Double double cation order in the high pressure perovskites MnRMnSbO6

Citation for published version:

Digital Object Identifier (DOI):
10.1002/anie.201603526

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Peer reviewed version

Published In:
Angewandte Chemie International Edition

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.
Double double cation order in the high pressure perovskites MnRMnSbO₆


Abstract: Cation order in ABO₃ perovskites adds to their chemical variety and can lead to properties such as ferrimagnetism and magnetoresistance in Sr₂FeMoO₆. Through high pressure and temperature synthesis we have discovered a new type of ‘double double perovskite’ structure in the family MnRMnSbO₆ (R = La, Pr, Nd and Sm). This tetragonal structure has 1:1 order of cations on both A and B sites; A-site Mn²⁺ and R³⁺ cations are ordered in columns while Mn²⁺ and Sb⁵⁺ have rock salt order on the B sites. The A-site Mn²⁺ positions are further divided into tetrahedral and square planar environments. The MnRMnSbO₆ double double perovskites are ferrimagnetic at low temperatures with additional spin-reorientation transitions. The ordering direction of ferrimagnetic Mn spins in MnNdMnSbO₆ changes from parallel to [001] below Tc = 76 K to perpendicular below the reorientation transition at 42 K at which Nd moments also order. Smaller rare earths lead to conventional monoclinic double perovskites (MnR)MnSbO₆ for Eu and Gd, where Mn²⁺ and R³⁺ are disordered over the A sites while Mn²⁺ and Sb⁵⁺ have rock salt order at the B sites.

ABO₃ perovskite oxides are a versatile class of materials with many notable physical and chemical properties. Further important variation arises from cation ordering within the basic structural arrangement. 1:1 cation order in perovskites can occur in (100) layered, (110) columnar, or (111) rock salt arrangements, with cations ordered parallel to the cubic perovskite planes indicated. All three types have been observed for both A-cation ordered AA’B'O₆ and for B-ordered AA’BB’O₆ double perovskites,¹ amongst which layered AA’B’O₆ and rock salt AA’BB’O₆ orders are the most common.² However AA’BB’O₆ ‘double double perovskites’ with simultaneous 1:1 cation order at both A and B sites are much rarer, and only one of the nine possible combinations has previously been reported. This type combines the common (100) A-cation layered and (111) rock salt B-cation orders in several examples such as NaLaMgWO₆ and NaLaScNbO₆.³ ⁴ We report here a new double double perovskite type that has been discovered as part of an investigation of perovskites with Mn²⁺ ion at A sites.

A²⁺ cations in perovskites synthesised at ambient pressure are typically large, non-magnetic atoms such as A = Ca, Sr, Ba, Pb. However, materials with the smaller high spin Mn²⁺ ion at A sites have recently been synthesised at high pressure and temperature conditions. This may introduce additional magnetic functionality as found in MnV₂O₇ perovskite which is metallic due to itinerancy of the V ³⁺ 3d² states as in CaV₂O₇ and SrV₂O₇, but also has a coexisting helimagnetic order of localised S = 5/2 Mn²⁺ spins.⁵ Several Mn₂BB’O₆ double perovskites have also been synthesised at high pressures.⁶ ⁷ Mn₆FeSbO₁₆ has a low temperature incommensurate antiferromagnetic Mn spin order.⁸ Mn₆FeReO₁₆ has a high Curie temperature of 520 K and similar ferrimagnetic and spin-polarised conducting properties to the much-studied magnetoresistive material Sr₂FeMoO₆, but also shows a novel switch from negative to large positive magnetoresistances at low temperatures driven by Mn²⁺ spin ordering.⁹ ¹⁰ In contrast, Mn₆MnReO₁₆ (Mn₆ReO₁₆) shows successive antiferromagnetic ordering transitions for Re and Mn spins at 99 and 109 K respectively.¹¹ Our subsequent investigation of possible rare earth (R) double perovskites Mn₂RSbO₆ has led to discovery of a new double double perovskite type for Mn₆MnSbO₆ with large R cations, as well as more conventional (MnR)MnSbO₆ double perovskites formed for smaller rare earths.

Mn₆MnSbO₆ materials were synthesized at 10 GPa pressure and 1473 K in a Walker-type multianvil apparatus. Further experimental details are given in ESI. Small single crystals of Mn₆NdMnSbO₆ were separated from the Pt capsule following a slow cooling experiment. Powder x-ray diffraction patterns (Figure 1a and b) collected at the ALBA synchrotron showed that two different perovskite-related structures are formed, with large R = La, Pr, Nd, Sm cations giving one type, while smaller Eu and Gd have a different arrangement. The latter structure was identified as a conventional AA’BB’O₆ double perovskite with a typical monoclinic P2₁/n distortion. Mn²⁺ and R³⁺ cations are disordered over the A sites while Mn²⁺ and Sb⁵⁺ have rock salt order over B and B’ sites.

The new double double Mn₆MnSbO₆ perovskite superstructure adopted by large R cations was solved through x-ray analysis of a Mn₆NdMnSbO₆ single crystal. Results are in Table I and the structure is shown in Figure 2. This tetragonal arrangement has a 2 x 2 x 2 perovskite supercell with P4/m symmetry and a very high degree of cation order, although a small excess of Mn was found at the Nd and Sb sites. Bond Valence Sum (BVS) calculations using the bond distances shown in Table I confirm the Mn²⁺Nd³⁺Mn²⁺Sb⁵⁺O₆ charge distribution with columnar Mn²⁺/Nd³⁺ order at A sites and rocksalt Mn²⁺/Sb⁵⁺ cation order at the perovskite B sites.

---

[a] Dr. A. M. Arévalo-López, Prof. J. P. Attfield
Centre for Science at Extreme Conditions (CSEC) and
School of Chemistry, University of Edinburgh, Mayfield
Road, Edinburgh EH9 3JZ (UK)
E-mail: j.p.attfield@ed.ac.uk
[b] E. Solana- Madruga, Dr. D. Ávila-Brande, Prof. R. Sáez-
Puche.
Dpto. Química Inorgánica I, Fac. Químicas, Universidad
Complutense de Madrid, 28040, Madrid, Spain.
[c] Dr. A. J. Dos santos-Garcia.
Dpto. Ingeniería mecánica, química y diseño industrial.
ETSIDI. Universidad Politécnica de Madrid, 28012,
Madrid, Spain.
[d] Dr. E. Urones-Garrote,
Centro Nacional de Microscopía Electrónica, . Universidad
Complutense de Madrid, 28040, Madrid, Spain.

Supporting information for this article is given via a link at the end of the document. Open data for this article are at http:...
A-type Mn$^{2+}$ cations in MnNdMnSbO$_6$ have two alternating inequivalent sites within their column and cooperative oxide displacements result in almost regular tetrahedral and square planar environments as shown at the bottom of Figure 2. In contrast, Nd cations are 10-coordinate. The MnNdMnSbO$_6$ structure is thus notable for having five different cation sites, with three occupied by Mn$^{2+}$ in tetrahedral, square planar, and octahedral environments. Bond angles are 102.5(1)° and 113.1(1)° in the Mn$_2$O$_6$ tetrahedron, and 90.2(1)° and 173.8(1)° in the Mn$_3$O$_6$ square plane. Mn$_2$O$_6$ octahedra have a slight tetragonal compression while Sb$_6$O$_{12}$ octahedra are very regular, but the B-site octahedra are highly tilted as shown in Figure 2.

Table 1. Refinement results (atomic coordinates, equivalent thermal factors, BVS’s, and bond lengths <3 Å) for MnNdMnSbO$_6$ at 120 K from single crystal structure analysis with Mo K$_\alpha$ radiation (space group P4$_2$/n; a = 7.8225(5) Å, c = 7.9077(5) Å; R$_{\text{obs}}$ = 2.24%, wR$_{2}$ = 5.04%, GOF = 1.20).

<table>
<thead>
<tr>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U$_{\text{el}}$ [Å$^2$]</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>M$_{n\alpha}$</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>0</td>
<td>0.005</td>
<td>1.9</td>
</tr>
<tr>
<td>M$_{n\beta}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.019</td>
<td>1.8</td>
</tr>
<tr>
<td>Nd$^*$</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>0.2674(4)</td>
<td>0.006</td>
<td>2.8</td>
</tr>
<tr>
<td>Mn$^*$</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>0.006</td>
<td>2.2</td>
</tr>
<tr>
<td>Sb$^*$</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>0.003</td>
<td>5.4</td>
</tr>
<tr>
<td>O1</td>
<td>0.3194(3)</td>
<td>0.0097(3)</td>
<td>0.2820(3)</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>0.4855(3)</td>
<td>0.2920(3)</td>
<td>0.1655(4)</td>
<td>0.009</td>
<td></td>
</tr>
<tr>
<td>O3</td>
<td>0.3192(4)</td>
<td>0.3004(4)</td>
<td>0.4855(3)</td>
<td>0.009</td>
<td></td>
</tr>
</tbody>
</table>

*Mn$_{\text{O3}}$(x4) 2.210(3) Mn$_{\text{O1}}$(x2) 2.118(3)
Mn$_{\text{O2}}$(x4) 2.091(3) Mn$_{\text{O2}}$(x2) 2.199(3)
Nd$_{\text{O1}}$(x2) 2.465(3) Mn$_{\text{O3}}$(x2) 2.196(3)
Nd$_{\text{O1}}$(x2) 2.397(3) Sb$_{\text{O1}}$(x2) 1.973(3)
Nd$_{\text{O2}}$(x2) 2.536(3) Sb$_{\text{O2}}$(x2) 1.987(3)
Nd$_{\text{O3}}$(x2) 2.762(3) Sb$_{\text{O3}}$(x2) 1.979(3)
Nd$_{\text{O3}}$(x2) 2.946(3)

Nd site has 6.3(6)% Mn occupancy and Sb has 7.6(6)% Mn. All other sites are occupied only by the element shown.

Structures of the MnRMnSbO$_6$ materials were further characterised using powder x-ray and neutron data and electron microscopy, and detailed results are in ESI. Electron diffraction confirms the $P4_2/n$ symmetry and no further superstructure was observed. The [110] lattice image of MnPrMnSbO$_6$ in Figure 3 shows microscopic order of both A and B site cations in the new double double perovskite arrangement.

Although the $P4_2/n$ perovskite supercell has been reported previously, for example, in double perovskites (SrNd)MnRuO$_6$ (M = Mg, Zn, Ni, Co), these materials do not have cation order at the A sites. The MnNdMnSbO$_6$ structure discovered...
here is thus notable as a new AA’BB’O₆ double double perovskite type and the first to have magnetic transition metal cations at A sites. It combines (110) columnar A-cation and (111) rocksalt B-cation orders. Columnar A-cation order is rare but has been reported previously in CaMTi₂O₆ (M = Fe, Mn) double perovskites, and columnar A-site charge order also occurs in the ambient pressure structure of BiNiO₃, with 1:1 columnar order thus appears to be favoured for accommodating A cations of very different coordination number, with 4-coordinate sites for transition metal cations like Mn³⁺ and 10-coordination for larger electropositive cations such as Ca²⁺ or the early rare earths. Combining this with usual size and charge differences for B cation rocksalt order stabilises the MnNdMnSbO₆ double double perovskite type. In contrast, the NaLaMgWO₅ type is found for less extreme cation size mismatch at the A sites, but with strong off-centre B-cation displacements (second order Jahn-Teller effect) for highly-charged d⁰ cations such as W⁶⁺.

**Figure 3.** High resolution [110] electron microscopy image of MnPrMnSbO₆ with the cation-ordered double double perovskite model from Figure 2 inset. The scanned intensities at the right from the boxed sections in the main image show the Sb-Mn₂A°-Mn₂B°-Sb and Mn₂Pr-Sb-Pr-Mn₂ repeat sequences parallel to [001], where electron-rich Pr and Sb columns appear as bright spots and Mn are faint. These scans and the simulation placed to the lower right confirm the high degree of cation order at perovskite A and B sites.

Low temperature magnetic susceptibility data for the MnRMnSbO₆ double double perovskites are shown in Figure 4 and ESI contains further magnetic results for all samples. These materials are paramagnetic at high temperatures and a Curie-Weiss fit to 150–300 K susceptibility for MnNdMnSbO₆ gives an effective paramagnetic moment of \( \mu_{\text{eff}} = 8.9 \) µB per formula unit, in good agreement with the theoretical value of 9.14 µB from \( S = 5/2 \) Mn³⁺ and \( I_{\text{eff}}/2 \) Nd³⁺ ground state contributions. A negative Weiss temperature (\( \theta = -80 \) K) shows antiferromagnetic interactions are dominant. All of the double double MnRMnSbO₆ perovskites show Curie transitions between 50 and 90 K (\( T_C \) values and other parameters are in ESI). The phases with magnetic R³⁺ cations also show a second magnetic transition as indicated on Figure 4. Magnetic hysteresis loops at 2 K show that the R = La and Sm materials have small saturated magnetisations of ~0.1 µB but R = Pr and Nd have more substantial values of 1.5 and 1.2 µB.

**Figure 4.** Magnetic susceptibilities of MnRMnSbO₆ double double perovskites in a 0.1 T field with arrows showing Curie and spin reorientation transitions. Sm susceptibilities are multiplied by 10 for visibility. Inset shows magnetisation hysteresis loops at 2 K.

In conclusion, this study shows that use of high pressure to stabilise Mn³⁺ at A-sites can lead to discovery of new cation ordered perovskite structure types. The new type of double double perovskite structure in the MnRMnSbO₆ (R = La, Pr, Nd and Sm) family has columnar order of A-site Mn³⁺ and R³⁺ cations while Mn⁵⁺ and Sb⁵⁺ have rock salt order on the B sites. Mn³⁺ cations are in tetrahedral and square planar A-site environments and octahedral B-sites. The MnRMnSbO₆ double double perovskites are ferrimagnetic at low temperatures with Curie transitions between 50 and 90 K and those with magnetic R³⁺ cations also show a second magnetic transition. Magnetic neutron data show that the direction of ferrimagnetic Mn spins in MnNdMnSbO₆ changes from parallel to [001] below \( T_C = 76 \) K to perpendicular...
below the reorientation transition at 42 K at which Nd moments also order. The tetragonal double double perovskite structure is stabilised by large R\(^{3+}\) cations and smaller rare earths lead to conventional monoclinic double perovskites (MnR)MnSbO\(_6\) for R = Eu and Gd, where Mn\(^{2+}\) and R\(^{3+}\) are disordered over the A sites while Mn\(^{2+}\) and Sb\(^{3+}\) have rock salt order at the B sites. Hence use of cation variety and size to control cation order and octahedral tilts under high temperature and pressure conditions may lead to the discovery of other new ordered perovskites with novel structures and properties.

![Diagram](attachment:image.png)

**Figure 5.** a) Magnetic contributions to the (200) and (002) neutron diffraction peaks at d = 3.91 and 3.95 Å respectively for MnNdMnSbO\(_6\). The onset of antiferromagnetic Mn spin order is marked by the appearance of (200) intensity at 60 K, and changes between 40 and 2 K show the reorientation transition driven by Nd spin ordering. b) Temperature variations of the ordered x and z components of the Mn and Nd moments, and of the polar angle \(\phi\) for Mn moments. \(\mu = 0\) below 20 K where the reorientation transition is complete. c) Magnetic structures of MnNdMnSbO\(_6\) at 60 and 2 K.

Acknowledgements

We acknowledge EPSRC, the Royal Society and STFC for support and provision of beam time at ISIS. MINECO and Comunidad de Madrid are also acknowledged for support through projects MAT2013-44964 and S-2013/MIT-1275. We thank Dr. P. Manuel and Dr. D. Khalyavin for assistance with neutron diffraction experiments on WISH. Synchrotron diffraction experiments were performed at ALBA beamline BL04-MSPD with the help of Dr. O. Vallcorba and Dr. C. Popescu. We thank the ICTS Centro Nacional de Microscopía Electrónica de U.C.M. for technical assistance.

**Keywords:** perovskite phases • high-pressure chemistry • magnetic properties • double perovskites

A new double double perovskite type structure is discovered in the family MnRMnSbO$_6$ (R = La, Pr, Nd and Sm). This has order of Mn$^{2+}$ and R$^{3+}$ cations in columns on perovskite A sites while Mn$^{2+}$ and Sb$^{5+}$ have rock salt order on the B sites. The A-site Mn$^{2+}$ positions are further divided into tetrahedral and square planar environments. The MnRMnSbO$_6$ double double perovskites are ferrimagnetic at low temperatures with additional spin-reorientation transitions.