Structural and magnetic properties of the solid solution (0 \leq x \leq 1) 
YMn_{1-x}(Cu_{3/4}Mo_{1/4})_xO_3

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Abstract
Recently, the ferroelectromagnet YMnO₃ has been the focus of interest because it exhibits both antiferromagnetism (Néel temperature \( \sim 80 \) K) and ferroelectricity (Curie temperature \( \sim 914 \) K). There have been no reports of complete YMn_{1-x}M_xO_3 solid solutions in which substitution of the foreign M cation preserves the hexagonal P6₃cm structure. In contrast there exist several homeotypic phases with the general formula, \( Ln_{1+n}Cu_nM_xO_{3+3n} \) (\( n = 1 \) (M = Ti), 2 (M = V) and 3 (M = Mo); \( Ln \): lanthanide). Several YMn_{1-x}(Cu_{3/4}Mo_{1/4})_xO_3 compounds have been synthesized. The solid solution, from YMnO₃ (\( x = 0 \)) to YCu_{3/4}Mo_{1/4}O₃ (\( x = 1 \)) has been characterized by X-ray diffraction and transmission electron microscopy study. For \( 0 < x < 0.9 \), the compounds are found to crystallize in the non-centrosymmetric structure, space group P6₃cm, of YMnO₃. The Mn-free end member, \( x = 1 \), crystallizes in a complex multiple cell, the superstructure being associated to Cu_{3+}/Mo_{6+} cationic ordering. Dilution of the Mn^{3+} magnetic array by the paramagnetic (Cu^{2+}) and diamagnetic (Mo^{6+}) cations is found to decrease the antiferromagnetic ordering temperature and it becomes undetectable for \( x \geq 0.5 \) compositions.

Keywords: Hexagonal structure; Electron Microscopy; Solid solution; Magnetic properties

1. Introduction
Among the fascinating properties of the perovskite manganites, the ferroelectricity of the hexagonal phase “type YAlO₃” has been revisited after the new interest of the solid state scientists for the search of new multiferroic materials (see Ref. [1] and references therein), which are promising materials for applications in the information storage spintronics and sensor. Those properties result from the strong interplay between spin, charge and orbital ordering, responsible for simultaneous ferromagnetism, ferroelectricity and ferroelasticity. The YMnO₃ hexagonal phase is a typical example of a magnetic ferroelectric with a magnetic Néel temperature \( T_N \sim 80 \) K and a ferroelectric Curie temperature \( T_C \sim 914 \) K [2–5]. For this phase a clear anomaly in the dielectric constant at \( T_N \) has been found [5].

From the structural point of view, the RMnO₃ hexagonal structure differs strongly from the ideal cubic and distorted orthorhombic perovskite and is generally stabilized for small enough R cation in RMnO₃ (R are lanthanides smaller than Tb^{3+}, Sc^{3+} and Y^{3+}) [2,6,7]. The Mn cations adopt a fivefold trigonal bipyramidal coordination contrasting with its octahedral one, with an unoccupied d_{0} orbital hybridized with the p_{z} orbital of oxygen along the c-direction. This has been previously proposed to be at the origin of a “one-dimensional d_{0}-ness” which is original compared to usual “d_{0}-ness criterion” for ferroelectricity [8].

There exist only a few reports describing substitutions at the Mn-site in YMnO₃, which preserve the hexagonal structure. As for the substitution of cobalt for manganese in YMnO₃, though...
the solubility range is important, the structure transforms to an orthorhombic one as soon as $x = 0.15$ in Y$\text{Mn}_{1-x}$Co$_x$O$_3$ [9]. In this respect, La$\text{Cu}_{3/4}\text{Mo}_{1/4}$O$_3$ is a very interesting phase since, despite the large ionic radius of La$^{3+}$, it also crystallizes in the hexagonal structure [10,11]. This provides a nice illustration of the unpredictability in solid-state chemistry. The “improbable” formation of many oxides has been explained on the basis of a balance between stable and unstable compositions [12]. In fact, there exists a large family of closely related oxides containing copper, that crystallize in hexagonal structure $\text{YAlO}_3$ and additional reflections involving a supercell derived from the $x = 1$ structure. The (Cu$_{3/4}$Mo$_{1/4}$)$_3^{\text{3+}}$ substitution for Mn$^{3+}$ is found to progressively decrease the Mn$^{3+}$-Mn$^{3+}$ antiferromagnetic interactions. For the end member, YCu$_{3/4}$Mo$_{1/4}$O$_3$, the cationic ordering is responsible for the very low effective paramagnetic moment observed.

2. Experimental

Polycrystalline samples of Y$\text{Mn}_{1-x}$\((\text{Cu}_{3/4}\text{Mo}_{1/4})\)O$_3$ ($0 \leq x \leq 1$ with $x = 0; 0.25; 0.5; 0.75; 0.85; 0.9; 0.95$ and 1) were synthesized at ambient pressure by solid-state reaction of stoichiometric amounts of Y$_2$O$_3$, Mn$_2$O$_3$, CuO and MoO$_3$. Powders were ground in an agate mortar, pressed in bars ($\sim 2$ mm $\times$ 2 mm $\times$ 10 mm) and heated to 1100 $^\circ$C at a rate of 1.5 $^\circ$C/min, held at this temperature for 24 hours and cooled to room temperature at a rate of 70 $^\circ$C/h.

The electron diffraction (ED) study was carried out on a JEOL 200CX electron microscope fitted with an eucentric gonimeter ($\pm 60^\circ$) equipped with an EDS analyzer. For the transmission electron microscopy study, the samples were crushed in alcohol and deposited on a holey carbon membrane supported by a nickel grid.

The powder X-ray diffraction (PXRD) data were recorded using a Philips vertical diffractometer, working with Cu K$\alpha$ radiation in the range $10 \leq 2\theta \leq 100^\circ$ with a step size of 0.02$^\circ$.

The magnetic properties have been studied by using a SQUID magnetometer. The sample under study was first cooled in the absence of magnetic field down to 5 K, temperature at which a magnetic field of 0.3 T was applied. The magnetic moment values were then collected as a function of temperature between 5 and 400 K. Additional isothermal magnetic field dependent magnetization curves were collected at 5 K.
The electron diffraction characterization was carried out for the YMnO$_3$-type solid solution. This article

Table 2 Lattice parameters obtained from PXRD refinement of YMn$_{0.15}$Cu$_{0.64}$Mo$_{0.21}$O$_3$

<table>
<thead>
<tr>
<th>x</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.1453</td>
<td>11.3714</td>
<td>371.90391</td>
</tr>
<tr>
<td>0.25</td>
<td>6.1831</td>
<td>11.3665</td>
<td>376.33094</td>
</tr>
<tr>
<td>0.5</td>
<td>6.2176</td>
<td>11.3521</td>
<td>380.0602</td>
</tr>
<tr>
<td>0.75</td>
<td>6.2483</td>
<td>11.3407</td>
<td>383.4372</td>
</tr>
<tr>
<td>0.85</td>
<td>6.2623</td>
<td>11.3293</td>
<td>384.7600</td>
</tr>
<tr>
<td>0.9</td>
<td>6.2629</td>
<td>11.3228</td>
<td>384.6231</td>
</tr>
<tr>
<td>0.95</td>
<td>6.2668</td>
<td>11.3131</td>
<td>384.7724</td>
</tr>
<tr>
<td>1</td>
<td>6.2645</td>
<td>11.3091</td>
<td>384.35409</td>
</tr>
</tbody>
</table>

For $x \geq 0.9$, one observes a variation of the parameters evolution: the $a$ parameter remains roughly constant whereas $c$ abnormally decreases. The volume remains constant despite the increase of the average $r_B$ size, suggesting a rearrangement of the B-cations. This hypothesis is reinforced by the presence of small extra reflections on the PXRD patterns.

3.2.2. The YMnO$_3$-type solid solution $0 \leq x < 0.9$

The electron diffraction characterization was carried out for all the samples with $x < 0.9$ at room temperature. The reciprocal space was reconstructed by tilting around the $c^*$ and

Table 1 Comparative data of the derivatives of YAI'O$_3$ type structures

<table>
<thead>
<tr>
<th>Composition</th>
<th>N.O. B, B' site</th>
<th>Sym. /Ref.</th>
<th>Lattice parameters</th>
<th>Z</th>
<th>$r_B$ (Å)</th>
<th>$r_A/r_B$</th>
<th>Ratio B$^{3+,6+}$ / $\sum$ (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YAI'O$_3$</td>
<td>III</td>
<td>Hex. Type I [4,18]</td>
<td>$a \approx 3.68$ Å, $c \approx 10.521$ Å</td>
<td>1</td>
<td>0.48</td>
<td>2.12</td>
<td>–</td>
</tr>
<tr>
<td>InMnO$_3$</td>
<td>III</td>
<td>Hex. Type II [21]</td>
<td>$a \approx 3.33$ Å, $c \approx 12.18$ Å</td>
<td>1</td>
<td>0.58</td>
<td>1.59$^a$</td>
<td>–</td>
</tr>
<tr>
<td>YMnO$_3$</td>
<td>III</td>
<td>Hex. [2]</td>
<td>$a \approx 6.14$ Å, $c \approx 11.41$ Å</td>
<td>3</td>
<td>0.58</td>
<td>1.76</td>
<td>0</td>
</tr>
<tr>
<td>YMn$<em>{0.15}$Cu$</em>{0.64}$Mo$_{0.21}$O$_3$</td>
<td>III/II/VI</td>
<td>Hex. This article</td>
<td>$a \approx 6.263$ Å, $c \approx 11.323$ Å</td>
<td>3</td>
<td>0.607</td>
<td>1.68</td>
<td>0.21</td>
</tr>
<tr>
<td>YCu$<em>{0.75}$Ti$</em>{0.25}$O$_3$</td>
<td>II/IV</td>
<td>Hex. [13]</td>
<td>$a \approx 6.17$ Å, $c \approx 11.48$ Å</td>
<td>3</td>
<td>0.59</td>
<td>1.72</td>
<td>–</td>
</tr>
<tr>
<td>YCu$<em>{0.75}$Mo$</em>{0.25}$O$_3$</td>
<td>II/VI</td>
<td>Monoocl. This article</td>
<td>$a \approx 7.2$ Å, $b \approx 6.2$ Å, $c \approx 11.8$ Å, $\beta \approx 107^\circ$</td>
<td>4</td>
<td>0.61</td>
<td>1.66</td>
<td>0.25</td>
</tr>
<tr>
<td>LaCu$<em>{0.75}$Mo$</em>{0.25}$O$_3$</td>
<td>II/VI</td>
<td>Monoocl. [16]</td>
<td>$a \approx 7.9$ Å, $b \approx 6.9$ Å, $c \approx 11$ Å, $\gamma \approx 90^\circ$</td>
<td>4</td>
<td>0.61</td>
<td>1.90</td>
<td>0.25</td>
</tr>
<tr>
<td>LaCu$<em>{2/3}$V$</em>{1/3}$O$_3$</td>
<td>II/IV</td>
<td>Hex. [12]</td>
<td>$a \approx 14.4$ Å, $c \approx 10.7$ Å</td>
<td>13</td>
<td>0.587</td>
<td>1.97</td>
<td>0.33</td>
</tr>
</tbody>
</table>

$^a$ Calculated for eightfold coordination of In$^{3+}$, but in the InMnO$_3$, the In$^{3+}$ coordination is octahedral.
Fig. 2. Powder X-ray diffraction data for YMn$_{1-x}$(Cu$_{3/4}$Mo$_{1/4}$)$_x$O$_3$ ($0 \leq x \leq 1$).

Fig. 3. Evolution of the lattice parameters and volume versus $x$ in YMn$_{1-x}$(Cu$_{3/4}$Mo$_{1/4}$)$_x$O$_3$.

$a^*$ axes. They confirm that the cell parameters, $a \approx 6.2$ Å and $c \approx 11.35$ Å, and the conditions of reflection of the P6$_3$cm space group ($h0\bar{h}l; l = 2n$) are in agreement with those of the undoped YMnO$_3$ phase [2]. The ED patterns of YMn$_{0.5}$(Cu$_{3/4}$Mo$_{1/4}$)$_{0.5}$O$_3$ recorded along [0001]; [11\bar{2}0] and [10\bar{1}0] are given as example in Fig. 4. For all the samples of the solid solution ($0 \leq x \leq 0.85$) one observes extra extinction with regard to the P6$_3$cm space group. The reflections indexed $h0\bar{h}0$ with $h \neq 3n$, are indeed systematically extinguished in the [0001] ED pattern (Fig. 4(a)) and barely visible in the [11\bar{2}0] ED pattern (Fig. 4(b)) owing to double diffraction phenomena. The extra extinction of the $h0\bar{h}0$ diffraction spots results from the particular atomic position ($x \approx 1/3$) of the B-cation. Considering only the (001) plane of the YMnO$_3$
is 3 times smaller (see Table 1). The experimental (0001)* ED pattern (Fig. 4(a)) recorded for YMnO₃₋ₓ(Cu₃/₄Mo₁/₄)ₓO₃₋ₓ appears therefore similar to the (0001)* ED pattern calculated for YAlO₃ (Z = 1) and to the (0001)* ED pattern calculated for YMnO₃ (Z = 3) with Mn located in (1/3 0 0). Considering the whole structure, the tilting of the MnO₅ polyhedra and the waving of the “[YO]” layer imply to use a triple cell (Z = 3) and a lower symmetry (P6₃cm instead of P6₃/mmc) for describing the hexagonal YMnO₃ structure. The important point highlighted by the ED study of YMn₁₋ₓ(Cu₃/₄Mo₁/₄)ₓO₃ is that the (Cu₃/₄Mo₁/₄)³⁺ substitution for Mn³⁺ allows stabilizing the sample whatever x (0 ≤ x ≤ 0.85) preserves the YMnO₃-type hexagonal structure. Accounting that there is only one site for the B-cation in the P6₃cm structure, it means that Mn³⁺, Cu²⁺ and Mo⁶⁺ are randomly distributed over a single site up to x < 0.9. Moreover, the extinction of the h₀l₀ with h ≠ 3n reflections in the ED patterns recorded on the samples 0 ≤ x ≤ 0.85 points out that these cations occupy similar x₀ with x ∼ 1/3 positions. The simulated electron diffraction patterns, calculated with the P6₃cm structure changing only slightly the x value of the B-site, showed indeed the great sensitivity of the intensity of the h₀l₀ reflections for tiny deviation with regard to the x = 1/3 peculiar position.

3.2.2. A new type of ordering for x = 1

For YCu₃/₄Mo₁/₄O₃ (x = 1), the ED patterns recorded on the manganese-free sample present extra reflections in addition to the reflections typical of the basic (Z = 1) YAlO₃-type structure. On the ED pattern recorded along [010], extra reflections are observed with regard to the hexagonal subcell, which imply to define a monoclinic cell with \( \tilde{a}_m = \frac{3}{4} \tilde{a}_h + \frac{1}{4} \tilde{b}_h \), \( \tilde{b}_m = \frac{\tilde{a}_h + \tilde{b}_h}{2} \) and \( \tilde{c}_m = \tilde{c}_h \), where the subscripts m and h designate the monoclinic and the simple hexagonal cells respectively. This monoclinic cell is then characterized by \( a \approx 7.2 \) Å, \( b \approx 6.2 \) Å, \( c \approx 11.8 \) Å and \( \beta \approx 107^\circ \) with the following conditions limiting the reflections: \( h0l: l = 2n \), compatible with the space groups P c, P 2/c or P 2₁/c. The ED patterns of the basis planes are given in Fig. 6. Most of the crystallites studied by electron diffraction present twinned domains. The additional spots which result from this twinning are indicated by white arrows on the (010)* ED pattern (Fig. 6(a)).
the subscript m refers to the monoclinic supercell. Due to twinned domains, the subscript h refers to the hexagonal unit cell while (c)

Fig. 6. ED patterns of YCu$_3$.2.3. Multiphased domain for $x$.

For this part of the diagram, some ED patterns exhibiting diffuse extra reflections, which are characteristic of $x = 1$ ordering, have been detected. However, these extra reflections are not systematically observed for all the crystallites and, even, different domains can be observed. The EDS analyses of these crystallites and domains do not exhibit significant deviation of the cationic ratio. One can conclude, that according to our conditions of synthesis, the $0.9 \leq x < 1$ domain is multiphased and symbolized by a grey rectangle in Fig. 3.

3.3. Structural remarks

On the basis of the electron diffraction study, structure refinements have been carried out for the solid solution $0 \leq x < 0.9$, using the powder X-ray diffraction data. The atomic parameters and reliability factors are given in Table 3. They are in agreement with the hypothesis of a random positions of the cations located in the B-site, namely Mn$^{3+}$, Cu$^{2+}$ and Mo$^{6+}$.

The monoclinic supercell of the YCu$_3$Mo$_1/4$O$_3$ ($x = 1$), has never been reported, at our knowledge. The $c$ parameters of numerous derivative structures, ordered or non-ordered, are of the same order as that of YAlO$_3$, ranging from 10.5 to 11.5 Å. The usual factors commonly explored for understanding the differences in the cell parameters and symmetry of structural families are compared in Table 1, namely the mismatch of the cationic radius between the A- and the B-sites, size mismatch on the B-site and the oxidation state of the cations:

- The role of the mismatch of the cationic radius between the A- and the B-sites appears crucial for $A^3B^3O_3$, as shown by comparing YAlO$_3$, YMnO$_3$ and InMnO$_3$. Decreasing $r_A/r_B$ by increasing $r_B$, from 2.12 YAlO$_3$ ($Z = 1$, SG = $P6_3/mmc$) to 1.76 for YMnO$_3$ induces a distorted triple cell ($Z = 3$, SG = $P6_3/mmc$) keeping the eightfold coordination of Y. In a different way, decreasing $r_A/r_B$ from 1.76 by decreasing $r_A$ from YMnO$_3$ ($Z = 3$, SG = $P6_3/mmc$) to 1.59 for InMnO$_3$ leads to a simple cell ($Z = 1$, SG = $P6_3/mmc$), which how differ from that of YAO$_3$ since the mismatch is accommodated by a smaller distance of next-nearest neighbor O anions, indium being in sixfold coordination (and significant decrease of $a$ and increase of $c$).

- The balance by introducing two cations in the B-site, $A^{3+}(B,B')^{3+}O_3$ properly selected to respect the $r_A/r_B$ criterion. For example, as reported by Floros et al. [13] the sample $Y_2CuTiO_6$ ($r_A/r_B = 1.72$ see Table 1) maintains hexagonal symmetry of the triple cell YMnO$_3$ ($Z = 3$,

<table>
<thead>
<tr>
<th>$x$</th>
<th>0</th>
<th>0.25</th>
<th>0.5</th>
<th>0.75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(1)</td>
<td>0.28(2)</td>
<td>0.273(2)</td>
<td>0.28(2)</td>
<td>0.278(2)</td>
</tr>
<tr>
<td>Y(2)</td>
<td>0.238(2)</td>
<td>0.237(2)</td>
<td>0.252(2)</td>
<td>0.255(1)</td>
</tr>
<tr>
<td>Mn</td>
<td>0.338(4)</td>
<td>0.330(3)</td>
<td>0.332(4)</td>
<td>0.332(3)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.293(4)</td>
<td>0.308(5)</td>
<td>0.302(8)</td>
<td>0.308(5)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.155(2)</td>
<td>0.161(2)</td>
<td>0.164(4)</td>
<td>0.155(3)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.651(4)</td>
<td>0.644(5)</td>
<td>0.660(9)</td>
<td>0.658(7)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.332(2)</td>
<td>0.346(2)</td>
<td>0.336(4)</td>
<td>0.339(3)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.464(5)</td>
<td>0.492(3)</td>
<td>0.506(5)</td>
<td>0.517(4)</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.015(4)</td>
<td>0.024(2)</td>
<td>0.040(4)</td>
<td>0.041(2)</td>
</tr>
</tbody>
</table>

$R_{Bragg} (%)$ | 7.65 | 8.47 | 8.60 | 12

The space group is $P6_3cm$. Atomic positions: Y(1) at 2$a$ (0,0,0), Y(2) at 4$b$ (1/3, 2/3, $z$), Mn; Cu and Mo randomly distributed at 6$c$ ($x$, 0,0), O(1) and O(2) at 6$c$ ($x$, 0,0), O(3) at 2$a$ (0,0,0) and O(4) at 4$b$ (1/3, 2/3, $z$).
SG = P6<sub>3</sub>cm) with no cationic ordering as in the title solid solution with three cations randomly distributed at the B-site, YMn<sub>1−x</sub>(Cu<sub>3</sub>/4Mo<sub>1/4</sub>)O<sub>3</sub> for x < 0.9.

- YCu<sub>3/4</sub>Mo<sub>1/4</sub>O<sub>3</sub> and LaCu<sub>3/4</sub>Mo<sub>1/4</sub>O<sub>3</sub>, which exhibit the same (BB') cations (by the way, same r<sub>B</sub>) but strongly different r<sub>A</sub>/r<sub>B</sub> (1.66 and 1.93, respectively), are both ordered. They both involve a quadrupling of the subcell, but the ordering mode are different as well in the (001) planes as in their stacking along [001].

On the basis of these remarks, it appears that, on the one hand, the distortion-type strongly depends on r<sub>A</sub>/r<sub>B</sub> and that, on the other hand, long range ordering is clearly generated by the presence, on the B-site, of two cations exhibiting very different oxidation states, a very high B<sup>5+</sup> or B<sup>6+</sup> and a lower one B<sup>2+</sup>. This mechanism is exactly the same as the one observed in the ordered perovskite. In both cases, the ratio between the two types of cations, B<sup>5+,6+</sup>/B<sup>2+</sup> is a critical parameter.

4. Magnetic properties

The T dependent inverse magnetic susceptibility (χ<sup>−1</sup>) measurements of YMn<sub>1−x</sub>(Cu<sub>3/4</sub>Mo<sub>1/4</sub>)O<sub>3</sub> samples are illustrated by the curves given in Fig. 7. For all compositions, the χ<sup>−1</sup>(T) curve can be fitted by a Curie–Weiss law of the type χ = C/θ<sub>p</sub> in the higher T region as shown by the straight lines in Fig. 7. The corresponding θ<sub>p</sub> and effective paramagnetic moment μ<sub>eff</sub> values are reported in Table 4.

As shown in the table, |θ<sub>p</sub>| decreases as x increases up to x = 0.75 in YMn<sub>1−x</sub>(Cu<sub>3/4</sub>Mo<sub>1/4</sub>)O<sub>3</sub>. This indicates that the Mn<sup>3+</sup>–O–Mn<sup>3+</sup> antiferromagnetic interactions are weakened as the Mn array is diluted by the (Cu<sub>3/4</sub>Mo<sub>1/4</sub>)<sup>3+</sup> less magnetic cation. However, for the fully substituted (x = 1) member, YCu<sub>3/4</sub>Mo<sub>1/4</sub>O<sub>3</sub>, |θ<sub>p</sub>| is higher, θ<sub>p</sub> = −294 K which is consistent with the very large absolute value deduced for LaCu<sub>3/4</sub>Mo<sub>1/4</sub>O<sub>3</sub>, θ<sub>p</sub> = −460 K. This is to be related to the strength of the Cu<sup>2+</sup>–O–Cu<sup>2+</sup> antiferromagnetic fluctuations, which dominates in YCu<sub>3/4</sub>Mo<sub>1/4</sub>O<sub>3</sub>.

As a consequence of this |θ<sub>p</sub>| decrease as x increases, the Néel temperature, T<sub>N</sub>, of YMnO<sub>3</sub>, which is indicated by an arrow in the insert of Fig. 7 (T<sub>N</sub> ~ 75 K), decreases rapidly down to T<sub>N</sub> ~ 30 K for x = 0.25. For the other compositions, x = 0.5 and x = 0.75, the χ<sup>−1</sup>(T) shape is different with a progressive rounding developing below ~ 200 K and without a bump as in YMnO<sub>3</sub>. This suggests a lack of long-range magnetic ordering, even for the lowest temperature, for both x = 0.5 and x = 0.75 compounds. This is a direct consequence of the magnetic disordering induced by the presence of the random distribution of three different cations on the B-site.

Finally, the shape of the χ<sup>−1</sup>(T) curve of the end member, YCu<sub>3/4</sub>Mo<sub>1/4</sub>O<sub>3</sub>, differs from that of the x = 0.5 and x = 0.75 compounds for T<sub>N</sub>.

Fig. 7. Temperature (T) dependence of the inverse magnetic susceptibility (χ<sup>−1</sup>) for representative samples of the YMn<sub>1−x</sub>(Cu<sub>3/4</sub>Mo<sub>1/4</sub>)O<sub>3</sub> series. The x values are labeled in the graph. The straight lines are for the fitting curves obtained by using the Curie–Weiss law (see text). The arrows for the x = 0 and x = 0.25 compounds are for T<sub>N</sub>.
Compounds (Fig. 8). For thus compounds, the metallic cations Cu^{2+} and Mo^{6+} are ordered on a triangular network. Taking into account the triangular frustration induced by the corner shared trigonal bipyramids, one would expect a lack of magnetic ordering as it was already reported for La_{4}Cu_{3}MoO_{12} [16] and La_{3}Cu_{3}VO_{4} [15]. Consequently, the magnetic state has been assumed to be also paramagnetic for YCu_{3/4}Mo_{1/4}O_{3}. Two linear $\chi^{-1}(T)$ regimes can be distinguished: one at high temperature, which has already been discussed with all the Cu^{2+} ($S = 1/2$) magnetic moments contributing to the paramagnetism, and, a second regime, at lower temperature, leading to $\mu_{\text{eff}} = 0.95 \mu_{B}/\text{Cu}$. From this experimental value, one obtains that only 30% of the Cu magnetic moments are detected. For this compound, the $T$ dependent magnetic behavior is just as if the Cu^{2+} cations are loosing 2/3 of their magnetic moment as $T$ decreases (at high temperature, $\mu_{\text{eff}} = 1.8 \mu_{B}/\text{Cu}$ instead of $\mu_{\text{eff}} = 1.73 \mu_{B}/\text{Cu}$ at low $T$, $\mu_{\text{eff}} = 0.95 \mu_{B}/\text{Cu}$). This is reminiscent of a triangular frustration: if three Cu^{2+} cations occupy the corners of the same triangle, two cations over three can be antiferromagnetically paired yielding no net magnetic contribution and only the third Cu^{2+} contributes. Such a situation neglects the presence of the d^5 Mo^{6+} cations which would release the frustration when occupying the corner of the triangle instead of copper. The only possibility would be thus that the Cu^{2+} form always triplet and that Mo^{6+} cations order in between these triangles. Such a magnetic distribution was found in the case of La_{4}Cu_{3}MoO_{12} which exhibits a supercell derived from the YMnO_{3} structure.

5. Discussion and concluding remarks

The present study of the structural and magnetic properties for the complex YMn_{1-x}(Cu_{3/4}Mo_{1/4})_{x}O_{3} system demonstrates that a disordered solid solution can be obtained for 0 $\leq x < 0.9$, the hexagonal structure of the limit member YMnO_{3} being preserved. This is an important result with regard to previous studies of different YMn_{1-x}M_{x}O_{3} series ($M =$ transition metal) which evidenced a phase transition from the hexagonal structure to the orthorhombic perovskite structure, for instance, as soon as $x \sim 0.15$ for Co. Note that the orthorhombic perovskite form can be also stabilized working under high pressure or in the form of thin films [19,20]. This shows that the role of transition or post transition metal is important and deserves to be investigated. The limit $x = 1$ member, YCu_{3/4}Mo_{1/4}O_{3}, exhibits a complex monoclinic and original superstructure different from the one reported for LaCu_{3/4}Mo_{1/4}O_{3} [16]. Thus, the electron diffraction study evidence the presence of the two types structures, disordered and ordered, depending on the $x$ value in YMn_{1-x}(Cu_{3/4}Mo_{1/4})_{x}O_{3}. The accurate determination of the cations ordering mechanisms for $x = 1$, using X-ray diffraction and high-resolution electron microscopy is in progress.

For all the “disordered” compounds ($x < 0.9$) it must be pointed out that the non-centrosymmetry ($P6_3$cm space group) is preserved. This could allow ferroelectricity to exist. Nonetheless, according to the magnetic dilution of the manganite network induced by the (Cu^{2+}/Mo^{6+}) cations one could speculate that the interplay between the charges and spins decreases as $x$ increases in YMn_{1-x}(Cu_{3/4}Mo_{1/4})_{x}O_{3}. Dielectric measurements as a function of $T$ are now under progress to test this hypothesis.

References