Double corundum-related polar magnets are promising materials for multiferroic and magnetoelectric applications in spintronics. However, their design and synthesis is a challenge, and magnetoelectric coupling has only been observed in Ni$_3$TeO$_6$ among the known double corundum compounds to date. Here we address the high-pressure synthesis of a new polar and antiferromagnetic corundum derivative Mn$_2$MnWO$_6$, which adopts the Ni$_3$TeO$_6$-type structure with low temperature first-order field-induced metamagnetic phase transitions ($T_N$ = 58 K) and high spontaneous polarization (~ 63.3 $\mu$C.cm$^{-2}$). The magnetostriction-polarization coupling in Mn$_2$MnWO$_6$ is evidenced by second harmonic generation effect, and corroborated by magnetic-field-dependent pyroresponse behavior, which together with the magnetic-field-dependent polarization and dielectric measurements, qualitatively indicate magnetoelectric coupling. Piezoresponse force microscopy imaging and spectroscopy studies on Mn$_2$MnWO$_6$ show switchable polarization, which motivates further exploration on magnetoelectric effect in single crystal/thin film specimens.
The structural features of corundum derivatives provide an ideal platform for designing polar and magnetic compounds, since magnetic ions can be incorporated into both the octahedral A- and B-sites to lead to strong magnetic interactions, accompanied by large spontaneous polarization ($P_s$) if the polar LiNbO$_3$ (LN, R3c), ordered ilmenite (OIL, R3), or Ni$_3$TeO$_6$ (NTO, R3) type structure is adopted. Remarkable physical properties, such as multiferroic, piezoelectric, pyroelectric and second harmonic generation (SHG) effect, have been demonstrated in these materials. For example, the coexistence of weak ferromagnetism and ferroelectricity has been observed in the high-pressure LN-type FeTiO$_3$ and in recently-reported GaFeO$_3$ 2, 14, and non-hysteretic colossal magnetoelectricity was found in collinear antiferromagnetic (AFM) NTO, is, to the best of our knowledge, the only experimentally observed magnetoelectric coupling in the double corundum family 2. In contrast to the off-centering displacement of $d^0$ B cations in the octahedra occurring in many ferroelectric perovskites 15-17, in corundum-type ABO$_3$ or A$_2$BO$_5$ materials, the polarization reversals are driven by the small A or B cations moving between oxygen octahedra 18, 19, hence the $d^0$ configuration is not required. Therefore, considering the potential combinations of A1, A2, B, and B’ in the (A1A2)B’B’O$_6$ corundum family (where A1, A2, and B, or any two of them could be the same element, or all cations could be different), a very large number of new multifunctional materials are anticipated with the assistance of high pressure (HP) synthesis techniques. However, to the best of our knowledge, only 14 polar and magnetic A$_2$B’B’O$_6$-type corundum-related compounds have been reported to date (see Supplementary Table 1); of these, 11 compounds were experimentally prepared: Ni$_3$TeO$_6$ 20, Ni$_3$ScSbO$_6$ 3, and Ni$_3$InSbO$_6$ 4 were synthesized at ambient pressure, while the rest can only be stabilized at HP. Zn$_2$FeO$_6$ 21 and A$_2$FeMoO$_6$ (A=Sc, Lu) 22 have only been predicted by first principle calculations to show considerable P$_s$.

In this work, we present the HP synthesis of a new polar and magnetic compound Mn$_2$MnWO$_6$ (Mn$_8^3+$Mn$^4$W$^6$O$_6$), which is predicted by first principles calculations to show switchable polarization in an anticipated ferrimagnetic ground state 23, 24. The crystal and magnetic structures, cationic oxidation states as well as the physical properties, including second harmonic generation (SHG), magnetic properties, piezo-, pyro-, ferroelectric and magnetoelectric responses, are extensively studied.

**Results**

**Crystal structure of Mn$_2$MnWO$_6$.** Earlier, Mn$_2$MnWO$_6$ single crystals prepared by CO$_2$-LASER technique in H$_2$-atmosphere at ambient pressure were reported with the Mg$_6$TeO$_6$-type structure (Supplementary Fig. 1) 25. The Mn$_2$MnWO$_6$ polymorph we report here, prepared at 1673 K and 8 GPa (see Methods), forms in a different crystal structure. Synchrotron powder x-ray diffraction (SPXD) and neutron powder diffraction (NPD) data collected on the as-made sample indicate a rhombohedral (R3, No. 146) majority phase with a small impurity. The phases were identified as a NTO-type Mn$_2$MnWO$_6$ main phase ($a = 5.3223(3) Å$, $c = 14.0589(1) Å$, $V= 345.01(1) Å^3$) and ~ 3.3(1)% wt -MnWO$_4$ wolframite 26, 27, from combined Rietveld refinements of SPXD and NPD data (Supplementary Fig. 2, $R_p/R_{wp} = 4.74/4.55%$, $\chi^2 = 3.67$). All the cation sites were set as fully occupied, since free refinements lead to less than 1% deviation. There is good contrast between Mn and W neutron scattering lengths (Mn = -3.73 fm, W = 4.86 fm) 28 and allowing Mn – W antisite disorder (with constraints to maintain stoichiometry) in combined SPXD and NPD refinements suggested no disorder (antisite occupancies refined to < 1% with no improvement in fit). The final refinement results are listed in Supplementary Table 2 and the crystal structure is shown in Fig. 1. Mn$_2$MnWO$_6$ is isostructural with Mn$_3$FeWO$_6$ and crystallizes in NTO-structure with three independent Mn- (Mn1, Mn2, and Mn3), one W-, and two oxygen sites (O1 and O2), giving the structural formula of Mn$^3+$Mn$^3+$W$^6+$O$_6$. The face-sharing Mn$^3+$-W$^6+$ and Mn$_2$O$_6$-Mn$_3$O$_6$ octahedral pairs are arranged alternatively along the c-axis and separated by octahedral vacancies. In the ab-plane, the edge-sharing Mn$_1$O$_6$-Mn$_3$O$_6$ and Mn$_2$O$_6$-W$_6$O$_6$ octahedral layers are connected alternatively to form a framework structure (see Fig. 1).

The paired face-sharing arrangement yields high octahedral distortions as reflected by the octahedral distortion parameter ($\Delta_m$) 29 and atomic displacement ($d_{mo}$ distance between cation and its octahedral centroid) along the c-axis (Supplementary Table 3). The largest $\Delta$ and $d$ values are observed at the Mn2 site with $\Delta_{Mn2} = 5.07 \times 10^{-3}$, $d_{Mo} = 0.517 Å$, which are very close to those of the Mn2 site ($5.45 \times 10^{-3}$ and 0.544 Å) in the Mn$_2$FeWO$_6$ analog 30, 31. These anisotropic atomic displacements induce a large $P_s$ (e.g. 63.3 $\mu$C/cm$^2$ at 290 K, as estimated by the point-charge displacement model) 30, 31, and give three long and three short metal-oxygen bond distances for each octahedron, varying from 2.061(1) to 2.377(2) Å for Mn-O and 1.867(2) to 1.999(1) Å for W-O. The average <Mn-O> distance lies between 2.196(2) and 2.217(2) Å, comparable to the <Mn-O> of 2.187(9) and 2.228(6) Å for Mn1 and Mn2 in Mn$_2$FeWO$_6$. The <W-O> value 1.933(9) Å is close to the <W-O> (1.925(9) Å) in Mn$_2$FeWO$_6$ 32, 33. Bond valence sums (BVS) calculations 30, 34-36 give +2.00, +2.06, +2.09, and +5.84 for Mn1, Mn2, Mn3, and W, respectively, supporting formal cationic oxidation states of Mn$^{3+}$/Mn$^{3+}$/W$^{6+}$/O$_6$ and well accounting for its slightly larger unit cell volume (345.01(1) Å$^3$, $r^{(Mn^{3+})} = 0.83 Å$) than that of the isostructural Mn$^{2+}$/Fe$^{2+}$/W$^{6+}$/O$_6$ (338.65(1) Å$^3$, $r^{(Fe^{2+})} = 0.78 Å$) 35. The large difference in ionic size and charge between Mn$^{2+}$ and W$^{6+}$ is...
Magnetic properties of Mn$_2$MnWO$_6$. The temperature-dependent magnetization $M(T)$ curves up to 400 K at 0.1 T (Fig. 2a) show that upon cooling the magnetization is enhanced below 80 K and a sharp AFM transition occurs at ~58 K. Below 20 K, the zero-field cooling (ZFC) and field-cooling (FC) curves diverge, indicating a small ferromagnetic component or canted spins in an anisotropic system along with domain effects. At higher temperatures, Mn$_2$MnWO$_6$ follows the Curie–Weiss (CW) law; the negative Weiss temperature ($\theta = -279.2 K$) is much lower than the AFM transition at $T_N$ ~ 58 K, again suggesting significant magnetic frustration/interaction. The effective magnetic moment ($\mu_{eff}$) derived from the CW fit of $1/\chi(T)$ over the paramagnetic region (inset of Fig. 2a) is 10.20 $\mu_B$·f.u.$^{-1}$ (f.u. = formula unit), which gives an average value of 5.89 $\mu_B$·f.u.$^{-1}$ for each Mn site, consistent with the theoretical value (5.92 $\mu_B$·f.u.$^{-1}$) of high-spin $d^5$-Mn$^{2+}$ state. Figure 2b shows the logarithmic-$M(T)$ curves collected in both ZFC and FC modes between 0.005 and 14 T up to 400 K. Below 1 T, the $M(T)$ plots manifest robust AFM transitions ~58 K as evidenced by: the inflection point (below the peak) in the $M(T)$ curve; the sharp peak in the $dM/dT$ curves shown in Supplementary Fig. 6; and the isothermal $M(H)$ hysteresis loops below 50 K in Fig. 2c and Supplementary Fig. 7. At 1 T, this AFM transition is weakened and moved to lower temperature as highlighted by the dashed line in Fig. 2b and Supplementary Figs. 6 and 8. Above 7 T this AFM order is substantially modified and the detailed character of the high field AFM state is uncertain. The $M(T)$ curves also evidence structure near 60 K at all fields indicating local magnetic correlations on this energy scale. The presence of a low temperature first-order field-induced metamagnetic phase transition (Supplementary Fig. 8), similar to that observed in Mn$_2$FeWO$_6$, is clear from the isothermal magnetization curves, $M(H)$, shown in Fig. 2c and in expanded views (with additional data) in Supplementary Fig. 7. The magnetization is far from saturation at 2 K and 14 T, and gives a value of only ~1.82 $\mu_B$·f.u.$^{-1}$, indicating that AFM order still strongly constrains the field response in this regime.

Magnetic structure of Mn$_2$MnWO$_6$. To better understand the magnetic behavior of Mn$_2$MnWO$_6$, NPD data at lower temperatures were recorded. Additional Bragg reflections were observed below ~55 K with intensity increasing smoothly on cooling (Supplementary Fig. 9). Some magnetic reflections were consistent with a magnetic unit cell commensurate with the nuclear crystal structure with magnetic propagation vector $k_f = (0 0 3/2)$ (T point of the first Brillouin zone) while other reflections were broader and consistent with an incommensurate modulation with $k_s = (0 0 0.3)$ ($\Lambda$ line of the first Brillouin zone) (Supplementary Fig. 9). Good fits to the 5 K NPD data were obtained for models of $R_3(00\gamma\delta)$ symmetry with the magnetic unit cell related to the nuclear cell through the transformation [(0-10)(110)(002)]. This magnetic superspace symmetry is a result of both the mT1 and m2LE2 irreps acting on all three manganese sites. Models with only one irrep acting on each site gave poor fits to the data and unphysical moments for Mn$^{2+}$ sites. Various models with AFM ordering of manganese moments along [001] (described by irrep mT1) with these moments tilted towards the $ab$ plane rotating around [001] (described by m2LE2 irrep), giving Mn moments arranged in cones around [001], gave good fits to the experimental data. Constraints were needed to give a stable refinement and convergence and the $x$ and $xy$ components of the Mn2 moments were constrained to be half and double those of the Mn1/Mn3 moments, respectively. This gives overall moments of 4.2(5) and 4.4(5) $\mu_B$ for Mn1/Mn3 and Mn2 sites at 5 K, respectively, with incommensurate propagation.
Fig. 3 Illustration of the nuclear and magnetic structures of Mn₂MnWO₆ at 5 K. Mn₁, Mn₂, Mn₃ and W sites and polyhedra are shown in green, purple, blue and grey, respectively, with Mn moments shown by red arrows (color online) (oxide ions are omitted for clarity). a shows the complete magnetic structure (showing six times the nuclear unit cell along c). b shows only the z component of Mn moments (described by commensurate mT₁ irrep) and c shows only the xy component of Mn₁ and Mn₃ moments (described by mÅ2LE₂ irrep) (showing six times the nuclear unit cell along c), also d showing view down along c axis of magnetic unit cell.
Temperature dependent spontaneous polarization (P_s) in Mn_2MnWO_6. a, Temperature dependent spontaneous polarization (P_s) calculated, and Mn2-Mn3 distance evolution in Mn_2MnWO_6 between 5 and 100 K. b, Pyro-current as a function of temperature between 10 and 80 K, and c, Pyroelectric polarization measured in 0 and 1 T upon warming and normalized to a common high temperature value. d, Temperature dependent dielectric data between 0 and 10 T show anomalies around T_N and indicate magnetoelectric coupling.

vector \( k = 0 0 0.6107(8) \) \( (k = 0 0 0.305 \) with respect to the nuclear unit cell). We cannot rule out the possibility of similar magnetic structures giving equally good fits to the data, but the constraints imposed give almost equal moments for each manganese site and across the magnetic structure as might be expected for this insulating oxide. The magnetic and crystal structures at 5 K are shown in Fig. 3 and refinement profiles in Supplementary Fig. 10. Refinement details and selected bond lengths and distances are given in Supplementary Tables 4 and 5.

Refinement were then carried out using short NPD scans collected at selected temperatures on warming (with no magnetic component included above \( T_N \)).

This zero-field magnetic structure can be described as a superposition of commensurate AFM ordering along [001] (mT1 irrep) and a helical component in the xy plane (mA2LE2 irrep) giving rise to the conical-AFM magnetic structure propagating along [001]. This magnetic structure can be thought of in terms of AFM coupling between Mn1 and Mn3 sites within the Mn1Mn3O_3 layers, with moments predominantly along [010]. The Mn2 moments are predominantly within the (001) planes in the opposite direction to the in-plane component in the Mn1Mn3O_3 layer directly above (this in-plane component is cancelled by that of other layers in the overall magnetic unit cell in this zero-field AFM structure). Manganese moments increase smoothly on cooling (Supplementary Figs. 11 and 12). The AFM arrangement of Mn1 and Mn3 moments predominantly along [001] within the Mn1Mn3O_3 layers satisfies the 90° super-exchange interactions expected to be AFM. The Mn2 site is magnetically coupled to this Mn1Mn3O_3 layer via ~120° Mn1 – O2 – Mn2 interactions and about 86° Mn3 – O2 – Mn2 interactions across the shared face. Both these exchange interactions are likely to be AFM leading to magnetic frustration, consistent with magnetic susceptibility measurements described above. This frustration is somewhat relieved by the incommensurate modulation that reorients the moments away from [001], particularly for the Mn2 site, allowing its in-plane component to be oriented antiparallel to the in-plane component in the nearest Mn1Mn3O_3 layer (which lies directly above).

**Magnetostriction-polarization coupling and magnetoelectric effect in Mn_2MnWO_6**. The unit cell volume of Mn_2MnWO_6 decreases smoothly on cooling until the lowest temperatures when slight negative thermal expansion is observed (Supplementary Fig. 13). This is due to expansion of the unit cell along the [001] direction below \( T_N \). This expansion is thought to be due to magnetostriction across the Mn2 – Mn3 face-shared polyhedra: the Mn2 – Mn3 distance increases below the AFM ordering temperature as the Mn3 site moves towards the O1 layer and away from the O2 layer within the shared face (Fig. 4a and Supplementary Fig. 13), similar to structural changes observed in other materials containing Mn_2O_4 dimers. This magnetostriiction gives a dramatic increase of \( P_s \) below \( T_N \), in line with the increase of the Mn2 – Mn3 distance below \( T_N \), giving computed \( P_s \) of 62.86 \( \mu \text{C cm}^{-2} \) at 60 K and 70.48 \( \mu \text{C cm}^{-2} \) at 30 K (Fig. 4a and Supplementary Figs. 13 and 14). The coupling between spin structure and the lattice anomalies is well known to play an important role for the observation of multiferroicity. The magnetostriiction-polarization coupling around \( T_N \) is also visible in the fluctuation of the SHG intensity (Supplementary Fig. 15).

Figure 4b and c show the finite pyrocurrent and pyroelectric polarization response at 0 and 1 T, respectively. A clear anomaly/discontinuity can be detected in the pyrocurrent (Fig. 4b and Supplementary Fig. 16), the pyroelectric polarization (Fig. 4c) and the dielectric (Fig. 4d) curves in the vicinity of the magnetic transition, qualitatively echoed by the magnetostriiction effects, which couple the macroscopic polarization of the structure to magnetism. The small difference between pyroresponse at 0 and 1 T suggests possible magnetoelectric coupling, however, one should be aware of experimental uncertainties by lack of a robust effect (~ 0.05 \( \mu \text{C cm}^{-2} \) compared with the theoretical value of ~ 70 \( \mu \text{C cm}^{-2} \) at 20 K) in such a random-distribution polycrystalline specimen as also observed in the magnetic-field-dependent polarization measurement results in Supplementary Fig. 17. However, the temperature-dependent dielectric measurements at several magnetic fields from 0 to 10 T evidence anomalies around
$T_N$ in Fig. 4d. The shift of the transition temperature with the magnetic field as well as the observed suppression in high magnetic fields clearly convince magnetoelectric coupling in Mn$_2$MnWO$_6$.

Switchable polarization of Mn$_2$MnWO$_6$. To further explore the polar and ferroelectric properties of Mn$_2$MnWO$_6$, piezoresponse force microscopy (PFM) imaging and spectroscopic studies were performed at room temperature, since the surface deformation does not depend on the contact radius$^{39, 40}$ and hence is a direct measure of local piezoelectric properties$^{41, 42}$. In conjunction with dual amplitude resonance-tracking (DART) imaging, or band excitation (BE)$^{34, 43}$ modes, PFM allows to obtain quantitative information on material properties. The surface topography and PFM images of a polished sample embedded in epoxy is shown in Supplementary Fig. 18, with clearly visible variation of DART PFM contrast at the grain boundaries, some grains show clearly visible domain structures, highly reminiscent of domain structures for materials such as BaTiO$_3$.$^{46, 47}$.

The switching properties of the materials were explored with BE PFM polarization spectroscopy measurements$^{48}$. The 750 × 750 nm region was first imaged by DART PFM as shown in Fig. 5a–c. Representative hysteresis loops of the amplitude and phase are shown in Fig. 5d. The clear hysteresis loops with the characteristic coercive biases of ∼ 50 V are observed. Note that the loops are not saturated, suggesting that formation of domains are largely unstable and rapidly relax in the bias-off state. Here, the measurements are performed over rectangular grid of points (35 × 35), giving rise to the 3D array of hysteresis loops. The latter can be processed to yield 2D maps of materials parameters such as coercive bias of polarization switching. The maps of remnant polarization for positive and negative coercive biases are shown in Fig. 5e and f, which bear some resemblance with underlying domain structure, suggesting the pinning of polarization by preexisting electroelastic fields. The final switching experiment was conducted on the region shown in Supplementary Fig. 19a. In this case, the surface is scanned by a strongly negatively (−100 V) biased tip within a 4 µm square, and subsequently with a strongly positively biased tip (+100 V) within a 2 µm square (Supplementary Fig. 19d). The polarization distributions after each poling measurement are shown in Supplementary Figs. 19b–e, f. Herein, it is conclusive that the polarization in Mn$_2$MnWO$_6$ is switchable, as further corroborated by the $P(E)$ loop measurements (Supplementary Fig. 20). For a quantitative image of the ferroelectric and magnetoelectric coupling effect, further exploration on single crystal sample is necessary.

Comparison of Mn$_2$MnWO$_6$ and isostuctural polar magnets. It is relevant to compare the magnetic structure of Mn$_2$MnWO$_6$ with that of other magnetic NTO materials. In Mn$_2$ScSbO$_6$ and Ni$_2$BSbO$_6$ (B = Sc, In), the non-magnetic ions create holes in the Mn/Ni magnetic sublattices preventing direct exchange between the magnetic sites$^{35, 36}$. All these systems order AFM, but with no face-shared magnetic $M_i$O$_9$ ($M_i$ = magnetic cation) dimers or magnetic frustration, it is unlikely that magnetostriction-driven changes in polarization occur. However, it is interesting that without nearest-neighbor exchanges, Ni$_2$BSbO$_6$ (B = Sc, In) is significantly more frustrated than Ni$_2$TeO$_6$ and adopts a non-collinear, helical magnetic structure with components of the Ni$^{2+}$ moments along both the $c$ direction and in the $ab$ plane$^5$. NTO systems with three magnetic cations include Mn$_2$FeWO$_6$$^7$, Mn$_2$FeMoO$_6$$^8$, and Ni$_2$TeO$_6$$^9$–$^{12}$ and exhibit complex magnetic behavior. All three materials differ from Mn$_2$MnWO$_6$ (described here) in that they are reported to have collinear magnetic structures with FM coupling between edge-shared magnetic sites within layers$^{49, 50}$. The chiral, polar material Ni$_2$TeO$_6$ has been the most thoroughly characterized and it is useful to compare its behavior with that of Mn$_2$MnWO$_6$. Theoretical studies on Ni$_2$TeO$_6$ suggest that edge-linked Ni1 and Ni2 sites are coupled FM ($J_1$) and that face-linked Ni2 and Ni3 sites are also coupled FM ($J_2$). AFM $J_3$, $J_4$ and $J_5$ interactions couple the Ni3 site (analogous to the Mn2 site in M$_2$MnWO$_6$) to Ni1 and Ni2 sites in adjacent layers via corner-linked exchange; the relative strengths of these exchange interactions results in a small degree of frustration, and the experimentally observed (zero-field) magnetic structure is collinear with Ni$^{2+}$ moments oriented along [001]$^{49, 50}$. Mn$_2$MnWO$_6$ differs in that the Mn1 – Mn3 coupling between edge-linked sites is AFM. This leads to frustration in the coupling with the Mn2 site through face-shared coupling to Mn3 and corner-linked interactions with Mn1 and Mn3 sites, giving a higher degree of frustration in Mn$_2$MnWO$_6$ compared with Ni$_2$TeO$_6$ (|$\theta$|/$T_N$ = 5 for Mn$_2$MnWO$_6$ and = 1 for Ni$_2$TeO$_6$). This higher level of frustration is likely to give rise to the non-collinear magnetic structure of Mn$_2$MnWO$_6$ with a significant in-plane component for the Mn2 moment to somewhat relieve this frustration. Oh et al. reported interesting magnetic field dependent behavior for Ni$_2$TeO$_6$ with an increasing magnetic field along [001] able to switch the system from a higher polarization state to a state with lower polarization$^5$. It is interesting that magnetostriction across the face-shared $M_i$O$_9$ dimers gives rise to a noticeable change in polarization in both these NTO materials and our variable-temperature NPD experiment allows us to study the magnetic and structural changes through the magnetic phase transition, clearly illustrating this effect (Fig. 4a, Supplementary Figs. 12 and 13). Both Ni$_2$TeO$_6$ and Mn$_2$MnWO$_6$ are polar as a result of the cation arrangement in this corundum-derived structure type, but the magnetic order modifies the existing electrical polarization$^{5, 49, 52}$. In Mn$_2$MnWO$_6$ the magnetic transition is driven by the one dimensional mT1 irreducible representation with order parameter $\mu$ and by the two dimensional mA2LE2 with order parameter $\eta_1, \eta_2$. Since the electrical polarization ($P$) is already present in the parent structure, it is possible to derive the coupling between the polarization and the magnetic order parameters as the product of $P$ and the magnetic free energy invariant. In this way, the linear quadratic coupling $P(\mu^2 + \eta_1^2 + \eta_2^2)$ is obtained. This coupling term is consistent with the magnetostriction observed experimentally in the neutron diffraction data and is at the basis of the change in the polarization at $T_N$.

In Ni$_2$TeO$_6$ the field-dependent behavior is ascribed to a spin-flop transition that reorients moments to within the $ab$ plane above a critical field along the polar $c$ axis, $H^c$.$^5$. Field-dependent neutron scattering experiments on the more frustrated Mn$_2$MnWO$_6$ (which already has some in-plane component for the moments) would be of interest to understand if a similar explanation might explain the field-depending observed in magnetic susceptibility measurements (Figs. 2b, c, Supplementary Figs. 7 and 8). Oh et al. describe how applying an electric field along the polar $c$ axis of Ni$_2$TeO$_6$ increases the polarization but decreases the magnetization along $c^5$, presumably due to the increased Ni2 – Ni3 separation (which weakens the FM $J_2$ interaction) and changes the balance between competing $J_1, J_2$ and $J_3$ interactions; with in-plane $J_1$ interactions relatively weak, this may be sufficient to cause reorientation of Ni3 sites as well as Ni1 and Ni2 sites$^{52}$. Single crystal experiments on Mn$_2$MnWO$_6$ would be valuable to investigate its (anisotropic) magnetic and dielectric behavior fully. Thus, our combined structural and magnetic study highlights the potential for NTO materials...
containing three magnetic cations to exhibit magnetostriction-influenced polarization changes and their complex field dependent behavior warrants further investigation to fully exploit their magnetoelastic coupling.

Discussions

In summary, we have prepared, by high pressure-high temperature techniques, a corundum derivative phase Mn2MnWO6, which is a new polar and antiferromagnetic ($P_s \sim 63.3 \ \mu$C cm$^{-2}$, $T_N = 58$ K) Ni$_3$TeO$_6$-type oxide with a low temperature first-order field-induced metamagnetic phase transition. The highly polarized spin structure shows antiferromagnetic coupling with magnetic moments predominantly along [001]. The magnetostriction-polarization coupling around the magnetic transition is echoed by the second harmonic generation effect and magnetostriction-polarization coupling around the magnetic moments predominantly along [001]. The magnetization measurements were carried out with a commercial Quantum Design superconducting quantum interference device (SQUID, up to 7 T) magnetometer and a physical property measurement system (PPMS, up to 14 T). The magnetic susceptibility was measured in zero-field-cooled (ZFC) and field-cooled (FC) conditions under 0.005-14 T magnetic fields.

Methods

Synthesis and crystal and magnetic structure determination. Polycrystalline Mn$_2$MnWO$_6$ was prepared from a stoichiometric mixture of MnO (99.99%, Alfa Aesar) and WO$_3$ (99.8%, Alfa Aesar) at 1673 K under 8 GPa for 1 h in a Multi-Anvil Press as used in our previous work. SPXD data were recorded on beam line X-16C ($\lambda = 0.69991 \ \text{Å}$) at the Brookhaven National Synchrotron Light Source. Diffraction data analysis and Rietveld refinement were performed with the TOPAS software package. NPD data were collected on 0.1063 g sample (placed inside a 3 mm diameter vanadium can with sample height around 4 mm) at the ISIS Neutron source (Rutherford Appleton Laboratory (UK)) on the WISH diffractometer located at the second target station. Data were collected at 290 K (~35 minute scans in 5 K increments to 80 K, then at 90 and 100 K). Rietveld refinements were carried out with Topas-Academic (for 290 K data) and Jana2006 (for 5 K and intermediate temperature nuclear and magnetic structures). The magnetic symmetry analysis was carried out using ISO-DISTORT. Double-frame data sets were collected at 5 and 100 K to confirm the presence of a magnetic Bragg reflection at $\sim 47$ Å below $T_N$. The Mn-K and W-L$_2$ XANES data were collected in both the transmission and fluorescence mode with simultaneous standards. All of the spectra were fitted to linear pre- and post-edge backgrounds and normalized to unity absorption edge step across the edge. All of the XANES were performed on beam line X-19A at the Brookhaven National Synchrotron Light Source with a Si(111) double crystal monochromator.

Magnetic properties measurements. Magnetization measurements were carried out with a commercial Quantum Design superconducting quantum interference device (SQUID, up to 7 T) magnetometer and a physical property measurement system (PPMS, up to 14 T). The magnetic susceptibility was measured in zero-field-cooled (ZFC) and field-cooled (FC) conditions under 0.005-14 T magnetic fields.

Fig. 5 PFM results on Mn$_2$MnWO$_6$. a Topography (scale bar 250 nm). b PFM DART amplitude and c phase. d average amplitude (i) and phase (ii) BE PFM switching spectroscopy loops determined from square regions indicated in the phase image in (c). Remnant e negative and f positive amplitudes determined from fitting $35 \times 35$ grid measurement. Scale bar is the same for Fig. 5a-c.
field, at temperatures ranging from $T = 5$–400 K. Isothermal magnetization curves were obtained at $T = 2$, 20, 50, 100 and 300 K under an applied magnetic field that varied from 0 to 14–17 T for 2 and 20 K and $\sim 7$–7 T for 50, 100, and 300 K. Magnetization curves at additional temperatures and maximum fields are presented in Supplementary Figs. 6 and 7.

SHG measurements. The SHG experiments were performed in the reflection mode on polished pellets (cylinder pellet with $98(1)$ % of the theoretical density and – 2 mm of diameter and thickness of – 0.3 mm) of the as-made polycrystalline Mn$_2$FeWO$_6$ (this is a widely used technique for determining non-centrosymmetry in material)\cite{34,35}. This is an optical technique in which two photons with fields $E_1$ and $E_2$ of frequency $\omega$ and directions $\mathbf{j}$ and $\mathbf{k}$, respectively, interact with a material with a non-zero $\chi^{(2)}$ tensor (non-centrosymmetric) forming a polarization $P^{(2\omega)}$ (nonlinear) of frequency $2\omega$ in the $\mathbf{j}$ direction. The SHG intensity, $I_{SHG}$ is detected using a Hamamatsu photomultiplier tube. A Ti:sapphire laser (Spectra-Physics) with a wavelength of 800 nm and a pulse width of 120 fs was used for this experiment. Temperature scans were performed with an Oxford cryostat (50–320 K) and a user customized heater (298–800 K).

Electric measurements. The pyro-current was measured with an electrometer (Keithley 6517) at cooling/heating rates of 1–3 K·min$^{-1}$ in a PPMX Cryo-Magnet (Quantum Design); the corresponding polarization data was gained by numerical integration. The ferroelectric P–E loops and magnetic-field dependent polarization measurements were recorded with a modified Sawyer-Tower circuit employing a Keithley 6517 electrometer with linear field ramping at rates of 100 (V·mm$^{-1}$)·s$^{-1}$ and 100 Oe·s$^{-1}$\cite{36}. The samples were sandwiched between Ag paste-deposited electrodes, in parallel plate geometry for the above measurements. It should be noted that due to the use of polycrystalline samples a pyroelectric can only be expected if one of the crystalline phases exhibit a similar polarization. The SHG intensity, $I_{SHG}$, the pyro-current, $I_{Pyr}$, and the magnetic field, $B$, were recorded with a modified Sawyer-Tower circuit employing a Keithley 6517 electrometer at cooling/heating rates of 1 K·min$^{-1}$ and a user customized heater (298–738 K). The pyro-current was measured with an electrometer (Keithley 6517) at cooling/heating rates of 1 K·min$^{-1}$ and a user customized heater (298–738 K).

PFM measurements. In PFM, application of the periodic electric bias to the conductive scanning probe microscopy tip in contact with the surface results in a surface deformation, due to converse piezoelectric effect. This deformation is detected as the periodic deflection of the tip via microscope electronics. This approach has been broadly used for imaging ferroelectric domains in a broad range of ferroelectric and piezoelectric crystals, ceramics, and thin films. The PFM measurements were performed at room temperature with $6 V_{pp}$ ac bias applied to a Pt/Cr-coated probe (Budget sensors Multi75E-G). For PFM imaging the drive frequency of the ac bias was centered at the contact resonance ($\sim 350$ kHz) and dual amplitude resonance tracking was then used to track the contact resonance as the tip was scanned across the sample surface\cite{37}. For the polarization switching experiments a band of frequencies ($\sim 80$ KHz) centered around the contact resonance were excited, as an additional DC bias was swept from $-90$ to $+90$ V. Extraction of the tip parameters were determined from fitting of the response to a simple harmonic oscillator model as described elsewhere\cite{38,39}. Data availability. The data that support the findings of this study are available from the corresponding authors on request.

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Supplementary Figures

Supplementary Figure 1 | Simulated lab XRD patterns and crystal structure of Mg$_3$TeO$_6$-type Mn$_2$MnWO$_6$. Crystallographic data: $R$-3, $a = 8.8931(18)$ Å, $c = 10.4782(19)$ Å, $V = 717.7(1)$ Å$^3$. Inset shows the polyhedral crystal structure with octahedral coordination of Mn and W.
Supplementary Figure 2 | Rietveld refinement profiles for Mn$_2$MnWO$_6$ at 290 K. a SPXD data b high resolution bank 5 (153°, ~0.7 – 4.8 Å) NPD data, c bank 4 (122°, ~ 0.7 – 5.4 Å) NPD data, d bank 3 (90°, ~ 0.7 – 6.6 Å) NPD data, e bank 2 (58°, ~ 1 – 9.6 Å) NPD data and f bank 1 (27°, ~ 1.6 – 17 Å) NPD data. Observed, calculated and difference profiles are shown by black points and with red and gray lines, respectively. Tick marks show the peak positions for the main phase (top) and impurity phase MnWO$_4$ (3.3(1)% by weight). For bank 5 data two Pawley phases were also included in the refinement to fit peaks from Al (~42000 μs, ~30000 μs, ~25000 μs) due to scattering from the cryostat.
Supplementary Figure 3 | The Mn-K edge XANES of Mn$_2$MnWO$_6$. a Spectra for Mn$_2$MnWO$_6$, the isostructural Mn$_2$Fe$^7$O$_6$ ($T = W$ and Mo) compounds, along with those of a series of standard compound spectra: Mn$^{2+}$O, LaMn$^{3+}$O$_3$, and CaMn$^{4+}$O$_3$. The energy range, labeled EI, where the Mn$_2$MnWO$_6$ exhibits extra intensity is relative to the $T = W$ and Mo compounds. Note the large arrow indicating the calibration energy at the peak of the MnO spectrum. b The Mn-K edge spectrum for Mn$_2$MnWO$_6$. The 2/3 ~A$^{2+}$ component was estimated from the 2/3 weighting of the isostructural (and iso-valent) Mn$_2$FeWO$_6$ Mn-K edge. Note the s-FeO spectrum is the FeO, Fe-K edge shifted down in energy so that its peak coincides with the MnO, Mn-K edge peak. The 1/3 ~B$^{2+}$ and 1/3 ~B$^{3+}$ spectral component estimates were obtained by applying this same energy shift to the Fe-K edges of Mn$_2$Fe$^{-2+}$WO$_6$ and Mn$_2$Fe$^{3+}$MoO$_6$ respectively (with the 1/3 weighting factor). The ~B$^{3+}$ has its spectral intensity lying at too high energy to consider it as a contributing component to the Mn$_2$MnWO$_6$ spectrum. The estimated spectrum (labeled est. in the figure) is a superposition of the 2/3 ~A$^{2+}$ and 1/3 ~B$^{2+}$ components.
Supplementary Figure 4  |  The Fe-K edge XANES of Mn$_2$Fe$^{2+}$WO$_6$ and Mn$_2$Fe$^{3+}$MoO$_6$ compounds. Along with those of a series of standard compound spectra are also shown: Fe$^{2+}$O, LiFe$^{2+}$PO$_4$, LaSrFe$^{3+}$TiO$_6$, and SrFe$^{4+}$O$_{3.8}$. It is important to note the very substantial broadening of the Fe-K edge spectra at the B site of these A$_2$BB’O$_6$ materials with the Ni$_3$TeO$_6$ (NTO, R3) structure. Despite this broadening the chemical shift between the Fe$^{2+}$ and Fe$^{3+}$ B-site spectra is very clear. The Fe-K Mn$_2$Fe$^{2+}$WO$_6$ spectrum, relative to the FeO peak energy, is used to estimate the B$^{2+}$-site contribution for Mn$_3$WO$_6$ in the main portion of this work. Note the large arrow indicating the calibration energy at the peak of the FeO spectrum.
Supplementary Figure 5 | The W-L₃ edge XANES of Mn₂MnWO₃. a Comparison of the series of W standard compounds in various d-configurations/valence states: the ~ d⁰-W⁶⁺ compound Sr₂MnWO₆, Mn₂FeWO₆ and WO₃; the ~ d⁲-W⁴⁺ compound WO₂; and elemental W. Note the systematic white line WL chemical shift to higher energy with increasing nominal W valence. Note also the bimodal A-B structure of WL-5d features in the W⁶⁺ compounds strong octahedral ligand field splittings. b The T-L₃ edges for a series of T(5d) compounds in various d-configurations/valence states from ~ d⁰ (t₂g⁰) to ~ d⁴ (t₂g⁴). c The W-L₃ edge XANES spectra for Mn₂MnWO₆, Mn₂FeWO₆, and Sr₂MnWO₆ shown on an energy range encompassing both the WL and the prominent fine structure C-feature regions. Inset shows the C-feature region on an expanded scale.
Supplementary Figure 6  |  The \(\frac{dM}{dT}\) derivatives for the FC and \(M(T)\) curves in Fig. 4b at a series of magnetic fields. For this comparison, the high field and low field plots are displayed on different vertical scales, and the \(H = 0.005\) T curve is multiplied by a factor 10. Note the sharp positive peaks indicating the magnetic ordering temperatures \(T_N\), for \(H \leq 1\) T. The \(T_N\) value at 0.005 T is 55.4 K in excellent agreement with the neutron diffraction results (see Supplementary Figure 11 caption). The similar broadened structure, labelled \(T'_N\) for the \(H = 7\) T curve, is interpreted here as tentative evidence for the presence of AFM order/correlations. Note the negative \(\frac{dM}{dT}\) peaks in the ~60 K range at all fields, are associate magnetic correlations above the ordering temperature. For \(H \leq 1\) T these negative peaks are quite sharp, however at higher fields they are strongly broadened. The negative \(\frac{dM}{dT}\) peaks and their widths (from Supplementary Figure 6) define a dash line boxed range where these field-coupled magnetic correlations (Mag. cor. in figure) appear operative.
Supplementary Figure 7  |  Expanded views of the positive field portion of the $M(H)$ loops. It is for this system made in different laboratories and with differing maximum field in the loop. a An expanded view of the data shown in Fig. 2c of the main text. b An expanded view of magnetization loop data collected between ±3.7 T, and except for the 100 and 50 K loops which were extended to ±7 T. The solid horizontal arrowheads indicate the inflection point associated with the field induced transitions. Noting that the detailed choice of temperature/field history will lead to differing phase admixtures and metastability limits in field induced transitions, the two sets of data are in admirable agreement. The presence of 1st-order/hysteretic field induced transitions for $T \leq 30$ K, along with an apparently continuous (2nd-order) at $T = 50$ K, is supported by the data. We note the slight offset in $H$ at the start of the 2 K field sweep measurement presumably caused by some remnant field at the start of this measurement, rather than starting in a true zero field state.
Supplementary Figure 8 | A schematic low temperature $H$-$T$ phase diagram for Mn$_2$MnWO$_6$ based upon the magnetic property measurements. The solid red line labelled $T_N$ is the onset of a c-AFM ordered state as indicated by the inflection point below the peak in the $M(T)$ data in Fig. 2b and the corresponding sharp positive $dM/dT$ peaks in Supplementary Figure 6. Here the c- prefix to conical-AFM conveys the conical and complex nature of the ordering found from the neutron scattering. The higher field dotted line (labeled $T'_N$) indicates the possible onset of a more different c-AFM’ state with a larger magnetic field response. In view of crystalline magnetic anisotropies, and the polycrystalline nature of the samples, any detailed comments on this phase would be speculative without finite -field neutron diffraction results. Also, the region labelled Mag. cor. indicates region where presumable local magnetic correlations, coupled to the magnetic field appear operative. The long range character in this region remains paramagnetic (PM).
Supplementary Figure 9  |  Film plot showing high d spacing region of bank 4 NPD data. They show intensity of commensurate (~85000 μs, ~4.6 Å) and incommensurate (~75000 μs (4.0 Å), ~79000 μs (4.2 Å) and ~97000 μs (5.2 Å)) magnetic reflections.
Supplementary Figure 10 | Rietveld refinement profiles for 5 K NPD data for Mn$_2$MnWO$_6$. a High resolution bank 5 (153°, ~0.7 – 4.8 Å) data; b bank 3 (90°, ~0.7 – 6.6 Å) data and c double-frame bank 1 (27°, ~1.7 – 60 Å) data showing magnetic reflection at ~47 Å (~235000 μs). Observed, calculated and difference profiles are shown by black points and with red and grey lines, respectively. Blue and green tick marks show Mn$_2$MnWO$_6$ commensurate and satellite peak positions, respectively. Excluded regions are shaded in grey, including peaks due to Al (~ 2000, ~ 30000, ~ 25000 μs) due to scattering from the cryostat in bank 5.
Supplementary Figure 11  |  Magnetic moments for Mn$_2$MnWO$_6$ as a function of temperature from Rietveld refinements (refinements using Jana2006 with bank 5 (153°), bank 3 (90°) and bank 1 (27°) data). The Mn$_2$MnWO$_6$ structure was described by a model of $R_1\beta(00g)t$ (hexagonal setting) symmetry with commensurate nuclear structure and incommensurate magnetic structure with moments on all Mn sites described by both mT1 and mA2LE2 irreps. Data points for Mn(1)/(3) sites are shown in blue and red (with esds approximately the same size as the points) and dotted lines are a guide to the eye showing fit to function $M_T = M_0 \left[1 - \left(\frac{T}{T_N}\right)^\beta \right]$ where $M_T$ is the sum of intensities at temperature $T$; for Mn(1)/(3): $M_0 = 4.46(7)$, $T_N = 55.7(1)$ K and $\beta = 0.42(2)$; for Mn(2): $M_0 = 4.60(4)$, $T_N = 56.6(2)$ K and $\beta = 0.41(1)$.
Supplementary Figure 12  |  Components of magnetic moments for Mn$_2$MnWO$_6$ as a function of temperature from Rietveld refinements using NPD data. Data points for $M_z$($\mu_B$) for Mn1/3 and Mn2 (Left) and $M_{xy}$($\mu_B$) for Mn1/3 and Mn2 (Right) sites are shown in blue and red, respectively (with esds approximately the same size as the points).
Supplementary Figure 13  |  Unit cell parameters and selected bond lengths and distances from refinements using short NPD scans (refinements using Jana2006 with bank 5 (153°), bank 3 (90°) and bank 1 (27°) data). a a-T; b c-T; c l-T; d (Mn1-O)-T; e (Mn2-O) -T; f (Mn3-O)-T; g (W-O)-T; h (Mn2-Mn3)-T. The Mn2MnWO6 structure was described by a model of $R_{13}(00\gamma)$ (hexagonal setting) symmetry with commensurate nuclear structure and incommensurate magnetic structure with moments on all Mn sites described by both mT1 and mΛ2LE2 irreps.
Supplementary Figure 14  |  Temperature dependent individual atomic $P_S$ contribution in Mn$_2$MnWO$_6$ between 5 and 100 K as calculated from point-charge-model method. The total net $P_S = P_S^\dagger$ (Mn1 + Mn2 + O1 + O2) − $P_S^\ddagger$ (Mn3 + W) regarding the formal oxidation state and atomic displacement direction along the c-axis in Fig. 1 ($P_S^\dagger$ (Mn1) = $P_S^\dagger$ (Mn2), $P_S^\dagger$ (O1) = $P_S^\dagger$ (O2) from point-charge-model calculations). The ‘+’ and ‘−’ represent the polarization directions denoted as blue (+) and red (−) symbols, respectively. $\Delta P_S^I$ and $\Delta P_S^II$ are for the $P_S$ evolution between 5 and 30 K and 60 and 100 K upon cooling, respectively. $P_S$ evolution of a Mn1/Mn2, O1/O2, Mn3, and W, and b Mn1/Mn2, (c) O1/O2, d Mn3, and e W. One should note that the polarization directions of (Mn1, Mn2, O1, O2) and (Mn3, W) are opposite. Apparently, the deceasing of $\Delta P_S^I$ (O1/O2) (1.158 μC•cm$^{-2}$) and increasing of $\Delta P_S^I$ (Mn3) (0.579 μC•cm$^{-2}$) in opposite direction are mainly responsible for the total $P_S$ drop of 1.59 μC•cm$^{-2}$ between 5 and 300 K. The $P_S$ values are almost identical between 60 and 100 K (0.01 μC•cm$^{-2}$ difference).
Supplementary Figure 15 | SHG measurements on Mn$_2$MnWO$_6$. a SHG intensity (arb. units) vs. temperature (K). b SHG (400 nm) peak and fundamental wavelength (800 nm) peak in the spectroscopic data at 300 K. The inset shows an expanded view of the temperature scan in (a) that reflects the magnetostriction-polarization coupling.
Supplementary Figure 16 | Temperature dependent pyrocurent measurements in different warming rate of 1, 3, and 5 K min⁻¹, spectively. These qualitatively confirm the expected scaling of the current with the rate of temperature change and thus exclude the possibility of ohmic, i.e. current related phenomena. (However the T-shift of the signature has to be attributed to the insufficient thermal coupling and thus denotes the experimental problems to determine e.g. a subtle shift of the feature in magnetic field as discussed above.) Also, the additional dielectric measurements now shown in Fig. 4d demonstrate that we indeed observe a change in polarization as this ac measurements are not subject to charge accumulation.
Supplementary Figure 17 | Magnetic-field-dependent polarization measurements of Mn$_2$MnWO$_6$ at 20 K. The error bar is addressed on the bottom figure. The small $\Delta P$ response indicates weak magnetoelectric coupling in Mn$_2$MnWO$_6$. 
Supplementary Figure 18 | PFM images of Mn$_2$MnWO$_6$. (a,b) AFM topography maps from two different representative areas of the polished Mn$_3$WO$_6$ sample (scale bar = 2 µm) collected in contact mode AFM. Simultaneously captured piezoresponse (c,d) amplitude and (e,f) phase maps are also shown. Piezoresponse force microscopy (PFM) was performed using dual amplitude resonance tracking (DART). DART-PFM was implemented on a commercial SPM system (Asylum Research Cypher). Measurements were performed using Pt–Ir coated (Multi75E-G Budgetsensors) cantilevers. An excitation voltage of 6 Vp-p consisting of two drive frequencies above and below (~ 3 KHz) the contact resonance frequency (~ 340 KHz) were supplied to the tip during DART-PFM. The contact resonance (c,d) amplitude and (e,f) phase maps were determined from fitting the DART responses at both drive frequencies to a simple harmonic oscillator model. The PFM amplitude maps show typical ferroelectric domain structures which are independent from topography, and also clearly visible domain walls at which the amplitude drops close to 0. Further, PFM phase images show 180° phase offsets between domains, which are indicative of ferroelectric domains with opposite polarization.
Supplementary Figure 19 | Topography and DART PFM images of Mn₂MnWO₆. (a,d)

AFM topography (scale bar = 2 µm) and piezoresponse (b,c) amplitude and (c,f) phase maps after poling the pristine region shown in Supplementary Fig. 18a-c. PFM poling was performed using a commercial SPM system (Asylum Research Cypher) coupled with a high voltage amplitude (x10), and local poling was achieved by contact mode scanning using a constant force setpoint between tip and surface while controlling the voltage supplied the conductive tip. Piezoresponse amplitude and phase maps after poling a 4 x 4 µm region with -100 V and subsequently poling a smaller 2 x 2 µm with +100 V is shown in (b,c) and (e,f) respectively. Modification of the PFM domain structure between pristine and positively or negatively poled regions is clearly evident. The phase is shown to change by 180° between positively and negatively poled regions indicated controlled ferroelectric switching in this material by PFM.
Supplementary Figure 20 | $P(E)$ loop measured on polycrystalline Mn$_2$MnWO$_6$ pellet between 10 and 150 K, showing very small switchable polarization (in the range of 0.005 μC·cm$^{-2}$). At 200 K the bulk conductivity dominates the polarization response of the sample: The dashed line is a double up-cycle of the electric field at the same temperature. The second up-cycle yields again a similar enhancement of polarization compared to the first which cannot be explained by the switching of intrinsic polarization but stems from ohmic contributions. However, at lower temperatures the residual conductivity of the sample decreases drastically and therefore this ohmic contribution vanishes leaving only the denoted remnant polarization.
## Supplementary Tables

| Compound       | Synthesis | Structure | Magnetism | $P_S$ (μC•cm$^{-2}$) | Ref. |
|---------------|-----------|-----------|-----------|----------------------|------|
| Mn$_2$FeNbO$_6$ | 1573 K, 7 GPa | LN, R3c   | $T_N = 90$ K | 32 | 1 |
| Mn$_2$FeTaO$_6$ | 1573 K, 7 GPa | LN, R3c   | $T_N = 80$ K | 23 | 1 |
| Mn$_2$FeMoO$_6$ | 1623 K, 8 GPa | NTO, R3   | $T_C = 337$ K | 68 | 2 |
| Mn$_2$FeMoO$_6$ | 1623 K, 8 GPa | OIL, R3   | $T_C = 229$ K | 55 | 3 |
| Mn$_2$FeWO$_6$ | 1673 K, 8 GPa | NTO, R3   | $T_N = 75$ K | 59.5/67.8 | 4 |
| Mn$_2$ScSbO$_6$ | 1523 K, 5.5 GPa | NTO, R3   | $T_C = 42$ K | 28.3 | 5 |
| Mn$_2$MnWO$_6$ | 1673 K, 8 GPa | NTO, R3   | $T_N = 58$ K | 62.9/69 | 6 |
| Ni$_2$NiTeO$_6$ | 1073 K, AP  | NTO, R3   | $T_N = 52$ K | 0.33$^b$ | 7,8 |
| Ni$_2$ScSbO$_6$ | 1073 K, AP  | NTO, R3   | $T_N = 60$ K | 7 | 9 |
| Ni$_2$InSbO$_6$ | 1073 K, AP  | NTO, R3   | $T_N = 76$ K | 7 | 9 |
| Zn$_2$FeTaO$_6$ | 1623 K, 9 GPa | LN, R3c   | $T_N = 22$ K | 50 | 10 |
| Sc$_2$FeMoO$_6$ | Theory     | NTO, R3   | $T_C = 923$ K | 7.1 | 11 |
| Lu$_2$FeMoO$_6$ | Theory     | NTO, R3   | $T_C = 895$ K | 8.7 | 11 |

**Supplementary Table 1** | Polar and magnetic oxides in A$_2$BB’O$_6$-type corundum family.  
The synthesis conditions, structure types, magnetic properties, and polarization values are list for comparing.
| Atom | Site | $x$  | $y$  | $z$      | $U_{iso} \times 100$ (Å$^2$) |
|------|------|------|------|----------|-----------------------------|
| Mn1  | 3$a$ | 0    | 0    | 0.2117(1)| 1.80(7)                     |
| Mn2  | 3$a$ | 0    | 0    | 0.7172(1)| 2.02(7)                     |
| Mn3  | 3$a$ | 0    | 0    | 0.4918(2)| 1.69(7)                     |
| W    | 3$a$ | 0    | 0    | 0*      | 1.83(6)                     |
| O1   | 9$b$ | 0.2766(3) | -0.0134(3) | 0.0933(1) | 2.09(7)                     |
| O2   | 9$b$ | 0.6544(2) | -0.0485(3) | 0.6009(1) | 2.00(6)                     |

Space group $R3$ (146), $Z = 3$, $a = 5.32323(3)$ Å, $c = 14.0589(1)$ Å, volume = 345.01(1) Å$^3$; $R_{wp} = 4.55\%$, $R_p = 4.74\%$, $\chi^2 = 3.67$. *$W$ z factional coordinate fixed to define origin along [001].

**Supplementary Table 2 | Structure parameters of Mn$_2$MnWO$_6$ at 290 K.** The data are from combined refinements of SPXD NPD data.
|                  | Mn1O₆     | Mn3O₆     | Wo6       |
|------------------|-----------|-----------|-----------|
| Mn1-O1 × 3       | 2.247(2)  | Mn3-O1 × 3| 2.085(2)  |
| -O2 × 3          | 2.150(2)  | -O2 × 3   | 2.308(2)  |
| 3                | 2.198(2)  | × 3       | 2.196(2)  |
| <Mn1-O>          | 2.00      | <Mn3-O>   | 2.09      |
| BVS              | 0.439     | BVS       | 0.308     |
| dₘₙ₁            | 0.49      | dₘₙ₃      | 2.58      |
| Δₘₙ₁ (× 10⁻³)    |           |           |           |
| Mn2O₆            |           |           |           |
| Mn2-O1 × 3       | 2.061(1)  | W-O1 × 3  | 1.999(1)  |
| -O2 × 3          | 2.377(2)  | -O2 × 3   | 1.867(2)  |
| 3                | 2.219(2)  | × 3       | 1.933(2)  |
| <Mn2-O>          | 2.06      | <W-O>     | 5.84      |
| BVS              | 0.517     | dₙ       | 0.193     |
| dₘₙ₂             | 5.07      | Δₙ (× 10⁻³)| 1.17      |
| Δₘₙ₂ (× 10⁻³)    |           |           |           |
| Mn1-W            | 2.976(2)  | Mn2-Mn3   | 3.169(3)  |
| O1-Mn1-O1        | 71.14(5)  | O1-Mn3-O1 | 102.12(4) |
| O2-Mn1-O2        | 107.42(5) | O2-Mn3-O2 | 80.67(4)  |
| O1-Mn1-O2        | 87.22(4)  | O1-Mn3-O2 | 87.17(1)  |
|                  | 88.00(5)  |           | 87.85(6)  |
|                  | 153.64(4) |           | 164.44(3) |
| O1-Mn2-O1        | 111.88(6) | O1-W-O1   | 81.65(6)  |
| O2-Mn2-O2        | 77.88(4)  | O2-W-O2   | 97.59(6)  |
| O1-Mn2-O2        | 74.01(3)  | O1-W-O2   | 87.83(4)  |
Supplementary Table 3 | Crystallographic data in Mn₂MnWO₆ at 290 K from combined SPXD and NPD data refinements. Selected interatomic distances (Å), bond valence sums (BVS), atomic displacement distance (Å) from its octahedral center (dₘ₀), octahedral distortion parameters (Δ), and bond angles (°) are shown.

| Atom | Site | x   | y   | z     | U_iso × 100 (Å²) | Mz (µB) | Mxy (µB) |
|------|------|-----|-----|-------|----------------|---------|----------|
| Mn1  | 6a   | 0   | 0   | 0.10664(8) | 1.92(6)†      | 3.742(7) | 1.87(1)  |
| Mn2  | 6a   | 0   | 0   | 0.85807(9)  | 1.92(6)†      | -1.871(4) | -3.94(2) |
| Mn3  | 6a   | 0   | 0   | 0.24404(9)  | 1.92(6)†      | 3.742(7) | 1.87(1)  |
| W    | 6a   | 0   | 0   | 0*     | 2.4(1)        |         |          |
| O1   | 18b  | 0.2886(3) | 0.2765(4) | 0.04743(6) | 2.51(8)       |         |          |
| O2   | 18b  | 0.3690(4) | -0.0098(4) | 0.13476(7) | 1.34(6)       |         |          |

* W z fractional coordinate fixed to define origin along [001]
† U_iso for Mn sites constrained to be equal to minimise correlation with Mn moments

Supplementary Table 4 | Crystallographic data for Mn₂MnWO₆ from Rietveld refinement using 5 K NPD data. Space group R₃(00g)t (hexagonal setting; assume R3c for nuclear structure), a = 5.31609(3) Å, c = 28.1388(4) Å, Volume = 688.69(1) Å³; Rwp = 5.73%, Rp = 6.64%, χ² = 7.29.
| Bond       | Length (Å)  | Bond       | Length (Å)  |
|------------|-------------|------------|-------------|
| Mn1 – O1   | 3 × 2.244(3)| Mn3 – O1   | 3 × 2.058(2)|
| Mn1 – O2   | 3 × 2.140(3)| Mn3 – O2   | 3 × 2.356(3)|
| Mn2 – O1   | 3 × 2.067(3)| W – O1     | 3 × 2.010(2)|
| Mn2 – O2   | 3 × 2.342(3)| W – O2     | 3 × 1.864(2)|
| Mn1 – W    | 3.001(2)    | Mn2 – Mn3  | 3.209(2)    |

**Supplementary Table 5 | Crystallographic data of Mn₃MnWO₆ at 5K.** Selected bond lengths and distances from Rietveld refinement using 5 K NPD data are listed.
Supplementary Notes

Supplementary Note 1  | Polar and magnetic oxides in A₂B₂'O₆-type corundum family.

Under specific experimental conditions, the formation of polar and magnetic corundum compounds can be governed by the electron configuration, spin structure, size and charge difference of cations, or a combination of these parameters. So far, only 14 polar and magnetic A₂B₂'O₆-type corundum-related compounds have been reported (Supplementary Table 1). The AFM and pyroelectric LN-type Mn²⁺Fe³⁺M⁵⁺O₆ (M = Nb, Ta) were prepared at 7 GPa; first-principles calculations indicated that the second-order Jahn-Teller (SOJT) distortion effects of the d⁰-configuration (Nb⁵⁺ and Ta⁵⁺) favor the polar LN-type rather than the centrosymmetric ilmenite (IL, R-3) structure as observed in Mn²⁺Fe³⁺Sb⁵⁺O₆ (ref. 12), considering the very similar ionic sizes of six-coordinated Nb⁵⁺ (0.64 Å), Ta⁵⁺ (0.64) and Sb⁵⁺ (0.60 Å)¹³. This finding has been corroborated by the synthesis of LN-type, AFM Zn²⁺Fe³⁺Ta⁵⁺O₆ at 9 GPa, which suggests a small switchable ferroelectric component at low temperature¹⁰. The polarized spin structure of the ferrimagnetic semiconductor Mn²⁺Fe³⁺Mo⁵⁺O₆ (T_C ~ 337 K) allows significant energy lowering to stabilize in the NTO-type structure versus IL-type, despite the comparable effective ionic size (\(V^\text{I}r(\text{Mo}^5\text{+}) = 0.61\ \text{Å}\)) and charge difference of B and B’ ions (2) compared to those in IL-type Mn₂Fe³⁺Sb⁵⁺O₆ and LN-type Mn₂Fe³⁺M⁵⁺O₆ (M = Nb and Ta)¹,¹². In the case of Ni₃TeO₆, the large charge difference between Ni²⁺ and Te⁶⁺ renders full ordering between both cations at B- and B’-sites. This cationic ordering is responsible for the polar, so-called NTO-type, structure (formally, Ni²⁺₂Ni²⁺Te⁶⁺O₆)⁷,⁸. Similarly, in Mn²⁺Fe²⁺W⁶⁺O₆, the high stability of octahedral W⁶⁺ (\(V^\text{I}r(W^6\text{+}) = 0.60\ \text{Å}\)) produces Fe²⁺ (\(V^\text{I}r(\text{Fe}^2\text{+}) = 0.78\ \text{Å}\)) oxidation state, and thus the large charge and size difference between W⁶⁺ and Fe²⁺ in B- and B’-sites favors the NTO-type structure⁴,¹³,¹⁴. The large effective ionic size differences between Sc³⁺/Sb⁵⁺ (0.15 Å) and In³⁺/Sb⁵⁺ (0.2 Å) seem to account for the cation-ordering and NTO-type structure in Ni₂ScSbO₆, Ni₂InSbO₆, and Mn₂ScSbO₆ (refs. 5,9) The ambient pressure form of
Mn$_2$FeMoO$_6$, which is obtained by a Mn/Fe cationic rearrangement when the HP NTO-structural polymorph is treated at unusually low-temperature (150 - 300 °C), is the only known OIL-type polar magnet in this family. The low-temperature transformation of HP-Mn$_2$FeMoO$_6$ is accompanied by dramatic physical property changes, including a ~ 120 K lower magnetic ordering temperature and three-orders of magnitude higher resistivity$^3$. Above room-temperature multiferroic properties were predicted for ferrimagnetic Zn$_2$Fe$^{3+}$Os$^{5+}$O$_6$ ($T_C$ ~ 394 K, $P_S$ ~ 54.7 μC·cm$^{-2}$), which was predicted to adopt the LN-type structure, but was found to adopt the NTO-type structure ($R3$) with Fe$^{3+}$ and Os$^{5+}$ ordering over B- and B’-sites$^{15}$. The NTO-type A$_2$FeMoO$_6$ (A = Sc, Lu) are predicted to be room-temperature ferroelectric ($P_S$ = 7.1 and 8.7μC·cm$^{-2}$ for A = Sc and Lu, respectively) and ferrimagnetic ($T_C$ ~ 923 and 895 K, respectively) insulators, by first-principles calculations$^{11}$.

Supplementary Note 2  |  X-ray absorption near edge spectroscopy (XANES).

Mn-K edge

The main edge features at 3-$d$ transition metal K edges are dominated by 1$s$ to 4$p$ transition peak features, along with a step-continuum-onset-feature. The 4$p$ features can be complicated by splitting into multiple features by the local atomic coordination/bonding and by admixed 3$d$ configurations. Nevertheless these features manifest a chemical shift to higher energy with increasing valence, allowing the use of the K edge to chronicle the evolution of the transition metal valence state in compounds$^{1,2,4,10,14,16-24}$. In Supplementary Fig. 3a the Mn-K main edge spectra for Mn$_2$MnWO$_6$ is compared to those of the isostructural Mn$_2$FeTO$_6$ ($T$ = W and Mo) compounds which contain Mn only on the A-site. The spectra for a series of octahedrally coordinated Mn standard compounds are also shown. The Mn$^{2+}$O standard on the other hand has edge sharing octahedra, which splits/broadens the main edge$^{24}$. Inspection of the Mn$_2$MnWO$_6$ Mn-K spectrum suggests the presence of an A-site Mn$^{2+}$FeWO$_6$ like
component, however there is a clear excess of spectral intensity in the energy range labeled EI in Supplementary Fig. 3a.

The Mn-K main edge of Mn$_2$MnWO$_6$ should be a superposition of an A-site Mn$^{2+}$$_2$FeTO$_6$ like component (with a weight factor of 2/3) and a B-site Mn$^{2+}$ component (with a weight factor of 1/3). To estimate the B-site component the Fe-K edge for the Mn$_2$Fe$^{3+}$WO$_6$ and Mn$_2$Fe$^{3+}$MoO$_6$ compounds (previously measured) were considered (see Supplementary Fig. 4). The shifting of the Fe-K edge spectra down in energy to the Mn-K edge was done using the difference in the peak energies of the NaCl structure Mn$^{2+}$O and Fe$^{2+}$O spectra (see Supplementary Fig. 3b). The estimated spectrum (est. in Supplementary Fig. 3b) is a superposition equal to the weighted sum of the components given by $\{2/3 \sim A^{2+} + 1/3 \sim B^{2+}\}$ .

For energies above 6.552 keV the estimated spectrum provides a remarkably good simulation of the Mn$_2$MnWO$_6$ Mn-K edge spectrum (particularly in view of the large Fe-K to Mn-K energy shifts). This energy range also includes the extra intensity EI region, noted above, and the spectral fall-off in intensity above it. This is the energy range in which the Mn$^{2+}$ character of the B-site needed confirmation. The underestimated spectral weight of the est. spectrum at the steeply rising portion of the edge is not surprising in view of the substantial approximations implicit in the 2/3 $\sim A^{2+}$ and 1/3 $\sim B^{2+}$ component estimation process. Thus the Mn-K data are consistent with both the Mn$^{2+}$ character at the A and B sites and with the very different spectral shapes at the two sites.

\textit{W-L$_3$ edge}

The L$_3$ edges of transition metals (T) are dominated by very intense white line (WL) features due to dipole transitions into final d states as shown in Supplementary Figs. 5a and b$^{1,4,10,14,18-23}$. The simplest signature of increasing T-valence states (decreasing d-count) is the chemical shift of the absorption edge to higher energy. Such an increasing-valence/increasing chemical shift of the centrum of the WL-feature has been observer in multiple
studies\textsuperscript{1,4,14,18-20-23}. In Supplementary Fig. 5a the W-L\textsubscript{3} edge for Mn\textsubscript{2}MnWO\textsubscript{6} is compared to those of a series of standard W compounds with varying $d$-configurations/valence states. The systematic chemical shift of the of the WL feature to higher energy, with increasing nominal W valence, is clear in the figure. Despite the bimodal A-B structure of WL-5$d$ features in the A\textsubscript{2}BWO\textsubscript{6} compounds their centrum chemical shift indicate a $\sim d^0$-W\textsuperscript{6+} configuration assignment (Supplementary Fig. 5c). Additional information on the W local environment can be gleaned from the W-L\textsubscript{3} edge XANES spectra on an energy range encompassing the prominent fine structure C-feature. This feature can be regarded as either the first of the ligand shell EXAFS oscillations (with multiple scattering) or as a continuum resonance due to the containment of the photoelectron by the filled shell ligand atoms. In either interpretation, the C-feature moves to higher energy with decreasing W-O bond lengths\textsuperscript{4,18,22}. The close correspondence in energy of the C-feature of Mn\textsubscript{3}WO\textsubscript{6} to that of the isostructural W\textsuperscript{6+} compound Mn\textsubscript{2}FeWO\textsubscript{6} provides additional support for the identification of the W\textsuperscript{6+}, $d^0$ state in the former. The double perovskite compound W\textsuperscript{6+}, $d^0$ has a simpler corner sharing local environment, as opposed to the face and edge sharing in the Ni\textsubscript{3}TeO\textsubscript{6} (NTO, R\textsubscript{3}) structure. Hence, the C-feature for this less distorted octahedron is more pronounced as well as indicating a shorter W-O bond length.

The bimodal A ($t_{2g}$ related)/B ($e_g$ related) structure of the L\textsubscript{3}-WL features arises from the robust octahedral O-ligand coordination ligand field (LF), splitting of the $d$-states, into lower energy, 6X degenerate, $t_{2g}$ and higher energy, 4X degenerate, $e_g$ multiplets. This LF splitting is most clearly illustrated in the $d^0$ compound spectra shown in Supplementary Figs. 5a and b. The systematic filling of the $t_{2g}$ orbitals with increasing 5$d$-orbital-count (decreasing hole-count) clearly leads to a systematic decrease of the A-feature ($t_{2g}$-hole coupled) intensity as is illustrated in Supplementary Fig. 5b for a series of compounds spanning $d^0$-$d^4$.\textsuperscript{1,4,10,14,18-24} Here the T-L\textsubscript{3} spectra of the various elements have been displaced to nominally align the A-B
features. Thus the greater A-feature intensity, relative to the B-feature, for Mn$_2$MnWO$_6$ also strongly supports its $\sim d^0$-$W^{6+}$ configuration assignment.

**Supplementary Note 3 | Magnetic Properties.** Referring to Supplementary Fig. 6, hysteretic 1$^{st}$-order field induced transition below 30 K are defined by the inflection points in the $M(H)$ plots. The metastability limits of these field induced transitions are indicated as dotted lines in the phase diagram in Supplementary Fig. 7. The lack of $M(H)$ hysteresis at $T = 50$ K (see Supplementary Fig. 6) indicates a 2$^{nd}$-order transition (as indicated in Supplementary Fig. 7), and lies very close to the thermal instability of the AFM low temperature phases. The region above the AFM phases has been labelled paramagnetic. It is worth noting that the $T = 58$ and 65 K curves show a disparate curvature, which suggest some field coupled magnetic correlations above the ordering temperature. The negative peak in the $dM/dT$ plots in Supplementary Fig. 6 fall in this temperature range and are tentatively associated with local magnetic correlations precursive to the ordering temperature. The loci and peak widths of these negative $dM/dT$ peaks are used to define a shaded region in the $H$-$T$ phase diagram where magnetic correlations appear operative. These magnetic correlations couple to the external field and presumably involve field induced spin canting, however, the finite field neutron diffraction would be required to determine their true character. The fluctuation of the SHG response in Supplementary Fig. 15 at around $T_N$ indicates the presence of spin-charge coupling, as shown in previous works.$^{25}$ This behavior is consistent with the magnetostriction-polarization coupling that is proposed.

**Supplementary Note 4 | SHG effect.** SHG experiments were performed on as-made pellets of Mn$_2$MnWO$_6$ in the reflection mode. The compound was observed to be SHG active between 6 K and 800 K (Supplementary Fig. 14a) as SHG intensity was significantly higher
than the background in this temperature range. As shown in Supplementary Fig. 14b, SHG intensity ($I_{2\omega}$) peak was observed at 400 nm wavelength in the spectroscopic data corresponding to the 800 nm fundamental wavelength that was irradiated on the pellet. The presence of the SHG peak confirms broken inversion symmetry in this compound. Following this experiment, temperature dependent SHG intensity was measured in a far-field SHG setup previously reported in Garten et al. 26.

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