Preparing materials which simultaneously exhibit spontaneous magnetic and electrical polarisations is challenging as the electronic features which are typically used to stabilise each of these two polarisations in materials are contradictory. Here we show that by performing low-temperature cation-exchange reactions on a hybrid improper ferroelectric material, Li$_2$SrTa$_2$O$_7$, which adopts a polar structure due to a cooperative tilting of its constituent TaO$_6$ octahedra rather than an electronically driven atom displacement, a paramagnetic polar phase, MnSrTa$_2$O$_7$, can be prepared. On cooling below 43 K the Mn$^{2+}$ centres in MnSrTa$_2$O$_7$ adopt a canted antiferromagnetic state, with a small spontaneous magnetic moment. On further cooling to 38 K there is a further transition in which the size of the ferromagnetic moment increases coincident with a decrease in magnitude of the polar distortion, consistent with a coupling between the two polarisations.
magnetoelastic multiferroic materials\textsuperscript{1,2}—those which exhibit spontaneous and coupled magnetic and electrical polarisations—offer the prospect of preparing a range of devices for the manipulation and storage of digital information, including low-power nonvolatile random-access memories\textsuperscript{3,4}. However, the preparation of magnetoelastic multiferroic materials is hampered by the contrasting electronic structures typically required for ferroelectric and ferromagnetic behaviour\textsuperscript{5}. Specifically, the noncentrosymmetric, polar crystal structures, which are a prerequisite for ferroelectric materials\textsuperscript{6,7}, are typically stabilised by second-order Jahn–Teller distortions\textsuperscript{8} of either d\textsuperscript{0} transition metals\textsuperscript{9} or ns\textsuperscript{2} post-transition metals\textsuperscript{10,11}, and these closed-shell electronic configurations are not consistent with magnetism.

The “hybrid improper” (HIP) mechanism offers an alternative method for inducing the noncentrosymmetric perovskite crystal structures necessary for ferroelectric behaviour\textsuperscript{16–20}. In this mechanism, two nonpolar structural distortions, typically the low-energy tilts of BO\textsubscript{6} octahedral units in AB\textsubscript{2}O\textsubscript{3} and A′ AB\textsubscript{2}O\textsubscript{3} layered perovskite phases, combine to break the inversion symmetry of the host framework and couple to a third polar-distortion mode, leading to a spontaneous electrical polarisation\textsuperscript{21–28}. A key feature of the trilinear coupling between the three distortion modes is that the polar-distortion mode is not the primary order parameter of the ferroelectric-phase transition of this class of material and is unstable in the absence of the two nonpolar distortions, hence the improper label.

As the HIP mechanism does not rely on the presence of d\textsuperscript{0} or ns\textsuperscript{2} diamagnetic ions, it should be easier, in principle, to combine magnetic behaviour with this class of ferroelectric. Indeed, one of the first materials predicted to exhibit HIP ferroelectric behaviour, Ca\textsubscript{3}Mn\textsubscript{2}O\textsubscript{7}\textsuperscript{16}, adopts a canted antiferromagnetic state (weak ferromagnet) below 115 K\textsuperscript{29}, in which magnetoelastic coupling has been observed\textsuperscript{24,30}, in line with theory predictions\textsuperscript{16}.

However, further investigation of the Ruddlesden–Popper and Dion–Jacobson phases that exhibit HIP ferroelectric behaviour reveals that large B-site cations are needed to stabilise the highly distorted perovskite frameworks required for the HIP mechanism to function\textsuperscript{21–27}. When combined with the high B-site charges needed in these frameworks, this size requirement rules out the inclusion of the vast majority of paramagnetic transition-metal cations, and to date, the only candidate magnetoelastic multiferroic materials based on the HIP mechanism are Ca\textsubscript{3}Mn\textsubscript{2}O\textsubscript{7}\textsuperscript{16,24,30} and [Ca\textsubscript{1.69}Sr\textsubscript{0.36}Fe\textsubscript{0.6}Ta\textsubscript{1.85}Fe\textsubscript{2}O\textsubscript{7}]\textsuperscript{10,15}Ca\textsubscript{3}Ti\textsubscript{2}O\textsubscript{7}\textsuperscript{31}, the latter of which uses the introduction of some large diamagnetic Ti\textsuperscript{4+} ions onto the perovskite B site, via alloying the magnetic iron phase with diamagnetic Ca\textsubscript{3}Ti\textsubscript{2}O\textsubscript{7}, to help stabilise the required distorted perovskite framework.

Recently we have been using the facile cation-exchange chemistry of the A′AB\textsubscript{2}O\textsubscript{7} Dion–Jacobson phases to tune the structural distortions of this family of materials to induce HIP ferroelectric behaviour\textsuperscript{15,21,24,30–35}. Here we describe how this cation-exchange chemistry can be used to substitute paramagnetic cations onto the A′-sites of HIP ferroelectric Ruddlesden–Popper oxides to yield an additional class of magnetoelastic multiferroic materials.

**Results and discussion**

Li\textsubscript{2}SrTa\textsubscript{2}O\textsubscript{7} was prepared by a ceramic synthesis route from a combination of Li\textsubscript{2}CO\textsubscript{3}, SrCO\textsubscript{3}, and Ta\textsubscript{2}O\textsubscript{5}. Neutron powder diffraction (NPD) data indicate that Li\textsubscript{2}SrTa\textsubscript{2}O\textsubscript{7} adopts a polar a\textsuperscript{-}a\textsuperscript{-}c\textsuperscript{-}/a\textsuperscript{-}a\textsuperscript{-}c\textsuperscript{-} distorted, n = 2 Ruddlesden–Popper structure, described in space group A\textsubscript{2}am, in which the lithium cations reside in pseudo tetrahedral coordination sites between the TaO\textsubscript{6} octahedra (Fig. 1a), and the Γ\textsubscript{p}′ polar-distortion mode, consistent with trilinearly coupled hybrid improper ferroelectric behaviour\textsuperscript{16}.

Mn\textsubscript{5}Ta\textsubscript{2}O\textsubscript{7} was prepared by reacting Li\textsubscript{2}SrTa\textsubscript{2}O\textsubscript{7} with MnCl\textsubscript{2} at 375 °C under an inert atmosphere to prevent the conversion of MnCl\textsubscript{2} to MnO or Mn\textsubscript{3}O\textsubscript{4}. Neutron powder diffraction data collected from the cation-exchanged material at room temperature\textsuperscript{36} (Fig. 1c) are consistent with this noncentrosymmetric structure, in contrast to previous reports\textsuperscript{37}. Analysis of the structure of Li\textsubscript{2}SrTa\textsubscript{2}O\textsubscript{7} reveals that it can be related to the undistorted aristotype Ruddlesden–Popper structure (space group I\textsubscript{4}mmm) by the introduction of the X\textsubscript{3}– and X\textsubscript{5}– distortion modes that tilt the TaO\textsubscript{6} octahedra (Fig. 1a), and the Γ\textsubscript{p}– polar-distortion mode, consistent with trilinearly coupled hybrid improper ferroelectric behaviour\textsuperscript{16}.

![Fig. 1 The polar oxide Li2SrTa2O7. a The polar crystal structure of Li2SrTa2O7 viewed down the [110] direction. b Observed (red crosses), calculated (green line), and difference (purple line) plots from the structural refinement of Li2SrTa2O7 against NPD data. Black, red, and blue tick marks indicate peak positions for the majority phase, the vanadium sample holder and a small quantity of Li3TaO4, respectively. c Particle-size dependent SHG data from Li2SrTa2O7 compared with an α-SiO2 standard.](image-url)
Fig. 2 Polar, incommensurate structure of MnSrTa$_2$O$_7$. a Reaction with MnCl$_2$ converts Li$_2$SrTa$_2$O$_7$ into MnSrTa$_2$O$_7$ via topochemical Mn-for-Li cation exchange. b Observed (red crosses), calculated (green line), and difference (purple line) plots from refinement of an A2$_{1}$am symmetry structural model against NPD data collected from MnSrTa$_2$O$_7$ at 300 K. A series of peaks (marked by arrows) are not fit by this model and can only be indexed with an incommensurate unit cell. c Half occupancy of the pseudo tetrahedral coordination sites by Mn$^{2+}$ ions allows two different local chequerboard orderings. d An approximate representation of the incommensurate intergrowth of the two Mn-ordering patterns, which propagates along the crystallographic y axis. Locally ordered regions are joined by doubly occupied/vacant stripes or “faul” which run parallel to the x axis.

(space group A$_2$$_1$am), but with the Li$^+$ cations replaced by a 50% occupancy of Mn$^{2+}$ ions, as shown in Fig. 2a. Refinement of this model gave a good fit to the NPD data, with a refined Mn occupancy of 0.496(6), consistent with the stated chemical formula, and the observed SHG activity (0.26 times α-SiO$_2$, Supplementary Fig. 2) of the material is consistent with the noncentrosymmetric structure, described in detail in the Supplementary Information.

Close inspection of the fit of this commensurate model to the NPD data revealed a series of weak diffraction peaks that could not be indexed by this model and that could not be assigned to impurity phases (Fig. 2b). However, these additional diffraction features could be indexed using an incommensurate unit cell in superspace group A$_2$$_1$am(0$\overline{8}$0)000 with a propagation vector $q = (0, 0.86, 0)$ compared with the previously refined commensurate A$_2$$_1$am symmetry unit cell—a situation that is clearer in a further NPD data set collected at 200 K using the WISH diffractometer.

A series of test structural models were constructed and refined against the data to establish which components of the MnSrTa$_2$O$_7$ framework led to the structural modulation. As shown in Fig. 2c, the Mn$^{2+}$ cations can adopt a chequerboard-ordered arrangement within the tetrahedral coordination sites, analogous to the arrangement of Na$^+$ cations in NaNdNb$_2$O$_7$27, resulting in an array of apex-linked MnO$_4$ units, which maximises the Mn–Mn separation. However, there are two distinct ways of ordering the Mn cations (A and B), which are simply related by switching the occupied and unoccupied tetrahedral sites. It was found that the best fit to the NPD data was achieved using a model with a Crenel modulation of the Mn$^{2+}$ occupancy, which corresponds to an incommensurate intergrowth of these two ordering patterns, as shown approximately in Fig. 2d, and described in detail in the Supplementary Information$^{38,39}$. In addition, there is a coupled modulation of the “equatorial” O$_4$ oxide ions that are adjacent to the tetrahedral coordination sites (Fig. 2a), and which move in response to the presence or absence of an Mn$^{2+}$ cation in the neighbouring coordination site. The resulting modulated structure is noncentrosymmetric and polar, consistent with the observed room-temperature SHG activity of...
the phase, with the electrical polarisation aligned parallel to the crystallographic x axis. The incommensurate modulated ordering of the Mn\(^{2+}\) cations over the two pseudotetrahedral coordination sites can be rationalised by noting that the commensurate, chequerboard ordering of the Mn cations, which maximises the Mn–Mn separation, is symmetry-incompatible with the polar a–a–c\(^{+}\)/a–a–c\(^{+}\) tilting of the TaO\(_{6}\) octahedra. This suggests that the observed modulated ordering pattern of the Mn cations is the optimum compromise between these two structural components\(^{32}\).

Zero-field-cooled (ZFC) and field-cooled (FC) magnetisation data collected from MnSrTa\(_{2}\)O\(_{7}\) (Fig. 3a) can be fitted by the Curie–Weiss law in the range 150 < \(T/\text{K}\) < 300 to yield a Curie constant of \(C = 4.37(1) \text{ cm}^3 \text{ K mol}^{-1}\), as shown in Fig. 4b. However, it can be seen from the data in Fig. 3b that magnetic scattering persists above this temperature. Close inspection of the data reveals that above 43 K, the magnetic scattering peaks broaden significantly as they diminish in intensity, and diffuse scattering features appear in the data, as highlighted in the Supplementary Information. This peak broadening/diffuse scattering is attributed to the persistence of strong 2D magnetic interactions in the xy plane above \(T_\text{N}\). Indeed, the value of the magnetic scattering peaks bro...
of the exponential term obtained from the power-law fit ($\beta = 0.27(1)$) is in excellent agreement with other systems that show strong 2D magnetic interactions, but weak 3D coupling40.

As noted above, the ZFC and FC magnetisation data diverge at $T_N = 43$ K (Fig. 4a). However, these data show a further feature at $38$ K, marked $T_A$, where the gradient of the ZFC and FC data increases sharply. Field-dependent magnetisation data (Fig. 4c) collected at 40 K (between $T_N$ and $T_A$) are nonlinear and exhibit weak hysteresis, consistent with a canted antiferromagnetic state below $T_N$. Equivalent data collected at 35 K and 30 K (below $T_A$) show a significant increase in both remnant magnetisation and coercive field consistent with a sharp increase in the ferromagnetic component (increased canting) of the magnetic state.

Signatures of the event at $T_A$ are also observed in the crystallographic data, with both the $b$ and $c$ lattice parameters exhibiting sharp minima at this temperature (Fig. 4a). A more detailed understanding of the structural changes occurring around $T_N$ and $T_A$ can be gained by analysing the changes to the magnitudes of the tilting distortion modes, $X_3^-$ and $X_2^+$, and the polar distortion mode, $\Gamma_5^-$, which relates the $a^a - c^- / a^- c^+$ distorted structure of MnSrTa$_2$O$_7$ to the corresponding undistorted aristotype structure.

**Fig. 4 Evidence for magnetoelectric coupling in MnSrTa$_2$O$_7$. a** Zero-field-cooled and field-cooled magnetisation data, lattice parameters, $X_3^-$, $X_2^+$, and $\Gamma_5^-$ distortion-mode magnitude (arbitrary units)45, 46 and Mn and Sr $\Gamma_5^-$ mode displacement of MnSrTa$_2$O$_7$ in the temperature range $0 < T/K < 50$. **b** $M = M_0 \left(1 - \frac{T}{T_N}\right)^\beta$ power law fit to ordered Mn moment (obtained by NPD data) as a function of temperature. **c** Expanded region around $H = 0$ of magnetisation-field data collected from MnSrTa$_2$O$_7$ in an applied field in the range $-50000 < H/Oe < 50000$. 
The $X_2^+$ mode, which corresponds to the $d\alpha d\rho c^+/d\alpha d\rho c^+$ tilting distortion of the Ta₆O₁₈ octahedra, is temperature dependent from 50 K to $T_N$ and then exhibits an almost linear decline of around 15% from $T_N$ to $T_A$, before becoming essentially temperature independent below $T_A$, as shown in Fig. 4a. This suggests that while the $X_2^+$ mode responds to the onset of magnetic order at $T_N$, changes to the magnitude of this mode are not responsible for the minima in the lattice parameters at $T_A$.

In contrast, the $X_3^−$ mode and the $Γ_5^−$ polar distortion mode are essentially temperature independent between 50 K and $T_A$, and thus do not appear to respond to the onset of magnetic order at $T_N$. However, on cooling below $T_N$, both modes show a step change: an increase of ~1% in $X_3^−$ and a sharp drop of around 5% in the magnitude of the $Γ_5^−$ mode, the latter change indicating a drop in the electrical polarisation of MnSrTa₂O₇ at this temperature (Fig. 4a). The drop in the magnitude of the $Γ_5^−$ mode can also be seen in sharp changes to the polar displacements of the Mn and Sr cations, also shown in Fig. 4a. The polar displacement of the Sr cations increases, while that of the Mn cations decreases, because the displacements of the Mn cations in the $Γ_5^−$ distortion mode oppose the establishment of a net polarisation as MnSrTa₂O₇. Therefore, $Γ_5^−$ can be thought of as a ferrielectric rather than a ferroelectric.

Taking all these observations together, we observe that at 300 K, MnSrTa₂O₇ adopts an incommensurate polar structure (although we note the incommensurate modulation of the structure is not the origin of the inversion symmetry breaking) in a paramagnetic state. On cooling below $T \sim 100$ K, 2-dimensional magnetic correlations build up, before the system undergoes a transition to 3-dimensional magnetic order at $T_N$ = 43 K. On cooling to $T_A = 38$ K, there is a further transition in which the magnitude of the ferromagnetic moment of the phase increases, the $X_3^−$ distortion increases, and the $Γ_5^−$ polar mode decreases.

A symmetry analysis of MnSrTa₂O₇ (see Supplementary Information) shows that the m$Γ_5^+$ weak ferromagnetic moment (which arises from the trilinear invariant of the primary antiferromagnetic m$X_2^+$ mode and the $X_3^−$ octahedral tilting) is directly coupled to the $Γ_5^−$ (HIP) polarisation through a quadrilinear coupling in the $mΓ_5^+$, $Γ_5^−$, m$X_2^+$ and the $X_3^−$ octahedral tilting. Data in Figs. 4a, b show that the magnitudes of the $Γ_5^−$, m$X_2^+$, and $X_3^−$ distortions undergo a step change at $T_N$, coincident with a sharp increase in the weak ferromagnetic moment (m$Γ_5^+$) of MnSrTa₂O₇, consistent with magnetoelectric coupling.

This quadrilinear coupling also gives an indication that it is possible to reverse both improper ferroic orders, leaving the energy of the system invariant. The actual switching mechanism is more complex and can include different paths, depending on the distortions involved. Indeed, the reversal of the improper ferroelectric polarisation, achievable by the application of an external electric field, requires the reversal of either the $X_3^−$ or the $X_3^−$ octahedral tilting due to the HIP mechanism. If the $X_3^−$ octahedral tilting changes sign, this will also require the reversal of the antiferromagnetic m$X_2^+$ mode or reversal of the weak ferromagnetic moment (m$Γ_5^+$), due to the quadrilinear coupling of these distortions to the $X_3^−$ tilting. This gives a clear path for the electrical control of the weak ferromagnetic moment via the $X_3^−$ tilting. The reverse mechanism, the magnetic control of the electrical polarisation, is less likely since the application of a magnetic field to switch the weak ferromagnetic moment will presumably result in the change of sign of the m$X_2^+$ anti-ferromagnetic mode and not in a change of the $X_3^−$ tilting.

The symmetry analysis and couplings detailed above are analogous to those described by Benedek and Fennie for Ca₃MnO₄. However, the appearance of a weak ferromagnetic moment at $T_N$ prior to the onset/enhancement of magnetoelectric coupling at $T_A$ does not appear to have an analogue in the observed behaviour of Ca₃MnO₄. Accurate theoretical investigations and switching experiments will be needed to identify the details of the coupling mechanism.

It should be noted that MnO₃ exhibits a magnetic ordering transition ($T_N = 41–43$ K) at a temperature similar to the magnetic events observed for MnSrTa₂O₇. However, as shown above, the only features observed in the magnetisation data collected from MnSrTa₂O₇ are observed at $T_N$ and $T_A$, which can be correlated to features in the NPD data collected from MnSrTa₂O₇ (Fig. 4) and attributed to symmetry-required changes of the weak ferromagnetic moment (m$Γ_5^+$) of MnSrTa₂O₇. Thus, we can conclude that even if small quantities of MnO₃ are present in the sample of MnSrTa₂O₇, any contribution they may make to the magnetisation data does not affect the veracity of the analysis presented above. We emphasise that there is no sign of any binary manganese oxide phases in any of the diffraction data collected from any of the samples prepared.

In conclusion, a directed cation-exchange reaction, which replaces the diamagnetic Li⁺ A-cations of the HIP ferroelectric phase Li₆SrTa₂O₇ with paramagnetic Mn⁺⁺ cations allows the preparation of a coupled magnetoelectric material, MnSrTa₂O₇. Given that this type of cation-exchange chemistry should be broadly applicable, this suggests that a wide variety of $M^2⁺$ transition-metal cations can be substituted into polar Li₆ABO₇ host phases, allowing the preparation of a large number of additional, potentially magnetoelectric, materials.

Methods

Synthesis. Polycrystalline samples of Li₆SrTa₂O₇ were prepared by combining suitable stoichiometric ratios of SrCO₃ (99.994%) and Ta₂O₅ (99.993%, dried at 900 °C) and a 10% stoichiometric excess of Li₂CO₃ (99.998%) to compensate for metal loss due to volatilisation at high temperature. This mixture was then heated at 600 °C in air for 12 h, reground, and pressed into pellets. The pellets were then heated to 1250 °C at a heating rate of 5 °C/min and kept at 1250 °C for 12 h, followed by cooling at 5 °C/min to room temperature. Samples were then reground, pressed into pellets, and heated at 1250 °C for 3 h, before being quenched to room temperature. Polycrystalline samples of MnSrTa₂O₇ were prepared by reacting Li₆SrTa₂O₇ with 5-mole equivalents of anhydrous MnCl₂ (98%). The mixture was ground together in an agate pestle and mortar in an argon-filled glovebox, loaded in a Pyrex tube, and heated for four days at 375 °C under flowing argon. The mixture was then washed with distilled water to remove the remaining chlorides, and dried for 12 h at 140 °C in air.

Characterisation. Reaction progress and the final sample purity were assessed using X-ray powder diffraction data collected using a PANalytical X’pert diffractometer incorporating an X’celerator position-sensitive detector (monochromatic Cu Kα₁ radiation). High-resolution synchrotron X-ray powder diffraction (SRXD) data were collected using instrument 111 at Diamond Light Source Ltd. using Si-calibrated X-rays with an approximate wavelength of 0.825 Å, from samples sealed in 0.3 mm-diameter borosilicate glass capillaries. Low-temperature X-ray powder diffraction data were collected using Rigaku Smartlab diffractometer fitted with a Ge crystal monochromator (Cu Kα₁) and an Oxford Cryosystems Phenix cryostat. Neutron powder diffraction (NPD) data were collected on the HRPD and WISH diffractometers at the ISIS neutron source, with the samples contained in indium-sealed vacuumum cans. Rietveld profile refinements were performed using IANA20065 and the GSAS suite of programs45. Symmetry analysis and distortion-model quantification was performed using the ISO-DISTORT software46,47.

Magnetisation data were collected using a Quantum Design MPMS-XL SQUID magnetometer. Zero-field-cooled (ZFC) and field-cooled (FC) data were collected in an applied field of 100 Oe. Powder second harmonic generation measurements were performed on a Kurtz-NLO system using a Nd:YAG laser with a wavelength of 1064 nm. The SHG signal was recorded and compared with a standard sample of α-SiO₂. A detailed description of the experimental setup and process has been reported elsewhere48.
Data availability
NPD data are available at https://doi.org/10.5286/ISIS.E.RB1910148. Other data are available on request to the authors.

Received: 10 May 2021; Accepted: 22 July 2021; Published online: 16 August 2021

References
1. Eisenstein, W., Mathur, N. D. & Scott, J. F. Multiferroic and magnetoelectric materials. Nature 424, 759 (2006).
2. Cheong, S. W. & Mostovoy, M. Multiferroics: a magnetic twist for ferroelectricity. Nat. Mater. 6, 13–20 (2007).
3. Bipes, M. & Barthelmy, A. Multiferroics: towards a magnetoelectric memory. Nat. Mater. 7, 425–426 (2008).
4. Scott, J. F. Data storage - Multiferroic memories. Nat. Mater. 6, 256–257 (2007).
5. Hill, N. A. Why are there so few magnetic ferroelectrics? J. Phys. Chem. B 104, 6694–6709 (2000).
6. Cohen, R. E. Origin of ferroelectricity in perovskite oxides. Nature 358, 138–139 (1982).
7. Nye, J. F. Physical Properties of Crystals (Oxford University Press, 1957).
8. Halasyamani, P. & Poeppelmeier, K. R. Noncentrosymmetric oxides. Chem. Mater. 10, 2753–2769 (1998).
9. Pearson, R. G. The 2nd-order Jahn-Teller effect. THEOCHEM J. Mol. Struct. 12, 25–34 (1983).
10. Cohen, R. E. Origin of ferroelectricity in perovskite oxides. Nature 358, 138–139 (1982).
11. Kunz, M. & Brown, I. D. Out-of-center distortions around octahedrally coordinated d8 transition-metals. J. Solid State Chem. 115, 395–406 (1995).
12. Lefebvre, I. et al. Electronic-properties of antimony chalcogenides. Phys. Rev. Lett. 59, 2471–2474 (1987).
13. Benedek, N. A., Malzer, J. M., Oliveira-Fourcade, J. & Jumas, J. C. Electronic structure of Tin monochalcogenides from SnO to SnTe. Phys. Rev. B 58, 1896–1906 (1998).
14. Seshadri, R. & Hill, N. A. Visualizing the role of Bi 6s lone pairs in the off-center distortion in ferromagnetic BiMnO3. Chem. Mater. 13, 2892–2899 (2001).
15. Schafar, M. W., Woodward, P. M., Seshadri, R., Klepeis, J. H. & Hurst, B. Structure and bonding in SnWO4, PbWO4 and BiVO4: lone pairs versus inert pairs. Inorg. Chem. 46, 3839–3850 (2007).
16. Benedek, N. A. & Fennie, C. J. Hybrid improper ferroelectricity: a mechanism for controllable polarization-magnetization coupling. Phys. Rev. Lett. 106, 107204 (2011).
17. Mulder, A. T., Benedek, N. A., Rondinelli, J. M. & Fennie, C. J. Tuning ABO3 antiferroelectrics into ferroelectrics: design rules for practical rotation-driven ferroelectricity in double perovskites and A2B6O13 Ruddlesden-Popper compounds. Adv. Funct. Mater. 23, 4810–4820 (2013).
18. Benedek, N. A., Mulder, A. T. & Fennie, C. J. Polar octahedral rotation: a pathway to new multifunctional materials. J. Solid State Chem. 195, 11–20 (2012).
19. Bouquet, E. et al. Improper ferroelectricity in perovskite oxide artificial superlattices. Nature 452, 732–736 (2008).
20. Benedek, N. A. Origin of ferroelectricity in a family of polar oxides: the Dion-Jacobson phases. Inorg. Chem. 53, 3769–3777 (2014).
21. Liu, M. F. et al. Direct observation of ferroelectricity in Ca3MnO5 and its prominent light absorption. Appl. Phys. Lett. 113, 022902 (2018).
22. Zhou, T. et al. Topological manipulation of perovskites: low-temperature reaction strategies for directing structure and properties. Adv. Mater. 23, 442–460 (2011).
23. Shaak, R. E. & Mailoux, T. E. Perovskites by design: a toolbox of solid-state reactions. Chem. Rev. 116, 1455–1471 (2016).
24. Hayward, M. A. & Halasyamani, P. S. Bulk characterization methods for non-centrosymmetric materials: second-harmonic generation, piezoelectricity, pyroelectricity, and ferroelectricity. Chem. Soc. Rev. 35, 710–717 (2006).
25. Fang, T. et al. Phase transition in the Ruddlesden-Popper layered perovskite Li3Sr2Ta2O9. J. Solid State Chem. 182, 317–326 (2009).
26. Petricek, V., Vanderlee, A. & Evain, M. On the use of Crenel functions for occupationally modulated structures. Acta Cryst. Sect. A 51, 529–535 (1995).
27. van Smaalen, S. Incommensurate Crystallography (Oxford University Press, 2007).
28. Bramwell, S. T. & Holdsworth, P. C. W. Magnetization and universal subcritical behavior in 2-dimensional XY magnets. J. Phys. Condens. Matter 5, L53–L59 (1993).
29. Guillou, F., Thotta, S., Prellier, W., Kumar, J. & Hardy, V. Magnetic transitions in Mn3O4 and an anomaly at 38 K in magnetization and specific heat. Phys. Rev. B 83, 094423 (2011).
30. Jensen, G. B. & Nielsen, O. V. Magnetic structure of Mn5O2 (Hausmannite) between 4.7 K and Neel point, 41 K. J. Phys. C. Solid State Phys. 7, 409–424 (1974).
31. Petricek, V., Dusek, M. & Palatinus, L. Crystallographic computing system JANA2000: general features. Z. Kristallographie-Crystalline Matter 229, 345–352 (2014).
32. Los Alamos National Laboratory. General Structure Analysis System. Los Alamos National Laboratory Report LAUR 86–748 (2000).
33. Campbell, B. J., Stokes, H. T., Tanner, D. E. & Hatch, D. M. ISODISPLACE: a web-based tool for exploring structural distortions. J. Appl. Crystallogr. 39, 607–614 (2006).
34. ISOTROPY Software Suite (iso.byu.edu, 2007).

Acknowledgements
Experiments at the Diamond Light Source were performed as part of the Block Allocation Group award “Oxford Solid State Chemistry RAG to probe composition-structure-property relationships in solids” (EE13284). Experiments at the ISIS pulsed neutron facility were supported by a beam time allocation from the Science and Technology Facilities Council (RR 191044, DIC:TO16286/ISIS.RB1911048). PSH and WZ thank the Welch Foundation (Grant E-1457) for support. We thank Dr. Gavin Stenning for helpful discussions with the collection of the low-temperature X-ray diffraction data in the Materials Characterisation Laboratory at the ISIS Neutron and Muon Source.

Author contributions
TZ prepared the samples and performed the bulk of the structural characterisation; FO supervised the project and wrote the paper.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-021-25098-1.

Correspondence and requests for materials should be addressed to M.A.H.

Peer review information Nature Communications thanks the anonymous reviewer(s) for their contribution to the peer review of this work.

Reprints and permission information is available at http://www.nature.com/reprints

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.
