**Introduction**

Spintronics (spin-based electronics or spin transport electronics) is an emergent new technology that takes advantage of the interaction between the charge and magnetic spins of the electrons in materials. Compared to conventional semiconductor charge-based electronics, devices based on spintronics consume less electric power, provide faster data processing speed and increased storage densities.\(^1\)\(^2\) Promising spintronic materials are ferromagnetic/ferrimagnetic semiconductors (FMS/FiMS) due to the possibility of spin-polarized carriers and facile combination with semiconductor devices.\(^1\) For practical application, the ideal
FMS/FiMS should exhibit magnetic ordering above room temperature (RT). Designing and finding such materials is still challenging for scientists in materials science, solid state chemistry, condensed matter physics, and related areas.\textsuperscript{5} To date, there are few FMS/FiMS materials with an ordering temperature near or above RT such as spinel Fe\textsubscript{0.5}Cr\textsubscript{0.5}S\textsubscript{2} (T\textsubscript{C} = 340 K),\textsuperscript{6,7} perovskite Sr\textsubscript{0.5}Y\textsubscript{0.5}CoO\textsubscript{3}\textsubscript{0.5} (T\textsubscript{C} = 335 K, 310 K for thin films),\textsuperscript{5,6} and double perovskites (DP) La\textsubscript{2}NiMnO\textsubscript{6} (T\textsubscript{C} ∼ 280 K) and Sr\textsubscript{2}CrOsO\textsubscript{6} (T\textsubscript{C} ∼ 700 K).\textsuperscript{7–9}

Compared to ferromagnets, antiferromagnets are more common in nature. Recent studies indicate that antiferromagnetic semiconductors (AFMS) could be alternatives to FMS in spintronics, which motivates further research into the AFM spintronics subfield.\textsuperscript{10–20} Several near/above RT candidates have been discovered including LiMn\textsubscript{2}O\textsubscript{4} (T\textsubscript{N} = 374 K),\textsuperscript{21} CuMn\textsubscript{3}O\textsubscript{8} (T\textsubscript{N} = 295 K),\textsuperscript{22,23} FeRh (T\textsubscript{N} ∼ 373 K),\textsuperscript{24} MnTe (T\textsubscript{C} = 310 K),\textsuperscript{25} and perovskite-type Sr\textsubscript{2}IrO\textsubscript{4} (T\textsubscript{N} = 240 K).\textsuperscript{26,27} However, further development of the AFM spintronics subfield requires the discovery of more AFMS with T\textsubscript{N} above RT.

As mentioned above, DPs are promising spintronic materials with high magnetic ordering temperatures. In particular, DP and corundum related oxides, A\textsubscript{2}BB\textsubscript{3}O\textsubscript{6} have demonstrated the required properties. Besides La\textsubscript{2}NiMnO\textsubscript{6} (T\textsubscript{C} = 280 K) and Sr\textsubscript{2}CrOsO\textsubscript{6} (T\textsubscript{C} = 700 K),\textsuperscript{7–9} we recently synthesized several Mn\textsubscript{2}Fe\textsubscript{3}B\textsubscript{2}O\textsubscript{6} (B = Nb, Ta, Mo, Re) phases under high-pressure and high-temperature, where both the A and B sites are transition metals.\textsuperscript{28–30} High pressure synthesis of Mn\textsubscript{2}Fe\textsubscript{3}B\textsubscript{2}O\textsubscript{6} obtained under 8 GPa is an FiMS with T\textsubscript{C} = 520 K.\textsuperscript{30} Following this trend, it was expected that Nb\textsuperscript{5+} (d\textsuperscript{0}) could also be substituted by Ru\textsuperscript{5+} (d\textsuperscript{3}) in Mn\textsubscript{2}Fe\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} for possible magnetic ordering above RT.

Here, we report that MnFe\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} can be synthesized under high-pressure and high-temperature. The crystal structure, formal oxidation states of cations, magnetic and electrical properties have been investigated. Neutron diffraction and Mössbauer spectroscopy data were also measured to elucidate the magnetic ordering in the structure. First principles calculations were undertaken to understand the electronic structure more thoroughly. Good agreement is found between the experiments and the DFT calculations.

**Experimental section**

**Starting materials and synthesis**

Polycrystalline MnFe\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} was prepared by high-pressure and high-temperature synthesis with a Walker-type Multi-Anvil press as described in our previous work.\textsuperscript{28–31} A stoichiometric mixture of MnO (wt 99.99%, Alfa Aesar), MnO\textsubscript{2} (wt 99.996%, Alfa Aesar), Fe\textsubscript{2}O\textsubscript{3} (wt 99.999%, Sigma Aldrich) and RuO\textsubscript{2} (wt 99.9%, Alfa Aesar) was first ground well at ambient pressure. The oxide mixture was then packed into a Pt capsule inside a MgO crucible, which was later assembled with other parts of the high-pressure apparatus. The reaction was carried out at 1873 K under 6 GPa for 0.5 h and then quenched to room temperature in a few minutes. After quenching, the pressure was slowly released. The resulting sample was a black pellet, with a total mass of ∼ 25 mg. To make enough sample (∼ 100 mg) for neutron experiment, four experiments were carried out with the same synthetic conditions, and the resulting samples were checked by X-ray powder diffraction (XRPD).

**Chemical analysis**

The chemical composition of the samples was determined by energy dispersive X-ray (EDX) analysis conducted on a JEOL 5510 scanning electron microscope equipped with an INCAx-sight 6587 system (Oxford Instruments). Mn-K, Fe-K and Ru-L lines were used for the composition quantification.

**Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)**

A powder sample of about 30 mg was loaded into an alumina crucible and measured in an SDT Q600 TA Instrument. The sample was tested from room temperature to 1000 °C at a heating and cooling rate of 10 °C min\textsuperscript{-1} under Ar flow. The remaining powder after the measurement was analyzed by XRPD.

**X-ray powder diffraction (XRPD)**

Samples were measured in the 2\theta range from 10° to 80° and collected for 1 h on a Bruker D8 Advance Diffractometer (Cu K\textsubscript{α}, λ = 1.5418 Å) with a SOL-X solid state detector. RT synchrotron powder X-ray diffraction (λ = 0.4126 Å) was collected in the 2\theta range from 0.5° to 50° at the 11-BM beam line at the Advanced Photon Source (APS) of Argonne National Laboratory. High-resolution powder X-ray diffraction data were also collected at room temperature on a Rigaku SmartLab X-ray diffractometer using a Ge220 monochromator to select the Cu K\textsubscript{α}, λ = 1.5406 Å wavelength.

**Neutron powder diffraction (NPD)**

NPD data were collected on ∼ 100 mg MnFe\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} powder sample placed inside a 3 mm diameter thin-walled cylindrical vanadium can at the ISIS neutron and muon source (Rutherford Appleton Laboratory, U.K.) on the WISH diffractometer located in the second target station.\textsuperscript{32} Multibank (153°, 122°, 90°, 58°, 27°) data were collected at 450 K (∼ 30 minutes) and the sample was then cooled to 5 K in a closed-cycle refrigerator (CCR) and a high quality dataset (∼ 2 hours) was recorded. Shorter scans were then collected on warming (∼ 15 minutes scans in 20 K increments to 75 K, and then at 25 K increments to 300 K, with longer 60 minutes scans collected at 60 and 125 K). Rietveld refinements were carried out with Topas Academic.\textsuperscript{33,34}
and the magnetic symmetry analysis was carried out with ISODISTORT.35

**Transmission electron microscopy (TEM)**

The samples for TEM analysis were prepared by mixing the powders with ethanol in an ultrasonic bath and depositing a few drops of the obtained suspension onto a holey TEM grid covered with carbon. Electron diffraction (ED) patterns were acquired with a Phillips CM20 microscope operated at 200 kV. High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images were acquired with a FEI Titan 80-300 “cubed” microscope operated at 300 kV. The simulated HAADF-STEM images were calculated with the QSTEM software.36

**Second harmonic generation (SHG)**

The measurements were done in far-field reflection geometry at normal incidence inside a cryostat. A pulsed laser beam from a Ti:sapphire femtosecond laser with a wavelength of 800 nm (pulse width 80 fs, repetition rate 80 MHz) was focused on a polished polycrystalline pellet sample with a 50 x objective onto a spot size of 0.5 μm. The reflected light was passed through a filter to eliminate the 800 nm fundamental, and then collected with a photomultiplier tube to detect any signal at the second harmonic of 400 nm.

**X-ray absorption near edge spectroscopy (XANES)**

XANES was carried out to confirm the formal oxidation state of the cations in MnFe0.5Ru0.5O3. Mn, Fe and Ru K-edge data were collected previously at X19A at (NSLS-I) are also included over most of the energy ranges.

**Magnetic measurements**

Magnetic properties were measured on polycrystalline sample with a Quantum Design SQUID MPMS-XL magnetometer. Field-cooled (FC) and zero-field-cooled (ZFC) magnetizations were measured between 1.8 and 300 K in a direct-current applied field. Field dependence of isothermal magnetization was measured with the applied field varying from -6 to 6 T.

**Mössbauer spectroscopy**

The 57Fe Mössbauer studies were performed with a conventional constant acceleration drive in transmission mode, in conjunction with a 50 mCi 57Co:Rh source. The absorber, MnFe0.5Ru0.5O3, was crushed to fine powder and put into a Perspex absorber holder. Measurements were performed while the absorber was in a cryostat with temperature stabilization (to 0.5 °C) in the range of 90 to 400 K. The obtained spectra were analyzed, in terms of a least square fit procedure, to simulated model spectra.

**Electrical resistivity**

Resistivity measurements were conducted with a Quantum Design Physical Property Measurement System (PPMS) with standard four-probe technique.

**DFT calculations**

Density functional theory (DFT) was used to investigate the type of crystal structure and magnetic order that give stable phases, to confirm the experimental findings. To treat the structural disorder observed in the experiments, the virtual crystal approximation (VCA) method37 implemented in Quantum Espresso code38,39 was employed within the Vanderbilt ultrasoft-pseudopotential scheme.40 The kinetic energy cutoffs for wave functions and charge density were set to be 50 and 400 Ry, respectively in the VCA calculations. After the stable crystal structure was found through the VCA calculations, the electronic structures have been studied with two different magnetic structures (antiferro- and ferro-magnetic ordering) using the full-potential linearized augmented plane-wave method implemented in WIEN2k.41 In the magnetic calculations, the structural disorder was ignored and the Fe occupancy was regarded to be 100% at the disordered sites for simplicity. Generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE)42 was used for the exchange–correlation functional and 25 x 25 x 7 k points were used for the Brillouin zone sampling. To obtain the correct ground state (including the magnetic moment of Fe3+ and an insulating phase), GGA+U was adopted within fully localized limit.43,44 The effective on-site Coulomb interaction parameter Veff = U − J = 4 eV was used.

**Results and discussion**

**Crystal structure and thermal stability**

Similar to the synthesis of Mn2FeMO6 (M = Nb, Ta, Mo, W, Re), MnFe0.5Ru0.5O3 was prepared at 1873 K under 6 GPa with a Walker-type Multi-Anvil press. Incident illumination, plane-polarized optical micrographs show the target phase with ~100 μm grain size, and traces of RuO2 and FeMnOx impurities (Fig. S2, ESI†). The XRPD pattern (Fig. S2, ESI†) indicates either a disordered α-Fe2O3-type (Fig. 1a, corundum, R3c) or

![Fig. 1](https://example.com/fig1.png)

Fig. 1 Crystal structures of MnFe0.5Ru0.5O3 with α-Fe2O3 type (a, corundum, R3c) and LN-type (b, R3c) viewed along the [110] direction. Color code: (Mn/Fe/Ru)O6 = orange in (a), MnO6/Fe3+/Ru3+O6 = gray/orange in (b), O = red spheres.
LN-type (Fig. 1b, R3c) as the main phase with a small amount RuO$_2$ impurity (~2%). Both structures give the same allowed reflections in diffraction experiments due to Friedel's law.

Both corundum and LN crystal structures have the same 3-dimensional (3D) construction based on distorted MO$_6$ (M = Mn, Fe, or Ru) octahedra. The centrosymmetric corundum crystal structure consists of symmetric dimers of MO$_6$ octahedra connected via face-sharing along the [001] direction and edge-sharing in [001] planes. All metal sites are disordered, and each MO$_6$ (M = Mn/Fe/Ru) is distorted with M cations displaced from the centers of octahedra, resulting in three long and three short M-O bond distances (Fig. 1a). The cation-ordered non-centrosymmetric LN structure is derived from this corundum structure, but with two cation sites, allowing ordering of Mn, Fe and Ru over these sites (e.g. a Mn site, and a mixed Fe/Ru site). This would give a LN model with distorted dimers of MnO$_6$ and MO$_6$ (M = Fe, Ru) octahedra face-sharing along [001] (Fig. 1b). Besides LN, other corundum derivatives are centrosymmetric ilmenite (IL, R3), noncentrosymmetric ordered ilmenite (OII, R3), and NTO (R3), which have the same 3D network of MO$_6$ octahedra but with different cation arrangements.45

The chemical composition of MnFe$_{0.5}$Ru$_{0.5}$O$_3$ was confirmed by EDX with the formula Mn$_{2.01(8)}$Fe$_{1.00(6)}$Ru$_{1.00(12)}$O$_{18e}$ and the thermal stability of this sample was measured by TGA-DSC. Above 800 °C, the sample starts decomposing into MnFe$_2$O$_4$, or FeMn$_2$O$_4$ and Ru$_2$O$_3$ (Fig. 3).

**X-ray and neutron powder diffraction**

Because Rietveld refinements with XRPD data gave similar fits to corundum (R3) or LN-type (R3c) structures (Fig. S2), and Fe and Mn are indistinguishable to Cu K$_\alpha$ radiation, RT XRPD data were used to determine only the distribution of Ru over the two cation sites in the LN model. Refinements suggested a statistical distribution of Ru over the two sites, with Ru occupancies of 0.27(2) at (0 0 3) and 0.23(2) at (0 0 0), respectively. The $R_w$ from this model is 7.12%, which is slightly smaller than that (7.15%) of this distorted LN model with Ru occupancies of 0.25 on both sites (Fig. S4 and Tables S1, S2, ESI†) analoguous to the corundum model due to cation disorder. Therefore, a statistical distribution of Ru seems most likely in MnFe$_{0.5}$Ru$_{0.5}$O$_3$ based on XRPD data analysis.

The Ru distribution was then fixed (Ru occupancies of 0.25 on both sites) in a starting LN model for multibank refinement using 450 K NPD data to refine the distribution of Fe and Mn over the two sites. NPD is expected to be very sensitive to this distribution, given the strong contrast in neutron scattering lengths (Mn = −3.73 fm, Fe = 9.54 fm, Ru = 7.21 fm).46 A fully disordered LN model (analogous to corundum) gave a good fit to the data ($R_w$ = 3.19%). Allowing the Fe and Mn distribution to refine resulted in a marginal improvement in fit ($R_w$ = 3.179%) but suggested an almost statistical distribution of Fe and Mn over the two sites, Ru/Fe/Mn occupancy of 0.25/0.227(3)/0.523(3) at (0 0 2), and 0.25/0.275(3)/0.477(3) at (0 0 0) (Fig. S5 and Table S3, ESI†). This analysis suggests that a fully disordered corundum model is most appropriate to describe the crystal structure of MnFe$_{0.5}$Ru$_{0.5}$O$_3$, at least at the length scale probed by diffraction techniques.

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**Table 1** Refinement details of corundum (R3c) model of MnFe$_{0.5}$Ru$_{0.5}$O$_3$ using 450 K NPD data with $a = 5.0870(1)$ Å, $c = 13.9306(3)$ Å; $R_w$ = 3.19%, $R_p$ = 3.04% and $\chi^2 = 2.27$

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<tr>
<th>Atom</th>
<th>Site</th>
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<th>y</th>
<th>z</th>
<th>Fractional occupancy</th>
<th>$U_{	ext{iso}} \times 100$ (Å$^2$)</th>
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<td>0.5/0.25/0.25</td>
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</tr>
<tr>
<td>O</td>
<td>18e</td>
<td>0.3073(1)</td>
<td>0</td>
<td>0.25</td>
<td>1</td>
<td>2.54(7)</td>
</tr>
</tbody>
</table>

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**Table 2** Selected bond lengths and angles from Rietveld refinement of corundum (R3c) model of MnFe$_{0.5}$Ru$_{0.5}$O$_3$ using 450 K NPD data

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M–O</td>
<td>3 x 1.997(1)</td>
<td>M–O(1)–M (within open face) 99.93(5)</td>
</tr>
<tr>
<td>M–O</td>
<td>3 x 2.090(1)</td>
<td>M–O(1)–M (from open to shared face) 91.01(1)</td>
</tr>
<tr>
<td>M–M</td>
<td>1 x 2.777(3)</td>
<td>M–O(1)–M (within shared face) 80.71(5)</td>
</tr>
</tbody>
</table>

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The disordered corundum model was then used for multibank refinement (153°, 122°, 90°, 58°, 27° banks of data) Rietveld refinement using 450 K NPD data, and the results are shown in Fig. 2 (122° bank data fit profile), Tables 1, 2, and Fig. S6 (ESI†) (all bank data fit profiles). Several small impurity phases were also included in the refinements, including RuO$_2$ (wt 3.2(1)%), FeMn$_2$O$_4$ (wt 2.1(1)%), and Mn$_2$O$_3$ (wt 4(1)%).

The refined unit cell parameters are $a = 5.0870$ (1) Å, $c = 13.9306(3)$ Å, $V = 360.5(8)$ Å$^3$ (Table 1). The unit cell parameter $a$ of MnFe$_{0.5}$Ru$_{0.5}$O$_3$ is much smaller than those of LN-type corundum derivative Mn$_2$FeMO$_6$ ($M = \text{Nb, Ta, } a \sim 5.27$ Å), while the $c$-axis is slightly larger than that of Mn$_2$FeTaO$_6$ ($c = 13.8892(3)$ Å), but smaller than that of Mn$_2$FeNbO$_6$ ($c = 13.9338(2)$ Å). The average M–O bond lengths are about 2.05 Å (Table 2), which is much shorter than those of Mn–O in Mn$_2$Fe$^{2+}$TaO$_6$ (2.16 Å) and Mn$_2$Fe$^{2+}$TaO$_6$ (2.22 Å). These values are also smaller than those (~2.2 Å) in other corundum derivative analogs such as Mn$_2$Fe$^{2+}$M$^{5+}$O$_6$ ($M = \text{Mo, Sb}$) and Mn$_2$Fe$^{2+}$W$^{6+}$O$_6$. The M–O bond length analysis indicates that Mn is likely not purely Mn$^{2+}$ in the structure. The average M–O bond length (~2.05 Å) is comparable with those in Mn$_2$Fe$^{2+}$TaO$_6$ (2.035 Å), Mn$_2$Fe$^{2+}$M$^{5+}$O$_6$ (2.035 Å), and Mn$_2$Fe$^{2+}$TaO$_6$ (2.035 Å), while the Mn–O bond length (~2.05 Å) is longer than those in Mn$_2$Fe$^{2+}$TaO$_6$ (2.035 Å), Mn$_2$Fe$^{2+}$M$^{5+}$O$_6$ (2.035 Å), and Mn$_2$Fe$^{2+}$TaO$_6$ (2.035 Å).
Mn$_2^{2+}$Fe$^{3+}$Ta$^{5+}$O$_6$ (2.01 Å), Mn$_2^{2+}$Fe$^{3+}$Mo$^{5+}$O$_6$ (2.033 Å), and Mn$_2^{2+}$Fe$^{3+}$Sb$^{5+}$O$_6$ (2.006 Å). However, they are shorter than those in Mn$_2^{2+}$Fe$^{3+}$W$^{6+}$O$_6$ (2.154 Å), which support Fe$^{3+}$ in MnFe$_{0.5}$Ru$_{0.5}$O$_3$. The detailed cation oxidation states will be discussed in the XANES results.

**Transmission electron microscopy**

To distinguish between LN-type $R_3c$ and corundum $R_3c$ models for MnFe$_{0.5}$Ru$_{0.5}$O$_3$, as shown in Fig. 1, TEM experiments were also carried out. Electron diffraction patterns of MnFe$_{0.5}$Ru$_{0.5}$O$_3$ are shown in Fig. 3 and Fig. S7 (ESI†), respectively. The patterns agree with the reflection conditions of the $R_3c$ and $R_3c$ space groups: $hkl$: $-h+k+l=3n$; $h0l$: $-h+k=3n$; $hhl$: $h+l=3n$, $l=2n$; $hhh$: $l=3n$; $00l$: $l=6n$. In Fig. S6 (ESI†), reflection 011 and its symmetrically equivalent reflections in the [211] zone and 00l: $l=3n$ in the [210] zone are due to double diffraction. Based only on selected area ED patterns, it is impossible to distinguish between $R_3c$ and $R_3c$ space groups. Therefore, we tested the models for the two space groups against experimental HAADF-STEM images.

In the LN $R_3c$ models, there are distinct columns of A and B/B’ sites of different stoichiometry, while in the corundum $R_3c$ model, all three atomic species are intermixed. There are two projections that allow separate visualization of the A and B/B’ columns in the $R_3c$ structure: [100] and [211]. On HAADF-STEM images, the brightness of the dots is proportional to the average atomic number of the projected column: $I \sim Z^2$. In MnFe$_{0.5}$Ru$_{0.5}$O$_3$, $Z_{Mn} = 25$, $Z_{Fe} = 26$, $Z_{Ru} = 44$ and therefore in case of ordering, columns with on average heavier cations should appear brighter.

HAADF-STEM images were taken along both those [100] and [211] directions (Fig. 3c and d). There is no systematic difference in the intensity of the different atomic columns. The ratio between the summed intensity of A and B/B’ sites, from profiles of 10 different rows of either A or B/B’, is very close to 1. Moreover, intensity profiles for ten rows with pairs of A and B/B’ columns (Fig. S8, ESI†) do not show any systematic difference in the intensities. The differences between the A and B/B’ peaks are random and can be explained by a statistical difference in the occupation of one column to the next. Therefore, there is no ordering between Mn, Fe and Ru cations in MnFe$_{0.5}$Ru$_{0.5}$O$_3$ and the results agree with an $R_3c$ (and not an $R_3c$) model, which is consistent with the results from XRPD and NPD analysis above, and with the disorder suggested by SHG, XANES and Mössbauer data below.

**Second harmonic generation**

SHG is a sensitive probe of inversion symmetry breaking in single crystal and polycrystalline materials. The SHG response of polycrystalline MnFe$_{0.5}$Ru$_{0.5}$O$_3$ was probed with SHG microscopy. Similar techniques have been used by the authors in the past to study inversion symmetry breaking in single crystal and polycrystalline complex oxides. Measurements were carried out at 300 and 25 K. There is no SHG signal above the background noise level at either temperature, which indicates that the material is centrosymmetric in this temperature range.

**X-ray absorption near edge spectroscopy**

XANES measurements were performed to probe the Mn, Fe, Ru oxidation state in MnFe$_{0.5}$Ru$_{0.5}$O$_3$. The Fe-K main-edge in MnFe$_{0.5}$Ru$_{0.5}$O$_3$ appears to correspond to ~Fe$^{3+}$ with somewhat broad main edge features bearing some similarity to the LN structure standard spectra for Mn$_2$FeMO$_6$ (M = Ta and Nb) (Fig. 4).

Interestingly, compared to Mn$_2$FeMO$_6$ spectra, the MnFe$_{0.5}$Ru$_{0.5}$O$_3$ spectrum manifests two features, an additional shoulder on the initial rising portion of the main edge (labeled “1” in Fig. 4a), and a prominent absolute-peak shifted to higher energy (labeled “2” in Fig. 4a). These two features are however present (albeit being more sharply defined) in the corundum (x-Fe$_2$O$_3$) standard spectrum. Thus, the Fe-K main-edge appears to support a corundum (x-Fe$_2$O$_3$) structure for MnFe$_{0.5}$Ru$_{0.5}$O$_3$.

The Mn-K main-edge in MnFe$_{0.5}$Ru$_{0.5}$O$_3$ is dramatically different from those of the LN structure standard spectra for Mn$_2$FeMO$_6$ (M = Ta and Nb) (Fig. 5), thereby precluding a Mn$^{2+}$, LN structure in this compound. In terms of chemical shift, the Mn-K main edge appears to be consistent with a substantial Mn$^{3+}$ component, which is similar to that of its Fe-K edge in Fig. 4a. A comparison of the near-edge and post-edge fine structure features (Fig. S9, ESI†) emphasize the similar features over the entire energy range, which suggests that the Mn and Fe sites in MnFe$_{0.5}$Ru$_{0.5}$O$_3$ are the same and are essentially the same as that in the corundum x-Fe$_2$O$_3$ compound. The notably larger shoulder (on the leading main-edge rise), and decreased intensity in the peak-region of spectrum (relative to the shifted Fe spectrum) indicates a greater admixture of Mn$^{3+}$ character at the Mn sites.

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**Fig. 3** Electron diffraction patterns (a and b) and HAADF-STEM images (c and d) of MnFe$_{0.5}$Ru$_{0.5}$O$_3$ along [100] and [211] directions.
The Mn-K pre-edge of MnFe$_{0.5}$Ru$_{0.5}$O$_3$ is substantially broadened compared to the pre-edges of the LN structure standards (Fig. 5b). Moreover, the pre-edges of the LN structures standards are significantly different from the MnFe$_{0.5}$Ru$_{0.5}$O$_3$ pre-edge, yet again arguing for a corundum structure and against a LN structure.

Based on the chemical shift of the Ru-K edge as compared with Ru and RuO$_2$ standards (Fig. 6a), the Ru valence state is close-to, or somewhat-less-than the Ru$^{4+}$ state in RuO$_2$. The L$_{2,3}$-edges of 4d transition metals are sensitive to the electron configuration both through the chemical shift and the structure of the intense near edge “white line” (WL) features.$^{48-54}$ The chemical shift of the Ru-L$_{2,3}$ edge spectra in MnFe$_{0.5}$Ru$_{0.5}$O$_3$, compared to the Sr$_2$YRuO$_6$ (Ru$^{5+}$, d$^0$), and Y$_2$CoRuO$_6$ (Ru$^{3+}$, d$^3$) standards (Fig. 6b), are clearly consistent with a ~d$^0$ Ru$^{4+}$ configuration. The intense WL-features at the L$_{2,3}$ edges of 4d transition metal sites in compounds with octahedral O-ligand coordination manifest a distinctly bimodal A/B feature structure due to transitions into empty $t_{2g}/e_g$ d-states. The filling of the $t_{2g}$-states with increasing d-electron count is reflected in the L$_{2,3}$ edge spectra by a systematic decrease in the A-feature intensity (relative to the B-feature) as illustrated in Fig. S10 (ESI$^{†}$) for L$_3$ edge spectra for a series of d$^0$ to d$^4$ compounds.

In Fig. 6b, the dramatic decrease in relative A-feature intensity between the Sr$_2$YRuO$_6$ (Ru$^{5+}$, d$^0$) and Y$_2$CoRuO$_6$ (Ru$^{3+}$, d$^3$) standards should be noted. For the MnFe$_{0.5}$Ru$_{0.5}$O$_3$ L$_{2,3}$ edge spectra, the A-feature intensity appears as an unresolved shoulder on the B-feature. In view of the multiple local environments in the Mn/Fe/Ru site distribution, the inhomogeneity broadening of the ligand field splitting (and the A/B-feature) is reasonable. The amplitude of the A-feature is consistent with a ~d$^4$ Ru$^{4+}$ configuration. Therefore, both the spectral chemical shift and WLA/B-feature are suggestive of a somewhat reduced Ru$^{4+}$ valence. These observations are consistent with the Fe$^{3+}$ and mixed Mn$^{2+}$/3$^+$ suggested by XANES results.
Magnetic properties

FC and ZFC magnetic susceptibilities of polycrystalline samples indicate a transition around 375 K (Fig. 7). As the temperature decreases, the FC magnetic susceptibility keeps increasing, and two slight transitions occur near 80 and 45 K, respectively. These two transitions are more obvious when the sample is measured with lower magnetic field (Fig. S11, ESI†). The observed divergence between ZFC-FC curves is due to the anisotropy in the sample, which decreases as the magnetic field increases (Fig. S11, ESI†).

Based on the above NPD analysis, the sample contains a small amount of FeMn$_2$O$_4$ ($T_C = 373$, 50 K),$^{55}$ and Mn$_3$O$_4$ ($T_N = 42$ K)$^{56}$ impurities. Temperature dependent NPD (Fig. 9) indicates that the sample orders AFM around 400 K. There are no additional magnetic transitions; no additional reflections or changes in the temperature behavior of the magnetic Bragg peaks were observed below 80 K, Fig. S12 (ESI†). Therefore, the high transition temperature near 375 K may stem from both the sample and possible impurity FeMn$_2$O$_4$ or isostructural Fe$_{1+x}$Mn$_{3-x}$O$_4$ ($0 < x < 1$). The small low temperature transitions can be attributed to impurities Fe$_{1+x}$Mn$_{2-x}$O$_4$ and Mn$_3$O$_4$. The above RT magnetic transition feature is reminiscent of those of Mn$_2$FeMoO$_6$ ($T_C = 337$ K),$^{29}$ and Mn$_2$FeReO$_6$ ($T_C = 520$ K).$^{30}$

The isothermal magnetization measured at 370 K (Fig. 7b) shows almost linear behavior above 50 Oe, and there is almost no hysteresis at this temperature. However, the magnetization measured at 300 and 5 K increased more abruptly at low field (below 2000 Oe) and hysteresis loops were observed at both temperatures. As the temperature decreases, the hysteresis loops enlarge, with larger remnant magnetization and coercivity (Fig. S13, ESI†). The overall maximum moment at 6 T is very small, which confirms the AFM ordering and possible FiM ordering from impurity Fe$_{1+x}$Mn$_{3-x}$O$_4$.

Magnetic structure

To understand the nature of the magnetic ordering, neutron diffraction data were recorded from 5 to 450 K. Compared to
the data collected at 450 K, additional magnetic Bragg reflections 021 at \( \sim 2.2 \) Å, 101 at \( \sim 4.2 \) Å, and 003 at \( \sim 3.6 \) Å were observed in NPD data collected at 5 K (Fig. 8 and Fig. S12, ESI†). These were indexed by a magnetic unit cell with the same dimensions as the nuclear unit cell. Magnetic intensity is observed for 00l reflections, indicating a significant component of the moments within the \( ab \) plane.

ISODISTORT\textsuperscript{15} was used to explore possible magnetic structures (Table S6, ESI†), and those with \( \Gamma \) modes predicted some intensity in the positions of the magnetic Bragg reflections. The data is best fit with the cation disordered (\( R3\bar{c} \)) nuclear structure and a \( P \bar{I} \) magnetic unit cell (Fig. S14, \( a_{mag} = b_{mag} = a_{mag} = \approx 5.48\) Å; \( c_{mag} = 101\) Å, 003); with magnetic moments in-plane described \( \Gamma_3 \) modes, and an additional out-of-plane (AFM) component described by a \( \Gamma_1 \) mode. This low symmetry magnetic model allows four independent in-plane magnetic \( \Gamma_3 \) modes that are highly correlated in analysis using powder diffraction data, since powder data are not sensitive to the in-plane spin direction.

The best fit was obtained with \( P \bar{I} \) magnetic model, with two in-plane \( \Gamma_3 \) modes (with constraints to give modes of opposite sign) and one mode (\( \Gamma_3 \), \( E^\ast \ 2(a) \)) constrained to be \( 1/\sqrt{2} \) in magnitude smaller than the other (\( \Gamma_3 \), \( E^\ast \ 1(a) \)). This gives a collinear AFM magnetic model with moments antiparallel and oriented along [120]. This constrained model gives an equivalent fit to the unconstrained model (\( R_{wp} \) values for the two models are identical to two decimal places), and gives equal moments on each site as expected for this cation-disordered semiconducting oxide (and avoids high levels of correlation for the unconstrained models). The fit is improved noticeably (\( R_{wp} \) decreased by \( \sim 1\% \)) if the out-of-plane (AFM) \( \Gamma_1 \) mode is also included, allowing the moments to cant out of the \( ab \) plane. The combination of in-plane AFM \( \Gamma_3 \) modes (Fig. S15a, ESI†) and an out-of-plane AFM \( \Gamma_3 \) mode (Fig. S15b, ESI†) give the resulting AFM structure (Fig. 9a).

The components of the moments along the \( P \bar{I} \) magnetic unit cell are \( a = \pm 1.256(5) \mu_B \), \( b = \pm 1.256(5) \mu_B \), \( c = \pm 1.59(1) \mu_B \). This is equivalent to components along Cartesian axes of \( \mu_x = \pm 2.618(5) \mu_B \), \( \mu_y = \pm 1.512(3) \mu_B \), \( \mu_z = \pm 1.340(8) \mu_B \), giving an overall in-plane moment \( \mu_{xy} = 3.023(6) \mu_B \) and an overall moment of \( 3.307(7) \mu_B \) per site at 5 K. The resulting ordered moment (\( 3.3 \mu_B \) at 5 K) in MnFe\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} is very close to that expected for a mixed \( \text{Mn}^{2\text{+}}/\text{Mn}^{3\text{+}}/\text{Fe}^{3\text{+}}/\text{Ru}^{4\text{+}} \) site (\( 3.28 \mu_B \)). We note that this combination of the two AFM irreducible representations (irreps) \( \Gamma_3 \) and \( \Gamma_1 \) allows the \( \Gamma_2 \), irrep, which describes a FM component along [001]. Although analysis of our diffraction data does not indicate the presence of this out-of-plane FM component, we cannot exclude its presence as a secondary order parameter. However, we note that the hysteresis loop measured for MnFe\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} (Fig. 7b) suggests that any such component must be very small. Details from the multibank refinement at 5 K are given in Tables S4, S5 and refinement profiles are shown in Fig. 8 and Fig. S16 (ESI†).

The collinear AFM magnetic structure described here for MnFe\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} (Fig. 9) is similar to the collinear FiM structure reported for Mn\textsubscript{2}FeSb\textsubscript{6} (II-type, \( R3 \)) at 150 K, in which Mn and Fe sublattices are coupled AFM in the \( ab \) plane.\textsuperscript{57} The absence of FiM in corundum MnFe\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} is due to cation disorder and the absence of two AF-coupled sublattices. AFM interactions also exist in related NTO-type (\( R3 \)) materials such as Ni\textsubscript{3}TeO\textsubscript{6}, Mn\textsubscript{2}FeWO\textsubscript{6}, Mn\textsubscript{2}FeMoO\textsubscript{6}, and Mn\textsubscript{2}MnWO\textsubscript{6}, which show more complicated magnetic structures as a result of three ordered metal sites leading to competition between the different magnetic sublattices.\textsuperscript{29,58–60} Ni\textsubscript{3}TeO\textsubscript{6} exhibits a collinear AFM structure with all Ni moments along the \( c \) axis with FM honeycomb planes.\textsuperscript{58,59} The magnetic structure of Mn\textsubscript{2}FeWO\textsubscript{6} is a collinear spin arrangement with Mn2 spins antiparallel to both Mn1 and Fe spins. In Mn\textsubscript{2}FeMoO\textsubscript{6}, a more complicated FiM is revealed with all spins parallel to the \( c \) axis but antiparallel between sub-lattices Fe, Mn1, and Mo. Mn\textsubscript{2}MnWO\textsubscript{6}, however, adopts a non-collinear AFM magnetic structure due to frustration.\textsuperscript{60} The canting of spins arrangement in MnFe\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} is also observed in the double perovskite Mn\textsubscript{3}FeReO\textsubscript{6}, where an AFM Mn lattice and a FiM Fe and Re lattice are cant rotated away from the \( c \) axis.\textsuperscript{30}
101 and 003, which smoothly decreases (Fig. S12, ESI†) as the temperature is warmed up from 5 to 445 K. Magnetic Bragg reflections are clearly observed in data collected at 395 K, but are absent at 420 K, which indicates that the transition temperature of the sample is around 400 K. Sequential refinements were then carried out with the 122° bank data which show that the moment per cation site decreases smoothly from 3.46(2) \( \mu_B \) per site at 5 K to 0.70(3) \( \mu_B \) per site at 395 K (Fig. 9b). The refined magnetic moments are close to zero at 425 and 445 K, at which no magnetic Bragg reflections are observed (Fig. S12a, ESI†). The slight change of slope in parameters derived from sequential Rietveld refinements (magnetic moment as a function of temperature, Fig. 9b; relative intensities of magnetic-only reflections, Fig. S12, ESI†) reflects the change in heating sequence and sample environment: NPD data were first collected on heating the sample from 300 K to 450 K in vacuum before the sample was cooled down to 2 K, with 150 mBar at RT of He as exchange gas, and further data collected on heating back up to 300 K.

Mössbauer spectroscopy

The experimental Mössbauer spectra of the \( \text{MnFe}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) absorber, show that at 97 K all Fe ions are equivalent, since all are in magnetic saturation (Fig. 10). The high field in saturation (490 KGAuss) proves that the Fe ions are all trivalent \((S = 5/2)\), which is in agreement with XANES results. The low temperature spectra \((T < 250 \text{ K})\) were fitted with absorption lines of Lorentzian lineshape, the absorption lines are slightly broadened as the temperature increases.

However, when the temperature is raised to above 250 K, the absorption line widths start to broaden to a large extent, as in the spectrum at 300 K (Fig. 10), and are most evident at 350 K (Fig. S17, ESI†). The 373 K spectrum contains a mixture of a sharp paramagnetic quadrupole doublet and a smeared magnetic subspectrum, which indicates that the magnetic phase transition is not sharp (Fig. 10). At 386 K, an almost pure quadrupole doublet with a tiny magnetic field (4 KGAuss) is still present. These results indicate that the Fe sublattice is already paramagnetic above \( T_C(\text{Fe}) = 390 \text{ K} \), consistent with the appearance of magnetic Bragg peaks in NPD data collected below 395 K.

The spectra at 300 and 350 K require the presence of a large hyperfine field distribution, indicating that the Fe ions are not all equivalent magnetically, and the spectra resemble the features of a spin glass structure, or spin fluctuation rates in the magnetic hyperfine splitting window. The temperature dependence of the average hyperfine field \((HF)\) is displayed in Fig. 11, in terms of \( HF(T)/HF(0) \), where \( T_C = 390 \text{ K} \) and \( HF(0) = 490 \text{ KGAuss} \). The fact that the temperature dependence of the experimental magnetic hyperfine field is quite different from a pure magnetic Fe\(^{3+}\) sublattice, indicates that Fe ions interact also with the Mn sublattice and possibly also with the magnetic Ru, present also in the Fe sublattice. The broadening phenomena in the Mössbauer spectra strongly support the disordered model of Fe/Mn/Ru in corundum \( \text{MnFe}_{0.5}\text{Ru}_{0.5}\text{O}_3 \).

Electrical conductivity

The resistivity was measured on a pellet as a function of temperature between 5–300 K without applying a magnetic field (Fig. 12). Above 40 K, the resistivity decreases as the temperature increases, indicating semiconducting behavior.
The high temperature data between 300 and 107 K can be linearly fitted with \( \ln \rho \) versus \( 1/T^{1/4} \), which agrees with the Mott’s variable range hopping (VRH) conduction mechanism:

\[
\rho = \rho_0 \exp \left( \frac{T_0}{T} \right)^{1/4} \]

The fitting yields the parameters \( \rho_0 \) and \( T_0 \) equal to 4.14 \( \times \) \( 10^{-3} \) \( \Omega \) cm and 2.03 \( \times \) \( 10^6 \) K, respectively. The high temperature resistivity behavior and the fitting results are similar to Mn\(_2\)FeMoO\(_6\), a FM VRH semiconductor. The abnormal feature around 40 K may be related to the magnetic anomaly seen in Fig. 7.

DFT calculations

Two possible crystal structures with \( \alpha\)-Fe\(_2\)O\(_3\) type, or LN-type were discussed in the diffraction analysis. To investigate which type of crystal structure is more stable energetically, DFT was utilized. The VCA method was employed to take into account the structural disorder. In the VCA calculations, Ru disorder was assumed not to be critical to determine the stable crystal structure. Hence, Ru disorder was not considered and was simply replaced by Fe and only the Mn/Fe disorder was taken into account in the calculations. As a result, the crystal structure with \( \alpha\)-Fe\(_2\)O\(_3\)-type has lower energy than that with LN-type with an energy difference of 10.58 eV per atom. Therefore, even if Ru disorder would be considered in the VCA calculations, it would be unlikely to reverse the energy order, due to the significant energy difference, in agreement with experimental results.

Fig. 13 shows the density of states for antiferromagnetic ordering in the \( \alpha\)-Fe\(_2\)O\(_3\) type crystal structure obtained from GGA+U calculations. The AFM order was adopted from Fig. 9. The GGA+U calculation with AFM order clearly shows a band gap of 1.91 eV, which supports the semiconducting behavior observed in the experiments. The magnetic structure with \( \alpha\)-Fe\(_2\)O\(_3\)-type possesses two symmetrically different Fe sites and the local moments of each Fe site are 4.06, 4.07 \( \mu_B \) per Fe, respectively. A weak ferromagnetic component with magnitude of 0.004 \( \mu_B \) per Fe is observed in the DFT calculation, which is consistent with the experiment. In Fig. 13, the red broken line corresponds to the partial DOS for Fe-I 3d orbital. The partial DOS for Fe-II has the opposite occupancy. Therefore, both Fe-I and Fe-II show Fe\(^{3+}\) (d\(^5\)) with high spin configuration. In comparing the total energies of AFM and FM states in the GGA+U calculations, the AFM state has a lower energy by 0.098 eV per atom from that of the FM state.

Comparison of MnFe\(_{0.5}\)Ru\(_{0.5}\)O\(_3\) and related Mn-BB\(^{\prime}\)O\(_6\)

To date, eight transition-metal-only A\(_2\)BB\(^{\prime}\)O\(_6\) (A = Mn, B = Fe, Mn, B\(^{\prime}\) = Nb, Ta, W, Re) oxides have been successfully prepared under high pressure (5–8 GPa) and high temperature (1573–1875 K) (Table 3). While Mn\(_2\)MnReO\(_6\) and Mn\(_2\)FeReO\(_6\) form highly distorted DP [AO\(_6\) with rock salt ordering of corner-linked BO\(_6\) and B\(^{\prime}\)O\(_6\)] other A\(_2\)BB\(^{\prime}\)O\(_6\) oxides form cation-ordered, non-centrosymmetric corundum derivatives, such as the LN and NTO
Table 3 Comparison of transition-metal-only A2BB’O6

<table>
<thead>
<tr>
<th>Compound</th>
<th>Synthesis</th>
<th>A, d^0, r^2</th>
<th>B, d^0, r</th>
<th>B’, d^0, r</th>
<th>Structure</th>
<th>T_c/T_N, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn2FeNbO6</td>
<td>MnO + Fe2O3 + Nb2O3, 1573 K, 7 GPa</td>
<td>Mn^{2+}, 3d^0 0.83 Å</td>
<td>Fe^{3+}, 3d^0 0.64 Å</td>
<td>Nb^{5+}, 4d^0 0.64 Å</td>
<td>LN, R3c</td>
<td>T_c ~ 90, T_N ~ 200</td>
</tr>
<tr>
<td>Mn2FeTaO6</td>
<td>MnO + Fe2O3 + Ta2O3, 1573 K, 7 GPa</td>
<td>Mn^{2+}, 3d^0 0.83 Å</td>
<td>Fe^{3+}, 3d^0 0.64 Å</td>
<td>Ta^{5+}, 5d^0 0.64 Å</td>
<td>LN, R3c</td>
<td>T_c ~ 80, T_N ~ 200</td>
</tr>
<tr>
<td>Mn2FeWO6</td>
<td>MnO + Fe2O3 + WO3, 1673 K, 8 GPa</td>
<td>Mn^{2+}, 3d^0 0.83 Å</td>
<td>Fe^{3+}, 3d^0 0.78 Å</td>
<td>W^{6+}, 5d^0 0.60 Å</td>
<td>NTO, R3</td>
<td>T_c ~ 75, T_N ~ 90</td>
</tr>
<tr>
<td>Mn2FeMoO6</td>
<td>MnO + Fe2O3 + MoO3, 1673 K, 8 GPa</td>
<td>Mn^{2+}, 3d^0 0.83 Å</td>
<td>Fe^{3+}, 3d^0 0.64 Å</td>
<td>Mo^{5+}, 4d^0 0.61 Å</td>
<td>NTO, R3</td>
<td>T_c ~ 337</td>
</tr>
<tr>
<td>Mn2FeReO6</td>
<td>MnO + Fe2O3 + ReO3, 1673 K, 8 GPa</td>
<td>Mn^{2+}, 3d^0 0.83 Å</td>
<td>Fe^{3+}, 3d^0 0.64 Å</td>
<td>Re^{5+}, 4d^0 0.61 Å</td>
<td>NTO, R3</td>
<td>T_c ~ 194</td>
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<tr>
<td>Mn2FeRuO6</td>
<td>MnO + Fe2O3 + RuO3, 1673 K, 8 GPa</td>
<td>Mn^{2+}, 3d^0 0.83 Å</td>
<td>Fe^{3+}, 3d^0 0.64 Å</td>
<td>Ru^{5+}, 4d^0 0.61 Å</td>
<td>NTO, R3</td>
<td>T_c ~ 520</td>
</tr>
<tr>
<td>Mn2FeMoO6</td>
<td>MnO + Fe2O3 + MoO3, 1673 K, 8 GPa</td>
<td>Mn^{2+}, 3d^0 0.83 Å</td>
<td>Fe^{3+}, 3d^0 0.64 Å</td>
<td>Mo^{5+}, 4d^0 0.61 Å</td>
<td>NTO, R3</td>
<td>T_c ~ 400</td>
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<tr>
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<td>MnO + Fe2O3 + ReO3, 1673 K, 8 GPa</td>
<td>Mn^{2+}, 3d^0 0.83 Å</td>
<td>Fe^{3+}, 3d^0 0.64 Å</td>
<td>Re^{5+}, 4d^0 0.61 Å</td>
<td>NTO, R3</td>
<td>T_c ~ 58</td>
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<tr>
<td>Mn2FeRuO6</td>
<td>MnO + Fe2O3 + RuO3, 1673 K, 8 Gpa</td>
<td>Mn^{2+}, 3d^0 0.83 Å</td>
<td>Fe^{3+}, 3d^0 0.64 Å</td>
<td>Ru^{5+}, 4d^0 0.61 Å</td>
<td>NTO, R3</td>
<td>T_c ~ 110</td>
</tr>
</tbody>
</table>

phases (with face- and corner-linked six-coordinated AO6, BO6 and B’O6 octahedra). In Mn2FeNbO6 and Mn2FeTaO6, the B and B’ sites disorder due to the small size difference between Fe^{3+} and Nb^{5+} ions (0.005 Å), but the overall structure of ordering of large Mn^{2+} ions on the A sites, is still polar LN-type which is stabilized by the second-order Jahn–Teller effect of d^0 Nb^{5+}/Ta^{3+} ions. Mn2FeWO6 and Mn2MnWO6 crystallize in the NTO-type structure with ordered B and B’ sites due to the large charge difference (4) and size difference (0.23 Å) between Fe^{2+} and W^{6+} ions. Although the charge difference (2) and size difference (0.035 Å) between Fe^{3+} and Mo^{5+} are small, Mn2FeMoO6 surprisingly also stabilizes in the NTO-type structure, which is attributed to FiM magnetic configuration that leads to the lowest energy state.

Mn2Fe0.5Ru0.5O3, as the mixed-valence of Mn^{2+}/3+, Fe^{3+} and Ru^{3+}/4+. The mixed-valence is thought to arise due to the small size and charge difference (0) electrons at the B sites due to the large charge difference (4) and size difference (0.23 Å) between Fe^{2+} and W^{6+} ions. Although the charge difference (2) and size difference (0.035 Å) between Fe^{3+} and Mo^{5+} are small, Mn2FeMoO6 surprisingly also stabilizes in the NTO-type structure, which is attributed to FiM magnetic configuration that leads to the lowest energy state.

Conclusions

MnFe0.5Ru0.5O3 is the first example of a cation-disordered corundum-derived oxide in the transition-metal-only A2BB’O6 series, which is synthesized by high-pressure and high-temperature. X-ray absorption K- and L-edges spectroscopy reveal that Mn2FeB0.5Ru0.5O3 contains Mn^{2+}, Fe^{3+} and Ru^{4+} formal oxidation states. The similar cation sizes and charges of metal ions provide a smaller driving force for ordering than in related systems containing small and highly charged B/B’ ions along with a high content of the large A-site Mn^{2+} ion. This is reflected in the unit cell parameters and bond lengths, with a much smaller in-plane parameter (and unit cell volume) and shorter Mn–O bond lengths for MnFe0.5Ru0.5O3 compared with ordered analogues such as Mn2FeB0.5Ru0.5O3, with shorter Mn–O bond lengths for Mn2FeB0.5Ru0.5O3 compared with ordered analogues such as Mn2FeB0.5Ru0.5O3, and shorter Mn–O bond lengths for Mn2FeB0.5Ru0.5O3.

The magnetic properties of MnFe0.5Ru0.5O3 are different from those reported for Mn2FeB0.5Ru0.5O3. Mn2FeB0.5Ru0.5O3 shows clear AFM ordering below 75–90 K, with weak FM ~ 210 K for B’ = Nb^{5+}, Ta^{3+}, W^{6+}, and Mn2FeMoO6 and Mn2FeReO6 exhibit FiM ordering above RT. The introduction of more d^0 (n > 0) electrons at the B’-site of Mn2FeB0.5Ru0.5O3 (B’ = Mo^{5+}, Re^{5+}) changes the AFM to FiM ordering and also increases the ordering temperature dramatically. The ideal Mn2FeB0.5Ru0.5O3 with an ordered polar structure is expected to show FM.
an ordering temperature above RT, MnFe$_{0.5}$Ru$_{0.5}$O$_3$ may be a potential candidate for spintronic applications.

Conflicts of interest

There are no conflicts to declare.

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References


