# Supplemental Material for "Local disorder and structure relation induced by

## magnetic exchange interactions in A<sub>2</sub>(Mo<sub>1-y</sub>Mn<sub>y</sub>)<sub>2</sub>O<sub>7</sub> pyrochlores"

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#### S1. An essential determination of the A<sub>2</sub>(Mo<sub>1-y</sub>Mn<sub>y</sub>)<sub>2</sub>O<sub>7</sub> pyrochlore compounds by XRD: effect on the

## crystal structure induced by the manganese partial substitution



Fig.S1. XRPD pattern of sample  $Gd_2(Mo_{0.90}Mn_{0.10})_2O_7$  collected at 30 K. Measured (black crosses) and calculated (red curves) intensities *I* are reported as well as the residuals (blue curves). The insert highlights the high angle (2 $\theta$ ) region of the pattern.

Sample	$Gd_2Mo_2O_7$	$Gd_2(Mo_{0.90}Mn_{0.10})_2O_7$	$Ho_2Mo_2O_7$	$Ho_2(Mo_{0.90}Mn_{0.10})_2O_7$
Phase	$Gd_2Mo_2O_7$	$Gd_2(Mo_{0.90}Mn_{0.10})_2O_7$	$Ho_2Mo_2O_7$	$Ho_2(Mo_{0.90}Mn_{0.10})_2O_7$
Space Group	Fd-3m	Fd-3m	Fd-3m	Fd-3m
a/ Å	10.35702(5)	10.31757(8)	10.26902(7)	10.20400(9)
X <sub>O1</sub>	0.3364(9)	0.3368(9)	0.339(1)	0.3363(9)
WF (%)	100	86.6(1)	100	82.8(1)
Phase		$Gd_5Mo_2O_{12}$		Ho <sub>5</sub> Mo <sub>2</sub> O <sub>12</sub>
Space Group		<i>C</i> 2/ <i>m</i>		<i>C</i> 2/ <i>m</i>
a		12.4272(9)		12.2426(7)
b		5.7649(5)		5.7033(6)
c		7.6044(5)		7.4861(4)
β		107.94(1)		107.95(1)
WF (%)		13.4(1)		17.2(1)
Uave/Å <sup>2</sup>	0.0047(2)	0.0066(2)	0.0094(2)	0.0121(2)
R <sub>p</sub>	0.140	0.135	0.170	0.121

Table S1: Refined structural parameters of patterns collected at 10K.

Figure S2a-b reports the X-ray powder diffraction patterns of the samples considered in the present manuscript, i.e.,  $A_2(Mo_{1-y}Mn_y)_2O_7$  with  $A = Ho^{3+}$ , and  $Gd^{3+}$  and y = 0.00, 0.05 and 0.10, respectively. In all cases, X-Ray diffraction data indicate that all samples take the pyrochlore face-centered cubic (*fcc*) structure, space group  $Fd\overline{3}m$  [1].

Samples with A = Gd, y = 0.00, 0.03 and 0.05 are single phase, while in the y = 0.10 solid solution some additional peaks appear; the two most intense among them are in the 27.5-29° range. In the Ho series, the undoped and the y = 0.03 compounds are single phase and very tiny peaks (just above the experimental resolution) appear in the same region in the y = 0.05 sample and grow up in the y = 0.10 sample. In both Gd and Ho cases the additional phase is isostructural to monoclinic  $Y_5Mo_2O_{12}$ , space group C2/m [2]. The structure of this latter phase is briefly discussed in the main text. The weight fractions (WF) of the impurity phase for y = 0.10 samples are reported in Table S1. As to the A = Ho, y = 0.05 sample, the WF of Ho<sub>5</sub>Mo<sub>2</sub>O<sub>12</sub>, as calculated by Rietveld refinement of the pattern reported in Fig.S2, is 3.6(2)%.

In order to provide evidence effect on the crystal structure induced by the manganese partial substitution, we retained as a quantitative parameter the structural distortion, using the lattice parameter "*a*". As shown in Figure S2c, the samples display an evolution of their lattice constants with both the concentration and ionic radii of the different rare earth *A*. Over the composition range examined, their lattice constants decrease with increasing manganese content, see Figure S2c. The introduction of the smaller Mn ions ( $r_{Mn}^{4+}$ : 0.53 Å,  $r_{Mo}^{4+}$ : 0.65 Å, for 6-fold coordination) [3] progressively reduces the lattice constants in the *A*<sub>2</sub>(Mo<sub>1-y</sub>Mn<sub>y</sub>)<sub>2</sub>O<sub>7</sub> system,

and even this small variation can induce a distortion in the material average. In the same way, the diffraction peaks progressively shift to a lower diffraction angle with the rare earth ionic radius ( $r_{Ho}^{3+}$ : 1.072 Å,  $r_{Gd}^{3+}$ : 1.107 Å, for 9-fold coordination) [3], as shown in the inserts of the Figs. S2a-b.

The continuous lattice parameters shrinking in both A = Gd and Ho compounds, shown in Figure S2c, testifies that the appearance of a spurious phase does not correspond to a saturation of Mn concentration in the pyrochlore phase. Moreover, in the y = 0.10 sample the T<sub>C</sub> and T<sub>f</sub> transitions have a consistent trend with that of the other samples and no anomalies attributable to impurities are identified.



Fig. S2. Structural Characterization of the  $A_2(Mo_{1-y}Mn_y)_2O_7$  pyrochlore compounds by X-ray diffraction: XRD patterns corresponding to the  $A_2(Mo_{1-y}Mn_y)_2O_7$  series where A is Ho<sup>3+</sup> (**a**) and Gd<sup>3+</sup> (**b**) as a function of y. On the right of each panel, the insert represents a detail of the XRD diffraction pattern in the 2 $\theta$  range 29.5° to 30.5°, corresponding to the (222) peaks of the cubic symmetry. (**c**) Evolution of the lattice parameter "*a*" as a function of the Mn<sup>4+</sup> content for Ho<sup>3+</sup> and Gd<sup>3+</sup> ions.

### **Supplementary References**

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