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

## magnetic exchange interactions in $\mathbf{A}_{\mathbf{2}}\left(\mathbf{M o}_{1-y} \mathbf{M n}_{\mathbf{y}}\right)_{2} \mathbf{O}_{7}$ pyrochlores"

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S1. An essential determination of the $\boldsymbol{A}_{\mathbf{2}}\left(\mathrm{Mo}_{1-\mathrm{y}} \mathrm{Mn}_{\mathrm{y}}\right)_{2} \mathbf{O}_{7}$ pyrochlore compounds by XRD: effect on the crystal structure induced by the manganese partial substitution


Fig.S1. XRPD pattern of sample $\mathrm{Gd}_{2}\left(\mathrm{Mo}_{0.90} \mathrm{Mn}_{0.10}\right)_{2} \mathrm{O}_{7}$ 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 (20) region of the pattern.

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

| Sample | $\mathrm{Gd}_{2} \mathrm{Mo}_{2} \mathrm{O}_{7}$ | $\mathrm{Gd}_{2}\left(\mathrm{Mo}_{0.90} \mathrm{Mn}_{0.10}\right)_{2} \mathrm{O}_{7}$ | $\mathrm{Ho}_{2} \mathrm{Mo}_{2} \mathrm{O}_{7}$ | $\mathrm{Ho}_{2}\left(\mathrm{Mo}_{0.90} \mathrm{Mn}_{0.10}\right)_{2} \mathrm{O}_{7}$ |
| :---: | :---: | :---: | :---: | :---: |
| Phase | $\mathrm{Gd}_{2} \mathrm{Mo}_{2} \mathrm{O}_{7}$ | $\mathrm{Gd}_{2}\left(\mathrm{Mo}_{0.90} \mathrm{Mn}_{0.10}\right)_{2} \mathrm{O}_{7}$ | $\mathrm{Ho}_{2} \mathrm{Mo}_{2} \mathrm{O}_{7}$ | $\mathrm{Ho}_{2}\left(\mathrm{Mo}_{0.90} \mathrm{Mn}_{0.10}\right)_{2} \mathrm{O}_{7}$ |
| Space Group | Fd-3m | Fd-3m | Fd-3m | Fd-3m |
| a/ $\AA$ | 10.35702(5) | 10.31757(8) | 10.26902(7) | 10.20400(9) |
| $\mathrm{X}_{\mathrm{O} 1}$ | 0.3364(9) | 0.3368(9) | 0.339(1) | 0.3363(9) |
| WF (\%) | 100 | 86.6(1) | 100 | 82.8(1) |
| Phase | -------- | $\mathrm{Gd}_{5} \mathrm{Mo}_{2} \mathrm{O}_{12}$ | -------- | $\mathrm{Ho}_{5} \mathrm{Mo}_{2} \mathrm{O}_{12}$ |
| Space Group | ------ | C2/m | ---- | C2/m |
| a | -------- | 12.4272(9) | -------- | 12.2426(7) |
| b | ------ | 5.7649(5) | ------ | 5.7033(6) |
| C | ------ | 7.6044(5) | ------ | 7.4861(4) |
| $\beta$ | -------- | 107.94(1) | ----- | 107.95(1) |
| WF (\%) | ----- | 13.4(1) | ----- | 17.2(1) |
| Uave/Å ${ }^{2}$ | 0.0047(2) | 0.0066(2) | 0.0094(2) | 0.0121(2) |
| $\mathrm{R}_{\mathrm{p}}$ | 0.140 | 0.135 | 0.170 | 0.121 |

Figure S2a-b reports the X-ray powder diffraction patterns of the samples considered in the present manuscript, i.e., $A_{2}\left(\mathrm{Mo}_{1-\mathrm{y}} \mathrm{Mn}_{\mathrm{y}}\right)_{2} \mathrm{O}_{7}$ with $A=\mathrm{Ho}^{3+}$, and $\mathrm{Gd}^{3+}$ 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 ( $f c c$ ) structure, space group $F d \overline{3} m[1]$.

Samples with $A=G d, y=0.00,0.03$ and 0.05 are single phase, while in the $\mathrm{y}=0.10$ solid solution some additional peaks appear; the two most intense among them are in the $27.5-29^{\circ}$ range. In the Ho series, the undoped and the $\mathrm{y}=0.03$ compounds are single phase and very tiny peaks (just above the experimental resolution) appear in the same region in the $\mathrm{y}=0.05$ sample and grow up in the $\mathrm{y}=0.10$ sample. In both Gd and Ho cases the additional phase is isostructural to monoclinic $\mathrm{Y}_{5} \mathrm{Mo}_{2} \mathrm{O}_{12}$, space group $\mathrm{C} 2 / \mathrm{m}$ [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 $A=\mathrm{Ho}, \mathrm{y}=0.05$ sample, the WF of $\mathrm{Ho}_{5} \mathrm{Mo}_{2} \mathrm{O}_{12}$, 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 ( $\mathrm{r}_{\mathrm{Mn}}{ }^{4+}: 0.53 \AA, \mathrm{r}_{\mathrm{Mo}}{ }^{4+}$ : $0.65 \AA$, for 6 -fold coordination) [3] progressively reduces the lattice constants in the $A_{2}\left(\mathrm{Mo}_{1-\mathrm{y}} \mathrm{Mn}_{\mathrm{y}}\right)_{2} \mathrm{O}_{7}$ 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 $\left(\mathrm{r}_{\mathrm{Ho}}{ }^{3++}: 1.072 \AA, \mathrm{r} \mathrm{Gd}^{3+}\right.$ : $1.107 \AA$, for 9-fold coordination) [3], as shown in the inserts of the Figs. S2a-b.

The continuous lattice parameters shrinking in both $A=G d$ 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 $T_{C}$ and $T_{f}$ 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 $A_{2}\left(\mathrm{Mo}_{1-\mathrm{y}} \mathrm{Mn}_{y}\right)_{2} \mathrm{O}_{7}$ pyrochlore compounds by X-ray diffraction: XRD patterns corresponding to the $A_{2}\left(\mathrm{Mo}_{1-\mathrm{y}} \mathrm{Mn}_{y}\right)_{2} \mathrm{O}_{7}$ series where $A$ is $\mathrm{Ho}^{3+}(\mathbf{a})$ and $\mathrm{Gd}^{3+}(\mathbf{b})$ 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 $29.5^{\circ}$ to $30.5^{\text {o }}$, corresponding to the (222) peaks of the cubic symmetry. (c) Evolution of the lattice parameter " $a$ " as a function of the $\mathrm{Mn}^{4+}$ content for $\mathrm{Ho}^{3+}$ and $\mathrm{Gd}^{3+}$ ions.

## Supplementary References

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