partially filled in one of the spin channel, and empty in other. The calculated electron configuration and $dp$ hybridization are found to hold good for a
variation of U value between 4-8 eV at the 3d transition metal sites (Mn and Fe), 1-4 eV at the 4d transition metal (Mo) site, confirming the robustness of the obtained results.

The ferromagnetic solution with spins of Mn, Fe, Mo all aligned parallel are found to be energetically unfavorable by a large energy difference of about 300 meV compared to the ferrimagnetic solution where the spins of two nonequivalent Mn sites (Mn1 and Mn2) are aligned antiparallel. The lowest energy magnetic structure, turned out to be the ferrimagnetic structure with spins of Mn1 and Fe aligned parallel, which are antiparallel to the spins of Mn2 and Mo, giving rise to layers of ferromagnetically ordered Mn1 and Fe, coupled antiferromagnetically to the next layer of ferromagnetically ordered Mn2 and Mo, in perfect agreement with the magnetic structure obtained from PND data analysis. This magnetic structure, cited as up-up-down-down (along the zig-zag chain) in the following, is found to be energetically lower compared to the ferrimagnetic solution with antiparallel alignment of Mn1 and Mn2, and parallel alignment of Fe and Mo, (up-up-down-up) by an energy difference of about 80 meV. This suggests a very strong antiferromagnetic exchange between Mn1 and Mn2 and a moderately strong antiferromagnetic exchange between Fe and Mo, mediated via the corner sharing super-exchange paths. We also computed the polarization, for the insulating solution assuming perfect ordering of Fe and Mn, in ground state magnetic configuration, using Berry phase formalism$^{46,47}$.

Mn$_2$FeMoO$_6$ lacks any $(n-1)d^{10}ns^0$ or $d^0$ ion, and adopts the polar Ni$_3$TeO$_6$ structure instead of others in the corundum family shown in Fig. S1, breaking the polarization rules in perovskite-related oxides. As far as we know, to date, all known polar perovskite-related and corundum based compounds, including the above LN, ordered IL, and Ni$_3$TeO$_6$ structures,
contain at least an \((n-1)d^{10}ns^0\) electronic configuration ion at the A-site (such as \(\text{Zn}^{2+}\) in \(\text{ZnSnO}_3\)\(^{25}\), \(\text{Sc}^{3+}\) in \(\text{ScFeO}_3\)\(^{48}\), and \(\text{In}^{3+}\) in \((\text{In}_{1-x}\text{M}_x)\text{MO}_3 (M = \text{Fe}_{0.5}\text{Mn}_{0.5})\)\(^{49}\)), or B-site (such as \(\text{Ge}^{4+}\) in \(\text{La}_2\text{MgGeO}_6\)\(^{8}\), \(\text{Sb}^{5+}\) in \(\text{Ni}_2\text{InSbO}_6\) and \(\text{Ni}_2\text{ScSbO}_6\)\(^{7}\), and \(\text{Te}^{6+}\) in \(\text{Ni}_3\text{TeO}_6\) and \(\text{Li}_2\text{ZrTeO}_6\)\(^{4-6}\)), or a lone pair electron ion at the A-site (such as \(\text{Bi}^{3+}\) in \(\text{BiFeO}_3\)\(^{50}\) and \(\text{Pb}^{2+}\) in \(\text{PbVO}_3\)\(^{51}\)), or a SOJT ion at the B-site (such as \(\text{Nb}^{5+}\) and \(\text{Ta}^{5+}\) in \(\text{Mn}^{2+}\text{Fe}^{3+}\text{M}^{5+}\text{O}_6 (M = \text{Nb, Ta})\)\(^{12}\) and \(\text{W}^{6+}\) in \(\text{NaLaFeWO}_6\)\(^{52}\)), no polarization was observed in oxides without any of the above ions, which either favor the essential hybridization between the metal \(nd\) and oxygen \(2p\) states\(^{53}\), or provide stereoactive lone pair electrons such as the \(6s^2\) lone pair electron in \(\text{Bi}^{3+}\) in \(\text{BiFeO}_3\)\(^{50}\). As far as we knew, the polar \(\varepsilon\)-\(\text{Fe}_2\text{O}_3\) is an exception but the crystal structure is different from perovksite/corundum and contains mixed \(\text{FeO}_6\) and \(\text{FeO}_4\) coordination environment\(^{54-66}\).

We calculated the total energy of different possible structural arrangements (Fig. S1) to reveal the reason for the formation of the \(\text{Ni}_3\text{TeO}_6\) structure. In order to check the influence of disorder on the electronic structure, we considered three different configurations in a supercell, which is three times the primitive unit cell, namely (i) perfect ordering (Fe-Mo-Fe-Mo-Fe-Mo), (ii) segregation (Fe-Fe-Fe-Mo-Mo), and (iii) mixed configuration (Fe-Fe-Mo-Fe-Mo-Mo). Our total energy calculations suggest that the ordered arrangement of Fe and Mo [case (i)] is preferred over the segregated arrangement of Fe-Mo [case (ii)] by a large energy difference of about 600 meV/f.u., and by an energy difference of about 150 meV/f.u. over the mixed configuration [case (iii)] when the magnetism is turned on. This result is evidence for the important role of magnetism in the finite \(d\) configuration of Fe and Mo in stabilizing the observed \(\text{Ni}_3\text{TeO}_6\) structure, which allows for two nonequivalent positions of B and B’ ions. Note that ilmenite (\(R-3\)) or \(\text{LiNbO}_3\) (\(R3\)\(c\)) structures do not allow for two nonequivalent positions of B and B’. The \(\text{Ni}_3\text{TeO}_6\) structure is also found to be stable over the ordered ilmenite (\(R3\)) structure.
by about 30 meV/f.u., which arises due to the large size mismatch between the ionic sizes of Mn$^{2+}$ in octahedral environment (~0.83 Å) and that of Fe$^{3+}$ or Mo$^{5+}$ (0.65 and 0.61 Å, respectively)\textsuperscript{67}. In the ordered ilmenite structure Mn1-Mn2 edge share within the layer, while in Ni$_3$TeO$_6$, the unlike atoms, e.g. Mn1 and Fe, edge share within the layer.

7. Dielectric and Polarization Measurements

Dielectric measurements were carried out in two-point geometry. For these investigations polycrystalline pellets were prepared as plate-like capacitors with typical area of 4 mm$^2$, a thickness of 0.5 mm and silver-paint electrodes. For the spectroscopic measurements in the frequency range from 1 Hz < ν < 1 MHz a frequency response analyzer [Novocontrol] was utilized; the polarization measurements at low temperatures were carried out in a Sawyer-Tower circuit using an electrometer (Keithley 6517) and linear E-field ramping with a frequency of one cycle per minute.

At high temperatures the dielectric properties are completely determined by the finite conductivity $\sigma'$, which effectively is connected to the measured imaginary part of the complex permittivity $\sigma' = 2\pi\nu\varepsilon_0\varepsilon''$. In addition to the experimental obstacles to perform polarization or pyro-current measurements in this conductive regime, and to precisely determine $\varepsilon'$ in the presence of a large dielectric loss $\varepsilon''$, one has to consider further intrinsic and non-intrinsic contributions to the dielectric response. On the one hand the presence of VRH as demonstrated in in Figure 3 will lead to a contribution to the real part of the permittivity $\varepsilon'$\textsuperscript{68,69}. On the other hand heterogeneities in the sample, i.e. grain boundaries and electrodes (contacts) will lead to highly
capacitive depletion layers, which (like Schottky diodes) give rise to highly dispersive dielectric response as they form effective RC-elements $^{68,69}$. Measurements of the complex dielectric permittivity are shown in Fig. S9. The high values of $\varepsilon'$ for high temperatures and small frequencies are accompanied by much higher values in $\varepsilon''$ denoting the influence of sample conductivity together with non-intrinsic resistivities and capacitances of contacts and grain boundaries. Nevertheless, one can try to evaluate the resulting effective conductivity as it is shown in Fig. S8 in the vicinity of the magnetic phase transition. The data is presented as Arrhenius-plot $\ln \sigma'(1/T)$ between 295 and 385 K to demonstrate the thermally activated nature of

$$\sigma' \sim e^{-\Delta/(k_B T)}$$

$$\Delta/k_B = 2135 \text{ K}$$

$$\Delta/k_B = 1830 \text{ K}$$

**Fig. S8** Logarithm of the conductivity measured at 1 Hz (left scale) and magnetization measured in a field of 0.1 T (right scale) plotted vs reciprocal temperature. The linear regions above and below the magnetic transition temperature of 337 K are fitted assuming thermal activation with an energy barrier $\Delta$. 

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Fig. S9 Real (upper frame) and imaginary (lower frame) part of the complex permittivity $\varepsilon^*$ vs temperature as measured in zero magnetic field for frequencies between 1 Hz and 1 MHz. the inset shows a $P(E)$-curve measured with a frequency of one cycle per minute.

the transport in this temperature regime. At the ferrimagnetic transition (which in Fig. S8 is nicely denoted by the onset of spontaneous magnetization) the effective energy barrier changes:
in the magnetically ordered regime the energy barrier is lowered. This meets the evaluation of
the magneto-resistive properties of the previous section, even though the details of this effect, e.g.
the role of inter-grain contacts, cannot be elucidated at this point.

For low temperatures and high frequencies the impact of the residual conductivity on the
dielectric properties is reduced. On cooling, the large values for $\varepsilon'$ drop via two steps (due to
electrode and inter-grain contacts) towards the intrinsic value of $\varepsilon' \approx 45$, which still is a relatively
high value compared to other transition metal oxides. In this low temperature regime the residual
conductivity $\sigma'$ vanishes and the dielectric loss $\varepsilon''$ becomes much smaller than $\varepsilon'$. Therefore it is
possible to conduct direct polarization measurements. The inset of Fig. S9 displays a P(E)-loop
measured at 2 K in fields up to 170 V/mm. No hint towards a ferroelectric component can be
found as denoted e.g. via switchable or at least non-linear polarization. However, these findings
do not exclude the presence of possible structurally induced pyroelectricity in the polycrystalline
sample.

References

1 Werfel, F. & Brümmer, O. Corundum structure oxides studied by XPS. *Phys. Scripta* **28**, 92
(1983).
2 Woodward, P. M., Sleight, A. W., Du, L.-S. & Grey, C. P. Structural Studies and order–disorder
phenomenon in a series of new quaternary tellurates of the type $A^{2+}M^{4+}Te^{6+}O_6$ and
3 Hoel, C. A. *et al*. High-pressure synthesis and local structure of corundum-type $In_{2-2x}Zn,SnO_3$ ($x
5 Živković, I., Prša, K., Zaharko, O. & Berger, H. $Ni_3TeO_6$ — a collinear antiferromagnet with
6 Choisnet, J., Rulmont, A. & Tarte, P. Les tellurates mixtes $Li_2ZrTeO_6$ et $Li_2HfTeO_6$: un nouveau
7 Ivanov, S. A. *et al*. Spin and dipole ordering in $Ni_3InSbO_6$ and $Ni_3ScSbO_6$ with corundum-related


Retuerto, M. et al. Magnetic and structural studies of the multifunctional material SrFe$_{0.75}$Mo$_{0.25}$O$_{3-δ}$. *Inorg. Chem.* **51**, 12273-12280 (2012).


Yamada, K. *et al.* The phase transition of \(\varepsilon\)-In\(_x\)Fe\(_{2-x}\)O\(_3\) nanomagnets with a large thermal hysteresis loop (invited). *J. Appl. Phys.* **111**, 07B506 (2012).


