Cation order and structural transition in La$_2$MnCoO$_6$

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Abstract. The value of $T_C$ and the magnetic behavior of La$_2$MnCoO$_6$ depend on preparation conditions, in particular on the cooling rate after the last calcinations process. The valence state and the degree of order of cobalt and manganese ions vary according. We expose here two samples of La$_2$MnCoO$_6$ sintered by solid state reactions with different cooling rates. The Rietveld refinement of neutron powder diffraction (NPD) data showed that our samples crystallize in a monoclinic structure with symmetry $P2_1/n$ up to room temperature and ferromagnetic transition around 230K. Sample with lower cooling rate presents a saturation magnetization of 5.58 $\mu_B$/f.u. besides the value of 4.41 $\mu_B$/f.u. for that with higher cooling rate.

1. Introduction

Perovskite-type oxides based on rare-earth and 3d-transition elements are promising materials for usage as electrodes, catalysts, membranes, etc. Their properties have fascinated thousand of scientists around the globe and hundreds of investigations have been carried out to find appropriate compositions with the best set of necessary properties for different applications. The ferromagnetic double-perovskites La$_2$MnCoO$_6$ exhibit a notable magnetodielectric behavior very near room temperature due to strong spin-lattice coupling. These are materials characterized by subtle structural distortions. The distortions are caused by concerted rotations of the BO$_6$ octahedra and displacements of the A and B cations within the cage. These distortions are temperature and pressure dependent and give rise to dramatic changes in properties such as dielectric properties, electrical resistivity and band gap. These important materials have received a large amount of academic interest and have potential applications in catalysis, magnetic media, electrical conductors and gas sensors.

2. Experimental details

We have prepared two polycrystalline samples of La$_2$MnCoO$_6$ by the solid-state reaction method, using high purity precursors, of La$_2$O$_3$, MnO$_2$ and CoO$_4$ in appropriate amounts. The mixture was calcined at 1000, 1100, 1200 and 1300 °C for 15 h in air and cooled down at 100 C/h. Taking into account that in the long-range order of Mn/Co with valences Mn$^{4+}$/Co$^{2+}$ are favored with the high oxygen content, annealing of the samples was done at high temperature under slow cooling [3,5]. In the last calcination the sample LMC-O was annealed at 1400°C under O$_2$ atmosphere and cooled at 8°C/h, later the sample was heat treated under high oxygen pressure (900°C with pO$_2$=200 bar during 24 hours; and 475°C with pO$_2$=150 bar during 12 hours). The LMC-D sample was annealed at 1400°C...
in air and cooled at 100ºC/h. The x-ray powder diffraction (XRD) of the sample was examined using a Siemens D-5000 Diffractometer, and found to be single phased and free from impurities. The resistivity, magnetotransport and magnetization were measured using a Physical Property Measurement System (PPMS-Quantum Design) and a Superconducting Quantum Interference Device (SQUID) system. Zero-field-cooled (ZFC) magnetic susceptibility data were obtained under field of 1000 Oe in the temperature range 10K≤T≤300K. Hysteresis loops in ZFC conditions were obtained at 10K varying the field between -50kOe≤H≤50kOe. The structure and magnetic order were determined by neutron scattering (D2B with λ=1.594Å, and D20 with λ=1.887Å).

3. Results and discussion

3.1. Crystallographic analysis

The structural characterization of La₂MnCoO₆ was made by NPD (Mn and Co are almost indistinguishable for X-Rays). The structural characterization reveals pure samples without impurities. Figure 1 shows the Rietveld refinement of NPD patterns at 300 K. Those data were taken in the D20 instrument (λ=1.8875Å). The refinement was performed using the model presented by R. I. Dass and J. B. Goodenough for an ordered sample [3].

![Figure 1. NPD pattern for LMC-O sample, refined by Rietveld analysis technique at 300K. The observed intensities are shown by dots and the calculated ones by solid line. The blue line at the bottom indicates the intensity difference between the experimental and the refined patterns. The positions of the Bragg reflections are shown by the small vertical lines below the patterns.](image1)

![Figure 2. Neutron thermodiffractogram for the (LMC-O) sample during the heating a) ramp from 10K up to 304K. b) Extension a low angles.](image2)

All the observed Bragg peaks can be indexed in the monoclinic space-group P 2₁/ n. Obtained cell parameters at RT are a=5.565519(10)Å, b=5.525861(10)Å, c=7.829581(16)Å y β=89.9158(3). NPD data show no structural changes between 5K and RT (figure 2a). This space group differentiates the ions at position B of the perovskite (Mn or Co) according the occupation of Wyckoff positions 2c and 2d. We have found that LMC-O has a 97.5% order Mn/Co, while LMC-D sample has 73% order Mn/Co. Information concerning valences Mn-Co can be obtained from bond distances. Bond angles and bond distances were calculated from the results obtained using the Rietveld analyses of the NPD. The average bond distances Mn-O and Co-O of both samples are also given in Table I. These values are
similar to those previous by reported for La$_2$MnCoO$_6$ (2.039Å for the Co and 1.918 Å for the Mn site) [6].

Table 1. Average bond distances at RT (D2B)

|     | $d_{\text{Mn}-\text{O}}$ (Å) | $d_{\text{Co}-\text{O}}$ (Å) | $<d>$ (Å) |
|-----|------------------------------|------------------------------|-----------|
| LMC-O | 1.8940                       | 2.0200                       | 1.9570    |
| LMC-D | 1.9047                       | 2.0467                       | 1.9757    |

3.2. Magnetic Order

The trace of a ferromagnetic transition is seen close at 230 K in the two samples. As it can be seen, the magnetization of both samples experiences a marked increase below $T_c = 230$K (see figure 3). The magnetization maximum at low temperature values for sample LMC-O (2.6 $\mu_B$/f.u) are considerably higher than those of sample LMC-D (1.62 $\mu_B$/f.u). The paramagnetic susceptibility in the temperature range of 210K $< T <$ 300K is fitted to Curie-Weiss law, $\chi = C/(T + \theta_C)$ (inset figure 3). In figure 4, the saturation magnetization (Ms) at 10K and 50 kOe of LMC-O sample reaches a value of 5.85 $\mu_B$/f.u.; close to the theoretical spin-only value of 6 $\mu_B$/f.u; expected for the ferromagnetic alignment of Mn$^{4+}$ and Co$^{2+}$ spins. In the LMC-D sample Ms is 4.41 $\mu_B$/f.u. The values obtained for $\theta_C$, and Ms are exposed in table II.

Figure 3. Temperature dependence Zero-field cooling (ZFC) and field cooling (FC) curves measured at 1000 Oe with (5K$\leq T \leq$300K) for samples LMC-O and LMC-D. Inset shows the temperature dependence of inverse magnetic susceptibility.

Figure 4. Magnetic field dependence of dc magnetization at 10 K to samples LMC-O and LMC-D, with $-50k\text{Oe} \leq H \leq 50k\text{Oe}$. The inset shows the coercive fields.

Table II. The magnetic properties of La$_2$CoMnO$_3$

|     | $\theta_C$ (K) | $H_c$ at 10T (kOe) | $Ms(\mu_B$/f.u) |
|-----|----------------|--------------------|-----------------|
| LMC-O | 233.067         | 1.5                | 5.85            |
| LMC-D | 220.525         | 6.75               | 4.41            |
Ordered magnetic moments have been obtained by NPD data. The increase of the integrated intensities of peaks (110) and (200) with the decrease of the temperature, as seen in figure 5, confirms the presence of ferromagnetic order at low temperatures. We obtained values average Mn/Co of 2.41 μₜₜ and 1.91 μₜₜ for LMC-O and the LMC-D respectively at low temperature through Rietved refinement. Value found for LMC-O is fairly comparable with values reported in the literature [7]. We can see decay in the values of magnetic moment when heating, indicating the disappearance of the ferromagnetism (figure 6).

![Figure 5](image)

**Figure 5.** Bragg reflections (110) and (200) for LMC-O (a) and LMC-D (b). Inset show the evolution of integrated intensities of (110) and (200) between 10 and 300K.

**Figure 6.** Magnetic moment in function of the Temperature for samples LMC-O and LMC-D.

4. Conclusions
We have produced various La₂MnCoO₆ samples with different cooling rates. We found a monoclinic phase from low temperature to room temperature accompanied by ferromagnetism below 230K. We
observed that the saturation magnetization strongly depends on the cooling rate after the last firing. The LMC-O sample got 97.5% of order Mn^{4+}/Co^{2+} with a magnetic moment of 2.41 \mu_B, while in the sample we have obtained a partially ordered 73% of order Mn^{4+}/Co^{2+} and a magnetic moment of 1.91 \mu_B. Our NPD data were unable to resolve the direction of the magnetic moment.

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