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Double double cation order in the high pressure perovskites MnRMnSbO$_6$

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Abstract: Cation order in ABO$_3$ perovskites adds to their chemical variety and can lead to properties such as ferrimagnetism and magnetoresistance in Sr$_2$FeMoO$_6$. Through high pressure and temperature synthesis we have discovered a new type of ‘double double perovskite’ structure in the family MnRMnSbO$_6$ (R = La, Pr, Nd and Sm). This tetragonal structure has 1:1 order of cations on both A and B sites; A-site Mn$^{2+}$ and R$^{3+}$ cations are ordered in columns 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. The ordering direction of ferrimagnetic Mn spins in MnNdMnSbO$_6$ 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. Smaller rare earths lead to conventional monoclinic double perovskites (MnR)MnSbO$_6$ for Eu and Gd, where Mn$^{2+}$ and R$^{3+}$ are disordered over the A sites while Mn$^{2+}$ and Sb$^{5+}$ have rock salt order at the B sites.

ABO$_3$ 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’O$_3$ and for B-ordered AB’BB’O$_6$ double perovskites, amongst which layered AA’B’O$_3$ and rock salt AB’BB’O$_6$ orders are the most common. However AA’BB’O$_6$ ‘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 NaLaMgWO$_6$ and NaLaScNbO$_6$. We report here a new double double perovskite type that has been discovered as part of an investigation of perovskites with Mn$^{2+}$ ion at A sites.

A$^{2+}$ 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 Mn$^{2+}$ ion at A sites have recently been synthesised at high pressure and temperature conditions. This may introduce additional magnetic functionality as found in MnV$_2$O$_5$ perovskite which is metallic due to itinerancy of the V$^{4+}$ 3d$^3$ states as in CaV$_2$O$_5$ and SrV$_2$O$_5$, but also has coexisting helimagnetic order of localised S = 5/2 Mn$^{2+}$ spins. Several MnBB’O$_6$ double perovskites have also been synthesised at high pressures. MnFeSbO$_6$ has a low temperature incommensurate antiferromagnetic Mn spin order, and MnFeReO$_6$ has a high Curie temperature of 520 K and similar ferrimagnetic and spin-polarised conducting properties to the much-studied magnetoresistive material Sr$_2$FeMoO$_6$, but also shows a novel switch from negative to large positive magnetoresistances at low temperatures driven by Mn$^{2+}$ spin ordering. In contrast, MnMnReO$_6$ (MnReO$_6$) shows successive antiferromagnetic ordering transitions for Re and Mn spins at 99 and 109 K respectively. Our subsequent investigation of possible rare earth (R) double perovskites Mn$_2$RSbO$_6$ has led to discovery of a new double double perovskite type for MnR MnSbO$_6$ with large R cations, as well as more conventional (MnR)MnSbO$_6$ double perovskites formed for smaller rare earths.

MnR MnSbO$_6$ 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 MnNdMnSbO$_6$ 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 A$_2$BB’O$_6$ double perovskite with a typical monoclinic P2$_1$/n distortion. Mn$^{2+}$ and R$^{3+}$ cations are disordered over the A sites while Mn$^{2+}$ and Sb$^{5+}$ have rock salt order over B and B’ sites.

The new double double MnR MnSbO$_6$ perovskite superstructure adopted by large R cations was solved through x-ray analysis of a MnNdMnSbO$_6$ 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$_2$/n 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 Mn$^{2+}$/Nd$^{3+}$/Mn$^{2+}$/Sb$^{5+}$/O$_6$ charge distribution with columnar Mn$^{2+}$/Nd$^{3+}$ order at A sites and rocksalt Mn$^{2+}$/Sb$^{5+}$ cation order at the perovskite B sites.
Refinement results (atomic coordinates, equivalent cell parameters, thermal factors, BVS’s, and bond lengths) for MnNdMnSbO₆ samples at 120 K from single crystal analysis with Mo Kα radiation (space group P4/z/n; a = 7.8225(5) Å, c = 7.9077(5) Å; Robs = 2.24%, wR = 5.04%, GoF = 1.20).

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U equivalent (Å²)</th>
<th>BVS</th>
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<td>5.4</td>
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<tr>
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<td>0.2920(3)</td>
<td>0.1655(4)</td>
<td>0.009</td>
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<tr>
<td>Sb</td>
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<td>2.188(3)</td>
<td>0.212(3)</td>
<td>0.019</td>
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</tr>
<tr>
<td>O</td>
<td>0.3192(4)</td>
<td>0.3004(4)</td>
<td>0.4855(3)</td>
<td>0.006</td>
<td>5.0</td>
</tr>
</tbody>
</table>

*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.

Figure 1. a) Low-angle powder synchrotron x-ray diffraction (SXRD) data (λ = 0.4421 Å) for MnRMnSbO₆ samples. The (110) peak (indexed on a 2 x 2 x 2 perovskite cell) characterises the columnar order of A-cations for the R = La, Pr, Nd and Sm P4/z/n double double perovskites and the (111) peak reveals rock salt type B-cation order, although this is split into (011) and (101) due to monoclinic distortion for R = Eu and Gd P2/z/n double double perovskites. The additional peak (*) is due to parasitic scatter from the diffractometer. b) Rietveld fit to synchrotron x-ray data for MnNdMnSbO₆; markers show additional contributions from TiO₂ (parasitic scatter from the detector) and ~3%wt NdMnO₂ secondary phase.

Table I. Refinement results (atomic coordinates, equivalent thermal factors, BVS’s, and bond lengths) for MnNdMnSbO₆ at 120 K from single crystal structure analysis with Mo Kα radiation (space group P4/z/n; a = 7.8225(5) Å, c = 7.9077(5) Å; Robs = 2.24%, wR = 5.04%, GoF = 1.20).

Figure 2. Double double perovskite structure of MnRMnSbO₆ oxides (R = La, Pr, Nd and Sm). B site MnO₆ and SbO₆ octahedra have a rocksalt type order while A site Mn and R are ordered in columns parallel to the unique z-axis. Mn A-sites are further split into MnA and MnA' environments with tetrahedral and square planar coordinations as shown below.

Structures of the MnRMnSbO₆ 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/z/n symmetry and no further superstructure was observed. The [110] lattice image of MnPrMnSbO₆ in Figure 3 shows microscopic order of both A and B site cations in the new double double perovskite arrangement.

Although the P4/z/n perovskite supercell has been reported previously, for example, in double perovskites (SrNd)MnRuO₆ (M = Mg, Zn, Ni, Co), these materials do not have cation order at the A sites. The MnNdMnSbO₆ 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 (Bi⁺⁺Bi⁺⁺Ni²⁺O₆). 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 Mn⁶⁺ and 10-coordination for larger electropositive cations such as Ca⁵⁺ 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 NaLaMgWO₆ 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-Mn₆A⁻A⁻Mn₆-Mn₆A⁻A⁻Sb and Mn₆-Pr-Sb-Pr-Mn₆ repeat sequences parallel to [001], where electron-rich Pr and Sb columns appear as bright spots and Mn are faint. The 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 MnRnMnSbO₆ 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 μₑₚ = 8.9 μₜ per formula unit, in good agreement with the theoretical value of 9.14 μₜ from S = 5/2 Mn⁶⁺ and 1/2 Nd⁴⁺ ground state contributions. A negative Weiss temperature (θ = -80 K) shows that antiferromagnetic interactions are dominant. All of the double double MnRnMnSbO₆ perovskites show Curie transitions between 50 and 90 K (Tc values and other parameters are in ESI). The phases with magnetic R⁴⁺ 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 μₜ but R = Pr and Nd have more substantial values of 1.5 and 1.2 μₜ.

Figure 4. Magnetic susceptibilities of MnRnMnSbO₆ 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 Mn⁶⁺ at A-sites can lead to discovery of new cation ordered perovskite structure types. The new type of double double perovskite structure in the MnRnMnSbO₆ (R = La, Pr, Nd and Sm) family has columnar order of A-site Mn⁶⁺ and R⁴⁺ cations while Mn⁶⁺ and Sb⁵⁺ have rock salt order on the B sites. Mn⁶⁺ cations are in tetrahedral and square planar A-site environments and octahedral B-sites. The MnRnMnSbO₆ double double perovskites are ferrimagnetic at low temperatures with Curie transitions between 50 and 90 K and those with magnetic R⁴⁺ 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 Tc = 76 K to perpendicular
below the reorientation transition at 42 K at which Nd moments also order. The tetragonal double double perovskites structure is stabilised by large R3+ cations and smaller rare earths lead to conventional monoclinic double perovskites (MnR)MnSbO6 for R = Eu and Gd, where Mn2+ and R3+ are disordered over the A sites while Mn2+ and Sb3+ 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.

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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.