**Electronic Supplementary information**

# Investigation of the magnetic spin correlations in the layered molybdenates, $Mn_2Mo_3O_8$ and $MnAMo_3O_8$ (A = Fe, Co, Zn)

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## Experimental Refinement details

**X-ray diffraction data:** Rietveld refinements of the data collected at both room temperature (298 K) and 12 K for $Mn_2Mo_3O_8$ were performed using the GSAS suite of programs[1,2] in the proposed $P6_3mc$ space group[3]. Refinements were performed for 26 variables which included lattice parameters, atomic positions, zero-point, 10 shifted Chebyshev background terms and peak shape fitted using a pseudo-Voigt function. The refinement also included the $MnMoO_4$ ($C2/m$) phase[4]. Room temperature refinements were performed in the same way for $MnFeMo_3O_8$ (26 variables), $MnCoMo_3O_8$ (23 variables) and $MnZnMo_3O_8$ (26 variables). For both $MnFeMo_3O_8$ and $MnZnMo_3O_8$ a $MnMoO_4$ secondary phase was also refined as described in the main text of the paper. Displacement parameters for all atoms in all refinements were fixed to 0.01 $U_{(iso)}/U_{(e)}$ x 100 (Å$^2$).

**Wish data:** All refinements of powder neutron diffraction (WISH) data were performed using the data collected from detector bank 4, covering a *d*-spacing of 1 Å to 6 Å. For refinement of the nuclear structure of $Mn_2Mo_3O_8$, 36 parameters, including background, phase fraction, unit cell and atomic positions were refined using the FULLPROF suite of programs[5]. The molybdenum z position was fixed to 0.25 to define the origin of the unit cell. Refining isotropic lead to non-physical values. For all temperature values these were fixed to values extracted from a multibank refinement of data collected for $Mn_2Mo_3O_8$ using detector banks 3 (1 Å to 7.5 Å), 4 (1 Å to 6 Å) and 5 (1 Å to 5 Å) at a temperature of 40 K (shown in figure S2 – refinement data is not included). A further constraint was used to fix all cation sites and all anion sites to have the same value. At all temperature points both the $Mn_2Mo_3O_8$ and $MnMoO_4$ nuclear

structures were included in the refinements[3,4]. Below 40 K the magnetic structure was determined for $Mn_2Mo_3O_8$ (***k*** = (0,0,0)) as described in the main paper. Below 10 K it was also necessary to incorporate the magnetic phase associated with $MnMoO_4$ (***k*** = (1,0,0.5))[4]. Refinements of the WISH data collected at 100 K and 2 K for $MnFeMo_3O_8$ and $MnCoMo_3O_8$ were refined in the same way as described for $Mn_2Mo_3O_8$. In order to determine cation order, a second set of atoms for Mn1 and Mn2 were incorporated with the fractional occupancies allowed to refine. For all refinements the isotropic atomic displacement parameters were constrained to have the same value for cations and anions respectively. Additionally, At 2 K for the $MnCoMo_3O_8$ and $MnFeMo_3O_8$ the atom positions, $U_{iso}$ and fractional occupancies were not refined and those determined at 100 K were used due to refinement complexities.

***GEM data*:** Powder neutron diffraction data were collected for $MnZnMo_3O_8$ through the GEM express route. Data were collected at temperatures of 200 K, 150 K, 100 K, 50 K and 5 K. Refinements were performed using the GSAS suite of programs[1,2]. Refinements were performed using the data collected using detector bank 3 (0.4 Å to 6.4 Å). A total of 39 variables were refined which included background (fitted using a linear interpolation function for consistency with the WISH data collected for $MnFeMo_3O_8$ and $MnCoMo_3O_8$), lattice parameters, atomic positions and thermal displacements. The peak shape was modelled using the pseudo-Voigt function (type 2 in GSAS) described by Howard, and Thompson *et al*[6,7]. For all of the refinements, the isotropic atomic displacement parameters ($U_{iso}$) were constrained together for cations and oxygen. The cation order was determined by introducing a second set of octahedral and tetrahedral sites and the site occupancy between the same site type was refined.

For context, In all refinements the $P6_3mc$ model describes the tetrahedral site as the Mn1 site and the octahedral site as the Mn2 site.

**Results**

***$Mn_2Mo_3O_8$:*** Table S1 provides the Rietveld refinement parameters for the XRD data collected at 12 K and 298 K for $Mn_2Mo_3O_8$. Refinement profiles are given in the main text of the paper as figure 2. Figure S1 shows the temperature dependence of $d\chi/dT$ for $Mn_2Mo_3O_8$ showing a sharp peak at ~40 K consistent with $T_N$ and variable temperature magnetometry data collected at applied fields of 0.1 T and 5 T. Full refinements profiles and data are given for the variable temperature study of $Mn_2Mo_3O_8$ in tables S2 through S5, and figures S3 and S4. Refinements were performed as described in the experimental refinement details section above and in the main text of the paper. Figures S5 and S6 give the temperature dependence of the lattice parameters, cell volume, Mn1_O3_Mn1 bond angle and tetrahedral and octahedral bond

lengths. Lastly figure S7 gives the temperature dependence of the magnetic moment and the fit to plot of ln $M_T/M_0$ vs. ln 1-($T/T_N$) from which the critical exponent, $\beta$ to be extracted.

***Table S1:*** *Rietveld refinement parameters for x-ray powder diffraction data collected at room temperature and 12 K for $Mn_2Mo_3O_8$, refined using the $P6_3mc$ model[3]. Refinements were performed incorporating a $MnMoO_4$ (C2/m) second phase[4]. Note: thermal displacement parameters were constrained for all atoms to values of* 0.01 $U_{(iso)}/U_{(e)}$ x 100 (Å$^2$).

| **Parameter** | **Temperature (K)** | |
|---|---|---|
| | **298** | **12** |
| **$\chi^2$** | 2.71 | 3.5 |
| **Rp (%)** | 5.74 | 6.3 |
| **wRp (%)** | 7.50 | 8.6 |
| **a (Å)** | 5.80066(2) | 5.79491(2) |
| **c (Å)** | 10.27314(6) | 10.2651(7) |
| **Cell Volume (Å$^3$)** | 299.35(2) | 298.53(2) |
| **Mn1 (⅓, ⅔, *z*)** | 0.9534(6) | 0.9671(8) |
| **Mn2 (⅓, ⅔ ,*z*)** | 0.5141(7) | 0.528(8) |
| **Mo1 (*x*, -*x*, ¼)** | 0.1459(1) | 0.1456(1) |
| **O1 (0, 0, *z*)** | 0.390(1) | 0.396(1) |
| **O2 (⅓, ⅔ ,*z*)** | 0.141(1) | 0.149(1) |
| **O3 (*x*, -*x* ,*z*)** | 0.488(1)<br>0.367(1) | 0.483(1)<br>0.381(1) |
| **O4 (*x*, -*x* ,*z*)** | 0.165(1)<br>0.631(6) | 0.164(1)<br>0.636(1) |

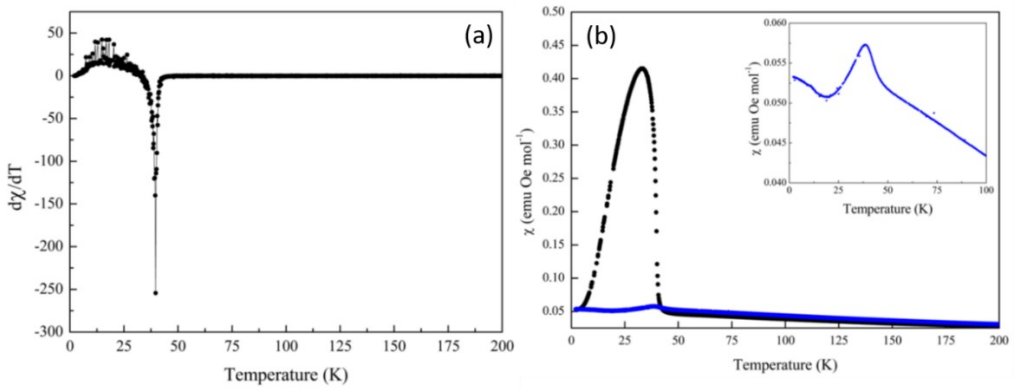


***Figure S1:*** *Magnetic susceptibility data collected for $Mn_2Mo_3O_8$ where (a) shows the derivative ($d\chi/dT$) of the zero field cooled data indicating a sharp feature at $T_N$ = 39.6(4) K and (b)Zero field cooled susceptibility data collected at applied fields of 0.1 T (black) and 5 T (blue and enlarged in inset) showing the sharpening of the magnetic transition.*

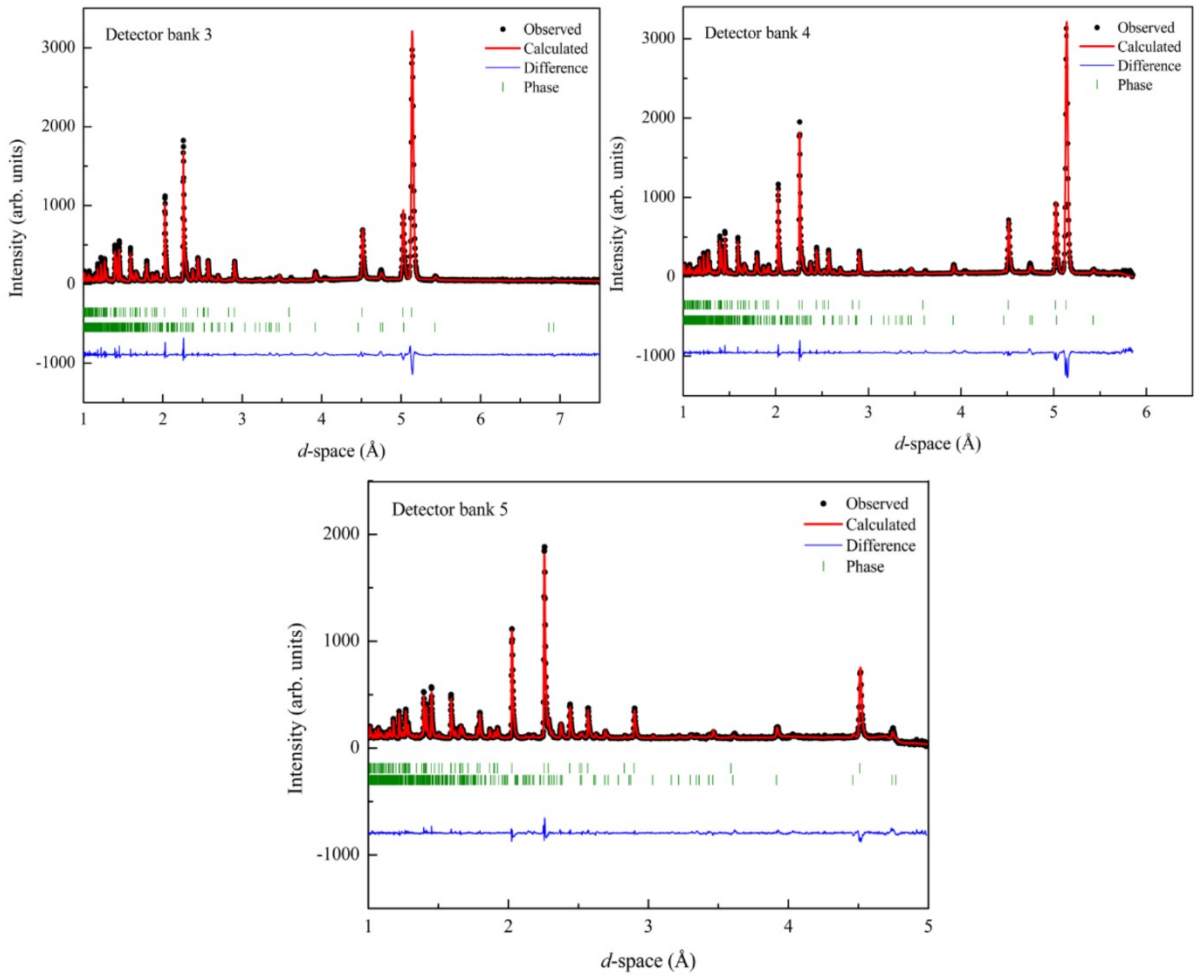


***Figure S2:*** *Rietveld refinement of the powder neutron diffraction data collected for $Mn_2Mo_3O_8$ at 40 K simultaneously fitted to the $P6_3mc$ model[3] using WISH detector banks 3, 4 and 5 (147 variables). Black crosses represent observed data, red line represents the calculated model and the blue line represents the difference between the observed and calculated data. From top to bottom the tick marks represent the following phases, $Mn_2Mo_3O_8$ nuclear and $MnMoO_4$ nuclear. Refinement residuals: Detector Bank 3 Rp: 17.2 %, Rwp: 14.6 % and $\chi$2: 7.8; Detector Bank 4 Rp: 14.1 %, Rwp: 12.6 % and $\chi$2: 6.1; Bank 5 Rp: 19.3 %, Rwp: 12.5 % and $\chi$2: 3.4.*

***Table S2:*** *Rietveld refinement parameters for powder neutron diffraction (WISH) data collected between 200 K and 40 K for $Mn_2Mo_3O_8$, refined using the $P6_3mc$ model[3].*

*Refinements were performed incorporating a $MnMoO_4$ (C2/m) second phase[4]. Note: thermal displacement parameters were constrained to values of* 023(5) and 0.58(4) $U_{(iso)}/U_{(e)}$ x 100 ($Å^2$) for cations and anions respectively as determined from the multibank refinement performed at 40 K.

| Parameter | Temperature (K) | | | | | |
|---|---|---|---|---|---|---|
| | **200** | **140** | **100** | **80** | **60** | **40** |
| **$\chi^2$** | 0.80 | 0.85 | 1.26 | 1.54 | 0.908 | 0.94 |
| **Rp (%)** | 11.5 | 11.5 | 12.5 | 13.1 | 11.3 | 11.9 |
| **wRp (%)** | 13.9 | 13.6 | 17.2 | 17.6 | 14.2 | 14.9 |
| **a (Å)** | 5.797520(6) | 5.796487(4) | 5.796128(6) | 5.796019(8) | 5.795445(6) | 5.795635(6) |
| **c (Å)** | 10.268250(9) | 10.266706(9) | 10.265966(9) | 10.26565(1) | 10.265269(9) | 10.265389(9) |
| **Cell Volume ($Å^3$)** | 298.89(1) | 298.74(1) | 298.68(1) | 298.66(1) | 298.63(1) | 298.61(1) |
| **Mn1 (⅓, ⅔, *z*)** | 0.953(2) | 0.955(1) | 0.954(1) | 0.953(2) | 0.953(1) | 0.951(1) |
| **Mn2 (⅓, ⅔ ,*z*)** | 0.512(2) | 0.513(2) | 0.512(2) | 0.511(2) | 0.512(2) | 0.510(2) |
| **Mo1 (*x*, -*x*, ¼)** | 0.1475(3) | 0.1475(3) | 0.1475(3) | 0.1474(4) | 0.1476(3) | 0.1473(3) |
| **O1 (0, 0, *z*)** | 0.3897(9) | 0.3895(9) | 0.3899(9) | 0.390(1) | 0.3893(9) | 0.3891(9) |
| **O2 (⅓, ⅔ ,*z*)** | 0.146(1) | 0.147(1) | 0.146(1) | 0.146(2) | 0.148(1) | 0.148(1) |
| **O3 (*x*, -*x* ,*z*)** | 0.4881(3)<br>0.3629(6) | 0.4879(3)<br>0.3631(6) | 0.4878(3)<br>0.3634(5) | 0.4880(5)<br>0.3629(9) | 0.4885(3)<br>0.3621(5) | 0.4877(3)<br>0.3623(6) |
| **O4 (*x*, -*x* ,*z*)** | 0.1659(4)<br>0.6333(6) | 0.1663(4)<br>0.6330(6) | 0.1662(4)<br>0.6335(6) | 0.1659(6)<br>0.6330(9) | 0.1664(4)<br>0.6323(6) | 0.1661(4)<br>0.6324(6) |

***Table S3:*** *Selected bond lengths and bond angles extracted from powder neutron diffraction (WISH) data collected between 200 K and 40 K for $Mn_2Mo_3O_8$, refined using the $P6_3mc$ model[3].*

| Bond Lengths and Angles | Temperature (K) | | | | | |
|---|---|---|---|---|---|---|
| | **200** | **140** | **100** | **80** | **60** | **40** |
| Mn1_O2 (Å) | 1.983(8) | 1.978(8) | 1.976(8) | 1.982(8) | 1.994(8) | 2.017(8) |
| Mn1_O3 (Å) | 2.019(7) | 2.025(7) | 2.021(7) | 2.02(1) | 2.019(7) | 2.012(7) |
| Mn2_O3 (Å) | 2.19(1) | 2.19(1) | 2.17(1) | 2.17(2) | 2.19(1) | 2.17(1) |
| Mn2_O4 (Å) | 2.09(1) | 2.09(1) | 2.09(1) | 2.10(1) | 2.08(1) | 2.09(1) |
| Mo_O1 (Å) | 2.062(7) | 2.060(7) | 2.062(7) | 2.06(1) | 2.059(7) | 2.056(7) |
| Mo_O2 (Å) | 2.148(6) | 2.143(6) | 2.148(6) | 2.15(1) | 2.140(6) | 2.146(6) |
| Mo_O3 (Å) | 2.084(4) | 2.084(4) | 2.085(4) | 2.083(6) | 2.080(3) | 2.079(4) |
| Mo_O4 (Å) | 1.984(4) | 1.988(4) | 1.984(4) | 1.985(6) | 1.992(4) | 1.991(4) |
| Mn1_O3_Mn2 (˚) | 108.0(4) | 107.6(4) | 108.2(4) | 108.3(6) | 107.8(4) | 108.9(4) |

***Table S4:*** *Rietveld refinement parameters for powder neutron diffraction (WISH) data collected between 35 K and 2 K for $Mn_2Mo_3O_8$, refined using the $P6_3mc$ model[3].*
*Refinements were performed incorporating a $MnMoO_4$ (C2/m) second phase[4]. Note: thermal*

*displacement parameters were constrained to values of* 023(5) and 0.58(4) $U_{(iso)}/U_{(e)}$ x 100 ($Å^2$) for cations and anions respectively as determined from the multibank refinement performed at 40 K.

| Parameter | Temperature (K) | | | | | |
|---|---|---|---|---|---|---|
| | **35** | **30** | **25** | **20** | **10** | **2** |
| **$\chi^2$** | 0.86 | 0.95 | 1.40 | 0.99 | 1.20 | 0.92 |
| **Rp (%)** | 10.8 | 10.4 | 10.1 | 10.0 | 9.64 | 8.65 |
| **wRp (%)** | 13.4 | 13.7 | 16.1 | 13.3 | 14.3 | 11.9 |
| **a (Å)** | 5.795433(5) | 5.795241(5) | 5.795142(5) | 5.794902(5) | 5.794941(5) | 5.794818(5) |
| **c (Å)** | 10.265319(9) | 10.265288(9) | 10.26536(1) | 10.265403(9) | 10.26549(1) | 10.265386(9) |
| **Cell Volume ($Å^3$)** | 298.59(1) | 298.57(1) | 298.56(1) | 298.54(1) | 298.54(1) | 298.53(1) |
| **Mn1 (⅓, ⅔, *z*)** | 0.950(1) | 0.950(1) | 0.949(2) | 0.949(1) | 0.948(1) | 0.953(1) |
| **Mn2 (⅓, ⅔ ,*z*)** | 0.511(2) | 0.510(2) | 0.511(2) | 0.510(2) | 0.510(2) | 0.511(2) |
| **Mo1 (*x*, -*x*, ¼)** | 0.1477(3) | 0.1477(3) | 0.1478(3) | 0.1482(3) | 0.1480(9) | 0.1479(3) |
| **O1 (0, 0, *z*)** | 0.3894(9) | 0.3892(9) | 0.390(1) | 0.3896(9) | 0.3897(9) | 0.389(1) |
| **O2 (⅓, ⅔ ,*z*)** | 0.148(1) | 0.148(1) | 0.148(1) | 0.0147(1) | 0.147(1) | 0.147(1) |
| **O3 (*x*, -*x* ,*z*)** | 0.4871(4)<br>0.3625(6) | 0.4867(4)<br>0.3629(5) | 0.4865(4)<br>0.3631(6) | 0.4872(4)<br>0.3627(5) | 0.4862(4)<br>0.3633(4) | 0.4884(5)<br>0.3639(6) |
| **O4 (*x*, -*x* ,*z*)** | 0.1661(4)<br>0.6325(6) | 0.1655(4)<br>0.6327(6) | 0.1656(4)<br>0.6325(6) | 0.1658(4)<br>0.6325(6) | 0.1657(4)<br>0.6329(6) | 0.1659(4)<br>0.6334(7) |

***Table S5:*** *Selected bond lengths and bond angles extracted from powder neutron diffraction (WISH) data collected between 35 K and 2 K for $Mn_2Mo_3O_8$, refined using the $P6_3mc$ model[3].*

| Bond Lengths and Angles | Temperature (K) | | | | | |
|---|---|---|---|---|---|---|
| | **35** | **30** | **25** | **20** | **10** | **2** |
| Mn1_O2 (Å) | 2.028(8) | 2.043(8) | 2.04(1) | 2.035(8) | 2.041(8) | 1.99(1) |
| Mn1_O3 (Å) | 2.015(7) | 2.013(7) | 2.012(8) | 2.007(7) | 2.011(7) | 2.008(8) |
| Mn2_O3 (Å) | 2.17(1) | 2.16(1) | 2.16(1) | 2.16(1) | 2.15(1) | 2.17(1) |
| Mn2_O4 (Å) | 2.09(1) | 2.10(1) | 2.10(1) | 2.10(1) | 2.11(1) | 2.10(1) |
| Mo_O1 (Å) | 2.061(7) | 2.059(7) | 2.062(7) | 2.066(7) | 2.065(7) | 2.060(7) |
| Mo_O2 (Å) | 2.138(6) | 2.135(6) | 2.136(6) | 2.137(6) | 2.138(6) | 2.139(6) |
| Mo_O3 (Å) | 2.077(4) | 2.078(4) | 2.078(4) | 2.075(4) | 2.077(4) | 2.087(4) |
| Mo_O4 (Å) | 1.990(4) | 1.986(4) | 1.988(4) | 1.990(4) | 1.987(4) | 1.984(5) |
| Mn1_O3_Mn2 (˚) | 108.8(4) | 109.3(4) | 109.4(5) | 109.5(4) | 109.9(4) | 108.9(5) |

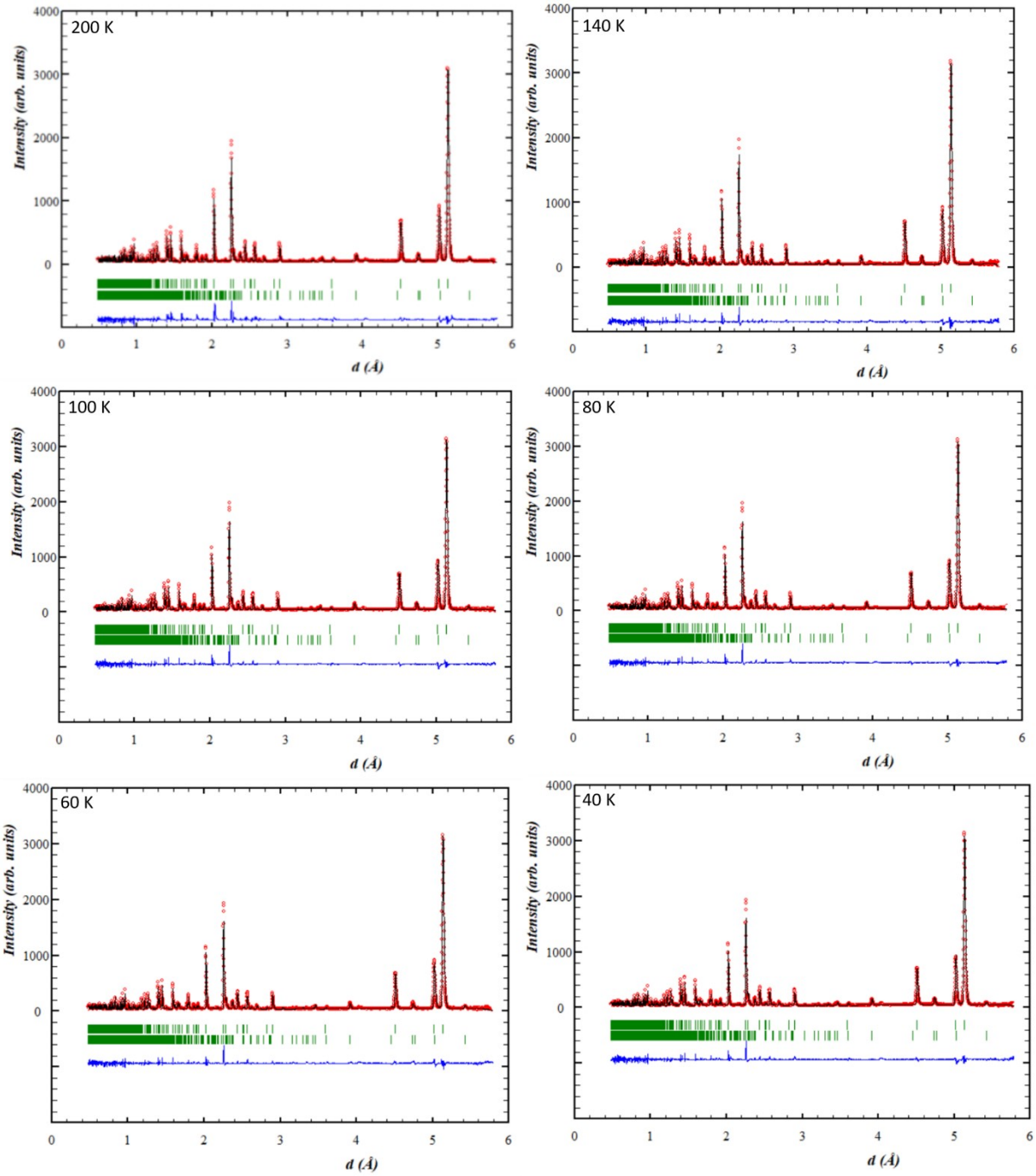


***Figure S3:*** *Rietveld refinement of the powder neutron diffraction data collected for $Mn_2Mo_3O_8$ at temperatures of 200 K, 140 K, 100 K, 80 K, 60 K and 40 K and fitted to the $P6_3mc$ model[3]. Black crosses represent observed data, red line represents the calculated model and the blue line represents the difference between the observed and calculated data. From top to bottom the tick marks represent the following phases, $Mn_2Mo_3O_8$ nuclear and $MnMoO_4$ nuclear.*

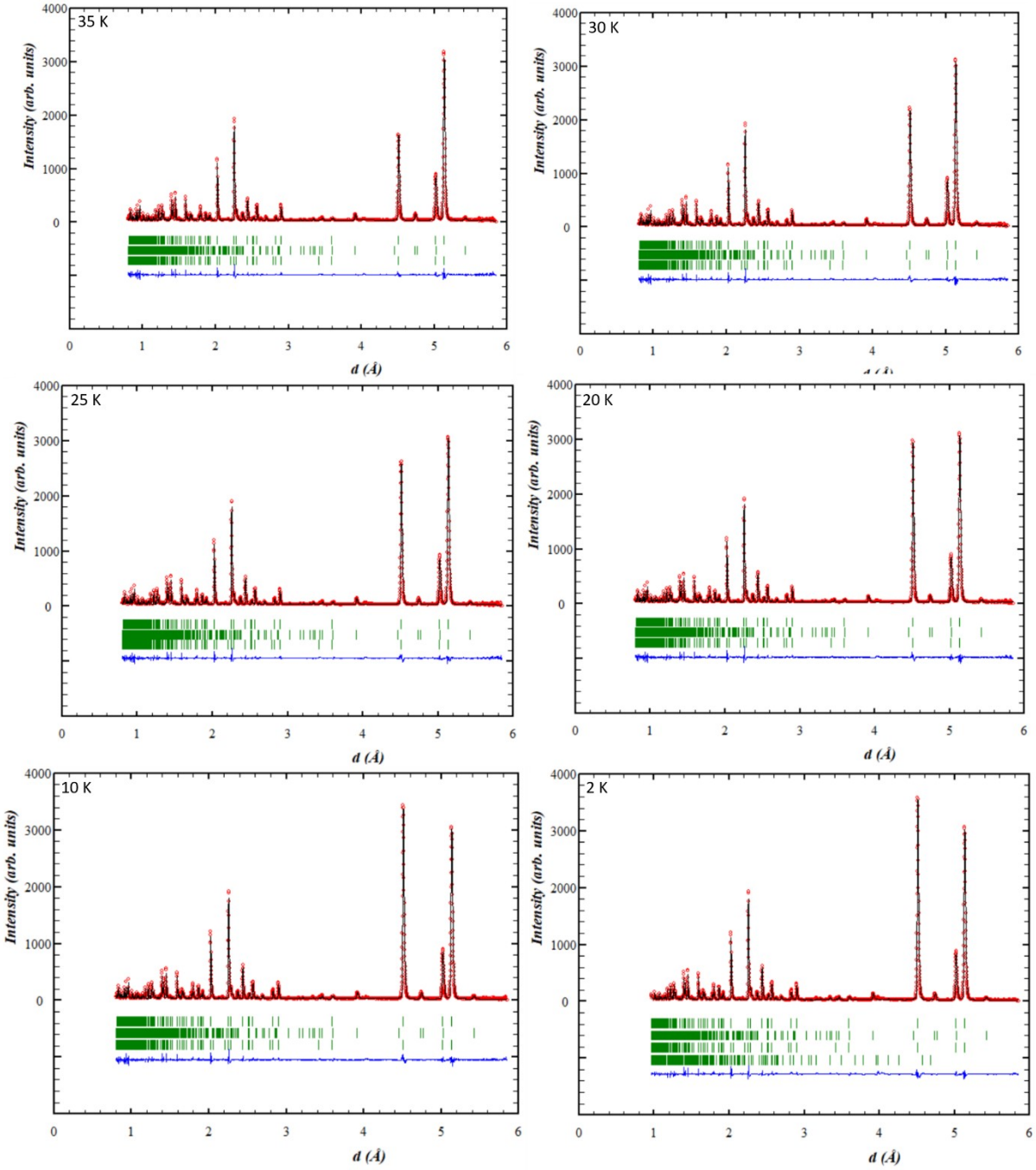


***Figure S4:*** *Rietveld refinement of the powder neutron diffraction data collected for $Mn_2Mo_3O_8$ at temperatures of 35 K, 30 K, 25 K, 20 K, 10 K and 2 K and fitted to the $P6_3mc$ model[3]. Black crosses represent observed data, red line represents the calculated model and the blue line represents the difference between the observed and calculated data. From top to bottom the tick marks represent the following phases, $Mn_2Mo_3O_8$ nuclear, $MnMoO_4$ nuclear, $Mn_2Mo_3O_8$ magnetic and $MnMoO_4$ magnetic (2 K only).*

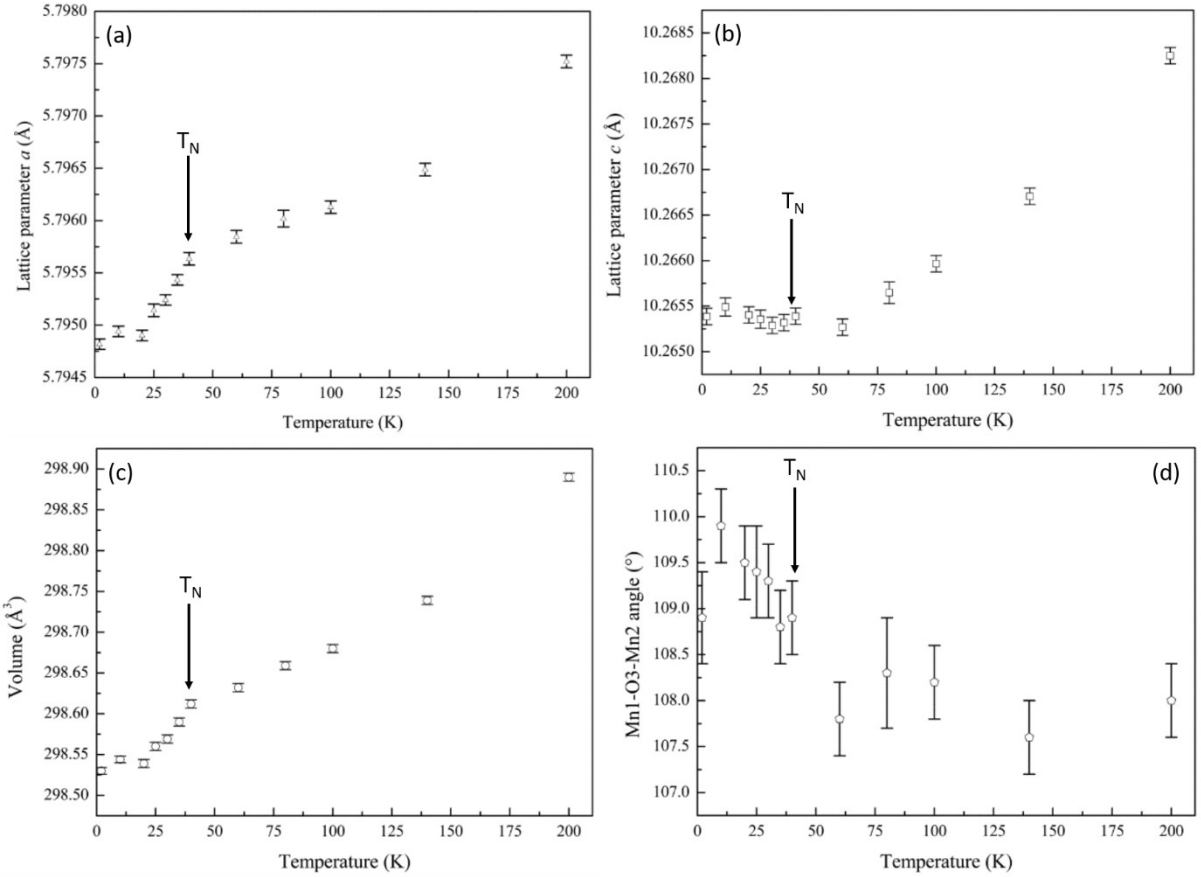


***Figure S5:*** *Temperature dependence of (a) lattice parameter, a, (b) lattice parameter, c, (c) cell volume and (d) $Mn_{tet}$-O-$Mn_{oct}$ bond angle for $Mn_2Mo_3O_8$ extracted from Rietveld refinement of the powder neutron diffraction data.*

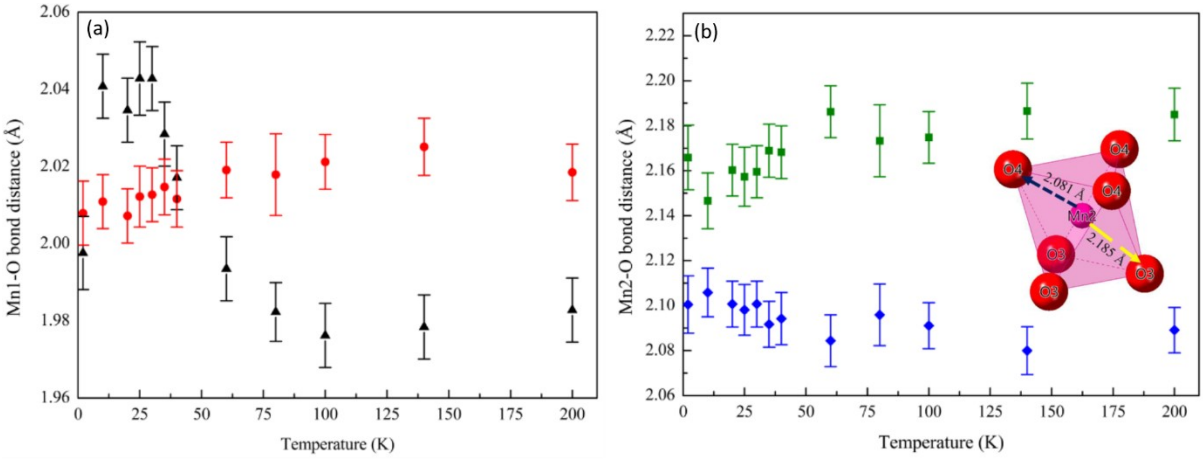


***Figure S6:*** *Temperature dependence of (a) the tetrahedral bond lengths Mn1-O2 (black, apex of tetrahedra) and Mn1-O3 (red, base of tetrahedra) and (b) octahedral bond lengths Mn2-O4 (blue) and Mn2-O3 (green) of the distorted octahedral unit shown in the inset of (b). Data extracted from the Rietveld refinement of the powder neutron diffraction data.*

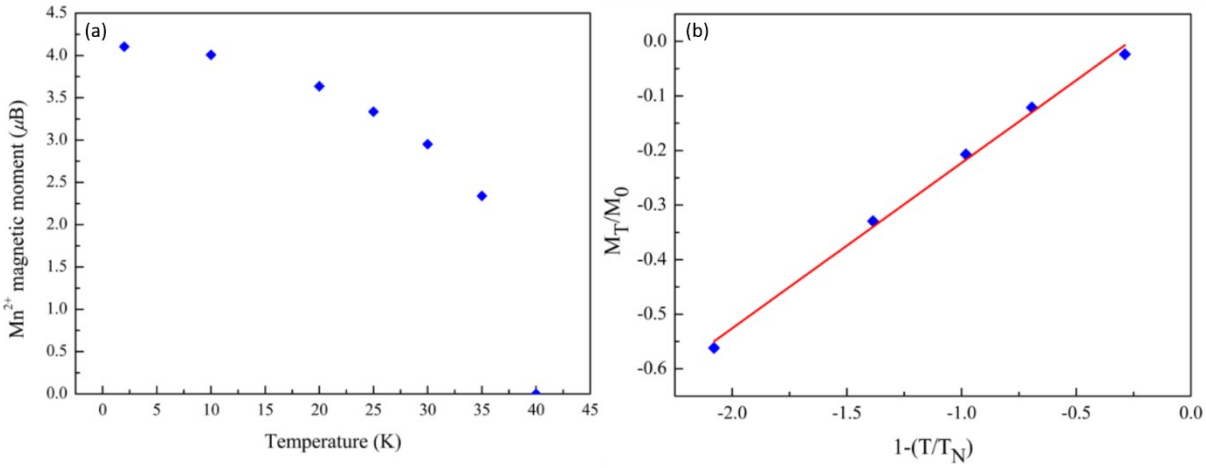


***Figure S7:*** *Temperature dependence of (a) the magnetic moment as extracted from the fitting of the powder neutron diffraction data collected over a temperature range of 2 K to 40 K and (b) plot of ln $M_T/M_0$ vs. ln 1-$(T/T_N)$ showing a linear relationship where β is given by the slope. Note the error bars in both plots are smaller than the point size.*

***$MnAMo_3O_8$:*** Rietveld refinement data (table S6) and profiles (figure S8) for the Rietveld refinement of the powder x-ray diffraction data collected for $MnFeMo_3O_8$, $MnCoMo_3O_8$ and $MnZnMo_3O_8$. Figures S9 and S10 provides the molar heat capacity data ($C_p$) measured in zero field and field dependent SQUID magnetometry data, respectively, collected for $MnFeMo_3O_8$, $MnCoMo_3O_8$ and $MnZnMo_3O_8$. Rietveld refinement data and profiles of the powder neutron (WISH) diffraction data collected for $MnFeMo_3O_8$ and $MnCoMo_3O_8$ are given in tables S7 and S8, and figure S11. Likewise, Rietveld refinement data and profiles of the powder neutron (GEM) diffraction data collected for $MnZnMo_3O_8$ are given in tables S9 and S10, and figure S12. Finally, temperature dependent behaviour of the lattice parameters and selected bond lengths/angles are given in figure S13 showing little variance confirming the lack of magnetic order in this material and by extrapolation magnetoelectric behaviour in $MnZnMo_3O_8$.

***Table S6:*** *Rietveld refinement parameters for x-ray powder diffraction data collected at room temperature and 12 K for $Mn_2Mo_3O_8$, refined using the $P6_3mc$ model[3]. Refinements were performed incorporating a $MnMoO_4$ (C2/m) second phase[4]. Note: thermal displacement parameters were constrained for all atoms to values of* 0.01 $U_{(iso)}/U_{(e)}$ x 100 ($Å^2$).

| Parameter | Sample | | |
|---|---|---|---|
| | **$MnFeMo_3O_8$** | **$MnCoMo_3O_8$** | **$MnZnMo_3O_8$** |
| **$\chi^2$** | 9.13 | 1.32 | 2.0 |
| **Rp (%)** | 5.47 | 8.17 | 7.59 |
| **wRp (%)** | 3.60 | 6.46 | 9.95 |
| **a (Å)** | 5.781(1) | 5.784(1) | 5.789(1) |
| **c (Å)** | 10.145(1) | 10.079(1) | 10.060(1) |
| **Cell Volume ($Å^3$)** | 293.69(1) | 292.02(1) | 292.44(1) |
| **Mn1 (⅓, ⅔, *z*)** | 0.949(1) | 0.946(1) | 0.950(1) |
| **Mn2 (⅓, ⅔ ,*z*)** | 0.505(1) | 0.510(1) | 0.512(1) |
| **Mo1 (*x*, -*x*, ¼)** | 0.146(1) | 0.146(1) | 0.145(2) |
| **O1 (0, 0, *z*)** | 0.392(1) | 0.399(2) | 0.409(1) |
| **O2 (⅓, ⅔ ,*z*)** | 0.150(1) | 0.1423(3) | 0.132(1) |
| **O3 (*x*, -*x* ,*z*)** | 0.489(1)<br>0.363(1) | 0.488(1)<br>0.361(2) | 0.492(1)<br>0.366(1) |
| **O4 (*x*, -*x* ,*z*)** | 0.177(1)<br>0.635(1) | 0.182(2)<br>0.633(2) | 0.173(1)<br>0.628(1) |

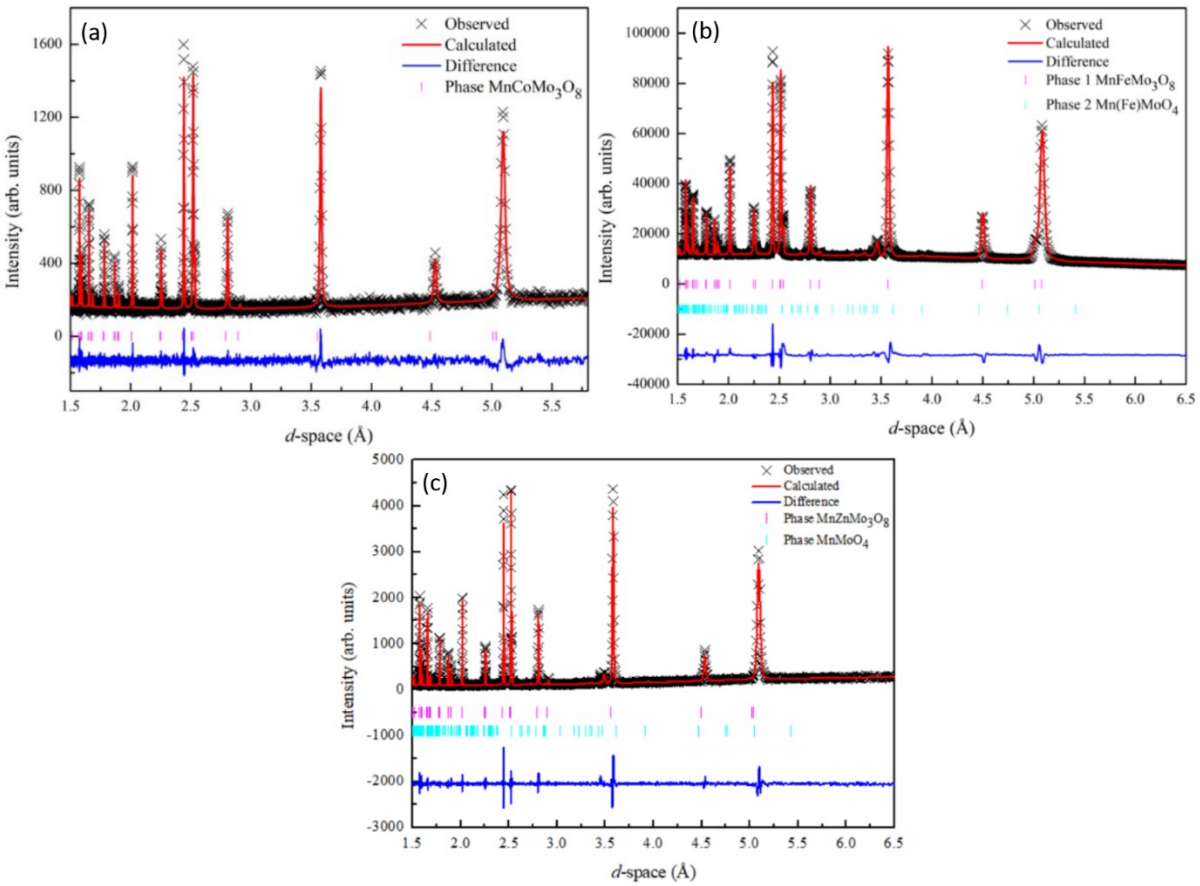


***Figure S8:*** *Rietveld refinement of the x-ray diffraction data collected at 298 K fitted to the $P6_3mc$ model[3] for (a) $MnCoMo_3O_8$, (b) $MnFeMo_3O_8$ and (c) $MnZnMo_3O_8$. Black crosses represent observed data, red line represents the calculated model and the blue line represents the difference between the observed and calculated data. $MnAMo_3O_8$ is represented by the magenta tick marks (top) and $MnMoO_4$ (for A = Fe and Zn) the cyan tick marks (bottom).*

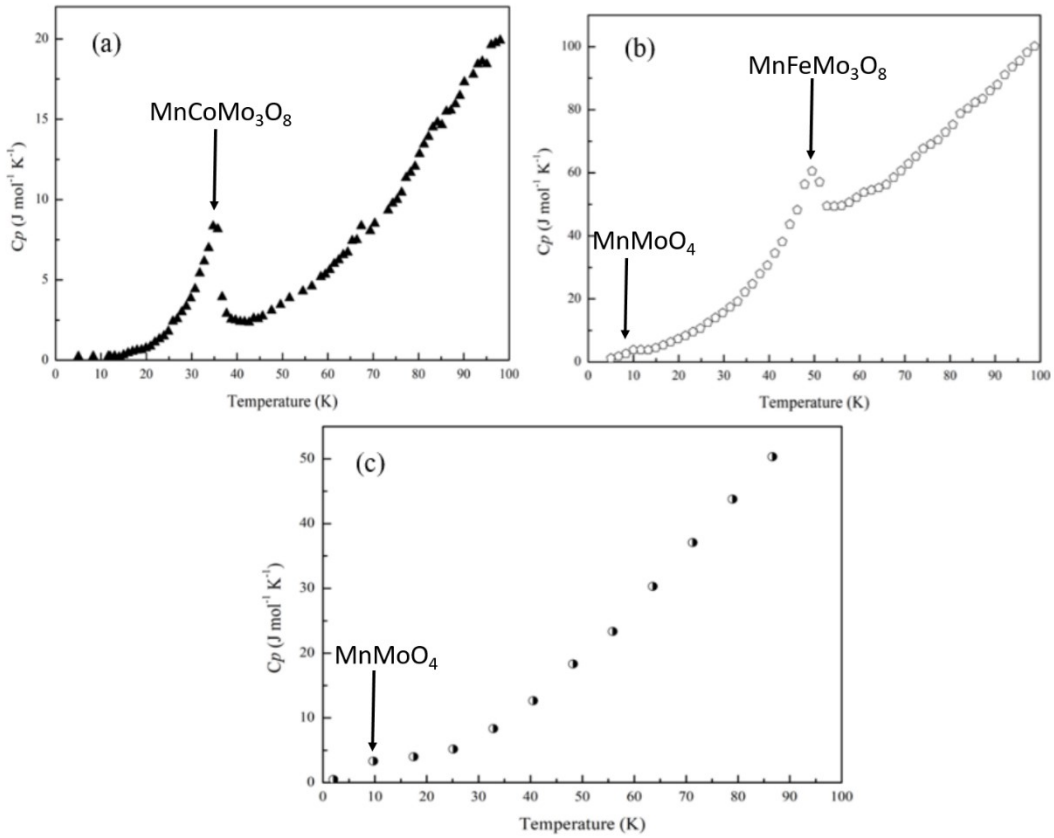


***Figure S9:*** *Molar heat capacity (Cp) data collected for (a) $MnCoMo_3O_8$ showing a sharp increase in Cp at approximately 35 K, (b) $MnFeMo_3O_8$ showing a sharp increase in Cp at approximately 50 K and a weaker inflection at ~10 K attributable to the magnetic transition in $MnMoO_4$ and (c) $MnZnMo_3O_8$ showing only a weak inflection at ~10 K attributable to the magnetic transition in $MnMoO_4$.*

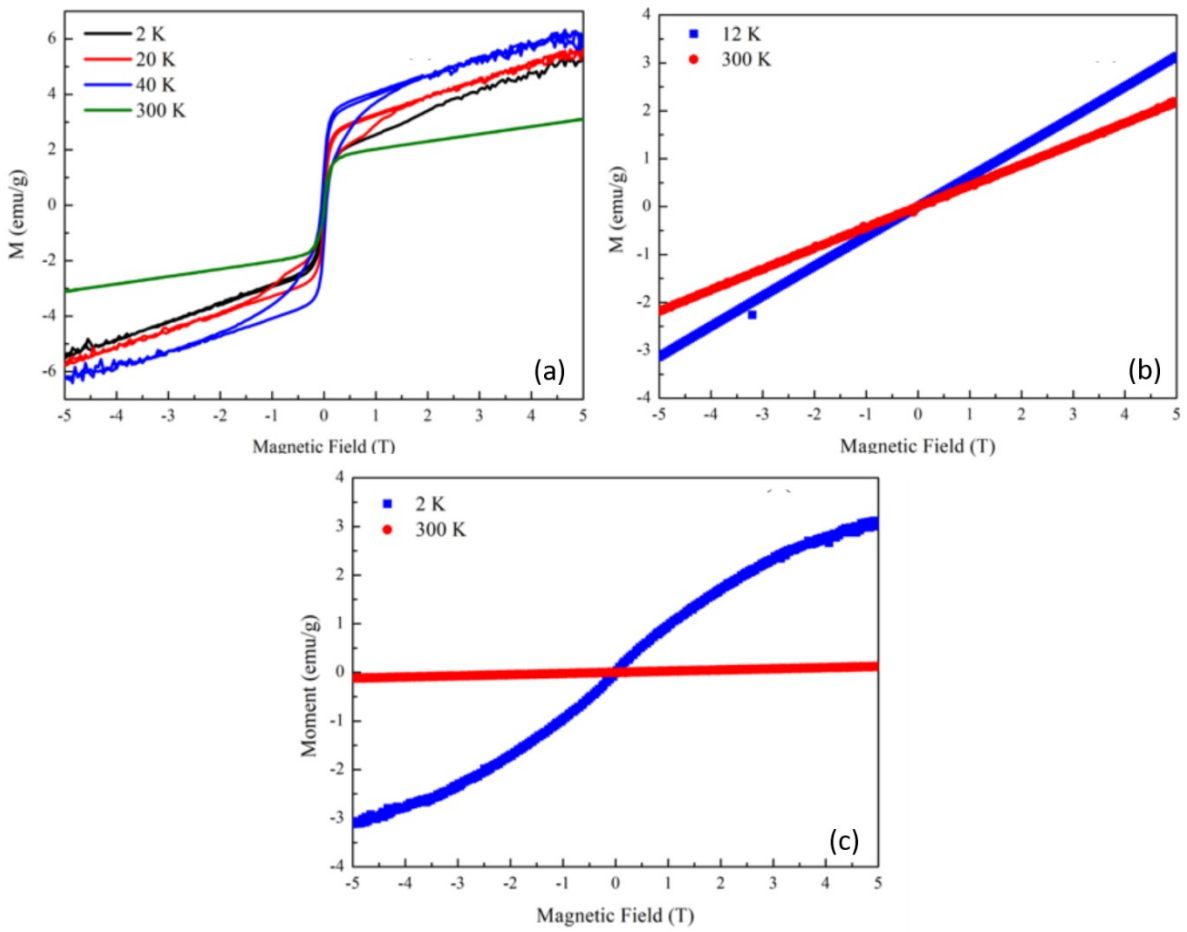


***Figure S10:*** *Field (H) dependent magnetisation data collected between 2 K and 300 K for (a) $MnFeMo_3O_8$, (b) $MnCoMo_3O_8$ and (c) $MnZnMo_3O_8$.*

***Table S7:*** *Rietveld refinement parameters for powder neutron diffraction (WISH) data collected at temperatures 200 K and 2 K for $MnFeMo_3O_8$ and $MnCoMo_3O_8$ refined using the $P6_3mc$ model[3]. Refinements were performed incorporating a $MnMoO_4$ (C2/m) and $Fe_3O_4$ secondary phases into $MnFeMo_3O_8$ and $MnMoO_4$ into $MnCoMo_3O_8$ refinement respectively. Note: thermal displacement parameters were constrained to have identical values for cations and anions respectively. Fractional occupancies are given with respect to Mn in FULLPROF settings, percentages are given in brackets. At 2 K the atom positions, $U_{iso}$ and fractional occupancies were not refined and those determined at 100 K were used.*

| Parameter | $MnFeMo_3O_8$ | | $MnCoMn_3O_8$ | |
|---|---|---|---|---|
| | Temperature (K) | | | |
| | 100 | 2 | 100 | 2 |
| $\chi^2$ | 1.01 | 3.18 | 0.56 | 1.85 |
| Rp (%) | 14.9 | 16.7 | 10.9 | 14.3 |
| wRp (%) | 15.3 | 20.1 | 10.7 | 15.7 |
| a (Å) | 5.786(1) | 5.785(1) | 5.792(1) | 5.7807(1) |
| c (Å) | 10.154(1) | 10.153(1) | 10.070(1) | 10.063(1) |
| Cell Volume (Å$^3$) | 294.46(1) | 294.33(1) | 291.60(1) | 291.23(1) |
| Mn1/A1 (⅓, ⅔, *z*) | 0.956(1) | 0.956(1) | 0.947(6) | 0.947(6) |
| Mn1/A1 $U_{iso}$ * 100 (Å$^2$) | 0.27(5) | 0.27(5) | 0.20(5) | 0.20(5) |
| Mn1/A1 Fractional occupancy | 0.0876(8) 53% | 0.0876(8) 53% | 0.097(1) (58%) | 0.097(1) (58%) |
| Mn2 (⅓, ⅔ ,*z*) | 0.509(1) | 0.509(1) | 0.476(7) | 0.476(7) |
| Mn2/A2 $U_{iso}$ * 100 (Å$^2$) | 0.27(5) | 0.27(5) | 0.20(5) | 0.20(5) |
| Mn2/A2 Fractional occupancy | 0.0700(8) 42% | 0.0700(8) 42% | 0.094(1) (57%) | 0.094(1) (57%) |
| Mo1 (*x*, -*x*, ¼) | 0.1459(1) | 0.1459(1) | 0.1468(3) | 0.1468(3) |
| Mo $U_{iso}$ * 100 (Å$^2$) | 0.27(5) | 0.27(5) | 0.20(5) | 0.20(5) |
| O1 (0, 0, *z*) | 0.1496(7) | 0.1496(7) | 0.3894(6) | 0.3894(6) |
| O1 $U_{iso}$ * 100 (Å$^2$) | 0.36(8) | 0.36(8) | 0.14(3) | 0.14(3) |
| O2 (⅓, ⅔ ,*z*) | 0.1496(7) | 0.1496(7) | 0.1459(7) | 0.1459(7) |
| O2 $U_{iso}$ * 100 (Å$^2$) | 0.36(8) | 0.36(8) | 0.14(3) | 0.14(3) |
| O3 (*x*, -*x* ,*z*) | 0.4878(3) 0.3618(5) | 0.4878(3) 0.3618(5) | 0.4873(2) 0.3624(5) | 0.4873(2) 0.3624(5) |
| O3 $U_{iso}$ * 100 (Å$^2$) | 0.36(8) | 0.36(8) | 0.14(3) | 0.14(3) |
| O4 (*x*, -*x* ,*z*) | 0.1617(4) 0.6345(4) | 0.1617(4) 0.6345(4) | 0.1662(4) 0.6342(4) | 0.1662(4) 0.6342(4) |
| O4 $U_{iso}$ * 100 (Å$^2$) | 0.36(8) | 0.36(8) | 0.14(3) | 0.14(3) |

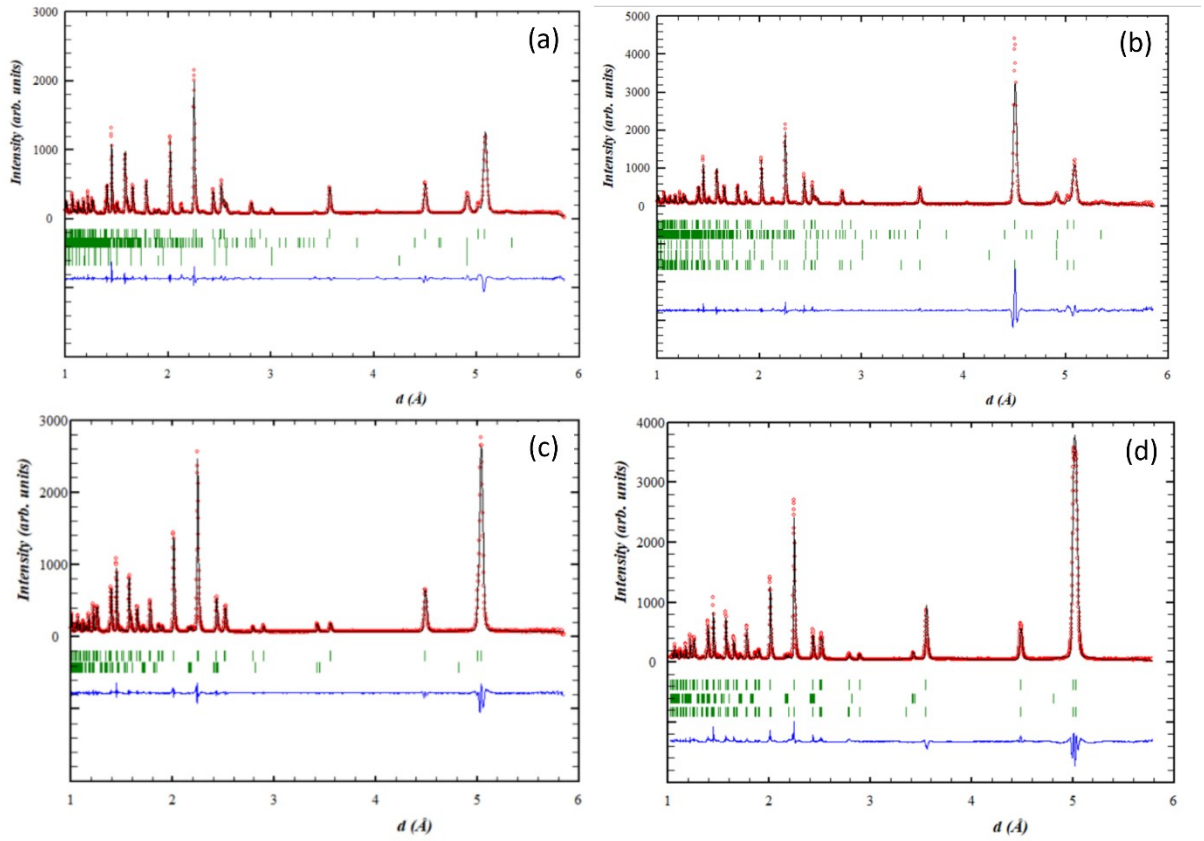


***Figure S11:*** *Rietveld refinement of the powder neutron diffraction data (WISH) fitted to the $P6_3mc$ model[3] for (a) $MnFeMo_3O_8$ at 298 K, (b) $MnFeMo_3O_8$ at 2 K, (c) $MnCoMo_3O_8$ at 298 K and (d) $MnCoMo_3O_8$ at 2 K. Black crosses represent observed data, red line represents the calculated model and the blue line represents the difference between the observed and calculated data. From top to bottom the tick marks represent the following phases, for (a) $MnFeMo_3O_8$ nuclear, $MnMoO_4$ nuclear, $Fe_3O_4$ nuclear, $Fe_3O_4$ magnetic and $MnCoMo_3O_8$ magnetic (2 K only) and (b) $MnCoMo_3O_8$ nuclear, $MnMoO_4$ nuclear and $MnFeMo_3O_8$ magnetic (2 K only). We see no evidence for the $MnMoO_4$ magnetic phase in these refinements.*

***Table S8:*** *Rietveld refinement parameters for powder neutron diffraction (GEM) data collected between 200 K and 5 K for $MnZnMo_3O_8$, refined using the $P6_3mc$ model[3] Refinements were performed incorporating a $MnMoO_4$ (C2/m) second phase[4]. Note: thermal displacement parameters were constrained for cations and anions respectively and allowed to refine. Values in parentheses indicate one standard deviation in the parameter.*

| **Parameter** | **Temperature (K)** | | | | |
|---|---|---|---|---|---|
| | **200** | **150** | **100** | **50** | **5** |
| **$\chi^2$** | 2.847 | 1.561 | 1.601 | 1.666 | 3.350 |
| **Rp (%)** | 2.00 | 2.53 | 2.55 | 2.59 | 2.14 |
| **wRp (%)** | 1.78 | 2.34 | 2.37 | 2.38 | 1.87 |
| **a (Å)** | 5.7928(3) | 5.7920(4) | 5.7914(3) | 5.7909(4) | 5.7917(3) |
| **c (Å)** | 10.075(1) | 10.073(1) | 10.074(1) | 10.070(1) | 10.072(1) |
| **Cell Volume (Å$^3$)** | 292.78(4) | 292.66(4) | 292.61(4) | 292.46(4) | 292.58(4) |
| **Mn1/Zn1 (⅓, ⅔, *z*)** | 0.948(1) | 0.949(1) | 0.948(1) | 0.946(1) | 0.948(1) |
| **Mn1/Zn1 $U_{(iso)}/U_{(e)}$ x 100 (Å$^2$)** | 0.06(5) | -0.04(6) | 0.08(7) | 0.00(6) | 0.00(5) |
| **Mn1/Zn1 fractional occupancies** | 0.135(5)<br>0.865(5) | 0.134(6)<br>0.866(6) | 0.128(6)<br>0.872(6) | 0.128(6)<br>0.872(6) | 0.131(5)<br>0.869(5) |
| **Mn2/Zn2 (⅓, ⅔ ,*z*)** | 0.5041(41) | 0.507(5) | 0.505(6) | 0.509(5) | 0.508(4) |
| **Mn2/Zn2 $U_{(iso)}/U_{(e)}$ x 100 (Å$^2$)** | 0.06(5) | -0.04(6) | 0.08(7) | 0.00(6) | 0.00(5) |
| **Mn2/Zn2 fractional occupancies** | 0.696(6)<br>0.304(6) | 0.702(7)<br>0.298(7) | 0.681(7)<br>0.319(7) | 0.694(7)<br>0.306(7) | 0.691(5)<br>0.309(5) |
| **Mo1 (*x*, -*x*, ¼)** | 0.1485(3) | 0.1480(3) | 0.1480(3) | 0.1481(3) | 0.1482(2) |
| **Mo1 $U_{(iso)}/U_{(e)}$ x 100 (Å$^2$)** | 0.06(5) | -0.04(6) | 0.08(7) | 0.00(6) | 0.00(5) |
| **O1 (0, 0, *z*)** | 0.3911(6) | 0.3914(7) | 0.3913(7) | 0.3904(7) | 0.3917(6) |
| **O1 $U_{(iso)}/U_{(e)}$ x 100 (Å$^2$)** | 0.16(3) | 0.14(4) | 0.05(4) | 0.10(4) | 0.09(3) |
| **O2 (⅓, ⅔ ,*z*)** | 0.1465(8) | 0.146(1) | 0.1458(9) | 0.1456(9) | 0.1471(7) |
| **O2 $U_{(iso)}/U_{(e)}$ x 100 (Å$^2$)** | 0.16(3) | 0.14(4) | 0.05(4) | 0.10(4) | 0.09(3) |
| **O3 (*x*, -*x* ,*z*)** | 0.4895(4)<br>0.3657(5) | 0.4895(5)<br>0.3655(6) | 0.4892(5)<br>0.3645(6) | 0.4897(5)<br>0.3653(6) | 0.4900(4)<br>0.3654(5) |
| **O3 $U_{(iso)}/U_{(e)}$ x 100 (Å$^2$)** | 0.16(3) | 0.14(4) | 0.05(4) | 0.10(4) | 0.09(3) |
| **O4 (*x*, -*x* ,*z*)** | 0.1642(4)<br>0.6328(4) | 0.1654(5)<br>0.6332(4) | 0.1642(5)<br>0.6325(4) | 0.1645(5)<br>0.6325(4) | 0.1644(4)<br>0.6331(3) |
| **O4 $U_{(iso)}/U_{(e)}$ x 100 (Å$^2$)** | 0.16(3) | 0.14(4) | 0.05(4) | 0.10(4) | 0.09(3) |
| **2$^{nd}$ phase %** | 4.1(8) | 3.8(2) | 3.9(2) | 3.8(2) | 4(1) |

***Table S9:*** *Selected bond lengths and bond angles extracted from powder neutron diffraction (GEM) data collected between 200 K and 5 K for $MnZnMo_3O_8$, refined using the $P6_3mc$ model[3].*

| Bond Lengths and Angles | Temperature (K) | | | | |
|---|---|---|---|---|---|
| | **200** | **150** | **100** | **50** | **5** |
| Mn1_O2 (Å) | 2.00(1) | 1.98(2) | 1.99(2) | 2.01(2) | 2.00(1) |
| Mn1_O3 (Å) | 1.960(7) | 1.967(9) | 1.970(9) | 1.954(9) | 1.960(7) |
| Mn2_O3 (Å) | 2.10(3) | 2.12(3) | 2.11(4) | 2.13(3) | 2.13(3) |
| Mn2_O4 (Å) | 2.14(3) | 2.12(3) | 2.13(4) | 2.10(3) | 2.12(3) |
| Mo_O1 (Å) | 2.059(4) | 2.057(5) | 2.057(5) | 2.051(5) | 2.061(4) |
| Mo_O2 (Å) | 2.128(5) | 2.135(6) | 2.135(6) | 2.134(6) | 2.127(5) |
| Mo_O3 (Å) | 2.085(9) | 2.086(4) | 2.080(4) | 2.085(4) | 2.086(3) |
| Mo_O4 (Å) | 1.968(3) | 1.969(3) | 1.967(3) | 1.969(3) | 1.966(2) |
| Mn1_O3_Mn2 (˚) | 113.4(9) | 112.3(9) | 112(1) | 113(1) | 112.4(8) |

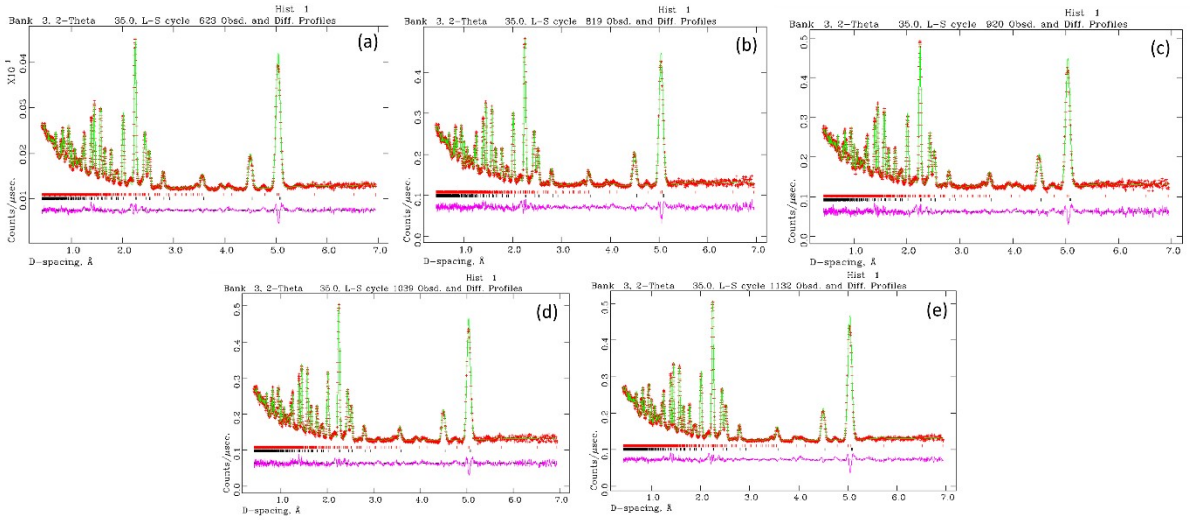


***Figure S12:*** *Rietveld refinement of the x-ray diffraction data collected for $MnZnMo_3O_8$ and fitted to the $P6_3mc$ model[3] at temperatures of (a) 200 K, (b) 150 K, (c) 100 K, (d) 50 K and (e) 5 K. Red circles represent observed data, green line represents the calculated model and the pink line represents the difference between the observed and calculated data. $MnZnMo_3O_8$ is represented by the black tick marks (bottom) and $MnMoO_4$ the red tick marks (top).*

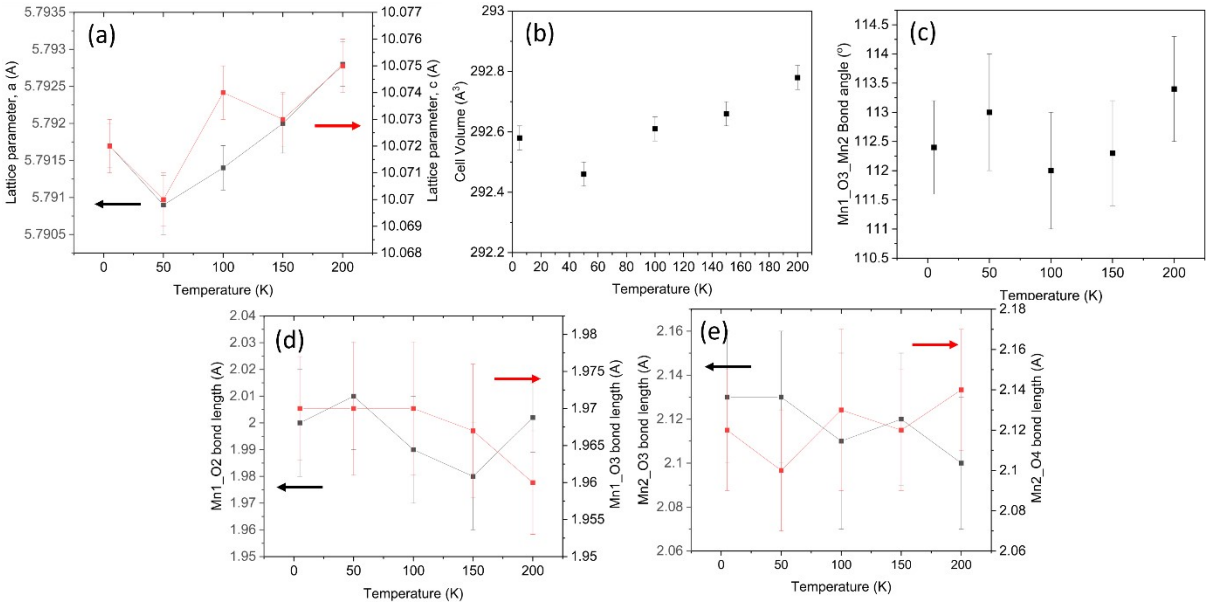


***Figure S13:*** *Data extracted from the Rietveld refinement of the powder neutron diffraction data collected for $MnZnMo_3O_8$ showing the temperature dependence of (a) Lattice parameters a and c, (b) cell volume, (c) Mn1_O3_Mn2 bond angle, (d) tetrahedral bond lengths Mn1_O2 and Mn1_O3 and (e) octahedral bong lengths Mn2_O3 and Mn2_O4.*

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