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Angel M. Arevalo-Lopez, Elena Solana-Madruga, Cintli Aguilar-Maldonado, Clemens Ritter, Olivier Mentré, Paul Attfield

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## Magnetic frustration in the high-pressure $\text{Mn}_2\text{MnTeO}_6$ ( $\text{Mn}_3\text{TeO}_6$ -II) double perovskite.

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Ángel M. Arévalo-López<sup>a\*</sup>, Elena Solana-Madruga,<sup>b</sup> Cintli Aguilar-Maldonado,<sup>a</sup> Clemens Ritter,<sup>c</sup> Olivier Mentré,<sup>a</sup> and J.Paul Attfield<sup>b\*</sup>

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**A new double perovskite  $\text{Mn}_2\text{MnTeO}_6$  has been obtained by high pressure phase transformation of a corundum-related precursor. It is antiferromagnetic below 36 K and develops a magnetic structure with magnetic moments of  $4.8 \mu_B$  and  $3.8 \mu_B$  for  $\text{Mn}^{2+}$  at the A and B sites respectively. This new polymorph accounts for a recently reported decrease in the bandgap of  $\text{Mn}_3\text{TeO}_6$  under pressure that may lead to useful light-harvesting properties.**

The  $\text{ABO}_3$  perovskite structure has proven to be very versatile, since it can accommodate several cations at both A and B sites. The consequent accessibility to a wide range of magnetic and electrical properties have attracted much attention. Perovskites show increasing distortion with decreasing ionic radius of the A-site cation, down to tolerance factors  $t = (r_A + r_O) / (\sqrt{2}(r_B + r_O))$  of 0.75, where  $r_A$ ,  $r_B$  and  $r_O$  are the ionic radii of the A, B and O ions<sup>1</sup>. However, the use of high pressures enables small cations such as  $\text{Mn}^{2+}$  ( $r = 0.96 \text{ \AA}$ )<sup>2</sup> to be accommodated at the A-sites, allowing complex electronic and magnetic interactions. For example  $\text{Mn}^{2+}\text{V}^{4+}\text{O}_3$  perovskite shows the coexistence of localized  $d^5$   $\text{Mn}^{2+}$  and itinerant  $d^1$  electron  $\text{V}^{4+}$  cations<sup>3</sup>. Further variety is achieved in high pressure double perovskites (DPVs)  $\text{Mn}_2\text{BB}'\text{O}_6$  with ordering of two cations on the B sites;  $\text{Mn}_2\text{BSbO}_6$  (B = Sc, Cr, and Fe)<sup>4,6</sup>,  $\text{Mn}_2\text{BREo}_6$  (B = Mn, Fe and Co)<sup>7-9</sup> and  $\text{Mn}_2(\text{Fe}_{0.8}\text{Mo}_{0.2})\text{MoO}_6$ .<sup>10</sup> Tellurium based oxides  $\text{M}_2\text{MTeO}_6$  (M = Mn, Co and Ni) have structures based on the corundum arrangement at ambient pressure (see Supplementary Figure 1) and show a variety of complex magnetic orders.  $\text{Mn}_3\text{TeO}_6$ -I crystallises in the  $\text{Mg}_3\text{TeO}_6$ -type structure.<sup>11</sup> Below 24 K it shows the coexistence of an elliptical helix and a sinusoidal spin density wave, both

being incommensurate with the crystal structure. This phase has shown a dielectric response below 21 K and so is a type-II multiferroic<sup>12</sup>.  $\text{Co}_3\text{TeO}_6$  has 5 independent Co sites, providing a rich magnetic phase diagram<sup>13</sup> and  $\text{Ni}_3\text{TeO}_6$  is a non-hysteretic colossal magnetoelectric material with a collinear antiferromagnetic (AFM) structure stabilised on stacked honeycomb layers<sup>14</sup>.

A recent study of light-harvesting properties of  $\text{Mn}_3\text{TeO}_6$ -I discovered an irreversible 39% bandgap reduction during in-situ measurements under pressure<sup>15</sup>. We have explored the possibility of transforming ambient pressure  $\text{Mn}_3\text{TeO}_6$ -I phase into a recoverable double perovskite using high pressure and high temperature conditions, and we report here the new double perovskite  $\text{Mn}_2\text{MnTeO}_6$ , which is likely to be responsible for the reported bandgap engineering.

$\text{Mn}_3\text{TeO}_6$ -I, prepared at 1270 K by the solid state synthesis method of reference 11 was packed into a Pt capsule, pressed at 8 GPa and heated at 1173 K using a Walker-type module in a multianvil press. After 20 minutes, the temperature was quenched and the pressure was slowly released. Synchrotron X-ray diffraction (SXRD) powder data were collected at room temperature using the BL04 beamline at ALBA, Barcelona. Neutron powder diffraction (NPD) data were taken on 6 combined high pressure samples ( $\approx 120 \text{ mg}$ ) at 50 K, 1.5 K and several intermediate temperatures using the D1B beamline at the ILL, Grenoble. Zero-field cooled and field cooled (ZFC and FC) magnetic susceptibilities and a magnetisation-field loop at 2 K were measured using a PPMS Dynacool from Quantum Design.

Preliminary laboratory X-ray diffraction evidenced the transition from  $\text{Mn}_3\text{TeO}_6$ -I into a new double perovskite,  $\text{Mn}_3\text{TeO}_6$ -II. This was found to have a monoclinic  $P2_1/n$  rock-salt B-site ordered DPV structure from Rietveld fitting of 300 K SXRD data (Fig. 1a). A few % of  $\delta$ - $\text{Mn}_3\text{O}_4$  ( $\text{CaMn}_2\text{O}_4$ -type) and Pt from the capsule are included in the refinements. The SXRD results are summarised in Table 1 and the structure is shown in Fig. 1b.

<sup>a</sup> Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France.

\*[angel.arevalo-lopez@univ-lille.fr](mailto:angel.arevalo-lopez@univ-lille.fr)

<sup>b</sup> Centre for Science at Extreme Conditions (CSEC) and School of Chemistry, The University of Edinburgh, EH9 3FD, U.K. \* [j.p.attfield@ed.ac.uk](mailto:j.p.attfield@ed.ac.uk)

<sup>c</sup> Institut Laue-Langevin, Avenue des Martyrs 71, 32042, Grenoble Cedex, France.

† Data that support the findings of this study have been deposited at <https://datashare.is.ed.ac.uk/handle/10283/838>.

‡ Electronic Supplementary Information (ESI) available: supporting figures and tables. See DOI: 10.1039/x0xx00000x

Antisite disorder between  $Mn_B$  and Te positions was checked but no mixing was found within error showing that  $Mn_3TeO_6$ -II is fully cation-ordered. The refined structural model shows that the  $Mn_BO_6$  octahedra are distorted while  $TeO_6$  octahedra are more regular (Table 1). Octahedral tilts  $\sim 20^\circ$  are comparable to those for other  $Mn_2BB'O_6$  double perovskites and reflect the significant distortion in agreement with the small  $t$ -value ( $t = 0.8$ ) for this high pressure polymorph.

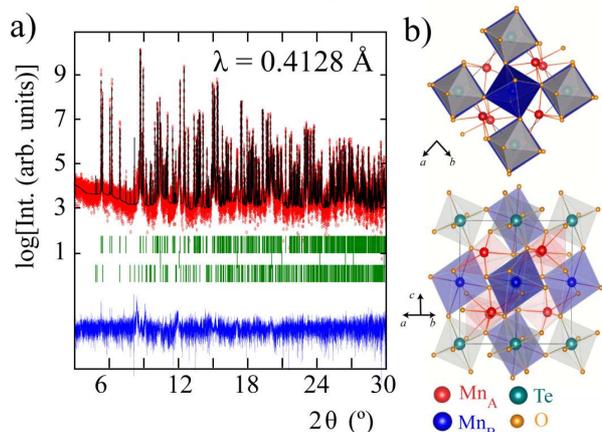


Figure 1. Rietveld fit (a) of the DPV structure of  $Mn_2MnTeO_6$  (b) from 300 K SXR data. Second and third rows of Bragg tick marks are minor amounts of Pt from the capsule (2.2(1) %) and  $\delta$ - $Mn_3O_4$  (1.9(1) %).

Table 1. Atomic positions and main interatomic distances and bond angles from the Rietveld fit of 300 K SXR data. S.G.  $P2_1/n$ ,  $a = 5.29370(1)$  Å,  $b = 5.45203(1)$  Å,  $c = 7.80894(1)$  Å,  $\beta = 89.62514(5)^\circ$ .

Site	x	y	z	Biso (Å <sup>2</sup> )	Occ
Te (2a)	0	0	0	0.43(1)	0.5
$Mn_B$ (2b)	0.5	0.5	0	0.56(2)	0.5
$Mn_A$ (4e)	0.4887(2)	0.0475(1)	0.2397(1)	0.66(2)	1
O1 (4e)	0.1677(8)	0.2784(7)	0.0808(6)	0.31(5)	1
O2 (4e)	0.7106(8)	0.1745(8)	-0.0520(5)	0.31(5)	1
O3 (4e)	0.8794(7)	0.9244(7)	0.2215(5)	0.31(5)	1
$d_{M-O}$ (Å)		$\langle M-O-M \rangle$ (°)			
2x ( $Mn_B$ -O1)	2.308(4)	$Mn_B$ -O1-Te	136.2(3)		
2x ( $Mn_B$ -O2)	2.133(5)	$Mn_B$ -O2-Te	144.9(3)		
2x ( $Mn_B$ -O3)	2.308(4)	$Mn_B$ -O3-Te	137.0(3)		
$\langle Mn_B$ -O $\rangle$	2.249(6)				
2x (Te-O1)	1.870(5)	$Mn_A$ -O1- $Mn_B$	96.5(1)		
2x (Te-O2)	1.851(5)	$Mn_A$ -O2- $Mn_B$	109.6(2)		
2x (Te-O3)	1.885(4)	$Mn_A$ -O3- $Mn_B$	98.7(1)		
$\langle Te$ -O $\rangle$	1.868(5)				
2x $Mn_A$ -O1	2.188(5) 2.458(5) 2.179(5)	$\phi$	21.5 <sup>o</sup>		
3x $Mn_A$ -O2	2.648(5) 2.660(5)	$\theta$	19.7 <sup>o</sup>		
2x $Mn_A$ -O3	2.178(5) 2.192(4)	$\Delta[Mn_BO_6]$	$2.30 \cdot 10^{-3}$		
$\langle Mn_A$ -O $\rangle$	2.358(4)	$\Delta[TeO_6]$	$1.04 \cdot 10^{-4}$		

Octahedral distortions calculated from  $\Delta[MO_6] = (1/n) \cdot \sum (d_i - d_{av})^2 / d_{av}$ . Tilt angles along [001]  $\phi$  and [110]  $\theta$  are calculated from  $(180 - \langle M-O-M \rangle) / 2$ .  $R_p = 16.8\%$ ,  $R_{wp} = 21.9\%$ ,  $R_f = 5.34\%$ ,  $R_B = 7.50\%$ ,  $\chi^2 = 2.22$  %.

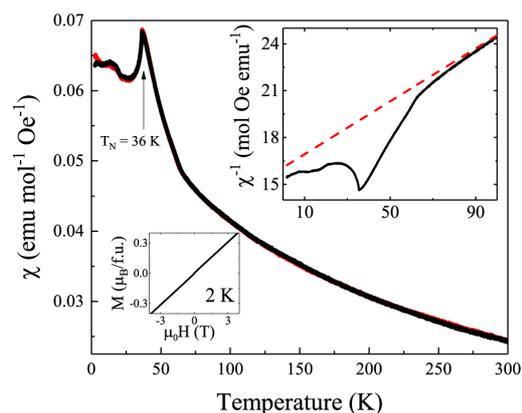


Figure 2. ZFC (black) and FC (red) magnetic susceptibility of  $Mn_2MnTeO_6$ . Insets show the reciprocal susceptibility with C-W from high temperature (red dashed line) (right) and the field dependent magnetisation at 2 K (left).

ZFC and FC magnetic susceptibilities were measured under an external field of 500 Oe (Figure 2). They show a single antiferromagnetic transition at  $T_N = 36(0.5)$  K. A Curie-Weiss fit to the inverse susceptibility in the 100 - 300 K temperature range gives  $\mu_{eff} = 5.6 \mu_B / Mn^{2+}$ , in good agreement with the theoretical value of  $5.92 \mu_B$  for spin only  $Mn^{2+}$  ( $S = 5/2$ ). The large negative Weiss constant  $\theta = -183(1)$  K indicates predominant antiferromagnetic interactions, and the linear dependence of magnetisation on applied field at 2 K (left inset in Figure 2), demonstrates the absence of a ferromagnetic component to the low temperature order. The upturn of the susceptibility observed below 25 K may be due to traces of the  $Mn_3TeO_6$ -I phase ( $T_N = 24$  K).

Rietveld fits to the NPD data collected at D1B at 50 K and 1.5 K are shown in Figure 3a. The large difference between neutron scattering lengths for Mn (-3.73 fm) and Te (5.80 fm) appear ideal to test for antisite disorder, thus the refinements confirmed the well-ordered structural model obtained from SXR. Oxidation states estimated from BVS calculations on the 50 K NPD model are 2.1, 1.7 and 6.0 for  $Mn_A$ ,  $Mn_B$  and Te sites respectively, demonstrating that the charge distribution is  $Mn_2^{2+}Mn^{2+}Te^{6+}O_6$ .

Prominent magnetic peaks observed below  $T_N$  can be indexed with the  $k = [\frac{1}{2} \ 0 \ \frac{1}{2}]$  propagation vector. The magnetic symmetry analysis was performed using the Baslreps tool implemented in the Rietveld refinement program FullProf Suite<sup>16</sup>. The resulting irreducible representations (Ireps) are summarised in Table S1 in the ESI and all four simple possible models were tested. The best fit is when both A- and B-site Mn spins follow Irep  $\Gamma_4$  and can be refined independently ( $R_B = 6.60\%$ ,  $R_f = 8.54\%$ ,  $R_{Mag} = 10.1\%$ ,  $\chi^2 = 1.233$  for  $T = 1.5$  K). The 1.5 K - 50 K difference pattern containing only magnetic intensity is shown as an inset in the lower panel of Figure 3a and magnetic refinement details are shown in ESI and Table S2.

The magnetic structure of  $\text{Mn}_2\text{MnTeO}_6$ -II, depicted in Figure 3b, can be described as  $ab$  layers of  $\text{Mn}_A$  spins AFM coupled with  $\text{Mn}_B$  spins perpendicular to the  $a$  direction in the magnetic unit cell. These layers are separated by diamagnetic  $\text{TeO}_6$  octahedra, stacked AFM along the  $c$  direction and with the spins confined in the  $ac$  plane. The  $90^\circ$  superexchange  $\text{Mn}_A\text{-O-Mn}_B$   $d^5\text{-}d^5$  interactions are assumed to be the dominant ones (see Table 1), and satisfy the Goodenough-Kanamori-Anderson rules (GKA).<sup>17</sup> The refined ordered magnetic moments at 1.5 K converge to  $\mu_A = 4.8(6)$   $\mu_B$  and  $\mu_B = 3.9(1)$   $\mu_B$  for A- and B-site  $\text{Mn}^{2+}$  respectively. The refined value for  $\text{Mn}_A$  agrees well with the expected ordered magnetic moment of 5  $\mu_B$  for  $\text{Mn}^{2+}$ , while the reduced value obtained for the  $\text{Mn}_B$  sublattice reflects some frustration present in the system, the later also supported by the ratio  $f = |\theta|/T_N \sim 5$ .

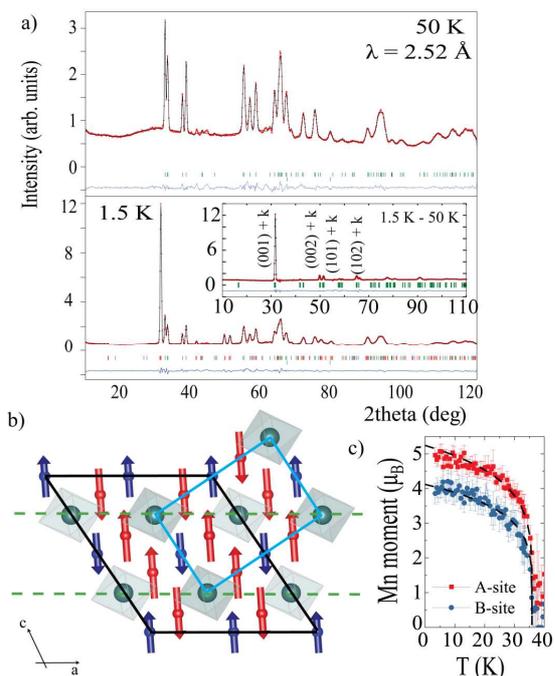


Figure 3. a) Rietveld fits of the nuclear and magnetic structures to the 50 K (top) and 1.5 K (bottom) NPD data. The right inset shows the fit of the magnetic model to the 1.5 K – 50 K difference pattern. b)  $ac$  plane of the magnetic structure of  $\text{Mn}_2\text{MnTeO}_6$  with  $\text{Mn}_A$  and  $\text{Mn}_B$  spins as red and blue arrows respectively. Magnetic unit cell  $t$  is delimited with a black line and related to the crystallographic cyan one via the transformation matrix:  $[(1\ 0\ -1), (0\ -1\ 0), (-2\ 0\ 0)]$  with an origin shift of  $(0, 0, 1/2)$  and magnetic space group  $Pc2_1/n$  (14.80). Green dashed lines show the AFM planes described in the text. c) Thermal evolution of the  $\text{Mn}^{2+}$  magnetic moments and fit to the critical law (dashed black line) as described.

The magnetic model was used to fit the NPD scans at intermediate temperatures giving the evolution of the magnetic moments at both sites, as shown in Fig. 3c. Their fit by the critical law  $\mu(T) = \mu(0) * [1 - (T/T_N)]^\beta$  in the  $(T_N/2) < T < T_N$  temperature range led to the parameters  $T_N = 35.8(1)$  K and  $\beta \approx 0.19(1)$ , confirming a simultaneous order of both sublattices, in agreement with magnetisation measurements. The small  $\beta$  value suggests a reduced dimensionality, being close to the

expected value of 0.23 for a 2D-XY model<sup>18</sup> and agreeing with the refined magnetic structure with spin directions confined into the  $ac$  plane.

In this context, the comparison with related high-pressure double perovskites  $\text{Mn}_2\text{BB}'\text{O}_6$  is remarkable. Table 2 summarises the main features of their magnetic behaviours, which suggests the essential role of the diamagnetic B' cation on the frustrated B-site magnetic moments of these compounds as detailed below.  $\text{Mn}_2\text{MnTeO}_6$ ,  $\text{Mn}_2\text{MnReO}_6$  and  $\text{Mn}_2\text{CoReO}_6$  are the only  $\text{Mn}_2\text{BB}'\text{O}_6$  compounds reported to stabilise a DPV structure with divalent B and hexavalent B' cations. The highest magnetic frustration is observed in  $\text{Mn}_2\text{MnTeO}_6$  and is released in  $\text{Mn}_2\text{BReO}_6$  by the presence of the paramagnetic cation  $\text{Re}^{6+}$ , which enables further superexchange pathways within the B sublattice and consequently increases  $T_N$ . Both  $\text{Mn}_2\text{CoReO}_6$  and  $\text{Mn}_2\text{MnReO}_6$  become ordered around 100 K into almost perpendicular AFM A and B sublattices with  $k = [\frac{1}{2}\ \frac{1}{2}\ 0]$  and with reduced moments in B.<sup>9,7</sup> The isoelectronic  $\text{Mn}^{2+}$  cations at A and B sites in  $\text{Mn}_2\text{MnReO}_6$  give rise to magnetoelastic effects that prompt Re magnetic ordering at lower temperatures than the Mn ( $f = 1.4$ ). However, in  $\text{Mn}_2\text{CoReO}_6$  with  $\text{Co}^{2+}$  in a high spin state, some GKA paths are blocked and it recovers some frustration increasing  $f$  up to 3.6. In  $\text{Mn}_2\text{FeReO}_6$  the strong coupling between  $\text{Fe}^{3+}$  ( $d^5$ ) and  $\text{Re}^{5+}$  ( $d^2$ ) leads to a ferrimagnetic ordering on the B/B'-sites at high temperatures into a simple  $k = [0\ 0\ 0]$  magnetic structure ( $f = 0.9$ ).<sup>8</sup> Likewise,  $\text{Mn}_2\text{Fe}_{0.8}\text{Mo}_{0.2}\text{MoO}_6$  shows almost no frustration ( $f = 0.3$ ) due to the B-sublattice disordering of cations and the presence of Mo in a 4+ and 5+ oxidation states.

Our comparison has to include compounds of type  $\text{Mn}_2\text{BSbO}_6$  ( $B = \text{Sc}, \text{Cr}$  and  $\text{Fe}$ ) due to the presence of a diamagnetic B' cation as in  $\text{Mn}_2\text{MnTeO}_6$ . All of them achieve high degrees of magnetic frustration with transitions lower than 60 K.  $B = \text{Sc}$ , where only  $\text{Mn}^{2+}$  at the A sites are paramagnetic, has a strong frustration ( $f = 4.3$ ) with AFM order at 22 K into a simple collinear magnetic structure with  $k = [0\ 0\ 0]$ .<sup>4</sup>  $B = \text{Cr}^{3+}$  shows the closest magnetic structure to that of  $\text{Mn}_2\text{MnTeO}_6$ , with  $k = [\frac{1}{2}\ 0\ \frac{1}{2}]$  and AFM  $d^5\text{-}d^3$  A-O-B superexchange interactions at  $90^\circ$ .<sup>5</sup> The weaker nature of these interactions compared to the  $d^5\text{-}d^5$   $\text{Mn}^{2+}_A\text{-O-Mn}^{2+}_B$  of  $\text{Mn}_2\text{MnTeO}_6$ , justifies the slightly lower frustration of  $\text{Mn}_2\text{CrSbO}_6$ . Finally,  $\text{Mn}_2\text{FeSbO}_6$  is isoelectronic to  $\text{Mn}_2\text{MnTeO}_6$  with both  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$   $d^5$  cations.  $\text{Mn}_2\text{FeSbO}_6$  presents an incommensurate helical magnetic structure with  $k = [0\ 0.426\ 0]$ .<sup>6</sup> The origin of this difference is that the exchange integral for  $\text{Fe}^{3+}$  is much larger than that for  $\text{Mn}^{2+}$ ,<sup>19</sup> inducing strong competitions between AFM  $d^5\text{-}d^5$  A-O-B and A-O-A interactions, thus frustrating the compound into a helical magnetic structure. In the case of  $\text{Mn}^{2+}$  the larger difference between these interactions, prevents the rotation of the spins and the release of the strong magnetic frustration, see Supporting Information for the interplays between A-A, B-B and A-B with frustrated topologies.

Finally,  $\text{Mn}_3\text{TeO}_6$  has been recently reported as a promising light-harvesting material due to an irreversible pressure-

induced phase transition occurring at 16–18 GPa, where an energy bandgap reduction of  $\Delta E_{\text{gap}} \approx 1$  eV is observed.<sup>15</sup> Our experimental plots of the Kubelka-Munk function of the UV-VIS reflectance spectra in Figure 4 show a  $\Delta E_{\text{gap}} \approx 0.8$  eV reduction from the  $\text{Mn}_3\text{TeO}_6$  precursor ( $E_{\text{gap}} = 2.6$  eV) to the  $\text{Mn}_2\text{MnTeO}_6$  perovskite ( $E_{\text{gap}} = 1.8$  eV) and we conclude that this is very probably the phase observed in the high pressure measurements. The change in connectivity from edge- to corner-shared octahedra between both polymorphs explains the decrease in the bandgap in the double perovskite.<sup>20</sup>

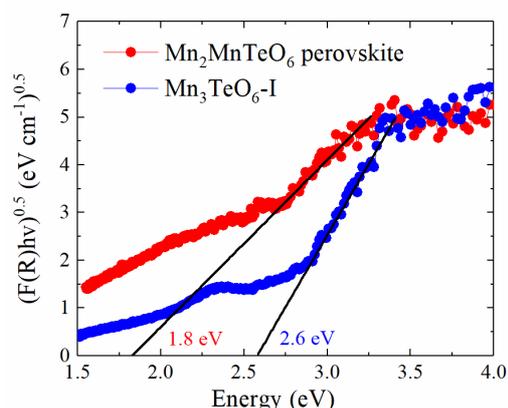


Figure 4. Kubelka-Munk plots (for an indirect bandgap) - for  $\text{Mn}_3\text{TeO}_6$ -I and the  $\text{Mn}_2\text{MnTeO}_6$  high-pressure double perovskite polymorph, both measured at ambient pressure and temperature.

Table 2. Main features of the magnetic behaviour for  $\text{Mn}_2\text{BB}'\text{O}_6$  double perovskites, including, electronic configuration of B and B' cations, transition temperature, Weiss constant ( $\theta$ ), frustration index ( $f = |\theta|/T_N$ ) and propagation vector ( $k$ ).

B	B'	$d_B$		$d_{B'}$	$T_N/T_C$ (K)	$\theta$	f	k
		$t_{2g}$	$e_g$					
Sc	Sb	0	0	10	22	94	4.3	0 0 0 <sup>4</sup>
Mn	Te	3	2	10	36	183	5.1	$\frac{1}{2}$ 0 $\frac{1}{2}$ * <sup>5</sup>
Cr	Sb	3	0	10	55	220	4.0	$\frac{1}{2}$ 0 $\frac{1}{2}$ <sup>5</sup>
Fe	Sb	3	2	10	60	180	3.0	0 $k_y$ 0 <sup>6</sup>
Co	Re	5	2	1	94	26	3.6	$\frac{1}{2}$ $\frac{1}{2}$ 0 <sup>9</sup>
Mn	Re	3	2	1	109	147	1.4	$\frac{1}{2}$ $\frac{1}{2}$ 0 <sup>7</sup>
$\text{Fe}_{0.8}\text{Mo}_{0.2}$	Mo	3	2	1	194	50	0.3	0 0 0 <sup>10</sup>
Fe	Re	3	2	2	520	452	0.9	0 0 0 <sup>8</sup>

\*This work

In conclusion, a new DPV  $\text{Mn}_2\text{MnTeO}_6$  has been prepared by high-pressure high-temperature transformation of the rhombohedral polymorph. Due to the large charge and size difference between  $\text{Mn}^{2+}$  and  $\text{Te}^{6+}$ ,  $\text{Mn}_2\text{MnTeO}_6$  shows a fully ordered B/B' rock-salt type DPV structure. It is AFM below  $T_N = 36$  K and it develops a complex magnetic structure with ordered magnetic moments of 4.8 (1)  $\mu_B$  and 3.8 (1)  $\mu_B$  at the A and B sites respectively. The magnetic structure describes AFM *ab* layers of A- and B-site spins, AFM coupled along the *c* axis, with the spins confined in the *ac* plane.  $\text{Mn}_2\text{MnTeO}_6$  shows the highest frustration index among the A-site manganites with

DPV structure. Replacement by non-magnetic B' cations proves to be a way to enhance the frustration and may be used as tuning parameter in partial B' substitutions. Formation of this DPV polymorph accounts for the previously reported bandgap reduction under pressure.

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**Conflicts of interest.** There are no conflicts to declare.

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