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$YBaMn_2O_5$: CRYSTAL AND MAGNETIC STRUCTURE REINVESTIGATION

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ABSTRACT

The ordered oxygen-deficient perovskite $YBaMn_2O_5$ has been synthesized as a monophasic sample. A variable temperature neutron diffraction study of this phase has been carried out. The crystal structure of this manganite was solved in the space group $P4/nmm$ ($a = 5.547$ Å and $c = 7.649$ Å). This oxide, which is closely related to the $YBaCuFeO_5$ structure, forms an alternate stacking of yttrium and barium layers along the c axis. It differs from the latter, however, by the existence of two distinct sites for manganese, corresponding to an ordering of the Mn^{3+} and Mn^{2+} cations, respectively. Elucidation of the magnetic structure of $YBaMn_2O_5$, from low temperature PND (powder neutron diffraction) data, leads to a G-type antiferromagnetic model; the superimposed Mn^{2+}/Mn^{3+} charge order results in ferrimagnetic behavior for this phase and explains its magnetic properties, as obtained from susceptibility measurements.

KEYWORDS: A. oxides, B. chemical synthesis, C. neutron scattering, D. crystal structure, D. magnetic structure

INTRODUCTION

A new oxygen-deficient perovskite $YBaMn_2O_5$ was recently reported by Chapman et al. [1] and McAllister and Attfield [2]. The authors showed that the structure of $YBaMn_2O_5$ is similar to that of $YBaCuFeO_5$ [3,4]. They solved it in the space group $P4/mmm$ ($a \approx 3.9$ Å

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and $c \approx 7.6$ Å), showing that it consists of double pyramidal manganese layers containing Ba^{2+} cations interleaved with yttrium layers. Studying the magnetic behavior of $YBaMn_2O_5$, the authors [1,2] suggested that the structure should be more complicated than expected from the PND study. Unfortunately, they were not able to carry out further investigation, due to the fact that the sample was polyphasic, containing 36.3% of $YMnO_3$, 24.9% of Ba_2SiO_4, 6.7% of MnO, and only 36.3% of $YBaMn_2O_5$ [2].

In a recent investigation of the La–Ba–Mn–O system, we synthesized three new perovskites $LaBaMn_2O_{6-x}$ [5], controlling the oxygen pressure during both the synthesis and post-annealing. Among these oxides, the perovskite $LaBaMn_2O_5$, obtained as a pure phase, was found to be closely related to $YBaCuFeO_5$. Nevertheless, its structure determination from PND data shows that it exhibits a different tetragonal cell ($a = 5.650$ Å and $c = 7.808$ Å), implying two different sites for manganese in the space group $P4/nmm$. These results suggest the possibility of similar behavior for $YBaMn_2O_5$.

In this paper, we report on the synthesis of the ordered oxygen-deficient perovskite $YBaMn_2O_5$ as a monophasic sample and the reinvestigation of its crystal and magnetic structures.

EXPERIMENTAL

The ordered oxygen-deficient tetragonal perovskite $YBaMn_2O_5$ was prepared by mixing the oxides Y_2O_3 and Mn_2O_3 with the carbonate $BaCO_3$, in stoichiometric proportions. The powders were sintered at 1500°C in a pure argon flow in order to avoid any oxidation of Mn^{3+} into Mn^{4+}. The products were then slowly cooled in the same atmosphere down to room temperature. Under these conditions, an oxygen-deficient perovskite with the formula $YBaMn_2O_{5+\varepsilon}$ was obtained with a very small oxygen excess (ε) with respect to the ideal formula O_5. Removal of this excess oxygen was achieved by annealing the obtained powder at 600°C in an evacuated silica ampoule, in presence of zirconium–titanium alloy chips for 12 h. The oxygen content of the sample was then determined by iodometric titration and found to be very close to the ideal stoichiometry O_5 ($YBaMn_2O_{5.0\pm0.1}$). It is worth pointing out that the oxygen content of this perovskite was confirmed by neutron diffraction refinements.

The purity of the samples was first checked from X-ray diffraction data registered with a Philips diffractometer using Cu Kα radiation. The ordered phase $YBaMn_2O_5$ was subsequently registered with the high-resolution neutron powder diffractometer D2B (room temperature, $\lambda = 1.594$ Å) and D1A (2 K, $\lambda = 1.911$ Å) at the Institut Laue-Langevin (ILL).

Nuclear and magnetic refinements were performed using the profile fitting program FULLPROF [6] ($b_Y = 0.775 \times 10^{-12}$ cm, $b_{Ba} = 0.525 \times 10^{-12}$ cm, $b_{Mn} = -0.373 \times 10^{-12}$ cm, and $b_O = 0.58 \times 10^{-12}$ cm) [7]. Magnetization measurement was made with a SQUID (MPMS Quantum Design) magnetometer. AC susceptibility was measured with a Lake Shore 7000 susceptometer ($8\ \text{Hz} \leq f \leq 666\ \text{Hz}$, $5\ \text{K} \leq T \leq 320\ \text{K}$, $10^{-2}\ \text{G} \leq h_{AC} \leq 10\ \text{G}$).

The thermogravimetric (TG) analysis was realized with a Setaram microbalance under an oxygen flow.

RESULTS AND DISCUSSION

Most of the reflections of the PND pattern of this phase, collected at room temperature in the paramagnetic domain, can be indexed with a tetragonal cell, space group $P4/mmm$ with $a = 3.9223$ Å and $c = 7.6498$ Å. This is in agreement with the previous study of Chapman et al.

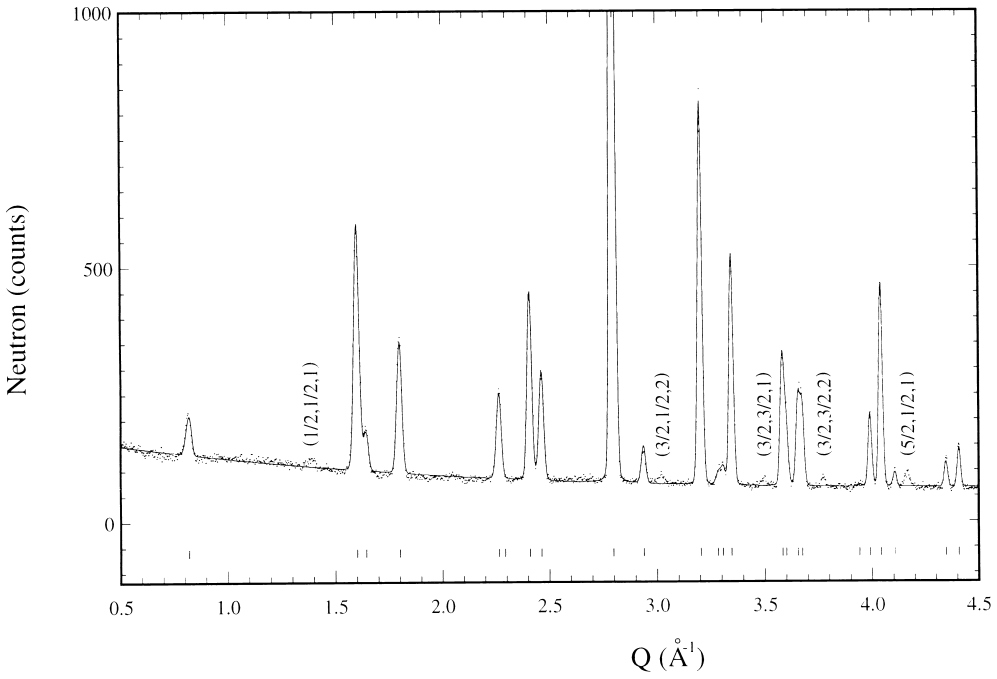

FIG. 1

Pattern matching refinement plot of the neutron diffraction data in the space group *P*4/*mmm* with the unit cell (a_p, a_p, $2a_p$).

[1]. The observed and calculated profiles are plotted in Figure 1. However, one observes that several reflections cannot be indexed in this unit cell (a_p, a_p, $2a_p$). All of these reflections (h = n/2 and k = n/2 with n odd) lead to a tetragonal cell with $a_p\sqrt{2}$, $a_p\sqrt{2}$, $2a_p$ parameters, consistent with the cell parameters and the space group proposed for $LaBaMn_2O_5$ [5]. At this level, the PND data were analyzed with a "whole pattern fitting" algorithm in order to determine accurately the cell parameters, the profile shape function, and the background. This preliminary study provided a good estimate of the R_{wp} and χ^2 that could be reached during the structure refinement. This whole pattern fitting led to R_{wp} = 4.86% and χ^2 = 1.45. 165 Bragg peaks were used to refine five positional parameters and five isotropic temperature factors, in the *P*4/*nmm* space group. The refinement converged to give an agreement factor R_{wp} = 5.87%, χ^2 = 2.12 and R_{nucl} = 5.74%. The observed, calculated, and difference profiles are plotted in Figure 2.

The structure of $YBaMn_2O_5$ is similar to that of $LaBaMn_2O_5$ [5]: double layers of apex-sharing MnO_5 pyramids, containing the Ba^{2+} cations, are interleaved with the oxygen-free yttrium layers. The resultant order of the Y^{3+} and Ba^{2+} cations forms layers parallel to (001). The final atomic coordinates for $YBaMn_2O_5$ are listed in Table 1 and the interatomic distances are given in Table 2. The Mn1 and Mn2 sites exhibit average Mn–O distances of 1.943 and 2.068 Å, respectively. Taking into consideration the ionic radii of Mn^{3+} and Mn^{2+} ions, it can be assumed that the Mn1 sites are occupied by Mn^{3+} ions and that the Mn2 sites are occupied by the Mn^{2+} ions. Each $Mn^{2+}O_5$ pyramid is linked to five $Mn^{3+}O_5$ pyramids

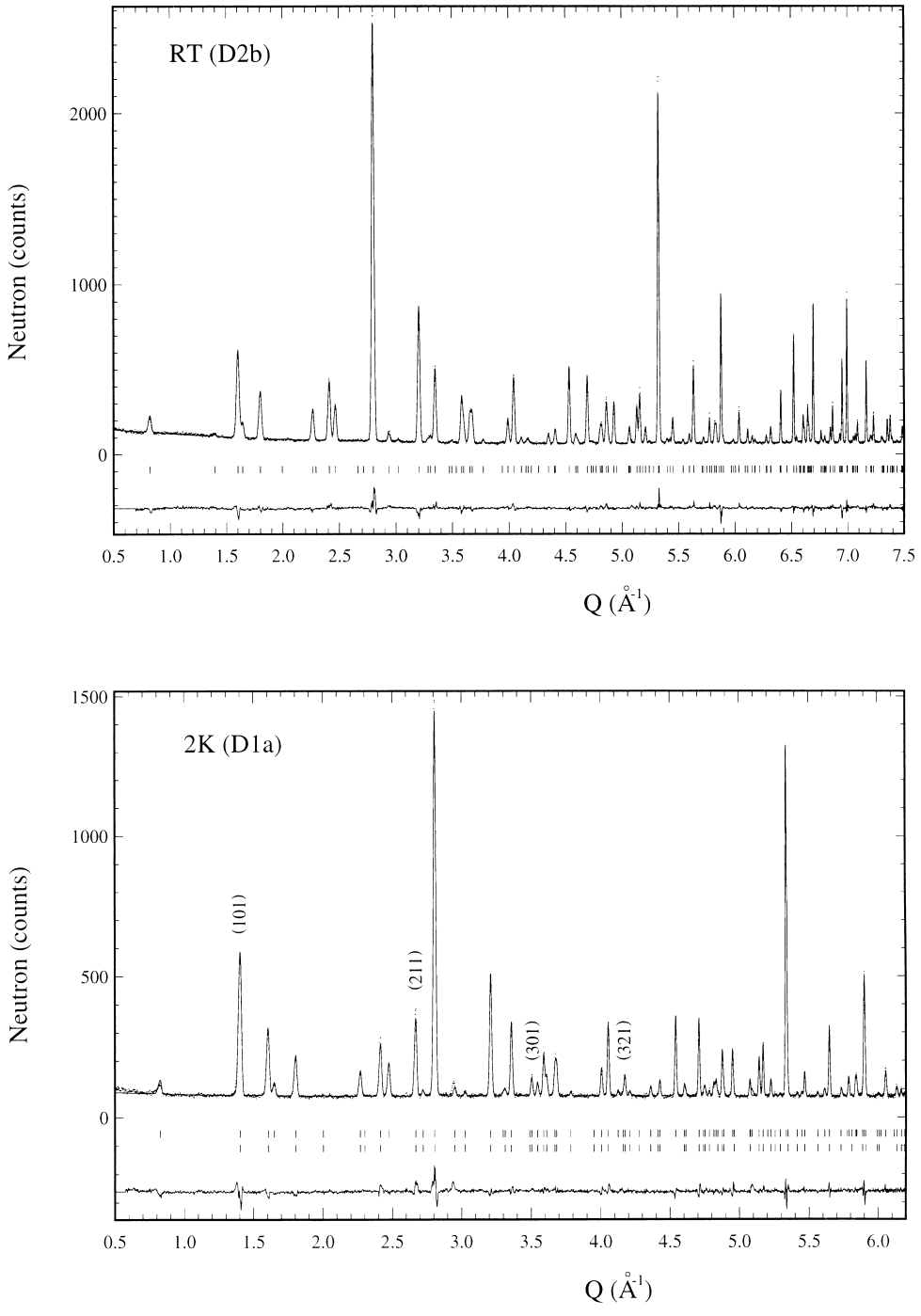

FIG. 2

Rietveld refinement plot of the neutron diffraction data of the ordered perovskite $YBaMn_2O_5$ in the space group *P*4/*nmm* (a) at room temperature and (b) at 2 K.

TABLE 1
Refined Structural Parameters of Ordered $YBaMn_2O_5$ (S.G. *P*4/*nmm*)

		T = 1.5 K (**D1a**)	T = 293 K (**D2b**)
Y	2b	B_{iso} = 0.19(9)[a]	B_{iso} = 0.65(9)[a]
Ba	2a	B_{iso} = 0.16(9)[a]	B_{iso} = 0.60(9)[a]
Mn1 = Mn^{III}	2c	*z* = 0.2794(9)	*z* = 0.2745(9)
		B_{iso} = 0.12(9)[a]	B_{iso} = 0.24(9)[a]
Mn2 = Mn^{II}	2c	*z* = −0.2514(9)	*z* = −0.2543(9)
		B_{iso} = 0.12(9)[a]	B_{iso} = 0.24(9)[a]
O1	8j	*x* = 0.4911(6)	*x* = 0.4910(6)
		z = 0.3164(3)	*z* = 0.3163(3)
		B_{iso} = 0.24(9)[a]	B_{iso} = 0.69(9)[a]
O2	2c	*z* = 0.0061(9)	*z* = 0.0069(9)
		B_{iso} = 0.20(9)[a]	B_{iso} = 0.67(9)[a]
a (Å)		5.5359(2)	5.5471(2)
c (Å)		7.6151(4)	7.6498(4)
μ_B	Mn1	2.9(1)	—
	Mn2	3.9(1)	—

[a] B_{iso} (Å^2).

(Fig. 3). For the pyramidally coordinated Mn^{3+}, considering the Mn–O bond lengths (four equatorial Mn1–O1 distances of 1.917 Å and one apical distance Mn1–O2 of 2.048 Å), the occupied d_z^2 orbital extends along [001], whereas the unoccupied $d_{x^2-y^2}$ orbital extends along [110] and [1$\bar{1}$0]. Considering the Mn–O bond lengths of the Mn2 site, an orbital order similar to the Mn1 site can be assumed for this site, but both the d_z^2 and the $d_{x^2-y^2}$ orbitals are occupied for the high-spin Mn^{2+} cation. If one considers the Goodenough–Kanamori rules [8] for magnetic interactions in manganese oxides, the expected magnetic order would be A-type: this arises from superexchange interactions between occupied $d_{x^2-y^2}$ orbitals on the Mn^{2+} site with empty $d_{x^2-y^2}$ orbitals on the Mn^{3+} site. Due to the charge order, each Mn^{2+} site has four Mn^{3+} neighbors in the plane leading to an expected ferromagnetic layer. The interactions between the occupied d_z^2 orbitals in the *c*-direction should be, as observed

TABLE 2
Selected Interatomic Distances and Angles of Ordered $YBaMn_2O_5$

	T = 1.5 K	T = 293 K	Multiplicity
Y–O1 (Å)	2.406(3)	2.414(3)	×8
Ba–O1 (Å)	3.105(3)	3.116(3)	×8
Ba–O2 (Å)	2.768	2.774	×4
Mn1–O1 (Å)	1.908(4)	1.917(4)	×4
Mn1–O2 (Å)	2.081(9)	2.048(9)	×1
Mn2–O1 (Å)	2.086(5)	2.086(5)	×4
Mn2–O2 (Å)	1.961(9)	1.998(9)	×1
Mn1–O1–Mn2 (°)	157.8(8)	157.3(8)	
Mn1–O2–Mn2 (°)	180	180	

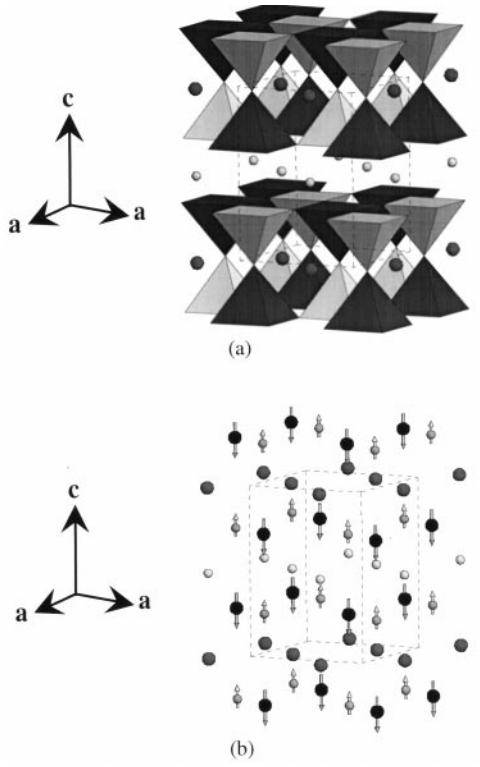

FIG. 3
(a) Structure of the perovskites $YBaMn_2O_5$ and (b) G-type magnetic structure of the perovskite $YBaMn_2O_5$.

experimentally, antiferromagnetic. However, as discussed below, the in-plane interactions are also antiferromagnetic, in spite of the ferromagnetic expectations. This is most likely due to a large deviation of the Mn–O–Mn angles away from the ideal 180° interactions assumed in the Goodenough–Kanamori scenario. This distortion can strongly influence the magnetic interactions, and is evidently great enough to drive the expected ferromagnetic interactions to become antiferromagnetic.

A comparison between the low temperature and the room temperature neutron diffraction data **(**Fig. 2**)** reveals an increase of the intensity of several reflections. These reflections can be indexed on the basis of the nuclear cell, i.e., the magnetic unit cell is $a_p\sqrt{2} \times a_p\sqrt{2} \times 2a_p$. These magnetic peaks correspond to *hkl* with $h + k = 2n + 1$ and 1 odd. The first extinction condition implies an antiparallel orientation of the spins within the (a_p, a_p) plane. The second extinction condition implies that, along the *c* axis, two magnetic atoms separated by *c*/2 have antiparallel magnetic moments. This leads to a G-type antiferromagnetic model (Fig. 3). The spin of the magnetic ions is parallel to the *c* axis ($R_{wp} = 6.09\%$, $R_{nucl} = 5.32\%$, $R_{mag} = 7.16\%$, and $\chi^2 = 2.16$ at $T = 1.5$ K). The magnetic moments of the two sites are 2.9(1) μ_B for Mn1 and 3.9(1) μ_B for Mn2. Each Mn^{2+} cation is linked via an Mn–O–Mn bridge to five Mn^{3+} cations, and vice versa. Thus, the order is ferrimagnetic as observed by the susceptibility measurement.

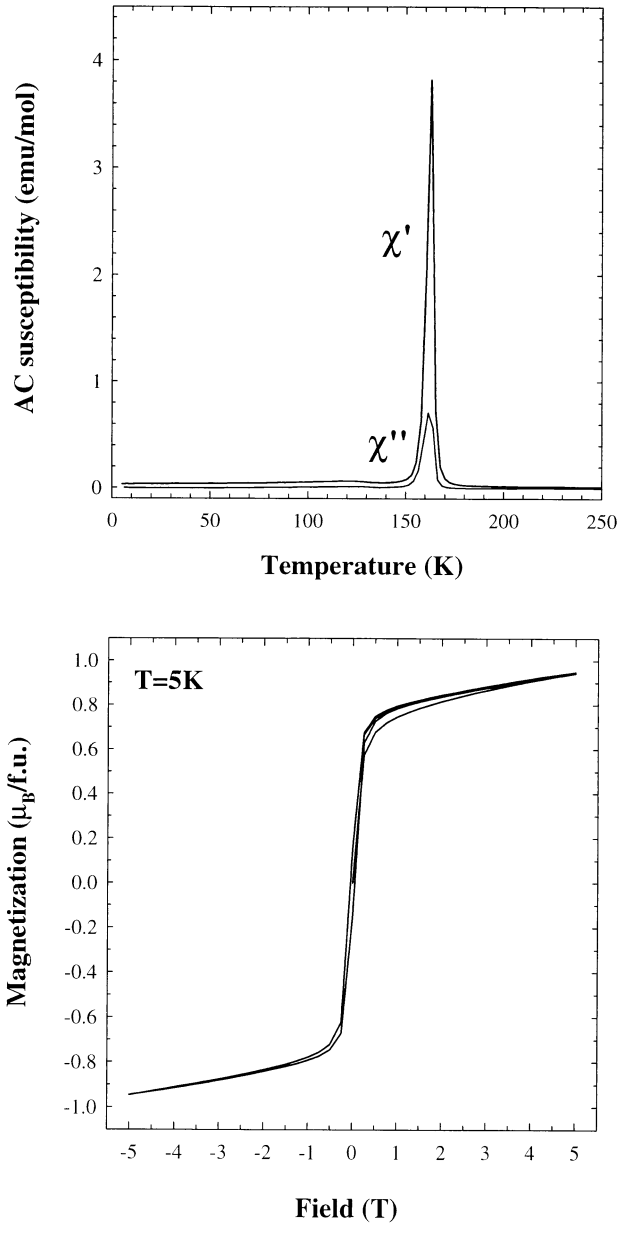

FIG. 4
AC and DC susceptibility of $YBaMn_2O_5$.

The AC and DC susceptibility measurements (Fig. 4) are easily explained by considering the Mn(II)/Mn(III) order. One observes a magnetic transition at 165 K, and a ferromagnetic component is clearly revealed by the peak in the imaginary part of the susceptibility. However, the saturated moment obtained from the DC measurement at 5 K is only 0.95 μ_B

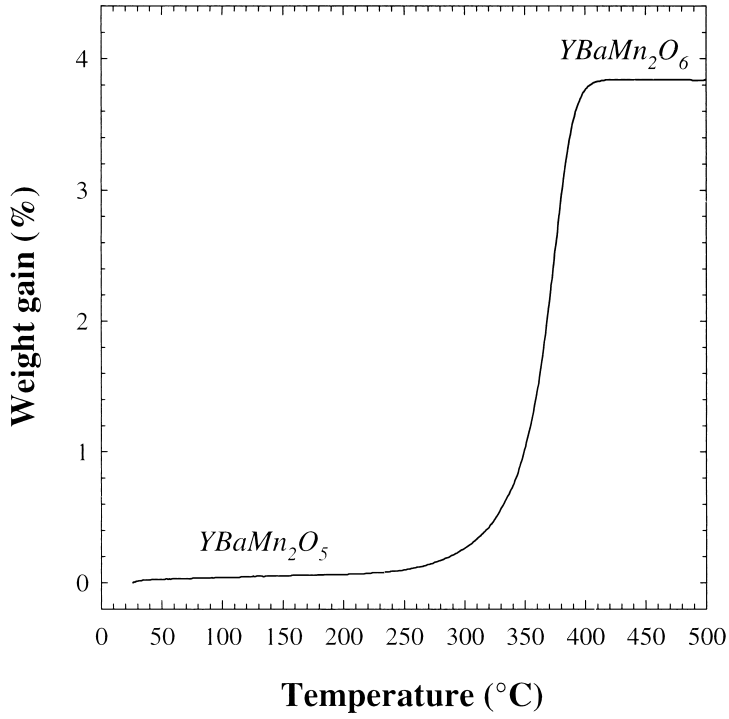

FIG. 5

TG weight gain vs. temperature under oxidizing atmosphere (O_2) for the ordered oxygen-deficient perovskite $YBaMn_2O_5$.

per $YBaMn_2O_5$ formula unit, which can be compared with the total moment of 9 μ_B per $YBaMn_2O_5$ that would result from a ferromagnetically ordered array of $S = 5/2$ Mn^{2+} and $S = 4/2$ Mn^{3+} spins. The neutron diffraction results show that the order is ferrimagnetic. If all of the $S = 5/2$ Mn^{2+} spins are antiparallel to the $S = 4/2$ Mn^{3+} spins, a saturated moment of 1 μ_B per $YBaMn_2O_5$ formula unit is expected. This is consistent with the observed value of 0.95 μ_B. As expected from the observed ordered arrangement of the species Mn^{2+}/ Mn^{3+}, $YBaMn_2O_5$ is an insulator.

In order to isolate the ordered stoichiometric tetragonal perovskite $YBaMn_2O_6$, we annealed the ordered oxygen-deficient phase at low temperature in the presence of oxygen. Thermogravimetric analysis (Fig. 5) revealed the oxidization begins at very low temperature, ~300°C, finishes near 400°C, and occurs in a single step. The weight gain of the thus-obtained sample determined from the TG analysis clearly shows that the oxygen content is close to O_6. The structure of this compound was studied and the results will be published later.

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