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# Preparation under high pressures and neutron diffraction study of new ferromagnetic $\text{RCu}_3\text{Mn}_4\text{O}_{12}$ ( $\text{R} = \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Tm}, \text{Yb}$ ) perovskites

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## Abstract

We report on the study of some new derivatives of the complex perovskite  $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ .  $\text{Ca}^{2+}$  cations can be replaced by rare earths in the  $\text{RCu}_3\text{Mn}_4\text{O}_{12}$  ( $\text{R} = \text{rare earths}$ ) family, implying an electron doping effect that dramatically affects the magnetic properties. These compounds must be prepared under high pressure conditions. We have synthesized for the first time, at 2 GPa in a piston–cylinder press, some new members of the family, with  $\text{R} = \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Tm}$  and  $\text{Yb}$ , for which we describe structural and magnetization data. The materials with non-absorbing rare earths have been studied by means of neutron powder diffraction, allowing us to determine the subtle structural features which are related to the observed physical properties. In fact, for most of the R cations, the ferromagnetic  $T_C$  increases remarkably up to 400 K.

## 1. Introduction

Among the rare ferromagnetic and half-metallic oxides, the complex perovskite  $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$  [1] is interesting because it exhibits a considerable low field magnetoresistance at room temperature, that is not coupled with  $T_C$  (355 K) [2]. This material and its derivatives form a family of compounds with potential technological applications. The crystal structure of  $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$  has the novelty of containing  $\text{Cu}^{2+}$  (or other Jahn–Teller transition metal cations, such as  $\text{Mn}^{3+}$ ) at the A positions of the  $\text{ABO}_3$  perovskite. This Jahn–Teller cation and  $\text{Ca}^{2+}$  are 3:1 ordered in a  $2\mathbf{a}_0 \times 2\mathbf{a}_0 \times 2\mathbf{a}_0$  cubic cell of  $Im\bar{3}$  symmetry ( $\mathbf{a}_0 =$  unit-cell vector of the perovskite aristotype). This perovskite is strongly distorted, showing an important tilting of the  $\text{MnO}_6$  octahedra that is given by the small size of the cations at the A positions. This material, and other compounds of the  $\text{A}'\text{A}_3\text{B}_4\text{O}_{12}$  family, have been prepared under high pressure (7 GPa), which is necessary to stabilize the small A cations in the twelfold positions of the perovskite. Recently, we have been able to synthesize well-crystallized (polycrystalline) samples of some new derivatives of  $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$  at moderate pressures of 2 GPa, starting

from very reactive precursors obtained by wet-chemistry procedures in the presence of  $\text{KClO}_4$  as an oxidizing agent [3]. In this system,  $\text{Ca}^{2+}$  cations can be replaced by rare earths in the  $\text{RCu}_3\text{Mn}_4\text{O}_{12}$  (R = rare earths) family, implying an electron doping effect that affects the magnetic and transport properties, as demonstrated for R = La, Ce, Nd and Th [4, 5]. With the aim of studying the structural and magnetic properties of this promising system, we have prepared new  $\text{RCu}_3\text{Mn}_4\text{O}_{12}$  compounds with R = Pr, Sm, Eu, Gd, Dy, Ho, Tm, Yb. These materials have been fully characterized by neutron powder diffraction (NPD), x-ray diffraction (XRD) and magnetic measurements.

## 2. Experimental details

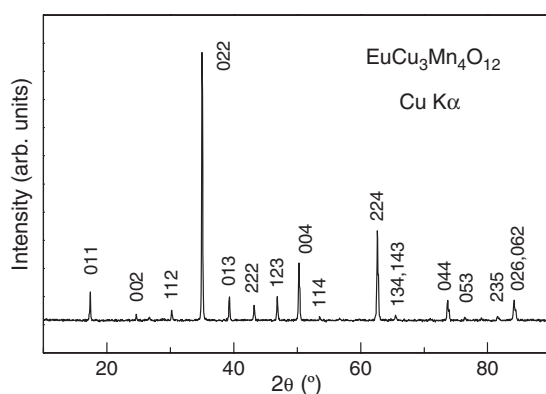
The elaboration of  $\text{RCu}_3\text{Mn}_4\text{O}_{12}$  compounds required the previous preparation of very reactive precursors obtained by wet-chemistry techniques. A mixture of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{MnCO}_3$  and the corresponding  $\text{R}_2\text{O}_3$  oxide was dissolved in citric acid; the solution was slowly evaporated and the resulting resin was decomposed at temperatures up to  $800^\circ\text{C}$ . These precursors were thoroughly ground with  $\text{KClO}_4$  (30% in weight), put into a gold capsule (8 mm diameter, 10 mm length), sealed and placed in a cylindrical graphite heater. The reactions were carried out in a piston–cylinder press (Rockland Research Co.), at a pressure of 2 GPa at  $1000^\circ\text{C}$  for 60 min. The ground product was washed in a dilute  $\text{HNO}_3$  aqueous solution, in order to dissolve KCl coming from the decomposition of  $\text{KClO}_4$ .

The products were initially characterized by means of laboratory XRD (Cu  $K\alpha$ ,  $\lambda = 1.5406 \text{ \AA}$ ) for phase identification and to assess phase purity. For the structural refinements, NPD patterns were collected at room temperature at the high resolution D2B neutron diffractometer of ILL-Grenoble. In spite of the relatively small amount of sample available (about 1 g), a good quality pattern could be collected with the high flux mode and a counting time of 4 h for each pattern. A wavelength of  $1.594 \text{ \AA}$  was selected from a Ge monochromator. Both crystallographic and magnetic structures were refined from the NPD by the Rietveld method, using the FULLPROF refinement program. The dc magnetic susceptibility was measured with a commercial SQUID magnetometer for powdered samples, in the temperature range 2–400 K under magnetic fields up to 16 T.

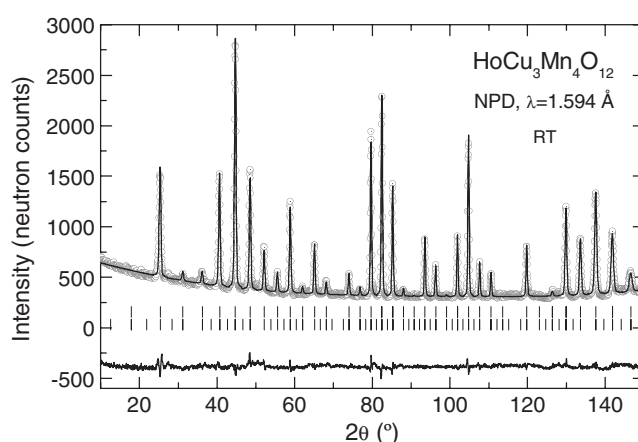
## 3. Results and discussion

A representative XRD diagram of  $\text{EuCu}_3\text{Mn}_4\text{O}_{12}$  is shown in figure 1. The pattern is characteristic of a body centred cubic perovskite, showing sharp, well-defined superstructure reflections due to the 1:3 ordering of rare earth and Cu cations. No impurity phases were detected from either XRD or NPD data. Identical diagrams were obtained for all the samples.

The materials with non-absorbing rare earths have been studied also by means of NPD at RT, allowing us to determine the subtle structural features which are related to the observed physical properties. The structural refinement from NPD patterns was performed in the  $Im\bar{3}$  (No 204) space group, with rare earth atoms at 2a (0, 0, 0) positions ( $A'$  site), Cu at 6b (0, 1/2, 1/2) positions (A site), Mn at 8c (1/4, 1/4, 1/4) (B site) and O at 24g (0, y, z) sites. No regions were excluded in the refinement. In the fit, the following parameters were refined from the high resolution D2B data: scale factor, background coefficients, zero-point error, unit-cell parameters, pseudo-Voigt parameters corrected for asymmetry, positional coordinates and isotropic thermal factors. As the materials are ferrimagnetically ordered at RT, the magnetic structure was included as a second phase in the final refinement, by considering Mn and Cu sublattices as antiferromagnetically coupled. Figure 2 shows an excellent agreement between



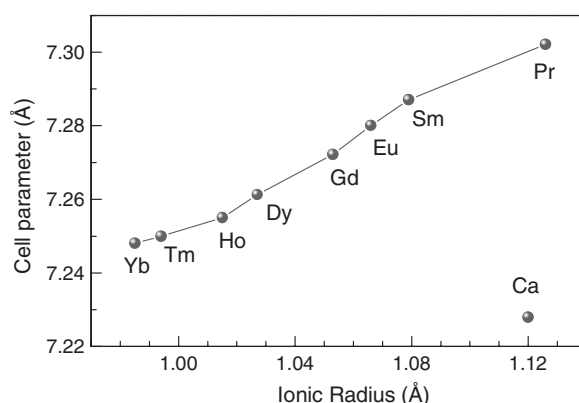
**Figure 1.** XRD pattern for  $\text{EuCu}_3\text{Mn}_4\text{O}_{12}$  indexed in a cubic unit cell with  $a = 7.2801(3) \text{ \AA}$ .



**Figure 2.** Observed (circles), calculated (full line), and difference (bottom) NPD Rietveld profiles for  $\text{HoCu}_3\text{Mn}_4\text{O}_{12}$  at room temperature. The second series of Bragg reflections corresponds to the magnetic structure.

the observed and calculated NPD profiles at RT for  $\text{HoCu}_3\text{Mn}_4\text{O}_{12}$  ( $R_1 \approx 8\%$ ). Similar fits have been obtained for all the samples. The subsequent refinement of the oxygen content gave no significant deviation from the full stoichiometry. Table 1 includes the main structural parameters for the full series, including the oxygen  $y$  and  $z$  positional parameters, Mn–O and R–O distances and Mn–O–Mn angles.

Figure 3 shows the dependence of the unit-cell parameter,  $a$ , as a function of the ionic radii of the rare earth in eightfold coordination [6]. Notice that the size of the cell is, in all cases, significantly larger than that of the undoped  $\text{Ca}^{2+}$  compound, which suggests that the main driving force for the unit-cell expansion is the electronic injection effect on bands of Mn–O origin. In fact, the Mn–O distances are considerably longer than that observed in  $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ , of  $1.911 \text{ \AA}$  [3]. A regular decrease of the cell size is observed across the rare earth series, as expected from the lanthanide contraction. This variation is mainly due to the contraction of the  $\text{RO}_{12}$  polyhedra, since the Mn–O distances and Mn–O–Mn angle vary insignificantly across the series, as observed in table 1. It is surprising that the Mn–O–Mn angle shows very little sensitivity to the size of the  $\text{R}^{3+}$  cation (unlike what happens in other



**Figure 3.** Unit-cell parameter evolution with the ionic radius of the rare earth cation. The parameter of  $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$  is given for the sake of comparison: the ionic radii of eightfold coordinated cations are considered in all cases [6].

**Table 1.** Main structural parameters of the perovskites  $\text{RCu}_3\text{Mn}_4\text{O}_{12}$  in the cubic  $Im\bar{3}$  (No 204) space group, for  $R = \text{Pr, Dy, Ho, Tm, Yb}$  from NPD data and for  $R = \text{Sm, Eu}$  and  $\text{Gd}$  from XRD data at 295 K.

	Pr	Sm	Eu	Gd	Dy	Ho	Tm	Yb
$a$ (Å)	7.30204(9)	7.2870(5)	7.2801(3)	7.2722(2)	7.2613(1)	7.2550(1)	7.2500(1)	7.2481(2)
$V$ (Å <sup>3</sup> )	389.343(8)	386.95(4)	385.85(3)	384.58(2)	382.86(1)	381.873(7)	381.07(1)	380.78(2)
$y$ (O)	0.3019(2)	0.304(2)	0.309(2)	0.308(2)	0.2982(3)	0.2981(2)	0.2983(3)	0.2968(3)
$z$ (O)	0.1806(2)	0.181(2)	0.186(2)	0.184(2)	0.1781(3)	0.1780(2)	0.1781(3)	0.1780(3)
R–O (Å) ( $\times 12$ )	2.569(1)	2.58(1)	2.625(7)	2.612(9)	2.522(2)	2.519(1)	2.519(2)	2.508(2)
Cu–O (Å) ( $\times 4$ )	1.957(9)	1.95(1)	1.94(1)	1.93(1)	1.954(3)	1.953(1)	1.951(2)	1.958(2)
Mn–O (Å) ( $\times 6$ )	1.932(1)	1.93(1)	1.926(8)	1.928(9)	1.921(3)	1.920(1)	1.918(2)	1.916(2)
Mn–O–Mn (deg)	141.75(2)	141.4(2)	141.8(1)	141.1(2)	141.78(3)	141.77(2)	141.79(3)	142.08(3)

R-containing perovskite series, such as  $\text{RNiO}_3$ ), since the tilting of the  $\text{MnO}_6$  octahedra is mainly determined by the presence of three  $\text{Cu}^{2+}$  versus a single  $\text{R}^{3+}$  cation at the  $A'$  positions.

Figure 4 shows the steep increase of magnetization with decreasing temperature characteristic of a spontaneous ferromagnetic ordering for all the samples. The inflection point in the magnetization, the ferromagnetic Curie temperature ( $T_C$ ), increases remarkably up to almost 400 K, well above the reported Curie temperature of the parent compound  $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$  ( $T_C = 355$  K) [2] or  $\text{CaCu}_{2.5}\text{Mn}_{4.5}\text{O}_{12}$  ( $T_C = 345$  K) [3]. The study of the magnetic structures demonstrates that Mn and Cu spins are coupled antiferromagnetically. At low temperatures ( $< 100$  K), the rare earth moment plays an important role in the total magnetization, as occurs for example in the Pr, Gd, Dy and Ho perovskites. The rare earth moment seems to become antiferromagnetically coupled with the Mn sublattice and therefore the magnetization undergoes an important decrease (figure 4). This magnetic coupling can be broken under sufficiently high magnetic fields (metamagnetic transition), as shown in the magnetization versus magnetic field plots (figure 5): the Gd sample does not reach a saturation value, at least up to 16 T. For  $R = \text{Sm}$  and  $\text{Eu}$  the saturation magnetization is reached for  $H < 1$  T, showing (figure 5) a behaviour characteristic of pure ferromagnets.

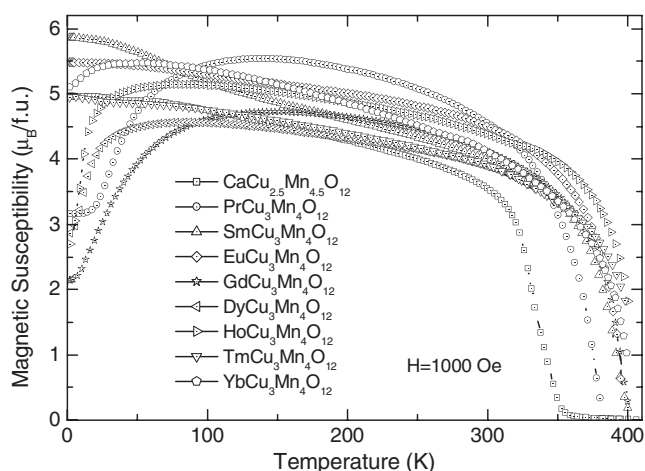


Figure 4. Temperature dependence of the dc magnetic susceptibility for  $RCu_3Mn_4O_{12}$  compounds.

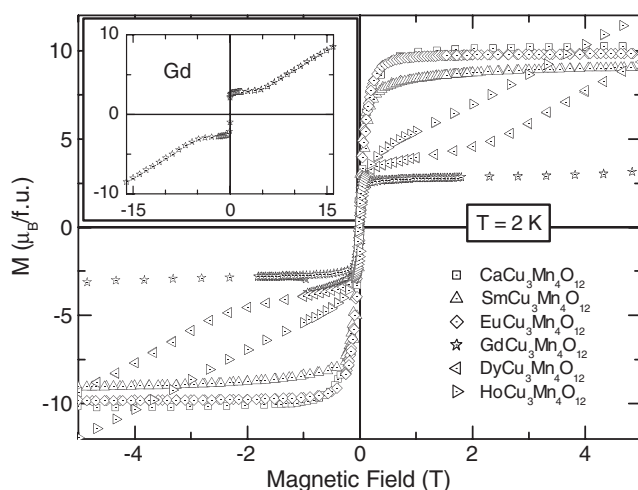


Figure 5. Magnetization versus magnetic field isotherms at 2 K for some selected samples. The inset shows the  $GdCu_3Mn_4O_{12}$  isotherm from  $-16$  to  $16$  T.

#### 4. Conclusions

We have synthesized some new derivatives of  $CaCu_3Mn_4O_{12}$  at moderate pressures of 2 GPa by replacing  $Ca^{2+}$  with  $R^{3+}$  rare earth cations; the concomitant electronic injection leads to a substantial increment of  $T_C$ . The crystal structures of the new materials were refined in the  $Im\bar{3}$  space group from NPD for the non-absorbing R cations. The unit-cell parameter scales with the ionic radius of the rare earth cation and is considerably expanded with respect to  $CaCu_3Mn_4O_{12}$ , as a result of the electronic injection. The room temperature magnetic structure displays a ferrimagnetic coupling between  $Mn^{3+/4+}$  and  $Cu^{2+}$  spins; additionally the contribution of the magnetic moment of the rare earth is very significant for  $R = Pr, Gd, Dy$  and  $Ho$  below 100 K, suggesting an antiferromagnetic coupling with the Mn sublattice, which substantially reduces the susceptibility and the saturation magnetization.

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