Physica B 404 (2009) 2717–2719

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

# New ferromagnetic $La_3Co_2TaO_9$ double perovskite: Structural and magnetic properties

V.C. Fuertes [a], M.C. Blanco [a], D.G. Franco [a], J.M. De Paoli [a], E.V. Pannunzio Miner [a], R.D. Sánchez [b], M.T. Fernández-Díaz [c], R.E. Carbonio [a,*]

[a] INFIQC, Dpto. de Fisicoquímica, Fac. de Ciencias Químicas, U.N.C., Córdoba 5000, Argentina
[b] Laboratorio de Resonancias Magnéticas. Centro Atómico Bariloche, Bariloche 8400, Río Negro, Argentina
[c] Institut Max Von Laue Paul Langevin, F-38042, Grenoble Cedex 9, France

ARTICLE INFO

*Keywords:*
Double perovskite
Crystal structure refinement
Rietveld method
Ferromagnetism
Magnetic characterization

ABSTRACT

The new double perovskite $La_3Co_2TaO_9$ has been prepared by a solid-state procedure. The crystal and magnetic structures have been studied from X-ray powder diffraction (XRPD) and neutron powder diffraction (NPD) data. Rietveld refinements were performed in the monoclinic space group $P2_1/n$. The structure consists of an ordered array of alternating $B'O_6$ and $B''O_6$ octahedra sharing corners, tilted along the three pseudocubic axes according to the Glazer notation $a^-b^-c^+$. Rietveld refinements show that at RT the cell parameters are $a = 5.6005(7)$ Å, $b = 5.6931(7)$ Å, $c = 7.9429(9)$ Å and $\beta = 89.9539(7)^\circ$, and the refined crystallographic formula of this "double perovskite" can be written as $La_2(Co)_{2d}(Co_{1/3}Ta_{2/3})_{2c}O_6$. Magnetization measurements and low-temperature NPD data show that the perovskite is a ferromagnet with $T_C = 72$ K. At high $T$ it follows the Curie–Weiss law with an effective magnetic moment of $3.82\mu_B$ per Co ion which is very close to spin only $Co^{2+}$ (HS).



## 1. Introduction

Perovskite compounds are very interesting materials because of their potential technological properties: Giant and colossal magnetoresistance in $La_{1-x}Ca_xMnO_3$ [1], superconductivity in $BaBi_{1-x}Pb_xO_3$ [2], ferroelectricity in $BaTiO_3$ [3], ceramic capacitors, actuators, transducers, magnetism, ion conductivity and many others. For these reasons perovskite compounds have show to be one of the most versatile structures.

The ideal cubic perovskite structure can be seen like a three-dimensional corner-sharing network of $BO_6$ octahedra, with a large A cation occupying the cuboctahedral cavities.

If two atoms, B′ and B″, are placed on two crystallographic different B sites, a double perovskite is formed with the general formula $A_2B'B''O_6$ [4]. These B′ and B″ atoms can be completely or partially order. Ordering can be in a rock salt pattern, with different cations occupying alternating $BO_6$ octahedra. Ordering of the B cations occurs when there is either large size dissimilarity or when the charge difference is greater than 2 [4].

Perovskites show several distortions when the A site cation is too small for the cuboctahedral cavity [5]. Distortions arise from three mechanisms: cation displacements within the $BO_6$ octahedra and distortions and tiltings of these octahedra [6].

Materials in which alkali-earth cations $A^{2+}$ had been partially replaced by $Ln^{3+}$ lanthanide had been synthesized too. However, there are few reports of double perovskite materials in which the A site ion had been totally replaced by a small $Ln^{3+}$ lanthanide [7–9].

Magnetic properties in double perovskites are strongly dependents order–disorder of their B cations [10].

In the present work we describe the synthesis, structure and magnetic characterization of a new compound-type double perovskite: $La_3Co_2TaO_9$.

## 2. Experimental

Dark brown $La_3Co_2TaO_9$ powder sample was prepared by conventional solid-state reaction. Stoichiometric amounts of $La_2O_3$ (99.9%), $Co_3O_4$ (99.9%) and $Ta_2O_5$ (99.9%) were ground in an agate mortar, and fired at 1400 °C for 24 h under Ar flow. The high phase purity was confirmed by X-ray powder diffraction (XRPD) on a Philips X'Pert PRO diffractometer (40 kV, 40 mA), in Bragg–Brentano reflection geometry with Cu Kα radiation ($\lambda = 1.5418$ Å).

The NPD patterns were collected at RT and 5 K in the D2B diffractometer at Institute Laüe-Langevin (ILL), Grenoble, France. The wavelength used was 1.5945 Å. The $2\theta$ range was from 0.1° to 159.9°, with increments of 0.05°.

* Corresponding author. Tel.: +54 351 433 4169/80; fax: +54 351 433 4188.
*E-mail address:* carbonio@mail.fcq.unc.edu.ar (R.E. Carbonio).

0921-4526/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2009.06.064

The refinement of the crystal structure was performed by the Rietveld method [11] using the FULLPROF program [12]. A pseudo-Voigt shape function was always adequate to obtain good fits for experimental data.

The magnetic measurements were performed in a commercial superconducting quantum interference device magnetometer (SQUID) on powdered samples, in the 10–300 K temperature range.

## 3. Results

### 3.1. Crystal structure

Fig. 1 shows XRPD data at RT for $La_3Co_2TaO_9$ as a main phase (94%) ($LaTaO_4$ and CoO are presents as minority phases).

Analysis of the NPD data showed $La_3Co_2TaO_9$ to crystallize with the monoclinic $P2_1/n$ structure commonly found in double perovskites. The $P2_1/n$ space group accommodates a rocksalt arrangement of Co and Ta described by the $a^-b^-c^+$ system of three octahedral tilts in the Glazer notation [13,14]. Refinements were performed by allowing oxide site occupancy and the Co/Ta distribution to vary, in order to model oxide non-stoichiometry and octahedral site disorder, respectively. There was negligible departure from unity for oxide sites and one of the B cation sites was fully occupied by Co, obtaining in this way the maximum order possible for this stoichiommetry. Thus, the crystallographic formula can be written as $La_2(Co)_{2d}(Co_{1/3}Ta_{2/3})_{2c}O_6$. The refined atomic positions and occupancies at RT are given in Table 1 and those at 5 K in Table 2.

Refined cell constants, selected bond lengths and bond angles at RT and 5 K are given in Table 3. The average La–O bond length do not change significantly, while the average Co–O and Co/Ta–O bond lengths do it between 5 and 300 K. The $BO_6$ octahedral tilt angles can be defined as $\delta = (180-\theta)/2$, where $\theta$ is a Co–O–Co/Ta bond angle. The average tilt angle does not change significantly with $T$.

### 3.2. Magnetic measurements and magnetic structure

$M$ vs. $T$ is shown in Fig. 2. The experimental saturation magnetization obtained is about $0.8\mu_B$/fu, much less than the theoretical one of $6\mu_B$/fu. Magnetic susceptibility data was fitted over the high temperature range (200 K $\leq T \leq$ 300 K) (Fig. 3) using the Curie–Weiss law, the obtained $\theta$ value was +41.7 K, clearly indicating that the main magnetic interactions are ferromagnetic. The $\mu_{eff}$ value is $3.82\mu_B$, and it is in good agreement with

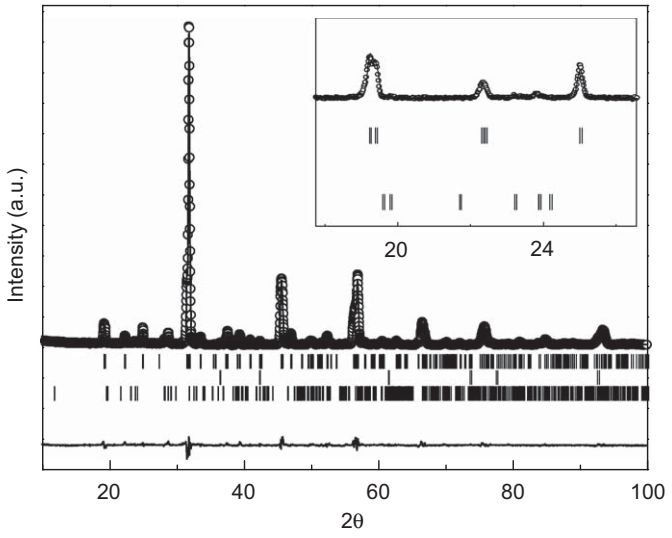


**Fig. 1.** Rietveld refinement of XRPD pattern for $La_3Co_2TaO_9$, (SG: $P2_1/n$). Dots: experimental pattern; solid line: calculated pattern; bottom solid line: difference; vertical bars: positions of Bragg reflections: main phase (top), $LaTaO_4$ (middle) and CoO (bottom). Inset: details for superstructure peaks at low angle.

**Table 1**
Refined atomic positions and occupancies for $La_3Co_2TaO_9$ at RT. Discrepancy factors: $\chi^2 = 0.476$; $R_{wp} = 5.43$, Rp = 4.30; $R_{Bragg} = 9.48$.

| Atom | $x$ | $y$ | $z$ | Occ |
|---|---|---|---|---|
| La (4e) | 0.497(1) | 0.5462(5) | 0.2461(1) | 1.000 |
| Co (2d) | $\frac{1}{2}$ | 0 | 0 | 0.500 |
| Co (2c) | 0 | $\frac{1}{2}$ | 0 | 0.167 |
| Ta (2c) | | | | 0.333 |
| O1 (4e) | 0.2925(2) | 0.3049(1) | 0.0368(1) | 1.000 |
| O2 (4e) | 0.2099(2) | 0.7763(1) | 0.0524(9) | 1.000 |
| O3 (4e) | 0.5815(7) | 0.9868(7) | 0.2467(2) | 1.000 |

**Table 2**
Refined atomic positions and occupancies for $La_3Co_2TaO_9$ at 5 K. Discrepancy factors: $\chi^2 = 0.538$; $R_{wp} = 5.64$, Rp = 4.49; $R_{Bragg} = 10.4$.

| Atom | $x$ | $y$ | $z$ | Occ |
|---|---|---|---|---|
| La (4e) | 0.4896(7) | 0.5465(4) | 0.242(1) | 1.000 |
| Co (2d) | $\frac{1}{2}$ | 0 | 0 | 0.500 |
| Co (2c) | 0 | $\frac{1}{2}$ | 0 | 0.167 |
| Ta (2c) | | | | 0.333 |
| O1 (4e) | 0.2959(1) | 0.2859(1) | 0.0443(9) | 1.000 |
| O2 (4e) | 0.2121(2) | 0.8060(1) | 0.0371(1) | 1.000 |
| O3 (4e) | 0.582(7) | 0.9817(6) | 0.2402(1) | 1.000 |

**Table 3**
Cell parameters, bond distances (Å) angles (deg) and octahedra tilting angle ($\delta$) for $La_3Co_2TaO_9$ at RT and 5 K.

| | RT | | 5 K | |
|---|---|---|---|---|
| $a$ (Å) | 5.6005(7) | | 5.5878(6) | |
| $b$ (Å) | 5.6931(7) | | 5.6935(6) | |
| $c$ (Å) | 7.9429(9) | | 7.923(1) | |
| $\beta$ (deg) | 89.9539(7) | | 90.015(6) | |
| ⟨La–O⟩ (Å) | 2.603(8) | | 2.595(7) | |
| $\langle Co–O\rangle_{(2d)}$ (Å) | 2.08(2) | | 1.98(2) | |
| $\langle Co/Ta–O\rangle_{(2c)}$ (Å) | 2.03(1) | | 2.11(2) | |
| | | $\delta$ | | $\delta$ |
| (Co)–O–(Co/Ta) | 152.9(8) | 13.6 | 153.1(8) | 13.5 |

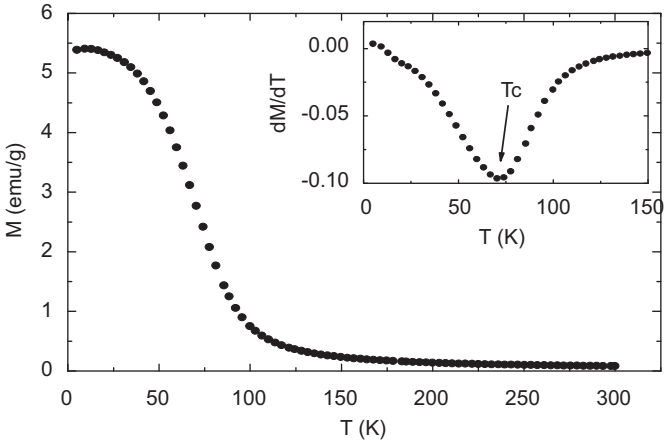


**Fig. 2.** Magnetization vs. temperature at 5 T. Inset: d$M$/d$T$ vs. $T$.

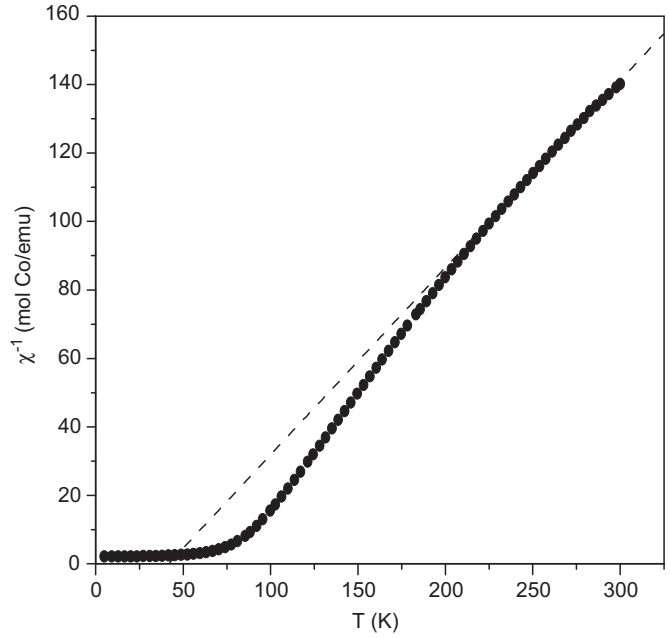


**Fig. 3.** Full circles show $\chi^{-1}$ vs. $T$ data. Dashed line represents the Curie–Weiss Law fit in the 200–300 K range.

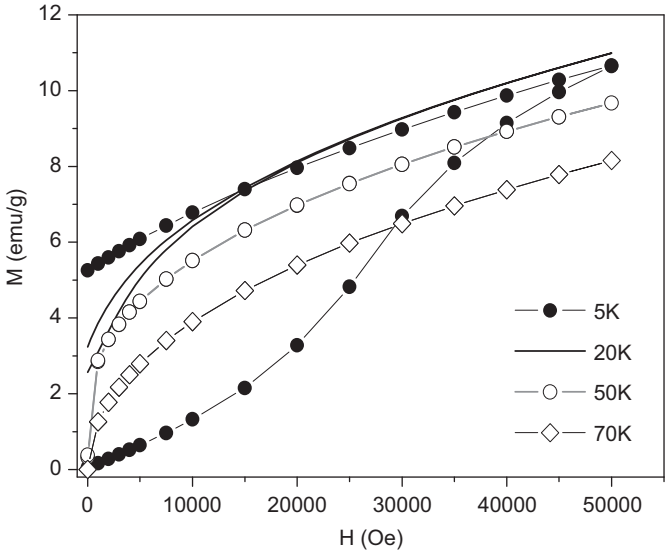


**Fig. 4.** Magnetic field dependences of the magnetization at 70, 50, 20 and 5 K for $La_3Co_2TaO_9$.

theoretically $\mu_{eff}$ calculated for spin only $Co^{2+}$ (HS) ($\mu_{eff} = 3.87\mu_B$). From d$M$/d$T$ (inset in Fig. 2) $T_C = 72$ K. The $M$ vs. $H$ data, (Fig. 4), measured at 70, 50, 20 and 5 K show a reversible FM behaviour without any difference between ZFC and FC dependences over 50 K, but there is a little irreversibility at 20 K which is complete and very clear at 5 K, which, together with the low $\mu_{sat}$, can be related to spin-glass behaviour and frustration in the system, probably due to the intrinsic disorder in the B sites in double perovskites with $A_3B'_2B''O_9$ stoichiommetry.

From NPD pattern at 5 K (not shown), it was possible to determine the magnetic cell for this new material (Fig. 5). The ferromagnetic structure was modelled with magnetic moments at the Co positions. The magnetic cell is coincident with the structural cell, so the propagation vector $\boldsymbol{k} = 0$. These results are thus in agreement with the magnetic measurements.

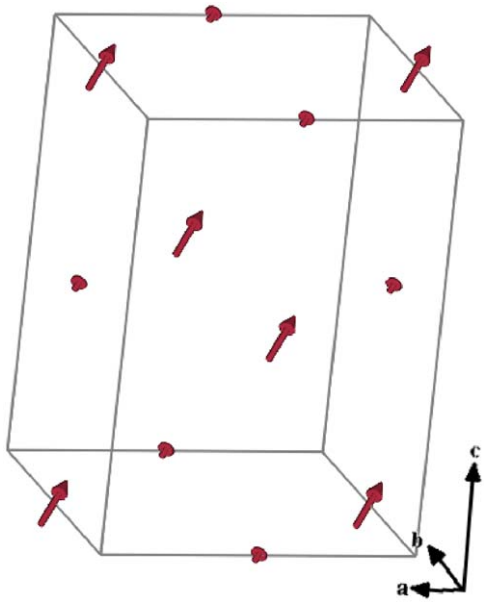


**Fig. 5.** Magnetic cell obtained from ND data at 5 K for $La_3Co_2TaO_9$. Larger arrows: $Co^{2+}$ ions (2d site); smaller arrows: $Co^{2+}/Ta^{5+}$ ions (2c site).

## 4. Conclusions

The double perovskites $La_2(Co)_{2d}(Co_{1/3}Ta_{2/3})_{2c}O_6$ with maximum possible B cations order and all A site occupied by La has been successfully synthesized by solid-state method, crystallizing in the monoclinic P $2_1/n$ space group (tilting system is $a^-b^-c^+$). The effective magnetic moment ($3.82\mu_B$) obtained by fiting the high temperature range (200–300 K) with the Curie–Weiss law is in agreement with spin only value for $Co^{2+}$ (HS). The positive value of $\theta$ indicates that the main magnetic interactions are ferromagnetic. The d$M$/d$T$ indicates that the ferromagnetic ordering occurs bellow $T_C = 72$ K.

## Acknowledgements

R.E.C. and R.D.S. thank ANPCYT (Projects PAV 22708, PICT 06-15102 and 21372) and CONICET (PIP 5767/05 and 5250/05). R. E. C. also thanks SECyT-UNC (Project 197/05). R.D.S. also thanks SEPCyT-UNCu. D.G.F., E.V. P.M. and J.M.D.P. thank CONICET for a fellowship. M.C.B. thanks ANPCYT-UnCu for a fellowship. We thank ILL (Grenoble, France) for access to D2B line.

## References

[1] B.T. Cong, P.N.A. Huy, N.H. Long, J. Magn. Magn. Mater. 262 (2003) 437.
[2] D.T. Marx, P.G. Radaelli, J.D. Jorgensen, et al., Phys. Rev. B 46 (1992) 1144.
[3] B.D. Stojanovic, C. Javalekic, V. Vukotic, A.Z. Simoes, J.A. Varela, Ferroelectrics 319 (2005) 291.
[4] K.L. Holman, Q. Huang, T. Klimczuk, K. Trzebiatowski, J.W.G. Bos, E. Morosan, J.W. Lynn, R.J. Cava, J. Solid State Chem. 180 (2007) 75.
[5] M.W. Lufaso, p.W. Barnes, P.M. Woodward, Acta Crystallogr. B 62 (2006) 397.
[6] L.O. San Martín, J.P. Chapman, L. Lezama, J. Sánchez-Marcos, J. Rodríguez-Fernández, M.I. Arriortua, T. Rojo, J. Mater. Chem. 15 (2005) 183.
[7] G. Blasse, J. Inorg. Nucl. Chem. 27 (1965) 993.
[8] Q. Lin, et al., J. Solid State Chem. 179 (2006) 2086–2092.
[9] S.A. Ivanov, N.W. Thomas, S. Ananta, R. Tellgren, H. Rundlof, J. Eur. Ceram. Soc. 20 (2000) 2325–2329.
[10] M.del.C. Viola, M.S. Augsburger, R.M. Pinacca, J.C. Pedregosa, R.E. Carbonio, R.C. Mercader, J. Solid State Chem. 175 (2003) 252–257.
[11] H.M. Rietveld, J. Appl. Crystallogr. 2 (1969) 65.
[12] J. Rodríguez-Carvajal, Physica B 192 (1993) 55.
[13] C.J. Howard, B.J. Kennedy, P.M. Woodward, Acta Crystallogr. B 59 (2003) 463.
[14] P.M. Woodward, Acta Crystallogr. B 53 (1997) 32.