

## Perovskites

## Double Double to Double Perovskite Transformations in Quaternary Manganese Oxides

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**Abstract:** Control of cation ordering in  $ABX_3$  perovskites is important to structural, physical and chemical properties. Here we show that thermal transformations of  $AA'BB'O_6$  double double perovskites, where both A and B sites have 1:1 cation order, to  $(A_{0.5}A'_{0.5})_2BB'O_6$  double perovskites with fully disordered A/A' cations can be achieved under pressure in  $CaMnMnWO_6$  and  $SmMnMnTaO_6$ , enabling both polymorphs of each material to be recovered. This leads to a dramatic switch of magnetic properties from ferrimagnetic order in double double perovskite  $CaMnMnWO_6$  to spin glass behaviour in the highly frustrated double perovskite polymorph. Comparison of double double and double perovskite polymorphs of other materials will enable effects of cation order and disorder on other properties such as ferroelectricity and conductivity to be explored.

Perovskite oxides have remarkable flexibility in accepting a wide variety of cations on the A- and B-sites leading to many properties such as ferroelectricity, ferromagnetism and superconductivity.<sup>[1–4]</sup> Further chemical variety arises through cation ordering, and layered, columnar and rock-salt arrangements have all been reported for the simplest 1:1 order at A or B sites,<sup>[5]</sup> leading to  $AA'B_2O_6$ <sup>[6]</sup> or  $A_2BB'O_6$ <sup>[7]</sup> double perovskite (DPv) structures. Such orders enable new physical properties to emerge, notably ferrimagnetism and half-metallicity with large magnetoresistance in  $Sr_2FeMoO_6$  and related  $A_2BB'O_6$  DPvs<sup>[8]</sup> where rock-salt B/B' ordering is driven by cation charge and size differences.<sup>[9]</sup> Combined 1:1 orders at both A and B sites to give an  $AA'BB'O_6$  double double (or doubly-ordered) perovskite (DDPv) are rarer but two types are known. A family with A-site layered and B-site rock-salt arrangements, for example,  $NaLaMgWO_6$ <sup>[10]</sup> and  $NaNiWO_6$ <sup>[11]</sup> is stabilised by the charge difference between

large  $A^+$  and  $A^{3+}$  cations. A second DDPv family with columnar A-site and rock-salt B site orders has recently been reported in  $RMnMnSbO_6$  (for rare earths  $R = La, Pr, Nd$  and  $Sm$ )<sup>[12,13]</sup> and several  $CaMnBB'O_6$  materials ( $B = Mn, Fe, Co, Ni$  for  $B' = Re$ ,<sup>[14–16]</sup> and  $B/B' = Fe/Ta$ ,<sup>[17]</sup>  $Cr/Sb$  and  $Fe/Sb$ <sup>[18]</sup>) synthesised at high temperatures and pressures. The A-site order in this tetragonal  $P4_2/n$  family is driven by cation size differences between  $R^{3+}$  or  $Ca^{2+}$  and  $Mn^{2+}$ .

Alternative cation-ordered double perovskite and disordered perovskite polymorphs have been synthesised for several materials, with consequent changes in properties. For example, the ferromagnetic Curie temperature where colossal magnetoresistance is maximal changes from  $T_C = 335$  K in A-site layered  $LaBaMn_2O_6$  to  $T_C = 270$  K for cation-disordered  $(La_{0.5}Ba_{0.5})MnO_3$ ,<sup>[19]</sup> and long range  $Fe^{3+}/Fe^{5+}$  charge order is observed in B-layered  $Ca_2FeMnO_6$ <sup>[20]</sup> but not in disordered  $Ca(Fe_{0.5}Mn_{0.5})O_3$ .<sup>[21]</sup> This raises intriguing questions of whether simple atomic order to disorder transitions, which are of fundamental interest in systems like  $\beta$ -brass ( $Cu_{0.5}Zn_{0.5}$  alloy), can be observed for the separate A and B cation pairs in double double perovskites, and if so whether disorder in one sublattice induces disorder in the other. The initial study found that  $RMnMnSbO_6$  double double perovskites were formed for  $R = La, Pr, Nd$  and  $Sm$ , whereas A-site disordered double perovskites  $(R_{0.5}Mn_{0.5})_2MnSbO_6$  were formed for  $R = Eu$  and  $Gd$ , but no double double—double phase coexistence or crossover transition was observed.<sup>[12]</sup> Furthermore, a study of the  $Ca_xMn_{2-x}FeReO_6$  system discovered large chemical miscibility gaps between double perovskites near  $x = 0$  and 2 and the double double phase formed around  $x = 1$  ( $CaMnFeReO_6$ ).<sup>[15]</sup> Our continuing research recently produced the first evidence of coexisting double and double double perovskites of the same chemical composition in the  $CaMnMnWO_6$  and  $SmMnMnTaO_6$  systems. These quaternary materials as representative compositions from both  $A = Ca$  and  $R$  families provide an ideal opportunity to study any coupling between A-site and B-site cation orders in  $AA'BB'O_6$  double double perovskites, as  $Mn^{2+}$  is common to both the A' and B sublattices so no A'/B disorder (observed in analogues such as  $CaMnFeTaO_6$ <sup>[17]</sup> and  $CaMnMSbO_6$ ;  $M = Cr, Fe$ <sup>[18]</sup>) can occur. We report here that complete double double to double perovskite structural phase transformations can be driven by temperature in both the  $CaMnMnWO_6$  and  $SmMnMnTaO_6$  systems at pressure enabling both polymorphs of each compound to be isolated, and we show that this structural change leads to a dramatic switch in magnetic properties for  $CaMnMnWO_6$ .

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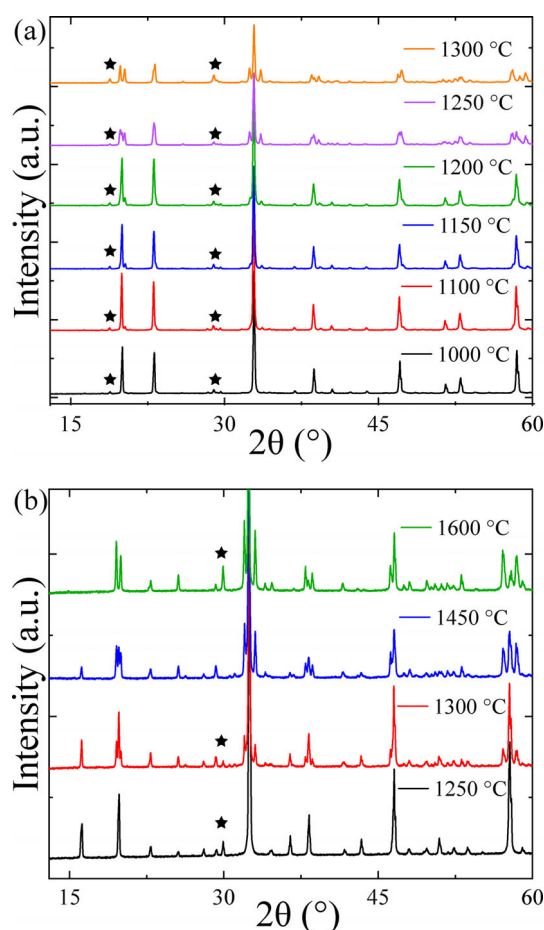
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$\text{CaMnMnWO}_6$  and  $\text{SmMnMnTaO}_6$  samples were prepared using stoichiometric mixtures of  $\text{CaWO}_4$  or  $\text{SmTaO}_4$  and  $\text{MnO}$ .  $\text{CaWO}_4$  was prepared by heating a stoichiometric pellet of  $\text{CaCO}_3$  and  $\text{WO}_3$  for 24 hours at  $1100^\circ\text{C}$ .  $\text{SmTaO}_4$  was prepared by heating a stoichiometric pellet of  $\text{Sm}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$  for 24 hours at  $1350^\circ\text{C}$ , with the  $\text{Sm}_2\text{O}_3$  dried in air at  $900^\circ\text{C}$  before use. The  $\text{AMnMnB}'\text{O}_6$  precursor mixtures were packed into a Pt capsule and heated at temperatures ranging from  $1000$  to  $1600^\circ\text{C}$  under  $10$  GPa pressure in a Walker-type multianvil apparatus. Samples were heated over  $10$  minutes to the target temperature and held there for  $30$  minutes which is sufficient to establish phase equilibrium, before quenching to room temperature, after which the pressure was slowly released.

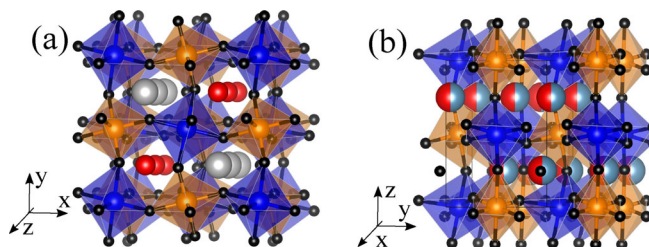
Samples were analysed by powder X-ray diffraction data collected at room temperature on a D2 Bruker diffractometer in the angular range  $2\theta = 10$  to  $110^\circ$  with step size  $0.01^\circ$  using a  $\text{Cu K}\alpha$  source. Powder neutron diffraction patterns for DDPv and DPv polymorphs of  $\text{CaMnMnWO}_6$  were collected from  $\approx 200$  mg samples using the D20 beamline at the ILL, Grenoble. High-resolution data were collected at  $300$  K using wavelength  $\lambda = 1.54 \text{ \AA}$  for structure refinement and scans at  $1.5$  and  $80$  K for the DDPv and at  $1.5$  and  $10$  K for the DPv polymorph with  $\lambda = 2.41 \text{ \AA}$  were used to investigate magnetic ordering. Magnetic symmetry analysis was carried out using BASIREPS<sup>[22]</sup> and X-ray and neutron diffraction patterns were refined through the Rietveld method using the Fullprof Suite.<sup>[23]</sup> Magnetic susceptibilities and magnetization-field hysteresis loops were measured on a Quantum Design MPMS-SQUID magnetometer.

Double double perovskite phases of  $\text{CaMnMnWO}_6$  and  $\text{SmMnMnTaO}_6$  were synthesised under  $10$  GPa pressure at  $1000$  and  $1250^\circ\text{C}$  respectively. Fits to powder X-ray data (Figures S1 and S2) confirmed that both compounds adopt the tetragonal  $P4_2/n$  structure described above. However, increasing temperature led to a mixture of double double (DDPv) and double perovskite (DPv) phases as shown in the powder X-ray data in Figure 1. All DDPv phases have the tetragonal  $P4_2/n$  structure (Figure 2a) and the DPVs adopt the monoclinic  $P2_1/n$  structure (Figure 2b) commonly found for rocksalt-ordered  $\text{A}_2\text{BB}'\text{O}_6$  double perovskites, e.g.  $\text{Ca}_2\text{MnWO}_6$ .<sup>[24]</sup> Complete conversion to the DPv phase was observed at  $1300^\circ\text{C}$  for  $\text{CaMnMnWO}_6$  and at  $1600^\circ\text{C}$  for  $\text{SmMnMnTaO}_6$ . Rietveld fits were used to extract the proportions of each perovskite phase (shown in Table S1). DPv samples of  $(\text{Ca}_{0.5}\text{Mn}_{0.5})_2\text{MnWO}_6$  and  $(\text{Sm}_{0.5}\text{Mn}_{0.5})_2\text{MnTaO}_6$  were, respectively synthesized at  $1300$  and  $1600^\circ\text{C}$ , and X-ray fits are shown in Figures S1b and S2b with results in Tables S2, S3, S7 and S8.

A/Mn disorders in the DDPv structure were refined in initial Rietveld X-ray fits but in all cases no A-site disorder was found to within  $\approx 1\%$  refinement errors. Hence the transformation from  $\text{AMnMnB}'\text{O}_6$  double double perovskite with all cation sites fully ordered to  $(\text{A}_{0.5}\text{Mn}_{0.5})_2\text{MnB}'\text{O}_6$  double perovskites where A/Mn cations are fully disordered over A-sites is discovered to occur entirely through a first order transition via coexistence of the two phases, but without any incipient A-cation disorder in either DDPv phase. The first order nature of the transition reflects the incompatible



**Figure 1.** Powder XRD patterns of a)  $\text{CaMnMnWO}_6$  and b)  $\text{SmMnMnTaO}_6$  at different synthesis temperatures showing progress of the DDPv-DPv structural phase transition. Black stars show secondary phase contributions from  $\text{CaWO}_4$  in (a) or  $\text{SmTaO}_4$  in (b).



**Figure 2.** Crystal structures of a)  $P4_2/n$  double double perovskite (DDPv) and b)  $P2_1/n$  double perovskite (DPv)  $\text{AMnMnB}'\text{O}_6$  structures. Ordered A/Mn cations in the DDPv structure are shown as grey/red spheres and  $\text{Mn/B}'\text{O}_6$  octahedra are blue/orange.

octahedral tilts between the two structures (Figure 2). The  $P4_2/n$  DDPv structure has two in-phase and one out-of-phase tilts of the  $\text{B/B}'\text{O}_6$  octahedra (written  $a^+a^+c^-$  in Glazer notation<sup>[25]</sup>) which creates the high (10) and low (4) oxide coordination numbers around the A-site Ca/Sm and Mn cations, respectively. However, the  $P2_1/n$  DPv structure has one in-phase and two out-of-phase tilts ( $a^-a^-c^+$ ) that provide a single 8-coordinate environment around all A cations. With no group-subgroup relation between the two structures, the transition is expected to be first order in Landau theory.

Nevertheless, the magnitudes of tilt angles  $\theta_{xy}$  in the  $xy$ -plane and  $\theta_z$  from the  $z$ -axis are virtually unchanged between the DDPv and DPv structures;  $\text{CaMnMnWO}_6$  has  $\theta_{xy}/\theta_z = 17.3(1)/18.9(1)^\circ$  in DDPv and  $18.3(1)/18.7(1)^\circ$  in DPv structures from neutron refinement, and  $\text{SmMnMnTaO}_6$  has  $\theta_{xy}/\theta_z = 17.4(2)/19.0(3)^\circ$  in DDPv and  $17.8(2)/18.7(3)^\circ$  in DPv from X-ray refinement.

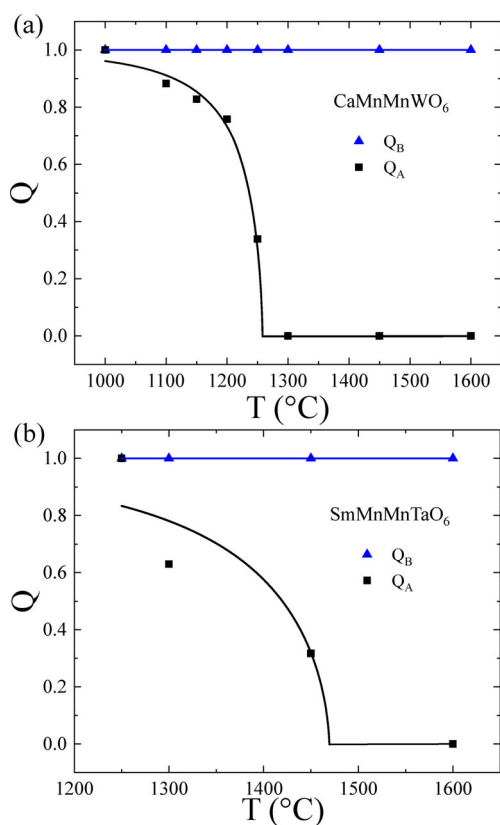
Despite the first order nature of the transition, the average A-cation occupancy order parameter across the two phases, calculated as  $Q_A = \% \text{DDPv} / (\% \text{DDPv} + \% \text{DPv})$  using phase proportions from Table S1, shows a continuous thermal variation for  $\text{CaMnMnWO}_6$  as shown in Figure 3. This was fitted using the function  $Q_A = \tanh(Wt^\beta) / \tanh(W)$ , where  $t = (T_C - T) / T_C$  for temperatures  $T$  in K and  $W$  is a fitting parameter to allow for higher order contributions to the Landau free energy expansion at large  $t$ .<sup>[26]</sup> Initial refinement gave  $\beta = 0.45(11)$  for  $\text{CaMnMnWO}_6$ , consistent with  $\beta = 0.5$  from mean field theory, and the critical exponent was fixed at the latter value giving the estimated upper temperature for the A-site order to disorder transition in  $\text{CaMnMnWO}_6$  as  $T_C = 1260^\circ\text{C}$ . Fewer points are available for  $\text{SmMnMnTaO}_6$  so the thermal variation is less clear, but a fit of the same function with  $\beta = 0.5$  gave  $T_C \approx 1470^\circ\text{C}$ . The higher transition temperature for  $\text{SmMnMnTaO}_6$  reflects the charge difference between A-site cations, as the (8-coordi-

nate) ionic radii of  $\text{Ca}^{2+}$  (1.12 Å) and  $\text{Sm}^{3+}$  (1.08 Å) are comparable, with the latter being closer in size to  $\text{Mn}^{2+}$  (0.96 Å).<sup>[27]</sup> Assuming ideal statistical entropy changes of  $R \ln 2$  per mol of perovskite at the transitions due to the cation disorder gives estimates of 8.8 and 10.0  $\text{kJ mol}^{-1}$  for the enthalpy changes in  $\text{CaMnMnWO}_6$  and  $\text{SmMnMnTaO}_6$  respectively.

Rock-salt B-site ordering in DDPv and DPv materials arises from cation size and charge differences. Previously reported  $\text{AA'BB'O}_6$  DDPvs with  $\text{B}^{3+}/\text{B}^{5+}$  cation combinations have large B/B' antisite disorder, up to 18% in  $\text{CaMnFeTaO}_6$ .<sup>[17]</sup>  $\text{B}^{2+}/\text{B}^{6+}$  combinations show much less disorder, for example, 4/3.6% for  $\text{M} = \text{Co/Ni}$  in  $\text{CaMnMReO}_6$ ,<sup>[16]</sup> but no Mn/B' antisite disorder to within refinement errors of  $< 1\%$  was observed in the X-ray studies of DDPv and DPv phases of  $\text{CaMnMnWO}_6$  and  $\text{SmMnMnTaO}_6$  in all samples of the present study. Hence the occupancy order parameter for the B-cations is  $Q_B = 1$  throughout as shown on Figure 3 so no coupling between  $Q_A$  and  $Q_B$  is apparent from our X-ray studies. Powder neutron refinement of the  $\text{CaMnMnWO}_6$  structures (Figure S4), where B/B' antisite disorder is less correlated with the scale factor than in X-ray refinements, found no disorder for the DDPv sample synthesised at  $1000^\circ\text{C}$  but gave 2.6(2)% Mn/W antisite disorder for the DPv polymorph made at  $1300^\circ\text{C}$ . This evidences a tiny influence of A-cation disorder and increased temperature on the B-cation ordering. Full neutron refinement results are in Tables S4 and S5.

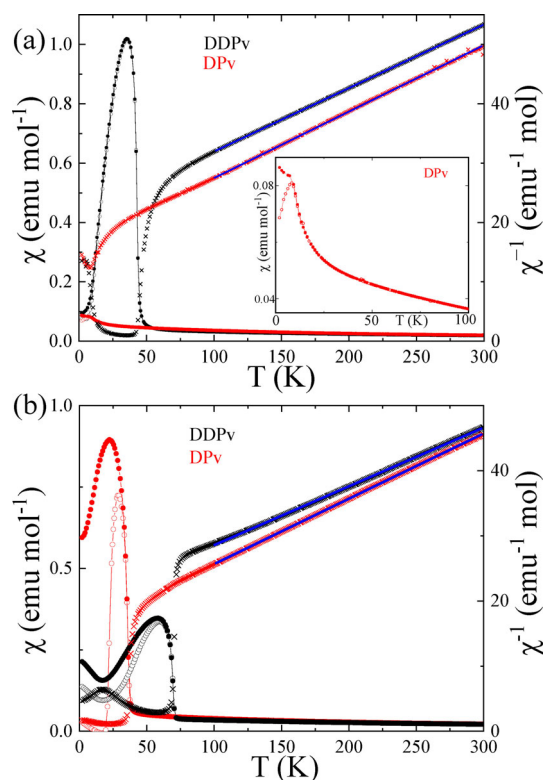
Magnetic properties of the DDPv and DPv polymorphs of  $\text{CaMnMnWO}_6$  and  $\text{SmMnMnTaO}_6$  were measured to discover how they are affected by the change from A cation order to disorder. High temperature susceptibilities of DDPv and DPv polymorphs of  $\text{CaMnMnWO}_6$  in Figure 4a show similar Curie–Weiss variations with fitted effective paramagnetic moments of 8.64 and 8.45  $\mu_B$  per formula unit, respectively, close to the theoretical value for high-spin  $3d^5 \text{Mn}^{2+}$  of 8.37  $\mu_B$ . Their respective Weiss temperatures are  $\theta = -198$  and  $-145$  K showing that antiferromagnetic  $\text{Mn}^{2+}$  spin-spin coupling is dominant, with some weakening of interactions in the DPv structure due to disorder. However very different ordering effects are apparent at low temperature. DDPv- $\text{CaMnMnWO}_6$  has a sharp Curie transition at  $T_C = 45$  K while the DPv polymorph shows a broader susceptibility peak (identified below as a spin glass transition) at  $T_g = 8$  K. This indicates moderate magnetic frustration in the DDPv material (frustration factor  $-\theta/T_C = 4.4$ ) whereas the DPv phase is highly frustrated ( $-\theta/T_g = 18$ ). Magnetisation-field loops at 5 K in Figure S3 show small hystereses with saturation moments of 0.05 and 0.03  $\mu_B$  and coercive fields of 500 and 100 Oe for DDPv and DPv polymorphs, respectively.

Low temperature neutron diffraction was used to explore long range magnetic ordering in the two polymorphs of  $\text{CaMnMnWO}_6$ . For the DDPv phase magnetic diffraction peaks indexed by propagation vector  $k = [0\ 0\ 0]$  appear below the Curie transition. The magnetic intensities are fitted well by a simple ferrimagnetic model in which A-site  $\text{Mn}^{2+}$  spins are antiparallel to B-site spins (Figures S6 and S7). A slight inequivalence of the opposed sublattice moments accounts



**Figure 3.** Cation occupancy order parameters  $Q$  from X-ray refinements averaged over the DDPv and DPv structures for a)  $\text{CaMnMnWO}_6$  and b)  $\text{SmMnMnTaO}_6$  plotted against synthesis temperature. Error bars are smaller than the points. Fits of the function described in the text to  $Q_A$  are shown, while  $Q_B = 1$  throughout as no B-site disorder was observed.





**Figure 4.** a) Magnetic susceptibilities (ZFC/FC = open/filled circles) and inverse ZFC susceptibilities (crosses) with Curie–Weiss fits (blue lines) shown for DDPv (black symbols) and DPv (red symbols) polymorphs of a)  $\text{CaMnMnWO}_6$  and b)  $\text{SmMnMnTaO}_6$ . Inset to (a) shows the spin glass transition of the DPv polymorph. Data were collected in a 0.1 T field for both materials.

for the small saturated moment in the magnetisation measurements. The refined average  $\text{Mn}^{2+}$  sublattice moment of  $3.9(2) \mu_{\text{B}}$  at 1.5 K is reduced from the ideal value of  $5 \mu_{\text{B}}$  reflecting the moderate frustration. In contrast, no magnetic diffraction peaks are observed for DPv- $\text{CaMnMnWO}_6$  at 1.5 K (Figure S5b), showing that the  $T_{\text{g}} = 8$  K peak is a spin glass transition rather than the onset of long range magnetic ordering. Further susceptibility measurements show that the peak broadens and shifts to lower temperature with increasing field and also shifts to slightly higher temperature with increasing frequency in AC measurements (Figure S8), both signatures of spin glass behaviour.

Magnetic susceptibilities for  $\text{SmMnMnTaO}_6$  in Figure 4b show that both DDPv and DPv polymorphs have ferrimagnetic transitions at  $T_{\text{C}} = 69$  and 35 K respectively. An additional transition observed at 18 K for the DDPv phase is likely due to ordering of the  $\text{Sm}^{3+}$  moments with possible reorientation of  $\text{Mn}^{2+}$  spins, as similar transitions were observed for  $\text{RMnMnSbO}_6$  analogues based on magnetic  $\text{R}^{3+}$  cations.<sup>[9]</sup> The inverse susceptibility plots show that the two polymorphs have significantly different slopes and Curie–Weiss fits give effective paramagnetic moments of  $9.41(2)$  and  $8.93(2) \mu_{\text{B}}$  for DDPv and DPv polymorphs. Subtraction of the theoretical  $\text{Mn}^{2+}$  contribution gives respective estimates of 4.3 and  $3.1 \mu_{\text{B}}$  for the  $\text{Sm}^{3+}$  moment, reflecting sensitivity to local environment which affects the contribution of low-energy higher  $J$ -

states to the paramagnetic moment. The fitted Weiss constants of  $-217$  and  $-156$  K give frustration factors of 3.1 and 4.5 for the DDPv and DPv phases showing that both are moderately frustrated, with greater frustration in the A-cation disordered DPv polymorph. Magnetisation-field loops at 5 K in Figure S3b show small saturation magnetisations of 0.01 and  $0.03 \mu_{\text{B}}$  for DDPv and DPv phases, and a change in coercive field from 1700 Oe at 35 K to 400 Oe at 5 K shown in Figure S3c is consistent with the likely  $\text{Sm}^{3+}$  moment ordering transition at 18 K in DDPv- $\text{SmMnMnTaO}_6$ .

The above results demonstrate that  $P4_2/n$ -type  $\text{AA}'\text{BB}'\text{O}_6$  double double perovskites can be thermally transformed at pressure to  $(\text{A}_{0.5}\text{A}'_{0.5})_2\text{BB}'\text{O}_6$  double perovskites in which A/A' cations are disordered but B/B' remain fully ordered. The transitions in  $\text{CaMnMnWO}_6$  and  $\text{SmMnMnTaO}_6$  are first order and proceed entirely via coexistence of the DDPv and DPv structures, without any incipient A/A' disorder being observed in the former. However the average A-site occupancy order parameter across the two structures follows a continuous mean field behaviour in  $\text{CaMnMnWO}_6$ , enabling the upper transition temperature to be estimated as  $1260^\circ\text{C}$  (and near  $1470^\circ\text{C}$  for  $\text{SmMnMnTaO}_6$ ). Both DDPv and DPv polymorphs of each material can thus be recovered by quenching under pressure from temperatures either side of the transition, and this strategy is expected to be applicable to many other double double perovskites provided the transition temperature is within experimental limits.

The ability to make double double and double perovskite polymorphs of the same chemical composition is important as it enables the effects of order or disorder of A/A' cations on physical properties such as magnetism in  $\text{CaMnMnWO}_6$  and  $\text{SmMnMnTaO}_6$  to be directly compared. The rocksalt type  $\text{MnB}'\text{O}_6$  B-site arrangement in these materials has an intrinsic geometric frustration from networks of edge-sharing  $\text{Mn}_4$  spin tetrahedra, and antiferromagnetic orders have been observed in  $\text{A}_2\text{MnWO}_6$  double perovskites below Néel temperatures of  $T_{\text{N}} = 8, 8, 13$  and 16 K respectively for  $\text{A} = \text{Ba},^{[28]} \text{Pb},^{[29]} \text{Sr},^{[30]}$  and  $\text{Ca}.^{[24]}$  The increase in  $T_{\text{N}}$  across the series reflects a decrease in frustration as crystal symmetry is lowered from cubic ( $\text{A} = \text{Ba}$ ) through orthorhombic (Pb), tetragonal (Sr) to monoclinic  $P2_1/n$  (Ca) symmetry due to A cation size decreasing plus  $\text{Pb}^{2+}$  off-centre distortion.<sup>[31]</sup> New magnetic ground states of the  $\text{MnWO}_6$  network are stabilised in the  $\text{CaMnMnWO}_6$  phases reported here. Ordering of cations in the DDPv polymorph is found to switch spin order in the  $\text{MnWO}_6$  network to ferromagnetic, with overall ferrimagnetism below  $T_{\text{C}} = 45$  K. However, Ca/Mn disorder in the double perovskite polymorph gives a spin glass with freezing temperature  $T_{\text{g}} = 8$  K. DPv- $\text{CaMnMnWO}_6$  is notable as a highly frustrated material featuring two types of frustrated sublattices, the randomly disordered Ca/Mn cations at the A-sites and the geometrically frustrated rocksalt Mn/W arrangement at the B-sites. The presence of large  $S = 5/2$   $\text{Mn}^{2+}$  spins leads to a spin glass ground state for  $\text{CaMnMnWO}_6$ , but analogous disordered double perovskites based on  $S = 1/2$  cations like  $\text{Cu}^{2+}$  could have quantum spin liquid ground states providing an exciting possibility for future research. For  $\text{SmMnMnTaO}_6$  the difference between Sm/Mn order and disorder is less dramatic as both cations are magnetic, and both DDPv and

DPv polymorphs appear to have ferromagnetic ground states although with greater frustration and suppression of a separate  $\text{Sm}^{3+}$  magnetic transition in the latter.

In conclusion, thermal transformations under pressure of two representative manganese-based  $P4_2/n$ -type  $\text{AA}'\text{BB}'\text{O}_6$  double double perovskites to  $(\text{A}_{0.5}\text{A}'_{0.5})_2\text{BB}'\text{O}_6$  double perovskites are demonstrated. The transition is first order due to incompatible octahedral tilts in the two structures and proceeds entirely via coexistence of the DDPv and DPv structures for both  $\text{CaMnMnWO}_6$  and  $\text{SmMnMnTaO}_6$ . The change from  $\text{A}/\text{A}'$  order to disorder leads to a dramatic switch of magnetic properties in  $\text{CaMnMnWO}_6$ , from ferrimagnetic order in the double double perovskite to a spin glass ground state in the highly frustrated double perovskite. The ability to generate both double double and double perovskite polymorphs of the same composition provides a systematic method for exploring how frustration of long range magnetic order can lead to spin glass or liquid ground states, and will enable the effects of cation order and disorder on other physical properties such as ferroelectricity and conductivity to be explored for other materials.

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### Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** double perovskites · high-pressure chemistry · magnetic properties · solid-state structures

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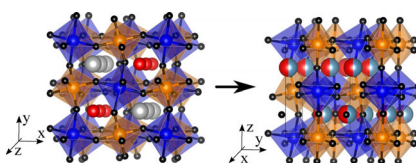
## Communications



## Perovskites

K. Ji, K. N. Alharbi, E. Solana-Madruga,  
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Double Double to Double Perovskite  
Transformations in Quaternary  
Manganese Oxides



Thermal transformations under pressure of  $AA'BB'O_6$  double double perovskites, where both A and B sites have 1:1 cation order, to  $(A_{0.5}A'_{0.5})_2BB'O_6$  double perovskites with disordered A/A' cations are demonstrated for  $\text{CaMnMnWO}_6$  and  $\text{SmMnMnTaO}_6$ , leading to a dramatic switch in magnetic properties from ferrimagnetic order to spin glass behaviour in the former.