Experimental Report

06/02/2014

Proposal: **5-31-2228** **Council:** 4/2012

Title: Crystal and magnetic structure of new materials belonging to the series of ferrimagnetic compounds RCrMnO5 (R= Nd, Tb, Ho and Er)

This proposal is a new proposal

Researh Area: Materials

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Samples:
NdCrMnO5
TbCrMnO5
HoCrMnO5
ErCrMnO5
La-Mn-MoO9
3x Y-Fe-Co-O3
La-Mn-MoO6
LaPbCoSbO6

Instrument	Req. Days	All. Days	From	To
D2B	2	2	29/10/2012	31/10/2012
D20	2	2	31/10/2012	02/11/2012

Abstract:

The compounds RMn2O5 have been informed to be magnetoelectric. Substitution of one Mn by Fe or Cr has been informed for RFeMnO5 (R= Y, Tb, Dy, Ho, Er and Yb) and RCrMnO5 (R= Y and Dy).
Here we propose the determination of the crystal and magnetic structures at RT and 4K in D2B and its evolution with temperature in D20 of some new compounds belonging to the family RCrMnO5 synthesized by us by the first time at high O2 pressure at temperatures in the range 900-1000 ˚C, where R= Nd, Tb, Ho and Er.
We expect to determine the influence of the Cr and Mn occupations on the octahedral and pyramidal sites on the magnetic structures and also to confirm the presence of R vacancies which were observed by Rietveld analysis of PXRD on these compounds and its influence on the structural and magnetic properties.

Introduction

Recently, numerous investigations focused on the magnetoelectric RMn_2O_5 (R= rare earths) materials [1-3]. These structures are extraordinarily flexible with regard to the substitutions of both R and Mn atoms allowing, for instance, the preparation of $RMnM'O_5$ (M'=transition metals) phases.

We recently prepared by the first time four new members of the family $RCrMnO_5$, where R is Tb, Ho or Er and Nd (with the stoichiometry $NdCr_{0.5}Mn_{1.5}O_5$).

Experimental

Neutron powder diffraction (NPD) measurements have been made with the aim of determinate the crystals structure, cation site occupancies and magnetic structure. These patterns were obtained at 300K and 4K at the D2B line (λ=1.594 Å). Besides, these samples were measured in the D20 instrument (λ=2.410 Å) from 3K to 300K. The FULLPROF program [4] was used to refine the crystal structure by the Rietveld method.

Results and discussion

A combined refinement of the crystal structure from NPD and XRD data at room temperature for the four compounds was carried out in the orthorhombic space group *Pbam*. The crystal structure of $YCrMnO_5$ was used as the starting model [5]. R atoms were placed at *4g* (x, y, 0) positions, Mn at *4f* (0, 1/2, z) sites, Cr at *4h* (x, y, 1/2), and the four crystallographically independent oxygen atoms at *4e* (0, 0, z), *4g*, *4h*, and *8i* (x, y, z) positions. This ideal atomic distribution gave rise to an unsatisfactory agreement between the calculated and observed patterns. The presence of antisite disorder between Cr and Mn cations was then checked; the refinement considerably improved. In fact, we found an extremely important degree of antisite disordering in these samples. Additionally, the partial occupancy of Cr/Mn at *4h* and *4f* positions was decoupled in the final refinement, allowing the independent refinement of the occupancy factor at both sites. By doing so, the final refined stoichiometry was somewhat apart from the nominal Cr/Mn = 1/1 composition, but the quality of the final refinement warrant the validity of these results (see **Fig. 1a** and **Table 1**). It is worth underlining that the refinement of the mixed occupancy factors of Cr and Mn over the same crystallographic site, which would be unfeasible by XRD, is very precise by neutron diffraction given the large difference in values of the scattering lengths for Cr (3.635fm) and Mn (-3.73fm). By the same reason, and given the comparable amount of Cr and Mn found in both sites, the average scattering length at both positions is very weak, and the error in the determination of the corresponding positions and thermal factors is huge. For this reason, a combined refinement from NPD and XRD data was essential to accurately determine the *4f* and *4h* positions. The goodness of fit of the NPD data for the sample $TbCrMnO_5$ is showed en **Fig. 1a**.

The neutron diffraction patterns collected at 3 K did not contains any additional information, extra peaks, or additional intensity on low-angle Bragg reflections that could be attributed to the establishment of a long-range ordered magnetic structure in any studied compounds. These patterns could be perfectly refined by considering the crystal structure alone. The experimental and calculated NPD patterns for $TbCrMnO_5$ are compared in **Fig. 1b**. The same is observed for the measurement taken on the D20 instrument, as can be seen in **Fig. 2** for the $TbCrMnO_5$.

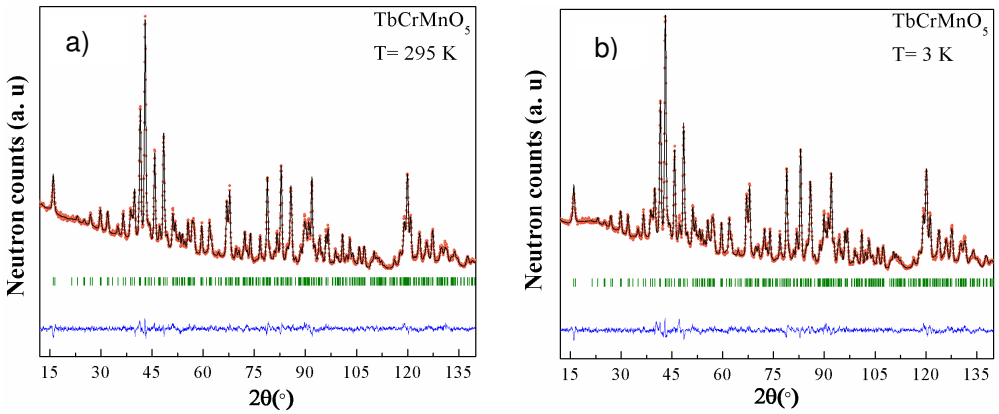

***Figure 1**: Observed (crosses), calculated (solid line) and difference (bottom line) NPD patterns at room temperature (a) and 3K (b).*

R (rare earth)	Refined Crystallographic Formula	Empirical Formula
Nd	$Nd[Cr_{0.152(1)}Mn_{0.614(1)}]_{4f}[Mn_{0.889(1)}Cr_{0.345(1)}]_{4h}O_5$	$NdCr_{0.497(1)}Mn_{1.503(1)}O_5$
Tb	$Tb[Cr_{0.594(1)}Mn_{0.406(1)}]_{4f}[Mn_{0.612(1)}Cr_{0.388(1)}]_{4h}O_5$	$TbCr_{0.982(1)}Mn_{1.018(1)}O_5$
Ho	$Ho[Cr_{0.544(1)}Mn_{0.456(1)}]_{4f}[Mn_{0.640(1)}Cr_{0.360(1)}]_{4h}O_5$	$HoCr_{0.904(1)}Mn_{1.096(1)}O_5$
Er	$Er[Cr_{0.522(1)}Mn_{0.478(1)}]_{4f}[Mn_{0.660(1)}Cr_{0.340(1)}]_{4h}O_5$	$ErCr_{0.862(1)}Mn_{1.138(1)}O_5$

***Table 1**: Empirical formula and refined crystallographic formula obtained from NPD data at room temperature for $RCrMnO_5$. 4f: octahedral site and 4h: pyramidal site.*

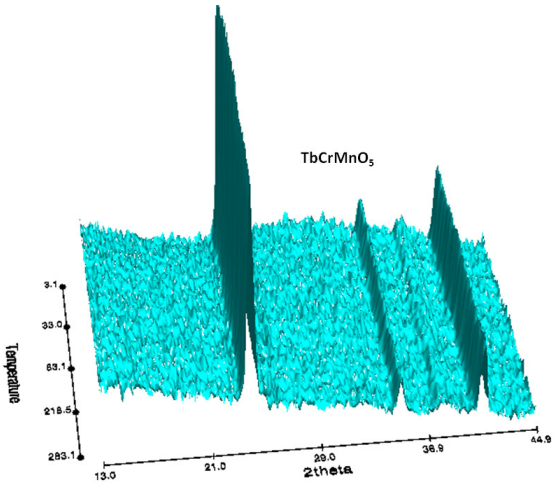

***Figure 2**: Measurement on the D20 instrument (λ=2.410 Å) from 3 K to 300 K for the sample with Tb, where we can see the absence of magnetic peaks at low angles.*

	295K			
	Nd	Tb	Ho	Er
$R^{3+}O_8$				
R-O1(x2)	2.5126(3)	2.3676(3)	2.3613(3)	2.3416(4)
R-O2	2.3929(4)	2.3322(4)	2.2750(4)	2.3153(6)
R-O2	2.4015(4)	2.4026(4)	2.4423(5)	2.3851(6)
R-O4(x2)	2.4664(3)	2.3733(3)	2.3445(3)	2.3490(4)
R-O4(x2)	2.5535(3)	2.4818(3)	2.4624(3)	2.4771(4)
<R-O>	2.4824	2.3975	2.3817	2.3795
$(Cr, Mn)^{4+}O_6$				
M-O2(x2)	1.9498(2)	1.9719(2)	1.9410(3)	1.9760(3)
M-O3(x2)	1.8480(2)	1.8691(2)	1.8767(3)	1.8311(4)
M-O4(x2)	1.9314(2)	1.9346(2)	1.9232(3)	1.9223(3)
<M-O>	1.9097	1.9252	1.9136	1.9098
$(Mn, Cr)^{3+}O_5$				
M'-O1(x2)	1.8378(3)	1.9228(2)	1.9271(3)	1.9122(3)
M'-O3	2.0074(6)	1.9109(3)	1.9262(4)	1.9314(6)
M'-O4(x2)	1.8266(3)	1.8852(2)	1.8848(3)	1.8681(3)
<M'-O>	1.8672	1.9054	1.9100	1.8984
M-M	2.9797(7)	2.9674(8)	2.7672(1)	2.6843(1)
M-M	2.7413(7)	2.7323(8)	2.9271(1)	3.0013(2)
M'-M'	2.8971(6)	2.8774(8)	2.8584(1)	3.0013(2)

***Table 2**: Main bond distances for the $RCrMnO_5$ samples at 295K.*

The more relevant bond distances are included in **Table 2**. In this table we can see that in all cases the average distance in octahedral sites is bigger than in pyramidal sites and this is just the opposite than in the compounds RMn_2O_5 [6]. This difference between $RCrMnO_5$

and RMn_2O_5 compounds can be explained if one assumes that the Mn^{3+} (r=0.645 Å) occupying the pyramidal site in RMn_2O_5 [5] is being replaced by Cr^{4+} (r=0.55 Å) and Mn^{4+} (r=0.53 Å) in the octahedral site is being replaced by Cr^{3+} (r=0.615 Å) in average. This could only be concluded using the precise bond distances obtained by PND.

In order to separate the magnetic effects from the Cr-Mn subsystem from the R subsystem, we have made measurements of M vs. T at 100 Oe (ZFC-FC). Although the magnetism of rare earths is very important in some members of the series, we took the separation between ZFC-FC curves (see inset on **Fig. 3**) as the ordering temperature (T_N) of Cr-Mn system (short range order). In **Fig. 3** we shows a lineal dependence of T_N as a function of ionic radius of the rare earth, suggesting a strong magnetic correlation between the Cr-Mn system and the changes in the crystal structure caused by the change in the size of R. For the samples with R=Gd, Eu and Sm we do not performed neutron diffraction experiments due to its know ability to strongly absorb neutrons.

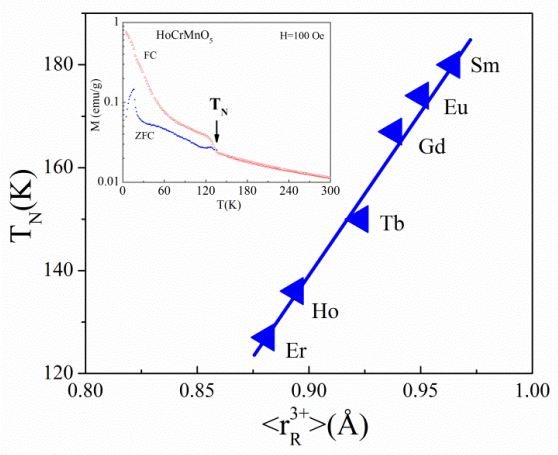

***Figure 3**: Lineal dependence of the T_N as a function of ionic radius of the rare earth. Inset: measurement of M vs. T at 100 Oe for the sample $HoCrMnO_5$, where we indicate the temperature (T_N) plotted in this figure.*

Conclusions

A high degree of antisite disordering has been found over the *4f* and *4h* sites. The oxidation states of the ions occupying the octahedral and pyramidal sites could be inferred by use of the average bond distances. The low temperature NPD patterns do not show any magnetic contribution in these compounds, indicating that long-range magnetic ordering is not established down to low temperature despite all the compounds show macroscopic magnetism with T_N dependent on the R nature.

References

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