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Cation distribution and ferromagnetic exchange in the $YMn_{0.5}Co_{0.5}O_3$ perovskite investigated by neutron powder diffraction

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Abstract

The synthesis and characterization of a polycrystalline $YMn_{0.5}Co_{0.5}O_{3-\delta}$ sample are reported. The oxygen-content, determined by the thermogravimetric method from complete reduction in flowing $5\%H_2/N_2$, shows some oxygen deficiency leading to the composition $YMn_{0.5}Co_{0.5}O_{2.87}$. Neutron powder diffraction shows some cation ordering at the six-coordinate site resulting in a monoclinic unit cell with $a = 5.241(1)$, $b = 5.594(1)$, $c = 7.468(1)$ and, $\beta \sim 90^\circ$ (space group $P2_1/n$) at 290 K. The sample undergoes a transition to a ferromagnetic phase at $T_c \sim 67$ K, with an ordered magnetic moment of 2.72(2) μ_B per formula unit aligned along [0 0 1].

Keywords: Manganites; Perovskite oxides; Thermogravimetry; Oxygen-content; Cation ordering; Neutron diffraction; Magnetic structure; Magnetic order

1. Introduction

Recent research into the phenomenon of colossal magnetoresistance (CMR) has increased interest in the structural and magnetic properties of mixed-metal perovskite manganites which can be formulated as $(Ln, A)MnO_3$, where *Ln* and *A* are usually lanthanide and alkaline-earth cations [1–3]. However, some authors investigated the structural and physical properties of *B*-site substituted manganites [4,5] attempting to obtain ferromagnetic behavior in double perovskites such as La_2NiMnO_6 ($LaNi_{0.5}Mn_{0.5}O_3$) and La_2CoMnO_6 ($LaCo_{0.5}Mn_{0.5}O_3$) by producing a 1:1 ordered cation array [6–8]. In our previous work including a study of the structural chemistry and magnetic properties of the $Y(Mn, Ni)O_3$ system, neutron powder diffraction (NPD) showed that the Mn and Ni cations in $YMn_{0.5}Ni_{0.5}O_3$ order in a 1:1 pattern [9,10]. At the same time, Bull et al. [11] and Dass et al. [12] demonstrated that the mixed transition ions order in La_2NiMnO_6 and La_2CoMnO_6, although annealing under high O_2-pressure was necessary to achieve full ordering in La_2CoMnO_6 [12].

In the present study, we aimed to ascertain the crystalline and magnetic structure of an $YMn_{0.5}Co_{0.5}O_{3-\delta}$ sample prepared by solid-state reaction and, compare our results to the data obtained on an $YMn_{0.5}Ni_{0.5}O_{3-\delta}$ sample [10]. Since standard X-ray is not convenient for such study, due to the similar scattering factors of Co and Mn [13] and, as anomalous powder X-ray is not adequate owing to comparable absorption energies of the 3d-ions, we used NPD to get better insight into the crystalline and magnetic structures of $YMn_{0.5}Co_{0.5}O_{3-\delta}$.

2. Experimental

A polycrystalline sample of $YMn_{0.5}Co_{0.5}O_{3-\delta}$ was prepared by solid-state reaction. Stoichiometric quantities of Y_2O_3, MnO_2 and CoO were intimately ground together by attrition milling, using isopropanol as liquid medium. The powders were pressed uniaxially into 1 cm-diameter pellets 2–3 mm thick and heated at 900 °C in air for a total of 24 h, with frequent regrinding, and finally at 1300 °C in air for 24 h, with intermittent regrinding. The progress of the reaction was monitored by X-ray powder diffraction,

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and was deemed to be complete when further firing produced no change in the diffraction pattern.

A CPS 120 INEL diffractometer with a flat geometry, operating with Cu-Kα_1 radiation and equipped with a position sensitive detector was used to collect X-ray data over the angular range $5 \leqslant 2\theta(\text{deg}) \leqslant 120$. NPD experiments were carried out at the Orphée reactor (LLB-Saclay) using the G4.1 two-axis diffractometer ($\lambda = 2.4266$ Å, 800 cells multidetector extending over the angular range $10 \leqslant 2\theta(\text{deg}) \leqslant 90^\circ$). The data were analyzed by the Rietveld method as implemented in the Fullprof program [14,15], using the scattering lengths: $b(\text{Y}) = 0.775$, $b(\text{Mn}) = -0.375$, $b(\text{Co}) = 0.25$ and $b(\text{O}) = 0.581$ ($\times 10^{-12}$ cm). The background was modelled by means of a linear interpolation and, a Gaussian function was used to describe the instrumental and sample contributions to the peak profile. The fractional occupancies of the transition metals were initialized as 50% Mn and 50% Co at the 2*c*- and 2*d*-sites of the space group $P2_1/n$ corresponding to a fully disordered model before being allowed to vary with their sum constrained to be unity throughout the refinement. The room temperature refined values were held constant during the analysis of the lower temperature neutron diffraction data to allow the refinement of the magnetic structure. Thermogravimetric analysis was carried out using a Setaram-TGDTA92 Thermogravimetric Analyzer. Samples weighing approximately 50–70 mg contained in silica crucibles were placed in the apparatus which was previously purged with 5%H_2/N_2 and, were subsequently heated to 950 °C at a rate of 2 °C min^{-1} under the gas flow and held at this temperature for up to 30 min before being allowed to cool to room temperature under the gas flow, at the cooling rate of the furnace. The raw data were corrected from the crucible contribution according to measurement for the empty crucible under the same conditions.

3. Results and discussion

3.1. Oxygen content and thermogravimetric analysis

The thermogravimetric curve obtained for $YMn_{0.5}Co_{0.5}O_{3-\delta}$ is shown in Fig. 1, and compared to that obtained for a $YMn_{0.5}Ni_{0.5}O_{3-\delta}$ sample annealed under similar conditions. The reduction of both samples heated to 950 °C under the 5%H_2/N_2 flow proceeds to completion, as clear plateaux are visible in the weight loss. Inspection of the X-ray diffraction pattern of the residue after this treatment reveals the presence of Y_2O_3, MnO and Co(or Ni) metals. The absence of a residual perovskite phase confirms that the reduction was complete. The total weight loss for $YMn_{0.5}Co_{0.5}O_{3-\delta}$, $\Delta m = 7.25\%$ is similar to that obtained for $YMn_{0.5}Ni_{0.5}O_{3-\delta}$, $\Delta m = 7.42\%$, leading to similar oxygen-deficient compositions; $YMn_{0.5}Co_{0.5}O_{2.87}$ and $YMn_{0.5}Ni_{0.5}O_{2.89}$. To approach oxygen stoichiometry, various annealing of the Co-sample under 1-atm O_2-pressure have been performed in the range 1000−1300 °C,

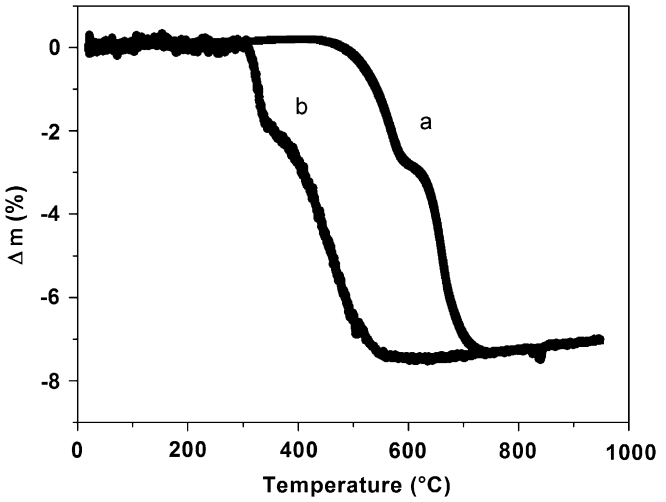

Fig. 1. Thermogravimetric curve of hydrogen reduction for $YMn_{0.5}Co_{0.5}O_{3-\delta}$ (a) in comparison to $YMn_{0.5}Ni_{0.5}O_{3-\delta}$ (b) in 5%H_2/N_2 flow; heating rate is 2 °C/min.

without significant increase of the oxygen-content. This result contrasts to that of the related $LaMn_{0.5}Co_{0.5}O_3$ perovskite which could be obtained stoichiometric under flowing O_2 [12].

Fig. 1 shows two gradual steps in the reduction process of $YMn_{0.5}Co_{0.5}O_{3-\delta}$ with onsets at temperatures $T_1 \sim 455$ °C and $T_2 \sim 590$ °C, higher than observed for the related $YMn_{0.5}Ni_{0.5}O_{3-\delta}$ sample, $T_1 \sim 305$ °C and $T_2 \sim 340$ °C.

3.2. Structural chemistry

Rietveld analysis of the X-ray powder diffraction patterns of $YMn_{0.5}Co_{0.5}O_{2.87}$ sample showed a single-phase, contrasting with the biphasic samples usually observed in the related $LaMn_{0.5}Co_{0.5}O_3$ and $LaMn_{0.5}Ni_{0.5}O_3$ samples [6,16]. Refinement of the data indicated that the space group was *Pbnm*(*Pnma*) orthorhombic with cell parameters $a = 5.241(1)$ Å, $b = 5.594(1)$ Å and $c = 7.468(1)$ Å. The absence of superlattice peaks, characteristic of cationic ordering was attributed to the reduced contrast between the scattering powers of Co/Mn constraining all the octahedral sites to be equivalent. However, the room temperature neutron diffraction pattern shows a weak reflection at $2\theta \sim 36.95^\circ$ ($d \sim 3.83$ Å) that could not be indexed in *Pbnm* but in monoclinic $P2_1/n$, resulting in some degree of cationic ordering over two distinguishable octahedral sites (Fig. 2), as reported for $YMn_{0.5}Ni_{0.5}O_{3-\delta}$ [10].

In order to determine the degree of ordering in $YMn_{0.5}Co_{0.5}O_{2.87}$, trial refinements with various starting values of the Mn/Co ions at the 2*c*- and 2*d*-sites converged to Mn(2*c*) = 0.34(1) and Mn(2*d*) = 0.66(1), reflecting some degree of cation ordering at the six-coordinate site. Since atomic order in double perovskites is usually governed by thermodynamic and kinetic parameters [17–19], various annealing of the $YMn_{0.5}Co_{0.5}O_{2.87}$ have been made in the