High-pressure preparation and characterization of new metastable oxides: the case of NdCu$_3$Mn$_3$MO$_{12}$ (M = Fe, Cr)

To cite this article: J Sánchez-Benítez et al 2011 J. Phys.: Conf. Ser. 325 012002

View the article online for updates and enhancements.

Related content
- Neutron diffraction, Mössbauer and magnetotransport study of Fe-substituted derivatives of CaCu$_3$Mn$_4$O$_{12}$ perovskite with colossal magnetoresistance
  H Falcon, J Sánchez-Benítez, M J Martínez-Lope et al.
- High-pressure preparation and characterization of (R,R')NiO$_3$ (R,R' = rare earths) perovskites: effect of the variance of the R$^{3+}$ ionic sizes
- Crystal structure, magnetic and electrical properties of CaCu$_3$Mn$_4-x$Ti$_x$O$_{12}$ (0.3<x<1) perovskites
  H Falcon, J A Alonso, J Sánchez-Benítez et al.

Recent citations
- Ferrimagnetism up to 200 K in Ti-rich double perovskites ACu$_3$Ti$_4-x$MnxO$_{12}$: Role of double exchange mechanism
  Md Motin Seikh et al.
- Correlation between the crystal structure and the Curie temperature in RCu$_3$(Mn$_3$Fe)$_2$O$_{12}$ (R = rare-earth) complex perovskites
  Paula Kayser et al.
High-pressure preparation and characterization of new metastable oxides: the case of NdCu$_3$Mn$_3$MO$_{12}$ (M= Fe, Cr)

J Sánchez-Benítez$^1$, P Kayser$^1$, M J Martínez-Lope$^1$, C de la Calle$^1$, M. Retuerto,$^1$ M T Fernandez-Díaz$^2$, J Á Alonso$^1$

$^1$Instituto de Ciencia de Materiales de Madrid, C.S.I.C., Cantoblanco E-28049 Madrid.
$^2$Institut Laue Langevin, BP 156X, Grenoble, F-38042, France

E-mail: jsb@icmm.csic.es, ja.alonso@icmm.csic.es

Abstract. High-pressure synthesis is a powerful technique to stabilize metastable oxides, either containing transition metals in unusual oxidation states, or favouring the formation of dense perovskite-related phases. Happily, many solids synthesized at high pressure-high temperature conditions (where they are thermodynamically stable) can be “quenched” to ambient conditions, where they are termodynamically metastable, yet they remain indefinitely kinetically stable. In this paper we illustrate the example of a new family of oxides derived from the CaCu$_3$Mn$_4$O$_{12}$ perovskite. We have studied the series of nominal composition NdCu$_3$(Mn$_4$M)$_{12}$ (M= Fe, Cr) where Mn is replaced by Fe(Cr) cations in the ferrimagnetic perovskite NdCu$_3$Mn$_4$O$_{12}$. These materials have been synthesized in polycrystalline form under moderate pressure conditions of 2 GPa, in the presence of KClO$_4$ as oxidizing agent. All the samples have been studied by neutron powder diffraction (NPD) below and above the ferrimagnetic Curie temperatures. These oxides crystallize in the cubic space group $Im3$m (No. 204). Mn$^{4+}$/Mn$^{3+}$ and Fe$^{3+}$/(Cr$^{3+}$) occupy at random the octahedral B positions of the perovskite structure. The materials have also been characterized by magnetic and magnetotransport measurements. All the samples are ferrimagnetic and show a decrease of $T_c$ upon Fe(Cr) introduction since these ions disturb the ferromagnetic interactions within this magnetic sublattice. The introduction of Fe changes the resistivity response from metallic to a semiconductor behavior. However, the magnetoresistance is still considerable at 300 K upon Fe doping, and it is enhanced at 100 K probably due to the decrease in the number of charge carriers from the pure oxide to the Fe-doped compound.

1. Introduction
Many transition metal oxides in unusual valence states (e.g. V(IV), Cr(IV), Mo(V), Fe(IV), Ni(III), Cu(III)) or intermediate valence (such as Cu(I)-Cu(III), Mn(II)-Mn(IV), Fe(II)-Fe(III)) present a metastable character and, given the difficulty of their synthesis, have been relatively little studied. However, they are very interesting materials presenting strong electronic correlations that are bound to exotic properties such as superconductivity, metal behavior, metal-insulator transitions or colossal...
magnetoresistance. The metastability of these compounds requires special synthesis conditions such as the application of high pressure.

Happily, many solids synthesized at high pressure-high temperature conditions (where they are thermodynamically stable) can be “quenched” to ambient conditions, where they remain indefinitely kinetically stable. Such preparation routes have attracted much attention since many materials of technological interest are metastable. Very well known examples are the high $T_c$-superconducting materials with infinite-layer structure, such as (Sr,Ca)CuO$_2$, or the high-$T_c$ superconductors of the Tl and Hg families, Tl$_2$Ba$_2$CuO$_6$ and HgBa$_2$Ca$_2$Cu$_3$O$_{8-\delta}$, this last exhibiting the highest $T_c$ ever reported of 135 K [1]. Also the CrO$_2$ oxide (containing Cr$^{4+}$), among the few ferromagnetic oxides above room temperature ($T_c= 410^\circ$ C), or the multiferroic BiMnO$_3$ or Bi$_2$NiMnO$_6$ perovskites.

In the last years we have paid much attention to a good number of metastable materials belonging to several families such as RNiO$_3$ (R= rare earths), Tl$_2$Mn$_2$O$_7$, RCu$_3$Mn$_4$O$_{12}$, ABO$_3$ (A= Se, Te, B= divalent transition metals), BaIrO$_3$, etc. In the study and correct characterization of these oxides it has been decisive the use of elastic neutron diffraction, most of the times in powder samples. This technique has allowed us to access to structural details typically related to the octahedral tilting in perovskite structures, the oxygen stoichiometry and order-disorder of the oxygen sublattice, the distinction between close elements in the Periodic Table, the resolution of magnetic structures and, in general, the establishment of a correlation between the structure and the properties of interest.

In this paper we illustrate the example of a new family of oxides derived from CaCu$_3$Mn$_4$O$_{12}$. Among the few oxide systems that have been described to exhibit colossal magnetoresistance, simultaneously showing ferromagnetic (FM) and half-metallic character, the complex perovskite CaCu$_3$Mn$_4$O$_{12}$ [2-5] is particularly appealing. It exhibits a ferromagnetic (FM) Curie temperature significantly above room-temperature (RT), with $T_c= 355$ K, and it shows good MR response at RT and low magnetic fields. This compound has been shown to be appropriate for real applications due to the magnitude and thermal stability of the MR [6].

CaCu$_3$Mn$_4$O$_{12}$ and other oxide materials belonging to the wide family of $A'A_3B_4O_{12}$ double perovskites have the particularity of containing two different $A$ cations 1:3 long-range ordered in a cubic body centered superstructure with doubled $a$ parameter (space group $Im\bar{3}$). The strong tilting of the $BO_6$ octahedra conforms very distorted oxygen coordination environment at the $A$ positions: the effective environment is reduced to a square-planar coordination, well suited for Cu$^{2+}$ and other Jahn-Teller cations such as Mn$^{3+}$ [7].

The metastability of CaCu$_3$Mn$_4$O$_{12}$ and related compounds requires high-pressure preparation techniques. Many previous studies have reported synthesis pressures up to 7 GPa; however we have been able to synthesize polycrystalline samples of the related oxide LaCu$_3$Mn$_4$O$_{12}$ at moderate pressures of 2 GPa, starting from very reactive precursors obtained by wet-chemistry procedures, in the presence of KClO$_4$ as in-situ oxidizing agent [8]. An important advantage of working at moderate pressures of 2 GPa is the accessibility to relatively large amounts of sample (around 0.8 g.) that allows a complete characterization including magnetotransport and neutron diffraction studies of the crystal and magnetic structure. LaCu$_3$Mn$_4$O$_{12}$ is ferrimagnetic below $T_c= 361$ K. We found that the magnetoresistance is enhanced with respect to that of CaCu$_3$Mn$_4$O$_{12}$ due to the effective electronic injection that dramatically reduces the bulk resistivity, thus promoting the grain boundary contribution to the electrical resistance. Values of low-field magnetoresistance close to 3% at room temperature are achieved for magnetic fields of 1T.

Previous investigations of colossal magnetoresistance (CMR) performed on materials chemically doped at the Cu site [9], La(Cu$_{3-x}$Mn$_x$)$_4$O$_{12}$ [10] as well as the octahedral Mn-site, in CaCu$_3$(Mn$_{4-x}$Fe$_x$)$_{10}$O$_{12}$ [11] stimulated our study of the LaCu$_3$(Mn$_{4-x}$Fe$_x$)$_{10}$O$_{12}$ ($x =0.5$, 1) series [12]. In the present paper we present the moderate-pressure synthesis of new perovskite oxides containing Nd at the $A'$ position, and we report on a structural and magnetic study from neutron powder diffraction data, complemented with magnetic and magnetotransport measurements.
2. Experimental

The access at moderate pressures to the NdCu$_3$(Mn$_3$M)O$_{12}$ (M= Fe, Cr) system required the previous preparation of very reactive precursors obtained by wet-chemistry techniques. A mixture of Cu(NO$_3$)$_2$$\cdot$3H$_2$O, MnCO$_3$, FeC$_2$O$_4$$\cdot$2H$_2$O (or Cr(NO$_3$)$_3$) and Nd$_2$O$_3$ oxide was dissolved in a citric acid aqueous solution with some droplets of HNO$_3$; the solution was slowly evaporated and the resulting resin was decomposed at temperatures up to 600 °C. These precursors were ground with KClO$_4$ (30% in weight). Then the mixture was located into a gold capsule (8 mm diameter, 10 mm length), sealed and placed into a cylindrical graphite heater. The reactions were carried out in a piston–cylinder press (Rockland Research Co.), at a pressure of 2 GPa at 1000 °C for 60 min. The decomposition of KClO$_4$ provides an “in-situ” high O$_2$ pressure that is necessary to stabilize Mn$^{4+}$ ions. A fraction of the raw products, obtained as dense, homogeneous pellets, was partially ground to perform the neutron diffraction and magnetic characterization; some as-grown pellets were kept for magnetotransport measurements. The ground products were washed in water, in order to dissolve KCl coming from the decomposition of KClO$_4$; then the powder samples were dried in air at 150°C for 1 h.

The products were initially characterized by laboratory x-ray diffraction (XRD) (Cu K$_\alpha$, $\lambda$= 1.5406 Å). NPD diagrams were collected at the Institut Laue-Langevin (ILL) in Grenoble (France). The crystal structures were refined from high-resolution NPD patterns, acquired below and above the Curie temperature at the D2B diffractometer with $\lambda$=1.594 Å. The magnetic structure of NdCu$_3$Mn$_3$FeO$_{12}$ at 2 K was determined from a NPD pattern collected in the D1B instrument ($\lambda$=2.52 Å). The refinements of both crystal and magnetic structures were performed by the Rietveld method [13], using the FULLPROF refinement program [14]. A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. The following parameters were refined in the final runs: scale factor, background coefficients, zero-point error, pseudo-Voigt corrected for asymmetry parameters, positional coordinates, isotropic thermal factors and magnitude of the Cu, Mn and Fe magnetic moments. The coherent scattering lengths for Nd, Cu, Mn, Cr, Fe and O were 7.690, 7.718, -3.750, 3.635, 9.45 and 5.805 fm, respectively.

The dc magnetic susceptibility was measured on powdered samples in a commercial SQUID magnetometer from Quantum Design, in the temperature range from 4 to 400 K under 0.1T magnetic field. Isothermal magnetization curves were obtained at 4 K for a magnetic field ranging from -5 to 5 T. The magnetotransport measurements were carried out in a Physical Properties Measurement System (PPMS) from 5 to 400 K and up to 9 Tesla.

3. Results and Discussion

3.1. Crystal structure

NdCu$_3$(Mn$_3$M)O$_{12}$ (M= Fe, Cr) samples were obtained as well crystallized powders. The X-ray patterns (figure 1) are characteristic of cubic perovskites with space group $Im\overline{3}$, showing sharp and well defined superstructure reflections owing to the 1:3 ordering between Nd and Cu cations at the A sublattice of the perovskite structure.

The refinement of the crystal structures has been carried out from four NPD patterns acquired in the high-resolution diffractometer D2B at T= 200 and 400 K for M= Cr and 230 and 450 K for M= Fe. For the refinement of the crystal structure, we have considered the structural model of LaCu$_3$Mn$_3$O$_{12}$ [8] that crystallizes in the cubic space group $Im\overline{3}$ (No. 204). Nd atoms occupy the 2a (0,0,0) Wyckoff sites, Cu the 6b (0,1/2,1/2), Mn and Fe (Cr) the 8c (1/4,1/4,1/4) and O the 24g (x,y,0) positions. A plot of the crystal structure is displayed in figure 2.
Figure 1. XRD patterns (Cu Kα, λ = 1.5406 Å) of NdCu₃Mn₄O₁₂ and NdCu₃(Mn₃M)O₁₂ (M= Fe, Cr) oxides.

We assume that Mn and Fe(Cr) atoms occupy the 8c site randomly, and the mixed occupancy factor has been refined. Neutron diffraction is specially suited to detect Fe at Mn positions, given the contrasting scattering lengths for both elements. For Mn and Cr the scattering lengths are also significantly different. In addition, we have also refined the possible random occupancy of the Cu²⁺ cations at 6b positions by some Mn³⁺ ions, which are also Jahn-Teller cations. After the refinement we have found a small amount of Mn over this site. It seems that the presence of Mn³⁺ at the A positions of the perovskite contributes to the stabilization of these materials under moderate pressure conditions.

Figure 2. View of the crystal structure of NdCu₃(Mn₃M)O₁₂ (M= Fe, Cr). Corner-sharing (Mn,M)O₆ octahedra are fairly tilted in the structure to optimize Nd-O and Cu-O bond-lengths; Cu atoms are bonded to four oxygens in a pseudo-square-planar coordination.
Also we have refined the occupancy factor for oxygen atoms and the results confirm a full stoichiometry. Some unidentified impurities were detected in both cases. The reasonable agreement between the observed and calculated NPD patterns above and below the Curie temperatures for NdCu$_3$(Mn$_3$M)O$_{12}$ (M= Fe, Cr) is presented in figure 3 and figure 4. Below $T_c$, the Rietveld fit includes the magnetic structures as second phases, which will be described in the following sub-section. According to the mixed occupancy refined at (Cu,Mn)$_{6b}$ and (Mn,M)$_{8c}$ sites above $T_c$, i.e. at $T= 400$ K for M= Cr and $T= 450$K for M=Fe, the crystallographic formula of the compounds are: Nd(Cu$_{2.64(2)}$Mn$_{0.36(2)}$)(Mn$_{2.98(1)}$Fe$_{1.02(1)}$)O$_{11.9(2)}$ and Nd(Cu$_{2.66(2)}$ Mn$_{0.34(2)}$)(Mn$_{3.55(4)}$Cr$_{0.45(4)}$)O$_{11.8(2)}$. Whereas the incorporated amount of Fe is close to the nominal stoichiometry, in the case of Cr only 0.5 atoms per formula unit result to be accommodated into the octahedral positions of the perovskite.

![Figure 3](image.png)

**Figure 3.** Observed (crosses), calculated (solid line) and difference (bottom) NPD Rietveld profiles for NdCu$_3$Mn$_3$FeO$_{12}$ at (a) 230K and (b) 450K. Second line of Bragg reflections at 230K corresponds to the magnetic structure.

![Figure 4](image.png)

**Figure 4.** Observed (crosses), calculated (solid line) and difference (bottom) NPD Rietveld profiles for NdCu$_3$Mn$_3$CrO$_{12}$ at (a) 200K and (b) 400K, collected at the high flux D2B-ILL diffractometer.

Table 1 lists the most important parameters considered after the refinement of the crystal structures at above and below the Curie temperatures for NdCu$_3$(Mn$_3$M)O$_{12}$ (M= Fe, Cr). The main bond distances and bond angles are listed in Table 2. The superstructure of perovskite contains several features that must be highlighted. At the $B$ substructure of the perovskite, (Mn,M$^{3+}$)$_{8c}$ cations occupy...
the centre of virtually regular octahedra. As shown in figure 2, the perovskite structure is fairly
distorted due to the small size of the Nd$^{3+}$ and (Cu$^{2+}$,Mn$^{3+}$)$_{6b}$ cations, which force the MnO$_6$ octahedra
to tilt in order to optimise the Nd–O and Cu–O bond lengths.

Table 1. Unit-cell, positional, thermal parameters, and ordered magnetic moments for
NdCu$_3$(Mn$_3$M)$_{12}$ (M = Fe, Cr) defined in the cubic $Im$
(no. 204) space group, $Z = 2$, from NPD data. Nd at $2a(0,0,0)$, Cu at $6b (0,\frac{1}{2},\frac{1}{2})$, Mn/M at $8c (\frac{1}{4},\frac{1}{4},\frac{1}{4})$, and O at $24g (x,y,0)$ positions.

<table>
<thead>
<tr>
<th>M</th>
<th>Fe</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>230</td>
<td></td>
<td></td>
</tr>
<tr>
<td>450</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>450</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>450</td>
<td>230</td>
</tr>
</tbody>
</table>

| a(Å)         | 7.3120(2) | 7.3255(1) | 7.2845(2) | 7.2967(3) |
| V(Å$^3$)     | 390.93(1) | 393.12(1) | 386.55(2) | 388.49(2) |

<table>
<thead>
<tr>
<th>Nd</th>
<th>B(Å$^2$)</th>
<th>0.40(4)</th>
<th>0.63(5)</th>
<th>0.56(6)</th>
<th>0.67(7)</th>
</tr>
</thead>
</table>

$\text{(Cu/Mn)}_{6b}$

| Occupancy Cu/Mn | 0.880(1)/0.120(1) | 0.880(1)/0.120(1) | 0.888(1)/0.112(1) | 0.888(1)/0.112(1) |
| B(Å$^2$)        | 0.94(2)          | 0.93(4)          | 0.70(5)          | 0.70(5)          |
| Magnetic mom. ($\mu_B$) | -0.26(6) | --- | -0.2(1) | --- |

$\text{(Mn/M)}_{8c}$

| Occupancy Mn/M | 0.124(1)/0.043(1) | 0.124(1)/0.043(1) | 0.148(1)/0.019(1) | 0.148(1)/0.019(1) |
| B(Å$^2$)       | 0.5              | 0.5              | 1.0(2)            | 0.6(1)            |
| Magnetic mom. ($\mu_B$) | 1.55(6) | --- | 1.9 (1) | --- |

<table>
<thead>
<tr>
<th>O</th>
<th>x</th>
<th>0.3036(2)</th>
<th>0.3036(3)</th>
<th>0.3031(4)</th>
<th>0.3040(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>y</td>
<td>0.1804(2)</td>
<td>0.181(2)</td>
<td>0.1813(4)</td>
<td>0.181884</td>
<td></td>
</tr>
<tr>
<td>B(Å$^2$)</td>
<td>0.91(2)</td>
<td>1.22(2)</td>
<td>1.16(2)</td>
<td>1.26(3)</td>
<td></td>
</tr>
</tbody>
</table>

Reliability Factors

| $\chi^2$ | 4.54 | 4.17 | 6.56 | 4.67 |
| Rp(%)    | 2.84 | 2.86 | 3.63 | 3.65 |
| Rwp(%)   | 4.10 | 4.23 | 5.13 | 5.16 |
| Rexp(%)  | 1.92 | 2.07 | 2.00 | 2.39 |
| Rmerge(%)| 23.72 | --- | 6.66 | --- |
| Rl(%)    | 7.66 | 7.47 | 6.75 | 7.67 |

Although the available structural data for the parent compound NdCu$_3$Mn$_4$O$_{12}$ are collected at 295
K [15] the comparison with the present Fe and Cr doped phases is interesting. The (Mn$_{8c}$–O) distances
are significantly longer for M= Fe (1.942(2) Å at 450 K; 1.938(3) Å at 230 K) than those reported for
NdCu$_3$Mn$_4$O$_{12}$ (1.9295(9) Å) [15]; this is consistent with the incorporation of the larger Fe$^{3+}$ cations in
the Mn$^{4+}$ substructure and the slight oxygen deficiency. For the Cr compound the amount of
incorporated Cr$^{3+}$ ions is smaller, and the (Mn,Cr)$_{8c}$–O distances are similar to those of the undoped
phase. The tilting Mn$_{8c}$–O–Mn$_{8c}$ angle of the octahedra (~141.80(7)$^\circ$ for the pure Nd phase) remains
constant with M doping. The Nd atoms are coordinated to 12 oxygen atoms, with equal Nd–O distances, while the oxygen environment for the (Cu$^{2+}$,Mn$^{3+}$)$_{6b}$ cations is highly irregular, with eight
rather long distances and an effective coordination number of four in a pseudo-square arrangement. As
mentioned, the 6b positions are especially appropriate to host Cu$^{2+}$ or other Jahn–Teller ions such as
Mn\(^{3+}\). The four short Cu-O distances remain pretty unchanged with M substitution (1.956(5) Å in NdCu\(_3\)Mn\(_4\)O\(_{12}\) [15]).

### Table 2. Main bond distances (Å) and selected angles (deg) for NdCu\(_3\)(Mn\(_3\)M)O\(_{12}\) (M=Fe, Cr) determined from NPD data.

<table>
<thead>
<tr>
<th></th>
<th>T(K)</th>
<th>Fe</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>NdO(_{12}) polyedra</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd-O(x12)</td>
<td>2.582(1)</td>
<td>2.589(2)</td>
<td>2.573(3)</td>
</tr>
<tr>
<td>(Cu/Mn)O(_{12}) polyedra</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Cu/Mn)-O(x4)</td>
<td>2.7429(8)</td>
<td>2.7442(8)</td>
<td>2.729(2)</td>
</tr>
<tr>
<td>(Cu/Mn)-O(x4)</td>
<td>1.950(2)</td>
<td>1.957(2)</td>
<td>1.950(3)</td>
</tr>
<tr>
<td>(Cu/Mn)-O(x4)</td>
<td>3.223(1)</td>
<td>3.226(2)</td>
<td>3.204(2)</td>
</tr>
<tr>
<td>O-(Cu/Mn)-O</td>
<td>85.1(1)</td>
<td>85.3(1)</td>
<td>85.3(2)</td>
</tr>
<tr>
<td>O-(Cu/Mn)-O</td>
<td>94.9(1)</td>
<td>94.7(2)</td>
<td>94.7(2)</td>
</tr>
<tr>
<td>(Mn/M)O(_6) octahedra</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mn/M)(_{8c})-O(x6)</td>
<td>1.938(3)</td>
<td>1.942(2)</td>
<td>1.928(3)</td>
</tr>
<tr>
<td>O-(Mn/M)(_{8c})-O</td>
<td>89.78(7)</td>
<td>89.88(8)</td>
<td>89.8(1)</td>
</tr>
<tr>
<td>O-(Mn/M)(_{8c})-O</td>
<td>90.22(9)</td>
<td>90.12(9)</td>
<td>90.2(1)</td>
</tr>
<tr>
<td>(Cu/Mn)(<em>{6b})-O-(Mn/M)(</em>{8c})</td>
<td>109.07(5)</td>
<td>108.99(6)</td>
<td>108.9(9)</td>
</tr>
<tr>
<td>(Mn/M)(<em>{8c})-O-(Mn/M)(</em>{8c})</td>
<td>141.28(2)</td>
<td>141.47(2)</td>
<td>141.69(4)</td>
</tr>
</tbody>
</table>

#### 3.2. Magnetic properties

The susceptibility vs. temperature curves for the samples NdCu\(_3\)Mn\(_3\)Fe\(_{12}\) and NdCu\(_3\)Mn\(_3\)Cr\(_{12}\) are represented in figure 5a compared with that of the parent NdCu\(_3\)Mn\(_4\)O\(_{12}\) oxide. The curves display, in all cases, a saturation characteristic of the spontaneous ferro- or ferri-magnetic ordering. For the undoped compound, NdCu\(_3\)Mn\(_4\)O\(_{12}\), T\(_{C}\) (given by the inflexion point in the magnetization) is 386 K [15]. T\(_{C}\) decreases slightly for M= Cr (T\(_{C}\)= 369 K), and more significantly for M= Fe (T\(_{C}\)= 319 K). In all cases the observed T\(_{C}\)'s are above RT.

![Figure 5.](image-url)
The isothermal magnetization curves measured at $T = 4$ K are presented in figure 5b. According to the curves, a small magnetic field produces a sharp saturation of the magnetization which corresponds to a ferro- or ferri-magnetic material; there is a negligible hysteresis for all the compounds. In both Fe and Cr-substituted samples there is a slight decrease of the saturation magnetization ($M_S$) respect to the undoped compound, suggesting the possible appearance of some antiferromagnetic interactions between the Fe$^{3+}$ and Cr$^{3+}$ and Mn$^{4+}$ spins, which would reduce the global magnetization.

3.3. Determination of the magnetic structure

The magnetic structure has been determined for NdCu$_3$Mn$_3$FeO$_{12}$ and NdCu$_3$Mn$_3$.Cr$_{0.5}$O$_{12}$ from NPD patterns collected below the respective $T_C$, i.e. at 230 K for M= Fe and 200 K for M= Cr. Figure 3a and figure 4a show a magnetic contribution on some low-angle crystallographic Bragg positions; therefore the magnetic structure is defined by a $k=0$ propagation vector. This means a parallel coupling between the $8c$ and $6b$ magnetic sublattices. On the other side, from a NPD experiment it is not possible to determine the absolute orientation of the magnetic moments in a cubic structure; we have considered that they are oriented along the $c$ direction. After the final refinement of the magnetic structure, including the modules and signs of the individual moments, it has resulted that the magnetic moment of the Mn/M atoms at the $8c$ site are antiferromagnetically coupled with the magnetic moments of the atoms (Cu$^{2+}$ and Mn$^{3+}$) at the $6b$ site. So the magnetic structure must be described as a ferrimagnetic structure like the undoped NdCu$_3$Mn$_4$O$_{12}$ compound [15]. At the mentioned temperatures the ordered magnetic moments of both sublattices are far from saturation, as shown in Table 1.

Additionally, we have collected a NPD diagram at 2 K at the D1B diffractometer for the NdCu$_3$Mn$_3$FeO$_{12}$ sample, where an extra reflection is observed at $2\theta=28^\circ$ (Figure 6). It corresponds to the magnetic ordering of Nd$^{3+}$ magnetic moments. The onset of magnetic ordering is probably indicated by the cusp in the susceptibility curve (figure 5a), at $T \sim 80$ K. The magnetic intensities can be explained in a model where Nd magnetic moments are antiferromagnetically coupled with Mn(Fe) spins, according to the scheme depicted in figure 7. At 2 K, the ordered magnetic moment of Nd$^{3+}$ is 1.1(4) $\mu_B$.

![Figure 6. Observed (crosses), calculated (full line) and difference (bottom) of the low angle region NPD Rietveld profile for NdCu$_3$Mn$_3$FeO$_{12}$ at 2K, collected at D1B-ILL diffractometer, showing the good agreement of the magnetic structure (second series of Bragg reflections).](image-url)
3.4. Magnetotransport properties

Figure 8a displays the resistivity of NdCu$_3$(Mn$_3$Fe)O$_{12}$ compared to that of the parent compound NdCu$_3$Mn$_4$O$_{12}$. It is noteworthy that whereas the Fe-undoped sample shows a metallic behaviour and exhibits a relatively low room-temperature resistivity of ~0.17 Ω·cm [15], the Fe-doped oxide exhibits a semiconducting behaviour in all the measured temperature range (4–400 K). It shows a room temperature resistivity of about 10 Ω·cm. In the parent compound, the low resistivity value is due to the mixed valence state of the Mn cations at B positions (Mn$^{3+}$–Mn$^{4+}$); it is important to recall that the average oxidation state of Mn ions in the NdCu$_3$Mn$_4$O$_{12}$ oxide is 3.75+. The huge increase in resistivity in the Fe doped sample is certainly related to the introduction of Fe$^{3+}$ at B positions. We believe that this doping substantially suppresses the Mn$^{3+}$–Mn$^{4+}$ mixed valence state at the octahedral sites, thus hindering the hopping mechanism between adjacent Mn$^{3+}$ and Mn$^{4+}$ that is the main responsible for the charge transport in the parent oxide [16].

Concerning to the changes in the resistance under a magnetic field we define $\text{MR}(H) = 100\times |(R(H) - R(0))/R(0)|$ as the magnetoresistive response of the samples. Figure 8b shows the
magnetoresistance isotherms at 100 and 300 K for NdCu$_3$(Mn$_3$Fe)O$_{12}$ compared with those of the undoped oxide; MR is negative for both compounds at both temperatures. The MR is significant at room temperature reaching values of $-6\%$ at 9 T. The undoped compound shows a strong component of low-field MR (defined for magnetic fields lower than 1 T) that is less noteworthy for the Fe-doped sample. However, it is remarkable that the magnetoresistance reaches a maximum value of about $-16\%$ at 100 K and 9 T for the Fe compound, significantly higher (in absolute value) than that of 12.5% exhibited by the pure compound, even if the $T_C$ of NdCu$_3$Mn$_4$O$_{12}$ is noticeably higher for this pure sample. We believe that the observed increase in MR is concomitant with a decrease in the number of charge carriers from the pure oxide to the Fe-doped compound, as predicted by Majumdar and Littlewood’s model [17]. In a semiconductor with low density of carriers ($n$) the conductivity, via polarons, is governed by the expression $\Delta \rho/\rho = C (M/M_s)^2$, where $\Delta \rho/\rho$ is the magnetoresistance, $M$ and $M_s$ are the magnetization and saturation magnetization of the sample, and $C$ is a constant proportional to $n^{-2/3}$. This model predicts, hence, an increment of MR associated with a decrease in the number of charge carriers, i.e. an increase of the resistivity. As commented above, we believe that the electron hopping between $\text{Mn}^{3+}$-$\text{Mn}^{4+}$ is hindered upon Fe introduction, given the energy difference between Fe and Mn 3e$_g$ orbitals, and we presume that the charge transfer between neighbouring $\text{Fe}^{3+}$ and $\text{Mn}^{4+}$ is negligible. Therefore, the chemical replacement of Mn by Fe leads to the blocking of the hopping mechanism between $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ involving a dramatic increase of the bulk resistivity and a concomitant increase of MR at low temperatures.

4. Conclusions

New materials of formula NdCu$_3$(Mn$_3$M)O$_{12}$ (M= Fe, Cr) with a complex perovskite superstructure have been synthesized at moderate pressures of 2 GPa in the presence of an oxidizing agent. The crystal structure has been refined from high-resolution NPD data. Owing to the contrast between the neutron scattering lengths of Mn and Fe(Cr), we could discern that Fe(Cr) cations occupy the B octahedral positions of the perovskite, and some Mn ions, adopting a trivalent oxidation state, are placed at the A (Cu$_{6b}$) sites. The substitution of Mn$^{8+}$ by Fe(Cr) ions gives rise to a decrease of the ferrimagnetic $T_C$ since these ions drastically reduce the FM interactions within this magnetic sublattice. The resistivity of the Fe-doped sample is semiconducting-like and presents a much higher magnitude than that of the undoped compound. The replacement of Mn cations by Fe$^{3+}$ within the octahedral sublattice partially suppresses the mixed-valence state ($\text{Mn}^{3+}$-$\text{Mn}^{4+}$) over the B (Mn$_{6b}$) positions, thus drastically hindering the hopping mechanism and the overall conductivity. We believe that the observed increase in MR at 100 K is concomitant with a decrease in the number of charge carriers from the pure oxide to the Fe-doped compound.

Acknowledgments

We thank the financial support of the Spanish Ministry of Science and Tecnology to the project MAT2010-16404 and of the Comunidad de Madrid to the project S2009PPQ-1551. We thank Dr. M. García-Hernández for the magnetic measurements and we are grateful to the Institut Laue-Langevin (ILL) for making all facilities available.

References