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Double double cation order in the high pressure perovskites MnRMnSbO₆

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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 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)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'B₂O₆ and for B-ordered A₂BB'O₆ double perovskites,¹ amongst which layered AA'B₂O₆ and rock salt A₂BB'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 MnVO₃ perovskite which is metallic due to itinerancy of the V⁴⁺ 3d¹ states as in CaVO₃ and SrVO₃, but also has 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} Mn₂FeSbO₆ has low temperature incommensurate antiferromagnetic Mn spin order.⁸ Mn₂FeReO₆ 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, Mn₂MnReO₆ (Mn₃ReO₆) 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 MnRMnSbO₆ with large R cations, as well as more conventional (MnR)MnSbO₆ double perovskites formed for smaller rare earths.

MnRMnSbO₆ materials were synthesised at 10 GPa pressure and 1473 K in a Walker-type multianvil apparatus. Further experimental details are given in ESI. Small single crystals of MnNdMnSbO₆ 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 A₂BB'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 MnRMnSbO₆ perovskite superstructure adopted by large R cations was solved through x-ray analysis of a MnNdMnSbO₆ 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 P4₂/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 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.

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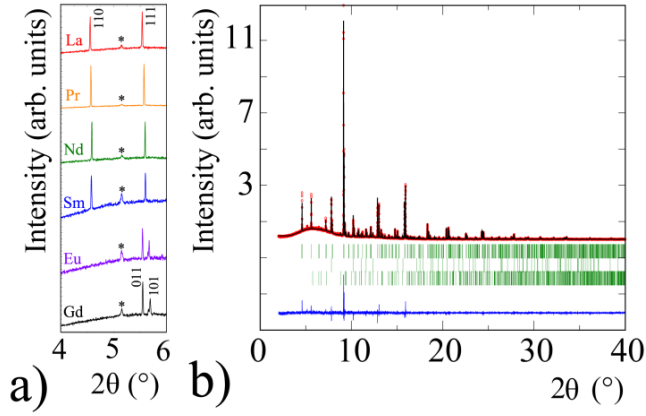


Figure 1. a) Low-angle powder synchrotron x-ray diffraction (SXRD) data ($\lambda = 0.4421 \text{ \AA}$) for MnRMnSbO₆ samples. The (110) peak (indexed on a $2 \times 2 \times 2$ perovskite cell) characterises the columnar order of A-cations for the R = La, Pr, Nd and Sm $P4_2/n$ double double perovskites 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 $P2_1/n$ 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 NdMnO₃ secondary phase.

Table I. Refinement results (atomic coordinates, equivalent thermal factors, BVS's, and bond lengths <3 Å) for MnNdMnSbO₆ at 120 K from single crystal structure analysis with Mo K_α radiation (space group $P4_2/n$; $a = 7.8225(5) \text{ \AA}$, $c = 7.9077(5) \text{ \AA}$; $R_{\text{obs}} = 2.24\%$, $wR_2 = 5.04\%$, GOF = 1.20).

	x	y	z	$U_{\text{eq.}} [\text{\AA}^2]$	BVS
Mn _A	½	½	0	0.005	1.9
Mn _{A'}	0	0	0	0.019	1.8
Nd*	½	0	0.2674(4)	0.006	2.8
Mn _B	¾	¾	¼	0.006	2.2
Sb*	¼	¼	¼	0.003	5.4
O1	0.3194(3)	0.0097(3)	0.2820(3)	0.007	
O2	0.4855(3)	0.2920(3)	0.1655(4)	0.009	
O3	0.3192(4)	0.3004(4)	0.4855(3)	0.009	
Mn _A -O3 (x4)	2.110(3)	Mn _B -O1(x2)	2.118(3)		
Mn _A -O2 (x4)	2.091(3)	Mn _B -O2(x2)	2.199(3)		
Nd-O1 (x2)	2.465(3)	Mn _B -O3 (x2)	2.196(3)		
Nd-O1 (x2)	2.397(3)	Sb-O1(x2)	1.973(3)		
Nd-O2 (x2)	2.536(3)	Sb-O2 (x2)	1.987(3)		
Nd-O3 (x2)	2.762(3)	Sb-O3 (x2)	1.979(3)		
Nd-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.

A-type Mn²⁺ cations in MnNdMnSbO₆ 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 MnNdMnSbO₆ structure is thus notable for having five different cation sites, with three occupied by Mn²⁺ in tetrahedral, square planar, and octahedral environments. Bond angles are 102.5(1) and 113.1(1)° in the Mn_AO₄ tetrahedron, and 90.2(1) and 173.8(1)° in the Mn_{A'}O₄ square plane. Mn_BO₆ octahedra have a slight tetragonal compression while SbO₆ octahedra are very regular, but the B-site octahedra are highly tilted as shown in

Figure 2. Similar large internal distortions are found when transition metal cations occupy 4-coordinate A sites in other perovskites. A-site Mn²⁺ has approximate tetrahedral coordination in the double perovskites Mn₂FeSbO₆, Mn₂FeReO₆, and Mn₂MnReO₆. The large family of A-cation ordered AA'₃B₄O₁₂ perovskites have square planar A' sites that may be occupied by Mn²⁺ for example in (La_{0.5}Na_{0.5})Mn₃Ti₄O₁₂.¹² Rock salt B-cation order can also occur in this family leading to AA'₃B₂B'₂O₁₂ double double perovskites including the spintronic material CaCu₃Fe₂Re₂O₁₂.¹³

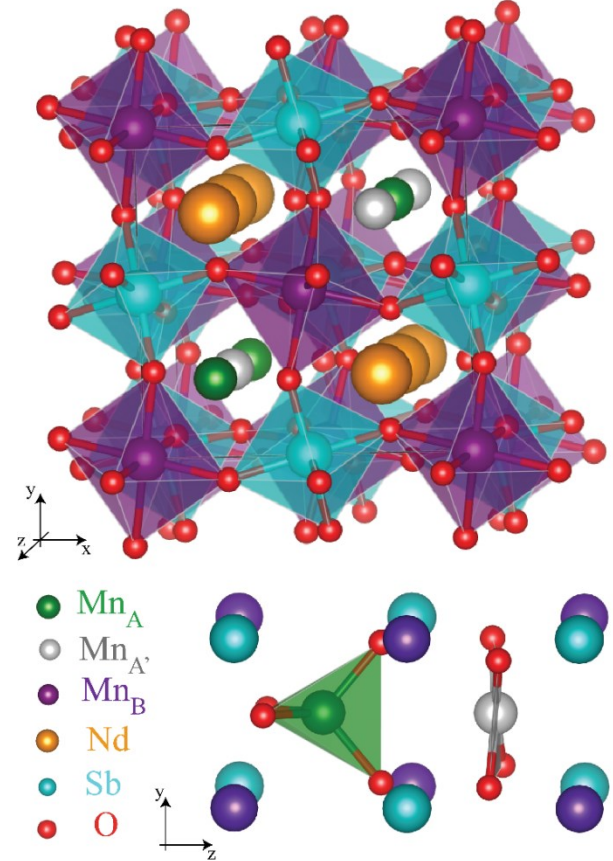


Figure 2. Double double perovskite structure of MnRMnSbO₆ oxides (R = La, Pr, Nd and Sm). B site MnO₆ and SbO₆ octahedra have a rocksalt type order while A site Mn and R are ordered in columns parallel to the unique z-axis. Mn A-sites are further split into Mn_A and Mn_{A'} environments with tetrahedral 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 $P4_2/n$ 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 $P4_2/n$ perovskite supercell has been reported previously, for example, in double perovskites (SrNd)MRuO₆ (M = Mg, Zn, Ni, Co),¹⁴ these materials do not have cation order at the A sites. The MnNdMnSbO₆ structure discovered

here is thus notable as a new $AA'BB'O_6$ 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 $CaMTi_2O_6$ ($M = Fe, Mn$) double perovskites,^{15,16} and columnar A-site charge order also occurs in the ambient pressure structure of $BiNiO_3$ ($Bi^{3+}Bi^{5+}Ni_2O_6$).¹⁷ 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 Mn^{2+} and 10-coordination for larger electropositive cations such as Ca^{2+} or the early rare earths. Combining this with usual size and charge differences for B cation rocksalt order stabilises the $MnNdMnSbO_6$ double double perovskite type. In contrast, the $NaLaMgWO_6$ 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 d^0 cations such as W^{6+} .

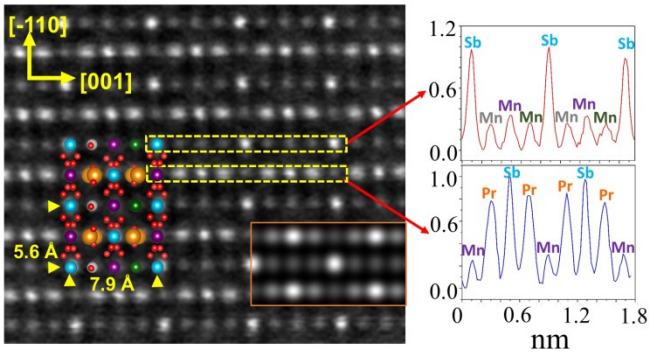


Figure 3. High resolution [110] electron microscopy image of $MnPrMnSbO_6$ with the cation-ordered double double perovskite model from Figure 2 inset. The scanned intensities at the right from the boxed sections in the main image show the $Sb-Mn_{A'}-Mn_B-Mn_{A'}-Sb$ and $Mn_B-Pr-Sb-Pr-Mn_B$ repeat sequences 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 $MnRMnSbO_6$ 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 $MnNdMnSbO_6$ gives an effective paramagnetic moment of $\mu_{exp} = 8.9 \mu_B$ per formula unit, in good agreement with the theoretical value of $9.14 \mu_B$ from $S = 5/2 Mn^{2+}$ and $4J_{9/2} Nd^{3+}$ ground state contributions. A negative Weiss temperature ($\theta = -80$ K) shows that antiferromagnetic interactions are dominant. All of the double double $MnRMnSbO_6$ perovskites show Curie transitions between 50 and 90 K (T_C values and other parameters are in ESI). The phases with magnetic R^{3+} 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 $\sim 0.1 \mu_B$ but $R = Pr$ and Nd have more substantial values of 1.5 and $1.2 \mu_B$.

Powder neutron diffraction data were used to explore the low temperature magnetic order in $MnNdMnSbO_6$. On cooling below $T_C = 76$ K, magnetic peaks such as (200) appear (Figure 5a). These are indexed by propagation vector (0 0 0) and the 60 K data are fitted well by a simple antiferromagnetic model in which Mn A-site spins are antiparallel to B site spins, with all moments in the c direction as shown in Figure 5c. This arrangement and the negative Weiss temperature are consistent with antiferromagnetic $Mn_{A'}-O-Mn_B$ interactions being dominant. On cooling below the second 42 K magnetic transition indicated by the magnetisation anomaly in Figure 4, (001) magnetic peaks such as (002) grow in intensity while (200) decreases. This reveals a spin reorientation transition driven by order of the Nd moments in the ab-plane, probably driven by single ion anisotropy of the Nd ion parallel to the a-axis. The Mn moments rotate from being parallel to the c -axis above the 42 K transition to perpendicular below 20 K as shown in Figure 5b. The 2 K magnetic structure has Mn^{2+} moments of $4.4 \mu_B$, close to the ideal value of $5 \mu_B$, but the ordered Nd^{3+} moment has a value of only $1.1 \mu_B$. This is consistent with the bulk magnetisations in Figure 4, as the A and B-site Mn spins approximately cancel so the net magnetisations result from the ordered R^{3+} moments which are significant ($\sim 1 \mu_B$) for Pr and Nd but zero or very small for La and Sm.

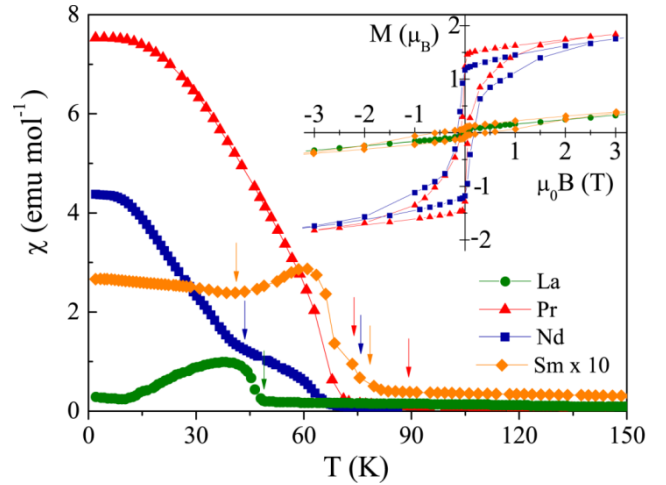


Figure 4. Magnetic susceptibilities of $MnRMnSbO_6$ double double perovskites in a 0.1 T field with arrows showing Curie and spin reorientation transitions. Sm susceptibilities are multiplied by 10 for visibility. Inset shows magnetisation hysteresis loops at 2 K.

In conclusion, this study shows that use of high pressure to stabilise Mn^{2+} at A-sites can lead to discovery of new cation ordered perovskite structure types. The new type of double double perovskite structure in the $MnRMnSbO_6$ ($R = La, Pr, Nd$ and Sm) family has columnar order of A-site Mn^{2+} and R^{3+} cations while Mn^{2+} and Sb^{5+} have rock salt order on the B sites. Mn^{2+} cations are in tetrahedral and square planar A-site environments and octahedral B-sites. The $MnRMnSbO_6$ double double perovskites are ferrimagnetic at low temperatures with Curie transitions between 50 and 90 K and those with magnetic R^{3+} cations also show a second magnetic transition. Magnetic neutron data show that the 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. 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^{5+} 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.

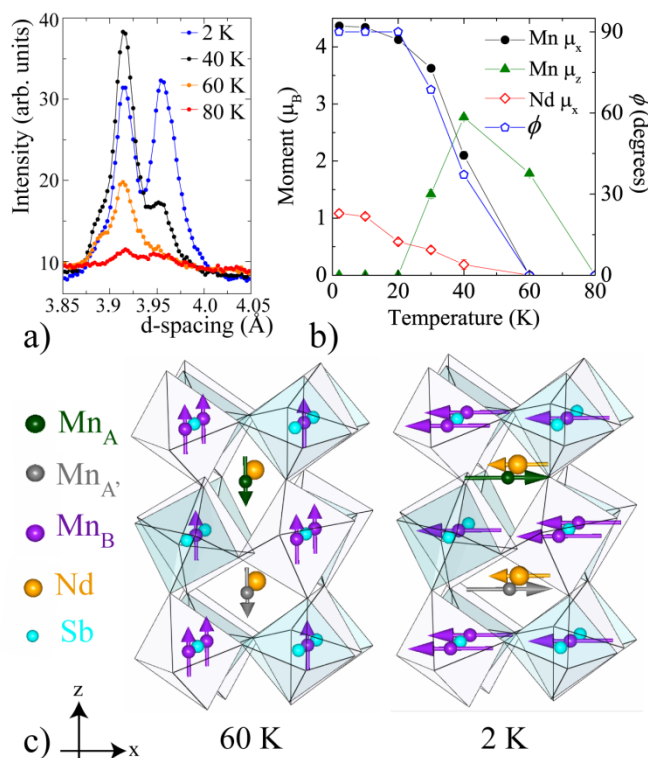


Figure 5. a) Magnetic contributions to the (200) and (002) neutron diffraction peaks at $d = 3.91$ and 3.95 Å respectively for $MnNdMnSbO_6$. The onset of antiferromagnetic Mn spin order is marked by the appearance of (200) intensity at 60 K, and changes between 40 and 2 K show the reorientation transition 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 ϕ for Mn moments. $\mu_z = 0$ below 20 K where the reorientation transition is complete. c) Magnetic structures of $MnNdMnSbO_6$ at 60 and 2 K.

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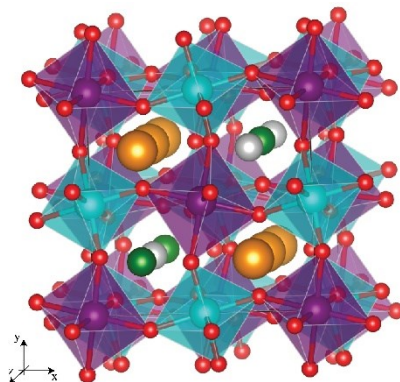
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Materials Synthesis

Elena Solana-Madruga, Ángel M. Arévalo-López, Antonio J. Dos santos-García, Esteban Urones-Garrote, David Ávila-Brande, Regino Sáez-Puche and J. Paul Attfield*

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A new double double perovskite type structure is discovered in the family MnRMnSbO_6 ($R = \text{La, Pr, Nd and Sm}$). 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.