THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Complex Ferrimagnetism and Magnetoresistance Switching in Ca-Based Double Double and Triple Double Perovskites

Citation for published version:

McNally, GM, Arevalo-Lopez, AM, Kearins, P, Orlandi, F, Manuel, P & Attfield, JP 2017, 'Complex Ferrimagnetism and Magnetoresistance Switching in Ca-Based Double Double and Triple Double Perovskites', *Chemistry of Materials*, vol. 29, no. 20, pp. 8870-8874.
<https://doi.org/10.1021/acs.chemmater.7b03556>

Digital Object Identifier (DOI):

[10.1021/acs.chemmater.7b03556](https://doi.org/10.1021/acs.chemmater.7b03556)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Chemistry of Materials

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

Complex Ferrimagnetism and Magnetoresistance Switching in Ca-based Double Double and Triple Double Perovskites

Graham M. McNally,[†] Ángel M. Arévalo-López,[†] Padraig Kearins,[†] Fabio Orlandi,[‡] Pascal Manuel[‡] and J. Paul Attfield^{*†}

[†]Centre for Science at Extreme Conditions (CSEC) and School of Chemistry, University of Edinburgh, Peter Guthrie Tait Road, Edinburgh EH9 3FD (UK)

[‡]STFC Rutherford Appleton Lab, ISIS Facility, Harwell Science and Innovation Campus, Didcot, OX11 0QX (UK)

ABSTRACT: Cation ordering in ABO_3 perovskites can lead to interesting and useful phenomena such as ferrimagnetism and high magnetoresistance by spin polarized conduction in Sr_2FeMoO_6 . We have used high pressures and temperatures to synthesize the cation ordered $AA'B'B'O_6$ perovskites $CaMnFeReO_6$, $CaMnMnReO_6$, and $Ca(Mn_{0.5}Cu_{0.5})FeReO_6$. These have columnar A/A' and rocksalt B/B' cation orders, as found in the recently discovered double double perovskite $MnNdMnSbO_6$, and partial Mn/Cu order over tetrahedral and square planar A' sites in $Ca(Mn_{0.5}Cu_{0.5})FeReO_6$ demonstrates that 'triple double' cation order is possible. Neutron diffraction reveals complex ferrimagnetic orders in all three materials; $CaMnFeReO_6$ and $Ca(Mn_{0.5}Cu_{0.5})FeReO_6$ have large room temperature magnetizations with low temperature switching of magnetoresistance in the latter material, and $CaMnMnReO_6$ displays a high coercivity of 1.3 T at low temperatures.

The ABX_3 perovskite structure is notable for giving rise to many materials with outstanding properties, and for the ability to accommodate many structural variations through cation order.¹ In double perovskites of the form $A_2BB'O_6$,² rocksalt order of 3d large spin B cations with small spin 4d or 5d B' cations can result in strong ferrimagnetism and half metallicity, such as in Sr_2FeMoO_6 (SFMO).³ This has a high Curie temperature ($T_C = 410$ K) and spin polarized conduction resulting in large, low-field tunnelling magnetoresistance (TMR, where magnetoresistance, $MR = [\rho(H) - \rho(0)] / \rho(0)$ for resistivities ρ measured in magnetic field H and at $H = 0$). Substitution of other cations such as A-site Ca or Ba and B-site Mo or Re gives rise to materials with similar properties.⁴⁻⁷

Recent studies have shown that high pressure synthesis can be used to stabilize small magnetic transition metal ions like Mn^{2+} at the A-sites of perovskites, in place of large, non-magnetic cations like Ca^{2+} and Sr^{2+} .⁸⁻¹⁰ This introduces a source of A-site magnetism that may change or improve the functionality of these materials. The double perovskite Mn_2FeReO_6 has similar room temperature ferrimagnetism to SFMO, but with enhanced magnetization and an unusual MR switching transition at low temperatures (~ 75 K), where MR switches from negative to positive.^{11,12} Mn_2FeSbO_6 and Mn_2MnReO_6 both have complex low temperature antiferromagnetic orders.¹³⁻¹⁵

Figure 1 – The double/triple double perovskite structure of $CaABReO_6$ materials in space group $P4_2/n$. Large Ca and small A_T/A_S cations are ordered in columns, with the latter alternating between tetrahedral A_T and square planar A_S sites as shown in the upper right view. BO_6 and ReO_6 octahedra order in a rocksalt arrangement and are tilted in system $a^+a^+c^-$ following Glazer notation.¹⁶

Double perovskites have also been reported in the form $AA'B_2O_6$ with columnar A-site order such as $CaATi_2O_6$ ($A = Mn, Fe$)^{17,18} and in addition, it was found that a new 'double double' cation order is stabilized in the series $MnRMnSbO_6$ ($R = La, Pr, Nd$ and Sm), with 1:1 columnar A-site and rocksalt B-site orders.¹⁹ Here we report that this structural type is surprisingly versatile, as $CaABReO_6$ type materials $CaMnFeReO_6$ and

CaMnMnReO₆ synthesized at high pressure have the same double double perovskite structure (space group $P4_2/n$, Fig. 1), and that a further partial ‘triple double’ cation order of three cations over A-sites and two over B-sites is achieved in Ca(Mn_{0.5}Cu_{0.5})FeReO₆. These materials all have different complex ferrimagnetic orders with up to four spin sublattices present.

Polycrystalline ~15 mg samples of CaMnFeReO₆, CaMnMnReO₆, and Ca(Mn_{0.5}Cu_{0.5})FeReO₆ were prepared by high pressure-temperature synthesis at 10 GPa and 1673 K in a Walker-type multianvil module. Variable temperature powder neutron diffraction (PND) data were collected from 60 mg aggregates of several samples of each material using the WISH diffractometer at the ISIS Neutron Facility. Powder synchrotron X-ray diffraction (PSXRD) data were also collected for CaMnFeReO₆ at the ALBA facility, and a small crystal of Ca(Mn_{0.5}Cu_{0.5})FeReO₆ was analyzed by single crystal X-ray diffraction (SCXRD). Magnetic properties were characterized by magnetization measurements up to temperatures of 650 K in fields up to 7 T. Experimental details are outlined in Supporting Information.

CaMnFeReO₆ (CMFR) was previously reported to be a semiconducting ferrimagnet with $T_C = 500$ K, saturated magnetization $\mu_{\text{sat}} = 4.3 \mu_B$ per formula unit (f.u.) and negative MR down to -32 % at 20 K and 7 T.¹¹ This material was originally proposed to be a 1:1 solid solution between the double perovskites Ca₂FeReO₆ and Mn₂FeReO₆, both of which have a monoclinically distorted $P2_1/n$ structure, with Ca/Mn disordered over the A-sites. However, we find that this model gives very poor fits to our PND data, whereas the $P4_2/n$ double double perovskite structure accounts for the neutron intensities well (Fig. 2a). Hence CaMnFeReO₆ is identified as the first Ca-based material to adopt the MnRMnSbO₆ type double double perovskite structure, and this discovery has inspired the synthesis of the other materials reported here. Structural and magnetic parameters for CaMnFeReO₆ are summarized in Table 1.

Table 1 – Summary of structural and magnetic parameters for the three CaABReO₆ double/triple double perovskites in this study.

		CMMR	CMFR	CMCFR
$a / \text{\AA}$		7.7136(7)	7.6311(5)	7.618(1)
$c / \text{\AA}$		7.7430(8)	7.6266(7)	7.629(1)
B-antisite / %		4.0(1)	3.0(1) †	1.3(5) †
Occ. A _S / %	PND	100 Mn	84(3) Mn/16 Fe	60(1) Cu/40 Mn
	SCXRD	-	-	61(4) Cu/39 Mn
Occ. A _T / %	PND	100 Mn	92(3) Mn/8 Fe	64(1) Mn/36 Cu
	SCXRD	-	-	77(4) Mn/23 Cu
BVS	A [‡]	1.7	1.6	1.8
	B	2.3	3.3	2.7
	Re	4.9	4.2	4.9
T_B / K		120	500	560
T_A / K		100	70	160
m_{sat} / μ_B (MvH)		3.4	4.3	4.8
m_{sat} / μ_B (NPD)		2.70(6)	3.63(1)	4.78(4)
$H_C / \mu_0 \text{T}$		1.3	0.04	0.06

Lattice parameters and Bond Valence Sums BVS at 300 K, occupancies of A_S and A_T sites. BVS and B-antisite disorder are from refinements of PND data unless stated otherwise.

†B-antisite disorder for CMFR obtained from PSXRD and by SCXRD for CMCFR. ‡Mean BVS for A_T and A_S sites.

Figure 2 – Rietveld fits to PND data at 2 K from the WISH diffractometer at the ISIS Neutron Facility (average of banks 2 and 9). The major phase (nuclear and magnetic) in each pattern is represented by magenta tick marks, with the minor impurity phases represented by green tick marks. Significant magnetic intensities are marked by "m". (a) CaMnFeReO₆ and (b) Ca(Mn_{0.5}Cu_{0.5})FeReO₆ both show MnFe₃O₅ as a magnetic impurity,²⁰ fit as an intensity matching le Bail phase. (c) CaMnMnReO₆ with an MnO impurity (3.6(2)%).

There is a very high degree of B cation order, with only 3.0(1)% Fe/Re antisite disorder obtained by PSXRD structure refinement. Ca²⁺ occupies the 10-coordinate A-sites and Mn²⁺ predominantly occupies the 4-coordinate A_T and A_S sites, although some Fe occupancy (8(3)% and 16(3)%, respectively) was found by PND, yielding a structural formula of Ca(Mn_{0.88}Fe_{0.12})FeReO₆ and allowing a small amount (<1 %) of MnFe₃O₅ to be detected. PND shows that at 300 K, CaMnFeReO₆ has magnetic order of only Fe³⁺ (3d⁵, $S = 5/2$) and Re⁵⁺ (5d², $S = 1$) spins in a collinear G-type ferrimagnetic arrangement like that found in SFMO and similar double perovskites. Magnetization measurements in Fig. 4a show that this order occurs below $T_B = 500$ K (we write the Curie temperature as $T_B = 500$ K to emphasize that only the B-site spins order below this transition) and a second transition is observed at low temperatures. This coincides with the appearance of new magnetic peaks in PND data below $T_A = 70$ K, and these are fitted by a second ferrimagnetic order of up A_T

and down A_S site Mn^{2+} ($3d^5$, $S = 5/2$) spins as shown in Fig. 3a. The magnitudes of A_T and A_S moments were found to be very similar and were constrained to be equal. Temperature variations of the refined moments are shown in Fig. 4a, the net moment of $3.63(1) \mu_B$ f.u.⁻¹ at 2 K agrees well with the saturated magnetization of $4.3 \mu_B$ f.u.⁻¹ from the M - H hysteresis measurement at 10 K in Fig. 3c. A-site spin order has a magnetoelastic effect on the lattice as the c -axis thermal expansion changes from negative to positive on warming through the transition, as shown in the inset to Fig. 4a. The ferrimagnetic A-site order of Mn^{2+} spins appears to reinforce the Fe/Re ferrimagnetic order, leading to a large negative tunnelling MR of -32% at 20 K and 7 T.¹¹ This is in contrast to the double perovskite Mn_2FeReO_6 where frustration between antiferromagnetic Mn-spin order and the Fe/Re ferrimagnetism leads to a low temperature switch from negative to positive MR.^{11,12}

The presence of distinct tetrahedral A_T and square planar A_S -sites within the double double perovskite structure in Fig. 1 suggests that two different transition metal cations might be ordered over these positions, and hence $Ca(Mn_{0.5}Cu_{0.5})FeReO_6$ (CMCFR) was investigated with the aim of ordering Mn^{2+}/Cu^{2+} cations at A_T/A_S -sites based on the stability of Cu^{2+} in square planar coordination. Single crystal structural analysis confirmed that this material has the $P4_2/n$ structure with a high degree of B-site Fe/Re order and only Ca at the Ca site. Refinements of Cu/Mn occupancies (Table 1) over square planar and tetrahedral sites using PND and SCXRD show that a partial order is achieved, with 60% Cu at A_S -sites in both analyses and 77% occupancy of Mn at A_T by SCXRD, the difference between A_T occupancy by SCXRD and PND likely indicates that a higher degree of order is promoted during crystal growth. Although the degree of ordering is small, it does verify the principle that two metals may be ordered over the A_T/A_S -sites of the $P4_2/n$ structure to generate ‘triple double’ perovskites, where three and two cations are respectively ordered over the A and B-sites of the ABO_3 lattice. It is notable that four different transition metals; Mn, Fe, Cu and Re; as well as Ca are at least partially ordered in the structure of $Ca(Mn_{0.5}Cu_{0.5})FeReO_6$. As in CMFR, a trace of $MnFe_3O_5$ (<1%) is found by PND.

The magnetic properties of $Ca(Mn_{0.5}Cu_{0.5})FeReO_6$ (CMCFR) are similar to those described above for $CaMnFeReO_6$ (CMFR), as shown in Table 1 and Fig. 3a and 4b. CMCFR has higher temperatures for Fe/Re spin order at $T_B = 560$ K, and at $T_A = 160$ K for A-site magnetic order. Weaker magnetoelastic effects at T_A are seen in CMCFR than in CMFR, probably due to dilution and disorder effects from replacing $S = 5/2$ Mn^{2+} by $S = 1/2$ Cu^{2+} . No significant magnetic moment was found at the square planar A_S sites in initial refinements, suggesting that Mn/Cu disorder frustrates spin order at this site, and so the moment was fixed to zero. The 2 K A_T moment refines to $2.70(6) \mu_B$ which is close to the ideal value of $3.2 \mu_B$ for alignment of 64% Mn^{2+} $S = 5/2$ spins. The predicted m_{sat} of $4.8 \mu_B$ from the 2 K neutron refinement agrees perfectly with the measured value from magnetization measurements. This is second only to the value of $5.0 \mu_B$ for Mn_2FeReO_6

among double perovskite materials with rocksalt order of transition metal cations.¹¹

Figure 3 – (a) The spin structure of $CaMnFeReO_6$, with $k = (0\ 0\ 0)$ propagation vector, showing ferrimagnetic G-type ordering of the Fe/Re sublattice along the c -axis and the collinear antiferromagnetic Mn A-site sublattice, with Mn_T orientating parallel to Fe and Mn_S antiparallel. $Ca(Mn_{0.5}Cu_{0.5})FeReO_6$ possesses a similar spin structure, however no moment on the A_S -site can be detected by NPD. (b) The spin structure of $CaMnMnReO_6$ also has $k = (0\ 0\ 0)$, with ferromagnetic A-site order and antiferromagnetic order of the Mn_B spins placed at 45° to the a, b -axes. Each successive plane has a $\pm 90^\circ$ rotation of the Mn_B spins around the c -axis. (c) Field dependence of the magnetization of $CaMnFeReO_6$ (CMFR), $CaMnMnReO_6$ (CMMR), and $Ca(Mn_{0.5}Cu_{0.5})FeReO_6$ (CMCFR) at various temperatures. (d) Resistivity in zero and 7 T fields and the derived MR for CMCFR.

The resistivity of a sintered pellet of CMCFR is $\sim 0.01 \Omega$ cm, indicative of metallic behavior, but with a small increase on cooling (equivalent to an activation energy of 3 meV) that is likely due to grain boundary re-

sistances (Fig. 3d). *MR* is positive at high temperatures, which is unusual in $A_2\text{FeReO}_6$ double perovskites, but begins to decrease below 70 K, before becoming negative below 40 K. This suggests that paramagnetic $\text{Mn}^{2+}/\text{Cu}^{2+}$ at A_T/A_S -sites promote spin-scattering of carriers that increases in applied field, with reduction of this effect below T_A enabling the negative TMR mechanism to dominate. Hence Cu-substitution into CMFR to give CMCFR promotes metallicity and leads to an increase in both ordering temperatures and saturated magnetisation.

Figure 4 – Magnetization versus temperature (field cooled, 5000 Oe) data of (a) CaMnFeReO_6 , (b) $\text{Ca}(\text{Mn}_{0.5}\text{Cu}_{0.5})\text{FeReO}_6$ and (c) CaMnMnReO_6 . Magnetic moments m are obtained from variable temperature PND. Combined total moments (m_{tot}) from A and B-sites for CaMnFeReO_6 and $\text{Ca}(\text{Mn}_{0.5}\text{Cu}_{0.5})\text{FeReO}_6$ (including Re moments) are shown, m_{AS} is zero for $\text{Ca}(\text{Mn}_{0.5}\text{Cu}_{0.5})\text{FeReO}_6$ and constrained to be

equal and opposite to m_{AT} for CaMnFeReO_6 . *Insets*: Thermal dependence of the lattice parameters a , c and $V^{1/3}$ for CaABReO_6 .

Fe^{3+} and Re^{5+} are present at the B-sites in the above materials, but the double perovskites $\text{Ca}_2\text{MnReO}_6^{21}$ and $\text{Mn}_2\text{MnReO}_6^{12}$ are found to have Mn^{2+} and Re^{6+} , so the composition CaMnMnReO_6 (CMMR) has been investigated to discover if the same charge configuration can be stabilized in the $P4_2/n$ double double perovskite arrangement. This phase was successfully synthesized with a small 3.6(2) % impurity of MnO and structure refinement against PND data reveals a high degree of cation order with 4.0(1)% of Mn/Re antisite disorder, and also 5.4(2)% Mn occupancy of the Ca site. The Bond Valence Sum (BVS)²² for B-site Mn confirms the $\text{Ca}^{2+}\text{Mn}^{2+}\text{Mn}^{2+}\text{Re}^{6+}\text{O}_6$ configuration, although there is little $\text{Re}^{5+}/\text{Re}^{6+}$ discrimination by BVS. Magnetic order in CaMnMnReO_6 is evidenced by an increase in magnetization below ~125 K, and two transitions were found from analysis of PND data at $T_B = 120$ K and $T_A = 100$ K (Fig. 4c). B-site spins lie in the *ab*-plane and successive antiferromagnetic layers are rotated by 90° to adjacent layers in the *c*-direction (Fig. 3b). PND also shows that the A-site Mn^{2+} square planar and tetrahedral moments order ferromagnetically parallel to the *c*-axis below $T_A = 100$ K. The perpendicular orientation of A-site to B-site moments shows that their orders are mutually frustrated. The net magnetization resulting from the A-site Mn^{2+} spins is predicted to be the refined A-site moment of $2.7 \mu_B \text{ f.u.}^{-1}$ which is comparable to the measured magnetization $3.4 \mu_B \text{ f.u.}^{-1}$ at 2 K and 7 T. *M-H* hysteresis loops for CaMnMnReO_6 in Fig. 3c show that a large coercive field develops at low temperatures, up to 1.3 T at 3 K. Similar behavior has been reported in some other Re based double perovskites, such as $\text{Sr}_{2-x}\text{Ca}_x\text{FeReO}_6$ which can show coercivity of up to 2 T that was attributed to magnetic anisotropy of Re^{5+} ions.⁶ However, in our CaABReO_6 double double perovskites the high coercivity is only observed for CMMR based on Re^{6+} , and not for the Re^{5+} materials CMFR and CMCFR. The difference most likely arises from electron delocalization in the latter spin-polarized ferrimagnetic materials, whereas CMMR has electron-localized Re^{6+} states. Coupling of magnetization to the lattice in CMMR is evidenced by magnetoelasticity below $T_B = 120$ K, similar to that of CMFR above.

The above results show that the recently-discovered $P4_2/n$ double double perovskite structure has a versatile chemistry as three different $\text{AA}'\text{BB}'\text{O}_6$ charge configurations are now exemplified by $\text{R}^{3+}\text{Mn}^{2+}\text{Mn}^{2+}\text{Sb}^{5+}\text{O}_6$,¹⁹ $\text{Ca}^{2+}\text{Mn}^{2+}\text{Fe}^{3+}\text{Re}^{5+}\text{O}_6$, and $\text{Ca}^{2+}\text{Mn}^{2+}\text{Mn}^{2+}\text{Re}^{6+}\text{O}_6$, with high degrees (>90%) of A/A' and B/B' cation ordering in all cases. In addition, this structure type offers the possibility of derived triple double perovskites by further order of two species over the tetrahedral and square planar sites within the A' cation column. This pattern of charge ordering was recently reported in RMn_3O_6 ($\text{R} = \text{Gd-Tm}$ and Y),²³ and the partial triple double order of five different cations is demonstrated here in $\text{Ca}(\text{Mn}_{0.5}\text{Cu}_{0.5})\text{FeReO}_6$.

This study also demonstrates that varied magnetic and electronic properties can be generated in double double perovskites, with all of the present materials showing separate spin ordering transitions for the A and B-site cations. CaMnFeReO_6 (CMFR) is remarkable as a 'double ferrimagnet' with ferrimagnetic order of antiparallel Fe and Re spins below $T_B = 500$ K, and a second ferrimagnetic order of opposed inequivalent tetrahedral and square planar Mn spins below $T_A = 70$ K. CMFR and $\text{Ca}(\text{Mn}_{0.5}\text{Cu}_{0.5})\text{FeReO}_6$ (CMCFR) preserve the ferrimagnetism and high Curie transition temperatures (500–600 K) of simple spin-polarized A_2FeReO_6 double perovskites ($A = \text{Ca}, \text{Sr}, \text{Ba}$), but enhance the saturated magnetization from $\sim 3 \mu_B$ up to $4.8 \mu_B$ in CMCFR. CMCFR is metallic with an unusual switch from positive to negative MR on cooling. CaMnMnReO_6 (CMMR) has very different magnetic order, with antiferromagnetism of B-site spins but ferromagnetic order in the A-site Mn columns. In conclusion, high pressure synthesis is likely to generate many further new materials in this double double, and even triple double, perovskite family, with notable magnetic or other physical properties.

ASSOCIATED CONTENT

Supporting Information.

Supporting information including tables of refined parameters are available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: j.p.attfield@ed.ac.uk

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We acknowledge EPSRC, the Royal Society and STFC for support and the provision of beam time at the ISIS Neutron Source. We also acknowledge the help of Dr. O. Vallcorba and Dr. C. Popescu during synchrotron X-ray beam time on BLo4-MSPD at ALBA.

REFERENCES

- King, G.; Woodward, P. M. Cation Ordering in Perovskites. *J. Mater. Chem.* **2010**, *20*, 5785.
- Vasala, S.; Karppinen, M. $\text{A}_2\text{BB}'\text{O}_6$ Perovskites: A Review. *Prog. Solid State Chem.* **2015**, *43*, 1–36.
- Kobayashi, K.-I.; Kimura, T.; Sawada, H.; Terakura, K.; Tokura, Y. Room-Temperature Magnetoresistance in an Oxide Material with an Ordered Double-Perovskite Structure. *Nature* **1998**, *395*, 677–680.
- Lue, C. S.; Kuo, Y.-K.; Horng, S.-N.; Peng, S. Y.; Cheng, C. Nuclear and Magnetic Structural Properties of $\text{Ba}_2\text{FeMoO}_6$. *Phys. Rev. B* **2005**, *71*, 64202.
- Michalik, J. M.; De Teresa, J. M.; Blasco, J.; Algarabel, P. A.; Ibarra, M. R.; Kapusta, C.; Zeitler, U. Temperature Dependence of Magnetization under High Fields in Re-Based Double Perovskites. *J. Phys. Condens. Matter* **2007**, *19*, 506206.
- Serrate, D.; De Teresa, J. M.; Algarabel, P. A.; Galibert, J.; Ritter, C.; Blasco, J.; Ibarra, M. R. Colossal Magnetoresistance in $\text{Ca}_x\text{Sr}_{2-x}\text{FeReO}_6$ Double Perovskites due to Field-Induced Phase Coexistence. *Phys. Rev. B* **2007**, *75*, 165109.
- Prellier, W.; Smolyaninova, V.; Biswas, A.; Galley, C.; Greene, R. L.; Ramesha, K.; Gopalakrishnan, J. Properties of the Ferrimagnetic Double Perovskites A_2FeReO_6 ($A = \text{Ba}$ and Ca). *J. Phys. Condens. Matter* **2000**, *12*, 965–973.
- Ovsyannikov, S. V.; Abakumov, A. M.; Tsirlin, A. A.; Schnelle, W.; Egoavil, R.; Verbeeck, J.; Van Tendeloo, G.; Glazyrin, K. V.; Hanfland, M.; Dubrovinsky, L. Perovskite-like Mn_2O_3 : A Path to New Manganites. *Angew. Chemie - Int. Ed.* **2013**, *52*, 1494–1498.
- Arévalo-López, A. M.; Attfield, J. P. Weak Ferromagnetism and Domain Effects in Multiferroic LiNbO_3 -Type MnTiO_3 . *Phys. Rev. B - Condens. Matter Mater. Phys.* **2013**, *88*, 1–6.
- Markkula, M.; Arevalo-Lopez, A. M.; Kusmartseva, A.; Rodgers, J. A.; Ritter, C.; Wu, H.; Attfield, J. P. Incommensurate Spin Order in the Metallic Perovskite MnVO_3 . *Phys. Rev. B - Condens. Matter Mater. Phys.* **2011**, *84*, 1–5.
- Arévalo-López, A. M.; McNally, G. M.; Attfield, J. P. Large Magnetization and Frustration Switching of Magnetoresistance in the Double-Perovskite Ferrimagnet $\text{Mn}_2\text{FeReO}_6$. *Angew. Chemie Int. Ed.* **2015**, *54*, 12074–12077.
- Li, M. R.; Retuerto, M.; Deng, Z.; Stephens, P. W.; Croft, M.; Huang, Q.; Wu, H.; Deng, X.; Kotliar, G.; Sánchez-Benítez, J.; Hadermann, J.; Walker, D.; Greenblatt, M. Giant Magnetoresistance in the Half-Metallic Double-Perovskite Ferrimagnet $\text{Mn}_2\text{FeReO}_6$. *Angew. Chemie - Int. Ed.* **2015**, *54*, 12069–12073.
- Dos Santos-García, A. J.; Ritter, C.; Solana-Madruga, E.; Sáez-Puche, R. Magnetic and Crystal Structure Determination of $\text{Mn}_2\text{FeSbO}_6$ Double Perovskite. *J. Phys. Condens. Matter* **2013**, *25*, 206004.
- Arévalo-López, A. M.; Stegmann, F.; Attfield, J. P. Competing Antiferromagnetic Orders in the Double Perovskite $\text{Mn}_2\text{MnReO}_6$ (Mn_3ReO_6). *Chem. Commun.* **2016**, *52*, 5558–5560.
- Li, M. R.; Hodges, J. P.; Retuerto, M.; Deng, Z.; Stephens, P. W.; Croft, M. C.; Deng, X.; Kotliar, G.; Sánchez-Benítez, J.; Walker, D.; Greenblatt, M. $\text{Mn}_2\text{MnReO}_6$: Synthesis and Magnetic Structure Determination of a New Transition-Metal-Only Double Perovskite Canted Antiferromagnet. *Chem. Mater.* **2016**, *28*, 3148–3158.
- Momma, K.; Izumi, F. VESTA 3 for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. *J. Appl. Crystallogr.* **2011**, *44*, 1272–1276.
- Leinenweber, K.; Parise, J. High-Pressure Synthesis and Crystal Structure of $\text{CaFeTi}_2\text{O}_6$, a New Perovskite Structure Type. *J. Solid State Chem.* **1995**, *114*, 277–281.
- Aimi, A.; Mori, D.; Hiraki, K.; Takahashi, T.; Shan, Y. J.; Shirako, Y.; Zhou, J.; Inaguma, Y. High-Pressure Synthesis of A -Site Ordered Double Perovskite $\text{CaMnTi}_2\text{O}_6$ and Ferroelectricity Driven by Coupling of A -Site Ordering and the Second-Order Jahn-Teller Effect. *Chem. Mater.* **2014**, *26*, 2601–2608.
- Solana-Madruga, E.; Arévalo-López, Á. M.; Dos Santos-García, A. J.; Urones-Garrote, E.; Ávila-Brandé, D.; Sáez-Puche, R.; Attfield, J. P. Double Double Cation Order in the High-Pressure Perovskites MnRMnSbO_6 . *Angew. Chemie - Int. Ed.* **2016**, *55*, 9340–9344.
- Hong, K. H.; McNally, G. M.; Coduri, M.; Attfield, J. P. Synthesis, Crystal Structure, and Magnetic Properties of MnFe_3O_5 . *Zeitschrift für Anorg. und Allg. Chemie* **2016**, *642*, 1355–1358.
- Corrêa, H. P. S.; Cavalcante, I. P.; Souza, D. O.; Santos, E. Z.; Orlando, M. T. D.; Belich, H.; Silva, F. J.; Medeiro, E. F.; Pires, J. M.; Passamai, J. L.; Martinez, L. G.; Rossi, J. L. Synthesis and Structural Characterization of the $\text{Ca}_2\text{MnReO}_6$ Double Perovskite. *Ceramica* **2010**, *56*, 193.
- Brown, I. D. *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*; Oxford University Press, 2002.

- (23) Zhang, L.; Matsushita, Y.; Yamaura, K.; Belik, A. A. Five-Fold Ordering in High-Pressure Perovskites RMn_3O_6 (R = Gd–Tm and Y). *Inorg. Chem.* **2017**, *56*, 5210–5218.

TOC FIGURE: