Effect of cationic order–disorder on the transport properties of LaBaCo$_2$O$_{6-\delta}$ and La$_{0.5}$Ba$_{0.5}$CoO$_3$$_{3-\delta}$ perovskites

Diana Garcés, Cristian F. Setevich, Alberto Caneiro, Gabriel Julio Cuello and Liliana Mogni

*J. Appl. Cryst.* (2014). *47*, 325–334

Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site or institutional repository provided that this cover page is retained. Republication of this article or its storage in electronic databases other than as specified above is not permitted without prior permission in writing from the IUCr.

For further information see http://journals.iucr.org/services/authorrights.html

Many research topics in condensed matter research, materials science and the life sciences make use of crystallographic methods to study crystalline and non-crystalline matter with neutrons, X-rays and electrons. Articles published in the *Journal of Applied Crystallography* focus on these methods and their use in identifying structural and diffusion-controlled phase transformations, structure-property relationships, structural changes of defects, interfaces and surfaces, etc. Developments of instrumentation and crystallographic apparatus, theory and interpretation, numerical analysis and other related subjects are also covered. The journal is the primary place where crystallographic computer program information is published.

Crystallography Journals Online is available from journals.iucr.org
Effect of cationic order–disorder on the transport properties of LaBaCo$_2$O$_{6-\delta}$ and La$_{0.5}$Ba$_{0.5}$CoO$_{3-\delta}$ perovskites

Diana Garcés, Cristian F. Setevich, Alberto Caneiro, Gabriel Julio Cuello and Liliana Mogni*

*Centro Atómico Bariloche, Instituto Balseiro–CNEA, Avenida Bustillo 9500, San Carlos de Bariloche, Rio Negro, 8400, Argentina, Departamento de Física, Universidad Nacional del Sur, Instituto de Física del Sur, Avenida Alem 1253, Bahía Blanca, Buenos Aires, 8000, Argentina,
Centro Atómico Bariloche, Instituto Balseiro–CNEA–CONICET, Avenida Bustillo 9500, San Carlos de Bariloche, Rio Negro, 8400, Argentina, and Diffraction Group, Institut Laue–Langevin, 6 rue Jules Horowitz, BP 156, Grenoble, Isère, 38000, France. Correspondence e-mail: mogni@cab.cnea.gov.ar

A-site cationic ordered LaBaCo$_2$O$_{6-\delta}$ and disordered La$_{0.5}$Ba$_{0.5}$CoO$_{3-\delta}$ perovskite phases were obtained by solid state reaction. Their structural properties were studied at room temperature and 673 K, by combining powder diffraction techniques, X-ray diffraction and neutron powder diffraction with an independent determination of the oxygen content of the samples by thermogravimetry. La$_{0.5}$Ba$_{0.5}$CoO$_{3-\delta}$ exhibits cubic symmetry with cations randomly distributed, whereas LaBaCo$_2$O$_{6-\delta}$ shows tetragonal symmetry with the La$^{3+}$ and Ba$^{2+}$ ions distributed in alternating layers. The diffraction data were analyzed using the Rietveld method and different structural and microstructural models. Bond valence and Fourier methods were used to determine bond distances and neutron/electron density maps. LaBaCo$_2$O$_{6-\delta}$ exhibits a higher concentration of oxygen vacancies than La$_{0.5}$Ba$_{0.5}$CoO$_{3-\delta}$, because the O atom is weakly bonded to the LaO layers. The anisotropic atomic displacement and the neutron density distribution suggest a two-dimensional O-migration path for LaBaCo$_2$O$_{6-\delta}$ and a three-dimensional path for La$_{0.5}$Ba$_{0.5}$CoO$_{3-\delta}$. The mechanism of electrical conductivity is via electron holes with high mobilities ($\mu_{\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}} = 2.49 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and $\mu_{\text{LaBaCo}_{2}\text{O}_{6-\delta}} = 1.48 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature) and low activation energy ($E_a^{\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}} = 0.019 \text{ eV}$ and $E_a^{\text{LaBaCo}_{2}\text{O}_{6-\delta}} = 0.030 \text{ eV}$). It has also been found that the higher electronic and ionic conductivities in La$_{0.5}$Ba$_{0.5}$CoO$_{3-\delta}$ compared to those in LaBaCo$_2$O$_{6-\delta}$ are due to the higher dimensionality of transport and to greater overlapping between the Co 3$d$ and O 2$p$ orbitals.

1. Introduction

In the past few years, cobaltites with perovskite structure and the related layered perovskites have been proposed as materials for high- and intermediate-temperature electrochemical devices.

This kind of material is attractive because of the presence of mixed ionic and electronic conductivities. The use of cobaltites with mixed conductivity as oxygen electrodes allows the oxygen reaction zone to be increased beyond the triple phase boundary, gas/electronic conductor/ionic conductor, to a gas/mixed conductor interface. Thus, (La,Sr)CoO$_3$ boundary, gas/electronic conductor/ionic conductor, to a gas/oxygen reaction zone to be increased beyond the triple phase interface. Thus, (La,Sr)CoO$_3$ mixed conductor interface. Thus, (La,Sr)CoO$_3$ mixed conductor interface.

Research papers

© 2014 International Union of Crystallography

J. Appl. Cryst. (2014). 47, 325–334
doi:10.1107/S1600576713031233

325

Research papers
between the ionic radii of Ba\(^{2+}\) (\(r_{Ba^{2+}} = 1.61\) Å) and Ln\(^{3+}\) ions (\(r_{Pr^{3+}} = 1.179\) Å, \(r_{Nd^{3+}} = 1.27\) Å, \(r_{Sm^{3+}} = 1.24\) Å, \(r_{Gd^{3+}} = 1.107\) Å). Fig. 1 shows an A-cationic disordered perovskite, where the La\(^{3+}\) and Ba\(^{2+}\) ions are randomly distributed (Fig. 1a), and an A-cationic ordered perovskite, where La\(^{3+}\) and Ba\(^{2+}\) are distributed in layers (Fig. 1b). The cubic and tetragonal unit cells are highlighted in these figures. As a consequence of the cationic ordering, the oxygen bond displays a different strength depending on whether it is located in BaO, CoO\(_2\) or LnO layers, giving rise to differentiated oxygen crystallographic sites: O1, O2 and O3, respectively. Thus, for example, Taskin et al. (2005) reported that the cationic ordered GdBaMn\(_2\)O\(_{6-\delta}\) perovskite exhibits a higher change of oxygen content and a higher rate of oxygen uptake than the cationic disordered GdBa\(_{1-x}\)Ba\(_x\)MnO\(_{3-\delta}\) perovskite. They assume that the cationic order in the crystal structure will reduce the oxygen bonding strength and will provide a disorder-free channel for ion motion. The reduction of oxygen bonding strength might also induce a two-dimensional distribution of oxygen vacancies in the (001) LnO layers (tetragonal symmetry, \(P4mm\)) of layered cobaltites (Taskin et al., 2005; Tarancon et al., 2008; Streule, Podlesnyak, Sheptyakov et al., 2006). In this way, linked Co—O—Co channels subsist in CoO\(_2\) layers even at high temperatures. Similarly to other perovskite-related oxides, the electronic conductivity in LnBaCo\(_2\)O\(_{6-\delta}\) occurs via electron hopping along Co—O—Co bonds with a double exchange process (Zhang et al., 2008). Thus, the presence of linked Co—O—Co channels permits high values of electrical conductivity to be achieved at high temperatures.

Despite this promoting characteristic of layered perovskites, recent work by Kim et al. (2009) shows that cationic disordered La\(_{0.5}\)Ba\(_{0.5}\)CoO\(_{3-\delta}\) displays better ionic and electronic conductivities than cationic ordered LnBaCo\(_2\)O\(_{6-\delta}\) (Ln = Pr, Nd, Sm), possibly because the former has a less distorted lattice. However, it is not clear if the improvement of transport properties is a consequence of cationic disorder or Ln nature.

Controlled syntheses of cationic ordered/disordered phases for the case Ln = La (\(r_{La^{3+}} = 1.36\) Å) (Nakajima et al., 2005; Rautama et al., 2009, 2008) have given the opportunity to study the effect of structure (independently of Ln nature) on high-temperature transport properties. Three characteristic structures were reported by Rautama et al. (2008) for this composition at room temperature: disordered cubic perovskite La\(_{0.5}\)Ba\(_{0.5}\)CoO\(_{3}\), perfectly ordered layered LaBaCo\(_2\)O\(_6\), and a nanoscale-ordered LaBaCo\(_2\)O\(_6\). These structures were studied by neutron diffraction (Nakajima et al., 2005), X-ray diffraction and electron diffraction (Rautama et al., 2009, 2008) below room temperature. However, to the best of our knowledge, structural characterization of cationic disordered La\(_{0.5}\)Ba\(_{0.5}\)CoO\(_3\) and cationic ordered LaBaCo\(_2\)O\(_6\) structures at high temperatures has not been performed yet. Recently, S. Pang and co-workers have reported a comparative study of electrical conductivity at high temperature (Pang, Li et al., 2012) and area-specific resistance (ASR) (Pang, Jiang, Li, Su et al., 2012; Pang, Jiang, Li, Wang & Su, 2012) properties for La\(_{0.5}\)Ba\(_{0.5}\)CoO\(_3-\delta\) and LaBaCo\(_2\)O\(_6-\delta\). These authors found that, while the electrical conductivity for the cationic disordered La\(_{0.5}\)Ba\(_{0.5}\)CoO\(_3-\delta\) phase is higher than that of ordered LaBaCo\(_2\)O\(_6-\delta\), the ASR is lower. The ASR reaches values of 0.0086 \(\Omega\) cm\(^{-2}\) for the ordered phase (Pang, Jiang, Li, Su et al., 2012) and 0.013 \(\Omega\) cm\(^{-2}\) for the disordered phase (Pang, Jiang, Li, Wang & Su, 2012) at 1073 K in air. These results suggest a strong influence of structural features on the electrochemical performance.

The electrochemical performance of cobaltites is influenced by O-ion and electron transport. The O-ion transport takes place with an O-vacancy mechanism involving hopping through the O sublattice, whereas the electron transport arises via electron holes in the Co—O 3d–2p band. Neutron diffraction makes it possible to obtain information about the oxygen sublattice of crystalline oxides given its high sensitivity to oxygen in the presence of heavier rare earth and transition metal elements. This structural characterization, complemented with X-ray diffraction, gives useful information about oxygen and cation sublattices. Therefore, significant structural information could be obtained by combining the two techniques, and this structural information could be related to O-ion and electron-hole transport. Thus, for example, the effects of oxygen vacancies on structures and the determination of the O-diffusion path in perovskites and related structures such as Ba\(_{0.5}\)Sr\(_{0.5}\)CoO\(_{3-\delta}\) (McIntosh et al., 2006; Itoh et al., 2009, 2010), SrFeO\(_3\) (Schmidt & Campbell, 2002), NdBaCoO\(_{5+x}\) (Hu et al., 2012), PrBaCo\(_2\)O\(_{5+x}\) (Chen et al., 2013) and Sr\(_2\)Fe(Fe,Co)NiO\(_{6+y}\) (Mogni et al., 2009) were studied from in situ neutron diffraction techniques.

In this work, we perform an in situ neutron powder diffraction study for cationic ordered LaBaCo\(_2\)O\(_6-\delta\) and cationic disordered La\(_{0.5}\)Ba\(_{0.5}\)CoO\(_3-\delta\) at room temperature and 673 K, in order to obtain detailed structural information that can be correlated with the intermediate-temperature properties of these oxides. The choice of 673 K as intermediate temperature is based on the fact that, at this temperature, the oxygen exchange and bulk diffusion in these materials are high enough to promote oxygen vacancy generation.

2. Experimental

Powder samples were prepared by the solid state reaction method (SSR). Stoichiometric amounts of La\(_2\)O\(_3\) and Co\(_3\)O\(_4\)
oxides and BaCO₃ carbonate were mixed using an agate ball mill. The cationic ordered LaBaCo₂O₆₋ₓ₋₄ phase was obtained by annealing at 1423 K under Ar flow for 24 h, with heating and cooling rates of 2 K min⁻¹. Then, the powders were annealed at 673 K in air for 6 h in order to reach the equilibrium oxygen content. The cationic disordered La₀.₅Ba₀.₅CoO₃₋₄ phase was obtained by heat treating at 1373 K in air for 12 h, with heating and cooling rates of 5 K min⁻¹.

X-ray powder diffraction (XRD) patterns were collected at room temperature with a Philips PW1700 diffractometer using Cu Kα radiation and a graphite monochromator. All reflection peaks of La₀.₅Ba₀.₅CoO₃₋₄ were indexed according to the cubic symmetry (space group Pm₃m) previously reported for this compound (Nakajima et al., 2005), while those corresponding to LaBaCo₂O₆₋ₓ₋₄ were assigned to the tetragonal unit cell (space group P4/mmm) reported by the same authors.

Neutron powder diffraction (NPD) measurements were carried out at Institut Laue–Landévin (ILL), Grenoble, France, using the D2B powder diffractometer (λ = 1.594 Å). A vanadium sample holder was used for the measurements at room temperature and a quartz tube for the measurements at high temperature. The quartz tube was open, allowing oxygen exchange with the surrounding air. The high resolution of this two-axis diffractometer allowed a precise determination of the positions and occupation numbers of O atoms. All patterns were refined by the Rietveld method using the FullProf suite tools (Rodríguez-Carvajal, 2000). Details of the refinements are given in the supporting information.¹ The XRD and NPD room-temperature data were refined simultaneously in order to obtain complementary information. The Bond_Str (bond-valence parameters) and GFourier tools of FullProf were used for calculating the distances and angles in the crystal structures and for obtaining the Fourier maps, respectively.

The oxygen content of samples was determined in situ as a function of temperature in air by thermogravimetry (TG) using a symmetrical thermobalance based on a Cahn 1000 function of temperature in air by thermogravimetry (TG). The data were obtained from the relation pO₂ = 2/(2 + e⁻βT), where β = 83.5 K atm⁻¹ is a temperature-dependent parameter. The high resolution of this high temperature. The quartz tube was open, allowing oxygen exchange with the surrounding air. The final products of reduction, La₂O₃, BaO and CoO, were checked by XRD. This oxygen content determination was used as an independent measure of total oxygen vacancies. The oxygen content determinations under an oxygen partial pressure of 10% H₂/Ar are given in the supporting information. These models included microstrain effects, considerations about isotropic or anisotropic atomic relative vibrational motion, and the location and values of oxygen vacancy defects.

The goodness of fits for the samples were improved by considering the phenomenological Stephens model (Stephens, 1999) for the anisotropic microstrain effect and including anisotropic and isotropic Debye–Waller coefficients for thermal atomic vibration for LaBaCo₂O₆₋ₓ₋₄ and La₀.₅Ba₀.₅CoO₃₋₄. Besides, in both compounds, the O content was fixed to equal the values obtained from independent TG measurement to avoid any correlation between the O occupation and thermal displacement.

Fig. 2 shows the normalized O content obtained from TG as a function of T for LaBaCo₂O₆₋ₓ₋₄ and La₀.₅Ba₀.₅CoO₃₋₄. The data at room temperature and 673 K are used to fit the NPD profile, obtaining the best agreement at 673 K. Figs. 3 and 4 show the NPD measured and calculated profiles, and the difference between the two, for La₀.₅Ba₀.₅CoO₃₋₄ and for LaBaCo₂O₆₋ₓ₋₄. Respectively. The structural data obtained from these refinements are discussed below.

Tables 1 and 2 show the structural and microstructural parameters determined from Rietveld analysis for La₀.₅Ba₀.₅CoO₃₋₄ and LaBaCo₂O₆₋ₓ₋₄, respectively. Structural features such as lattice parameters (a, b and c), specific atomic positions (x, y, z) and occupancies (gatom), and the equivalent thermal displacements (Biso), are shown for both samples at different temperatures.

³ Supporting information for this article is available from the IUCr electronic archives (Reference: FSS049).

Fig. 2
Oxygen content of samples as a function of T, obtained by in situ thermogravimetric measurement. Black squares: La₀.₅Ba₀.₅CoO₃₋₄; black circles: 2 × (3 − δ), La₀.₅Ba₀.₅CoO₃₋₄.

J. Appl. Cryst. (2014). 47, 325–334
Diana Garcés et al. • Effect of cationic order–disorder

327
room temperature and 673 K. Values of anisotropic atomic displacement parameters and information about the refinements are included in the supplementary data. In both samples, as the temperature increases, the O occupancies ($g_{O}$) decrease, while the mean atomic displacements increase. The two parameters might be strongly correlated, in which case, fixing the oxygen content with an independent technique would allow a better resolution of $B_{iso}$. For the cationic ordered phase, three different oxygen positions can be distinguished, O1, O2 and O3, located in BaO, CoO$_2$ and LaO.

Table 1
Structural parameters of La$_{0.5}$Ba$_{0.5}$CoO$_3$ at room temperature and 673 K.
The space group is cubic Pm$ar{3}$m.

| Atom         | Room temperature | 673 K |
|--------------|------------------|-------|
|              | $g_{atom}$ B$_{iso}$ (Å$^2$) | $g_{atom}$ B$_{iso}$ (Å$^2$) |
| Co (1/2, 1/2, 1/2) | 1 0.25 (5)      | 1 0.95 (5) |
| Ba (0, 0, 0)    | 0.5 0.43 (3)    | 0.5 1.01 (5) |
| La (0, 0, 0)    | 0.5 0.43 (3)    | 0.5 1.01 (5) |
| O (1/2, 1/2, 0) | 0.97 (1) 1.39 (4) | 0.96 (1) 1.98 (3) |
| Lattice parameters (Å) | $a = b = c = 3.89151$ (5) | $a = b = c = 3.91979$ (4) |
| O content      | 3–$\delta = 2.91$ | 3–$\delta = 2.88$ |
| $V_w$ (Å$^3$)  | 58.932 (3) 60.227 (2) |
| $\rho$ (Mg m$^{-3}$) | 6.8627 (3) | 6.7065 (2) |
| Max-strain (%%)$^{\dagger}$ | 35.4 (1) | 33.1 (4) |

$^{\dagger}$ The symbol (%%) indicates that the unit is divided by 10 000.

Table 2
Structural parameters of LaBaCo$_2$O$_{6-\delta}$ at room temperature and 673 K.
The space group is cubic P4$_{mmm}$.

| Atom         | Room temperature | 673 K |
|--------------|------------------|-------|
|              | $g_{atom}$ B$_{iso}$ (Å$^2$) | $g_{atom}$ B$_{iso}$ (Å$^2$) |
| Co (1/2, 1/2, z) | 0.2490 (9) 1 0.17 | 0.2486 (1) 1 0.97 |
| Ba (0, 0, 0)    | – 1 0.06 | – 1 0.52 |
| La (0, 0, 1/2)  | – 1 0.75 | – 1 1.43 |
| O1 (1/2, 1/2, 0) | 0.2694 (3) 1 0.89 | 0.2693 (3) 1 1.75 |
| O2 (1/2, 1/2, 0) | – 0.77 (1) 0.13 | – 0.71 (1) 0.96 |
| O3 (1/2, 1/2, 1/2) | – | – |

| Lattice parameters (Å) | $a = b = 3.91468$ (3), | $a = b = 3.93654$ (4), |
| $\delta$ (Å$^2$) | $\rho$ (Mg m$^{-3}$) | $\rho$ (Mg m$^{-3}$) |
| $\rho$ (Mg m$^{-3}$) | 6.8446 (3) | 7.7604 (4) |
| Max-strain (%%)$^{\dagger}$ | 20 (5) | 18 (5) |

$^{\dagger}$ The symbol (%%) indicates that the unit is divided by 10 000.

Figure 3
NPD profile fitting at (a) room temperature ($\chi^2 = 4.49$, $R_p = 16.1$ and $R_{wp} = 13.7$) and (b) 673 K ($\chi^2 = 1.73$, $R_p = 19.9$ and $R_{wp} = 11.6$) for La$_{0.5}$Ba$_{0.5}$CoO$_3$ with anisotropic strain, isotropic vibration and O content fixed.

Figure 4
NPD profile fitting at (a) room temperature ($\chi^2 = 5.09$, $R_p = 15.7$ and $R_{wp} = 13.3$) and (b) 673 K ($\chi^2 = 2.80$, $R_p = 17.2$ and $R_{wp} = 12.0$) for LaBaCo$_2$O$_{6-\delta}$ with anisotropic strain and vibration and O content fixed.
layers, respectively. Initially, the O vacancies were fully located on O3 sites. The \( B_{oa} \) values of the O1 and O2 sites were larger than that of the O3 site, suggesting that these O-atom sites could collaborate with the oxygen migration diffusion path. Considering this, the occupancies \( g_{o1} \) and \( g_{o2} \) were also released to be adjusted, and it was found that only the O2 and O3 sites can accept O vacancies. Therefore, it is possible to assume that, similar to the isostructural LnBaCo\(_2\)O\(_6\) (Ln = Pr, Nd, Sm, Gd) compounds, the oxygen vacancies are mainly located in LaO layers (Streule, Podlesnyak, Pomjakushina et al., 2006), while the O atoms located in CoO\(_2\) layers facilitate the oxygen diffusion process. Recent studies of the diffusional pathway of \( O^{2-} \) ions in PrBaCo\(_2\)O\(_{6-\delta}\) (Chen et al., 2013) and NdBaCo\(_2\)O\(_{6-\delta}\) layered perovskites (Hu et al., 2012) by in situ neutron diffraction at temperatures higher than 873 K are consistent with our results.

Comparing the O content of cationic ordered and disordered phases in Fig. 2 and Tables 1 and 2, one can observe that the concentration of oxygen vacancies is higher for the LaBaCo\(_2\)O\(_{6-\delta}\) ordered phase than for the La\(_{0.5}\)Ba\(_{0.5}\)CoO\(_3\)\(_{3-\delta}\) phase over the whole temperature range. However, the O-atom displacement in the cationic disordered phase is larger than that in the ordered one, suggesting a higher delocalization or mobilization degree for O in the La\(_{0.5}\)Ba\(_{0.5}\)CoO\(_3\)\(_{3-\delta}\) structure.

From the point of view of microstructural features, it was possible to obtain information about size and microstrains effects on peak profile by using a calibration function. While the size of domain seems to have a negligible effect on the broadening, the microstrain effect is evident in both structures. The maximum strains (Max-strain) are the average values calculated using the reciprocal lattice directions. In this way, the symmetry of each phase is taken into account and the standard deviations of Max-strain are a measure of the degree of anisotropy. Therefore, despite the fact that LaBaCo\(_2\)O\(_{6-\delta}\) shows less stress than La\(_{0.5}\)Ba\(_{0.5}\)CoO\(_3\)\(_{3-\delta}\), the cationic order renders a more anisotropic strain. Fig. 5 shows the Williamson–Hall plots of integral breadth as a function of reciprocal distance for LaBaCo\(_2\)O\(_{6-\delta}\) and La\(_{0.5}\)Ba\(_{0.5}\)CoO\(_3\)\(_{3-\delta}\) samples at 673 K. The relative strain of the two samples and its anisotropic characteristic can be observed in these plots. These results are similar to those obtained at room temperature. The lower degree of anisotropy for the cationic disordered phase compared to ordered LaBaCo\(_2\)O\(_{6-\delta}\) might be related to the cubic symmetry of this phase. In the cationic ordered phase, the more strained reflections are those corresponding to Miller indices \( h00 \), \( 0k0 \) and \( hk0 \). The preferential strain direction suggests that some kind of local cationic disorder should be present in these directions despite the global ordering along the \( c \) axis. Besides, additional strain effects associated with some degree of ordering in the O sublattice should not be discarded. The O vacancies located in LaO layers could be ordered in chains along the \( a \) or \( b \) direction like in other isostructural LnBaCo\(_2\)O\(_6\) (Ln = Pr, Nd, Sm, Gd) perovskites (Streule, Podlesnyak, Pomjakushina et al., 2006). In the LnBaCo\(_2\)O\(_6\) (Ln = Pr, Nd, Sm, Gd) compounds, the O-vacancy order is responsible for the existence of a low-temperature orthorhombic phase. Likewise, but with a minor degree of anisotropy, the highest strain is present along the \( (h00) \) plane and the equivalent \( (0k0) \) and \( (00l) \) planes in the cubic phase. The high strain present in the La\(_{0.5}\)Ba\(_{0.5}\)CoO\(_3\)\(_{3-\delta}\) sample might suggest that the cationic ordered LaBaCo\(_2\)O\(_{6-\delta}\) phase is structurally more favorable.

### 3.2. Oxygen vacancy structure and O-migration path

Fig. 2 shows that the concentration of oxygen vacancies is higher in the cationic ordered LaBaCo\(_2\)O\(_{6-\delta}\) phase than in cationic disordered La\(_{0.5}\)Ba\(_{0.5}\)CoO\(_3\)\(_{3-\delta}\) in the whole temperature range. Therefore, we might assume that oxygen is more strongly bonded to the lattice in La\(_{0.5}\)Ba\(_{0.5}\)CoO\(_3\)\(_{3-\delta}\) than in LaBaCo\(_2\)O\(_{6-\delta}\). Besides, as has been observed from the structural analysis in the previous section, the oxygen vacancies of LaBaCo\(_2\)O\(_{6-\delta}\) are preferentially located in O3 sites along LaO layers. These behaviors might be explained in the frame of the bond valence formalism.

Table 3 shows the bond valence sum (BVS) and some characteristic distances between atoms for both structures at room temperature and 673 K. The BVS of the oxygen sites follows the sequence \( O_{P4 nnm} < O_{Pmnnm} \approx O_{P4/mmm} < O_{Pn3m} \). In addition, these values decrease as temperature increases for both samples. Lower BVS values indicate that O is weakly bonded to the lattice (Chen et al., 2013). Therefore, this result is in agreement with the fact that cationic order induces a highly defective structure with oxygen vacancies distributed along LaO layers.

In addition, the atomic displacements become anisotropic as a consequence of cationic order. Fig. 6 shows the atomic displacement (75% probability surface) at 673 K for both phases. Two unit cells of La\(_{0.5}\)Ba\(_{0.5}\)CoO\(_3\)\(_{3-\delta}\) were included for comparison with LaBaCo\(_2\)O\(_{6-\delta}\). The anisotropic atomic displacement in layered LaBaCo\(_2\)O\(_{6-\delta}\) suggests that the O1 sites \( (U_{11} = U_{22} > U_{33}) \) move parallel to the BaO plane,
Co—O planes in La0.5Ba0.5CoO3, respectively. As observed, while all the Co—O planes, and (200) [or (020)] Co—O planes, the O—Co—O angle is 180°. The Fourier maps were obtained from the structure factors with NPD data using GFourier tools. Figs. 7(a) shows the Fourier maps of the CoO layers corresponding to (200) Co—O plane in cubic perovskite LaBaCo2O6. The O—Co—O angle is 180°, which is consistent with the cubic symmetry. Figs. 7(b) and 7(c) show the Fourier maps of the CoO layers corresponding to (200) and (004) planes, respectively. As observed, both the Co—O planes in the LaBaCo2O6 structure and that normal to the c direction in the LaBaCo2O6 structure exhibit an isotropically distributed neutron density, the neutron densities of Fourier maps parallel to the c direction are concentrated toward the LaO planes. The Fourier maps and the O-atom displacements suggest a two-dimensional character.

Table 3

| Bond valence sums (BVSs) and characteristic atomic distances (d) and angles obtained at room temperature and 673 K for La0.5Ba0.5CoO3 and LaBaCo2O6. |
|-----------------|-----------------|-----------------|-----------------|
| BVS             | d (Å), angles (°) | BVS             | d (Å), angles (°) |
|-----------------|-----------------|-----------------|-----------------|
| La0.5Ba0.5CoO3. | 293 K 673 K     | 293 K 673 K     | LaBaCo2O6       |
| Co 3.161 (1)    | 3.022 (1)       | Co—O (x6)       | Co—O (x6)       |
| O 2.070 (1)     | 1.978 (1)       | O—Co—O          | O—Co—O          |
|                 |                 | 180.000 (3)     | 180.000 (3)     |
|                 |                 | 2.75171 (2)     | 2.771130 (20)   |

whereas the O2 sites (U13 > U21 × U32) distort the CoO6 octahedra, moving along the c axis toward the O3 sites, which exhibit a shorter and almost isotropic atomic displacement. The O-atom displacement in the LaBaCo2O6 structure is larger than those of LaBaCo2O6. Therefore, we might assume that the O atoms in LaBaCo2O6 are more mobile than O2 and O3 in LaBaCo2O6 because although they are more strongly bonded to the lattice (high BVS) than O2 and O3—O3 hopping because these distances are shorter than the O3—O3 distances.

Kim et al. (2009) compared the ionic and electronic conductivity of disordered La0.5Ba0.5CoO3 with those of cationic ordered LnBaCo2O6 (Ln = Pr, Nd, Sm, Gd, Y). Despite the difference between absolute values of ionic conductivity reported in the two works, σion follows the series La0.5Ba0.5CoO3 >> SmBaCo2O6 > GdBaCo2O6 > NdBaCo2O6 > PrBaCo2O6 > LaBaCo2O6.
Co$_2$O$_6$–δ. Therefore, the diffusion mechanism proposed in this work, involving a three-dimensional pathway for La$_{0.5}$Ba$_{0.5}$-CoO$_{3–δ}$ and a two-dimensional one for LaBaCoO$_{6–δ}$, would explain the higher ionic conductivity for the cationic disordered phase in spite of their lower O-vacancy concentration.

### 3.3. Electrical conductivity and electron-hole transport

The equilibrium electrical conductivities (σ) of LaBaCoO$_{6–δ}$ and La$_{0.5}$Ba$_{0.5}$CoO$_{3–δ}$ dense samples have been measured as a function of temperature between 293 and 1173 K in air. Usually in these cobalt-rich perovskites, the ionic conductivity ranges from $10^{-2}$ to $10^{-1}$ S cm$^{-1}$ and the electronic conductivity is between 10$^{-11}$ and 10$^{-10}$ S cm$^{-1}$ (Zhang et al., 2008; Kim et al., 2009); therefore it is a good approximation to consider that the electron conductivity almost equals the total electrical conductivity. Fig. 8(a) shows the σ versus T curves. As observed, the conductivity remains almost constant with T below 523 K for both samples. On increasing T above 523 K, the conductivities decrease, exhibiting a metallic like behavior. Besides, the electrical conductivity of LaBaCoO$_{6–δ}$ is lower than that of La$_{0.5}$Ba$_{0.5}$CoO$_{3–δ}$, but both are higher than those reported for other perovskites, which achieve maximum conductivity values around 200–500 S cm$^{-1}$ at 673 K (Tai et al., 1995; Zhang et al., 2008; Suntsov et al., 2011). The fact that the electrical conductivity of LaBaCoO$_{6–δ}$ is lower than that of La$_{0.5}$Ba$_{0.5}$CoO$_{3–δ}$ is in agreement with the previous results reported by Pang, Li et al. (2012).

Comparing Figs. 2 and 8(a), it is possible to correlate the behavior of σ with T to the change of oxygen content. In such a case, the conductivity would be p-type, with electron-hole (h) charge carriers (Pang, Li et al., 2012) hopping from Co$^{4+}$ to Co$^{3+}$ ions through the Co 3d–O 2p band (Zhang et al., 2008). Therefore, using the Kroger–Vink notation, oxygen vacancies V$_O^-$ are created as T increases, consuming the electron holes according to

$$O_2^+ + 2h \leftrightarrow V_{O^–} + \frac{1}{2}O_2 \uparrow.$$  

(1)

Combining electrical conductivity data with oxygen content data as a function of T, the dependence of σ versus ‘normalized’ oxygen content (6–δ) is plotted in Fig. 8(b), showing that, effectively, for both samples the conductivity increases with 6–δ.

One can notice from Fig. 2 that the oxygen content in La$_{0.5}$Ba$_{0.5}$CoO$_{3–δ}$ is higher than that of LaBaCoO$_{6–δ}$ at the same temperature, rendering higher conductivity values (see Fig. 8). However, one additional factor influencing the conductivity behavior seems to be present. With the aim of discriminating some structural effect on conductivity, in addition to the O-vacancy effect, a different in situ condition was selected for the cationic disordered phase. The oxygen content for this sample was determined using the thermobalance coupled to a gas blending system. This system allowed the determination of the oxygen content at pO$_2$ = 0.002 atm between room temperature and 1173 K. From these experiments we were able to determine that, at 673 K and pO$_2$ = 0.002 atm, the unit formula of the cationic disordered phase is La$_{0.5}$Ba$_{0.5}$CoO$_{2.36}$. This 3–δ value corresponds to the same normalized oxygen content as for the cationic ordered phase LaBaCoO$_{5.72}$ at 673 K in air. Then, fixing pO$_2$ at 0.002 atm the equilibrium electrical conductivity was measured at 673 K. This unique point is also included in Figs. 8(a) and 8(b) (marked as open triangles). It was found that the electronic conductivity in the cationic disordered phase (La$_{0.5}$Ba$_{0.5}$-CoO$_{3–δ}$) is higher than that in cationic ordered LaBaCoO$_{6–δ}$, regardless of the oxygen vacancy concentration, the structural properties being key to controlling the electron transport.

The metallic like behavior and the decrease of conductivity as the concentration of oxygen vacancies decreases (at constant temperature) suggest the presence of an electron-hole mechanism controlling the electrical transport. Most cobaltites with perovskite structure show a small polaron mobility controlling the electron-hole mechanism (Tai et al., 1995; Zhang et al., 2008; Sehlin et al., 1995). In these cases, the electron holes move slowly along the polar oxides, dragging a polarization cloud. Then, a thermally activated dependence is observed for conductivity data:

---

*J. Appl. Cryst.* (2014), 47, 325–334

Diana Garcés et al. • Effect of cationic order–disorder
versus $T$ is the electron-hole concentration per unit-cell volume, $p$ where $e$ is the electron charge, $\mu$ is the electron-hole mobility, $p$ is the electron-hole concentration per unit-cell volume, $E_a$ is the activation energy and $k_B$ is the Boltzmann constant. Under constant electron-hole concentration, if the activation energy is low, the exponential pre-factor depending on $T$ would dominate, causing the conductivity to decrease as $T$ increases.

The inset in Fig. 8(a) shows both Arrhenius plots $[\ln(\sigma T) \text{ versus } T^{-1}]$. The $E_a$ values of LaBaCo$_2$O$_{6-\delta}$ and La$_{0.5}$Ba$_{0.5}$Co$_{O_{3-\delta}}$ were computed between room temperature and 523 K, where the oxygen content and the electron-hole concentration remain almost constant. The activation energies obtained, $E_a$LaBaCo$_2$O$_{6-\delta}$ = 0.019 eV and $E_a$La$_{0.5}$Ba$_{0.5}$Co$_{O_{3-\delta}}$ = 0.030 eV, are almost negligible, suggesting that these are not thermally activated processes. Therefore, the electron-hole transport should correspond to a large polaron.

The main difference between small and large polarons is their mobility values. In the first case the interaction between electron hole and lattice is strong, rendering the highest localization of charge. The electron holes, occupying a narrow band, hop between Co$^{4+}$ and Co$^{3+}$ sites. The characteristic mobility values for small polarons are between $10^{-4}$ and $10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$. In the case of the large-polaron mechanism, the charge carriers are itinerant, moving almost freely along a wide band. The behavior is metallic like, but the mobility ($1$–$10$ cm$^2$ V$^{-1}$ s$^{-1}$) is still lower than that of metallic conductors. Therefore, from the mobility for both phases computed using equation (2) and conductivity data, the electron transport mechanism could be proposed.

In both La–Ba–Co–O systems studied in this work, the negative charges Ba$_{2+}$ ions produced when La$^{3+}$ ions are partially replaced by Ba$_{2+}$ ions must be compensated for by electron-hole creation at the Co sites ($h$) and oxygen vacancy generation at O sites ($V_O$). The charge balance is

$$2[V_O] + [h] = [Ba^{4+}].$$

The electron-hole concentration $p = h/V_{uc}$ ($V_{uc}$ is the unit-cell volume) can be estimated considering $V_O = \delta$ and Ba$_{2+}$ equal to 1 and 0.5 for LaBaCo$_2$O$_{6-\delta}$ and La$_{0.5}$Ba$_{0.5}$Co$_{O_{3-\delta}}$, respectively. Therefore, the mobility values are obtained from equation (2) using the electron-hole concentration estimated from oxygen content. In the third column of Table 4 the electron-hole mobility values estimated at 293 and 673 K are listed. On one hand, in both samples the mobility decreases with $T$. This behavior and the mobility values themselves are typical of large-polaron behavior. On the other hand, the electron-hole mobility in the cationic disordered phase is almost twice that of the cationic ordered phase at both temperatures. Analyzing the Co–O distances and angles given in Table 3, the differences between them are not sufficient to explain the difference between mobility values.

If the two-dimensional character of layered perovskites as opposed to the three-dimensional structure of cubic perovskites is considered, it might be probable that, instead of six equivalent directions to electron-hole movements, in layered perovskites there are only four. The electronic density of these compounds was studied from the XRD Fourier maps. The results of this study are shown in Fig. 9. Figs. 9(a) and 9(b) show the Co–O layers corresponding to the (002) and (200) planes of La$_{0.5}$Ba$_{0.5}$Co$_{O_{3-\delta}}$, respectively, whereas Figs. 9(c) and 9(d) show the Co–O2 and Co–O (O1, O2 and O3) layers corresponding to the (004) and (200) planes of LaBaCo$_2$O$_{6-\delta}$, respectively. The electronic density is more isotropically distributed in the cationic disordered phase than in the cationic ordered one, where the $e$ direction shows a lack of electronic density around the O3 site. Therefore, it is plausible to assume that the oxygen vacancies, preferentially located in the LaO layer, work as a barrier blocking the charge carrier movement through the Co 3d–O 2p band in the c-axis direction. This way, it is possible to define a lineal mobility such as $\mu_{\text{lineal}}$La$_{0.5}$Ba$_{0.5}$Co$_{O_{3-\delta}}$ = $\mu/6$ for the cubic symmetry and $\mu_{\text{lineal}}$LaBaCo$_2$O$_{6-\delta}$ = $\mu/4$ for the tetragonal one. The lineal mobility values are also shown in Table 4.

The lineal mobility of the cationic ordered phase is slightly lower than that of the cationic disordered phase. The differences between electron-hole mobility arise from the octahedral distortion produced by La–Ba cationic order. As
observed in Table 3 and Fig. 9, in cationic ordered phases the O—Co—O angles are lower than 180°, locating these atoms out of the ab plane. This fact, as well as the increment in the Co—O distances (see Table 3), reduces the overlapping between the Co 3d and O 2p orbitals in LaBaCo₂O₆₋₅ compared to La₀.₅Ba₀.₅CoO₃₋₅, decreasing the electron-hole mobility.

Therefore, although these cobaltites are better electronic conductors than other perovskites, the structural difference between them improves the electronic conduction in La₀.₅Ba₀.₅CoO₃₋₅ compared to LaBaCo₂O₆₋₅. This would be due to the fact that, in LaBaCo₂O₆₋₅, the conductivity is two dimensional instead of three dimensional. Besides, the loss of overlapping between the Co 3d and O 2p orbitals due to the octahedral distortion hampers the electron-hole transport.

4. Conclusions

The effect of cationic ordering or disordering on ionic and electronic transport properties of cobalt perovskites was analyzed in relation to the structural features determined by NPD and XRD techniques. Two compounds with the same cationic ratio but different structures have been studied: cationic disordered La₀.₅Ba₀.₅CoO₃₋₅ with cubic symmetry and cationic ordered LaBaCo₂O₆₋₅ with tetragonal symmetry.

The cationic LaBaCo₂O₆₋₅ ordered phase shows lower strain values but a higher degree of anisotropy than the cationic La₀.₅Ba₀.₅CoO₃₋₅ disordered one. The minor degree of anisotropy for the cationic disordered phase was related to its cubic symmetry. The origin of the stress has been associated with the local order/disorder of La and Ba and the local concentration of oxygen vacancies, which produce a distribution of lattice parameters of the unit cell. Therefore, the minor strain in LaBaCo₂O₆₋₅ suggests that the distribution of cations in layers is structurally more favorable than cations randomly distributed.

NPD has allowed us to obtain precise information on the O sublattice and O-migration path. The oxygen vacancies of LaBaCo₂O₆₋₅ are mainly located in LaO layers. However, the O ions located in the CoO₂ layer are highly delocalized, contributing to the O-diffusion process. Rietveld refinement and bond valence sum methods suggest that O3 is more weakly bonded than the O1 and O2 O-atom sites in the LaBaCo₂O₆₋₅ structure and also than the O atoms in cubic La₀.₅Ba₀.₅CoO₃₋₅. The atomic displacement and Fourier maps suggest a two-dimensional diffusional path for oxygen migration in LaBaCo₂O₆₋₅, whereas this migration is isotropic along three dimensions in La₀.₅Ba₀.₅CoO₃₋₅. The lowest dimensionality for the O-migration path harms the ionic conductivity in the tetragonal LaBaCo₂O₆₋₅ structure compared to the cubic La₀.₅Ba₀.₅CoO₃₋₅.

Both LaBaCo₂O₆₋₅ and La₀.₅Ba₀.₅CoO₃₋₅ compounds exhibit high electrical conductivity values with a metallic-like behavior. The combination of electrical conductivity with oxygen content data indicates that the conductivity mechanism is via electron-hole charge carriers. Two structural features are detrimental to the electrical conductivity of the cationic ordered phase in contrast to La₀.₅Ba₀.₅CoO₃₋₅:

(a) The two-dimensional instead of three-dimensional conductivity. This lower dimensionality for the electron-hole transport was associated with the blocking of the c direction owing to the existence of a high concentration of oxygen vacancies in the LaO layers.

(b) The loss of overlap between the Co 3d and O 2p orbitals, since the octahedral distortion enlarges the Co—O₂ distance and decreases the O₂—Co—O₂ angles.

This work was supported by CONICET, CNEA, ANPCyT and Fundación Balseiro from Argentina, through PICT 2010-0850 and PIP 11220080100120, and by Institut Laue–Langevin through ILL research proposal 47269. We also thank Professor N. Gonzalez and M. C. Ferreiro from Balseiro Institute for their help in the English revision of the manuscript.

References

Chen, Y., Yashima, M., Peña-Martínez, J., & Kilner, J. A. (2013). Chem. Mater., 25, 2638–2641.
Frontera, C., Caneiro, A., Carrillo, A. E., Oró-Solé, J., & García-Muñoz, J. L. (2005). Chem. Mater., 17, 5439–5445.
Hu, Y., Hernández, O., Brout, T., Bahout, M., Hermet, J., Ottochian, A., Ritter, C., Geneste, G., & Dezaanneau, G. (2012). J. Mater. Chem., 22, 18744–18747.
Ishihara, T., Fukui, S., & Nishiguchi, H. (2002). Solid State Ionics, 152–153, 609–613.
Itoh, T., Hirai, T., Yamashita, J., Watanabe, S., Kawata, E., Kitamura, N., Idemoto, Y., & Igawa, N. (2010). Physica B, 405, 2091–2096.
Itoh, T., Shirasaki, S., Fujie, Y., Kitamura, N., Idemoto, Y., Osaka, K., Hiroswa, I. & Igawa, N. (2009). Electrochemistry, 77, 161–168.
Kim, J.-H., Mogni, L., Prado, F., Caneiro, A., Alonso, J. A., & Manthiram, A. (2009). J. Electrochem. Soc., 156, B1376–B1382.
Kim, J., Prado, F. & Manthiram, A. (2008). J. Electrochem. Soc., 155, B1023–B1028.
McIntosh, S., Vente, J. F., Haije, W. G., Blank, D. H. A., & Bouwmeester, H. J. M. (2006). Chem. Mater., 18, 2187–2193.
Mogni, L. V., Prado, F. D., Cuello, G. J., & Caneiro, A. (2009). Chem. Mater., 21, 2614–2623.
Nakajima, T., Ichihara, M., & Ueda, Y. (2005). J. Phys. Soc. Jpn., 74, 1572–1577.
Pang, S., Jiang, X., Li, X., Su, Z., Xu, H., Xu, Q., & Chen, C. (2012). Int. J. Hydrogen Energy, 37, 6836–6843.
Pang, S., Jiang, X., Li, X., Wang, Q., & Su, Z. (2012). Int. J. Hydrogen Energy, 37, 2157–2165.
Pang, S. L., Li, X. N., Wang, Q., & Zhang, Q. Y. (2012). Mater. Chem. Phys., 131, 642–645.
Petric, A., Huang, P., & Tietz, F. (2000). Solid State Ionics, 135, 719–725.
Rautama, E., Boullay, P., Kundu, A. K., Caignaert, V., Pralong, V., Karpipinen, M., & Raveau, B. (2008). Chem. Mater., 20, 2742–2750.
Rautama, E., Caignaert, V., Boullay, Ph., Kundu, A., Pralong, V., Karpipinen, M., Ritter, C., & Raveau, B. (2009). Chem. Mater., 21, 102–109.
Rodriguez-Carvajal, J. (2000). FullProf 2000. Laboratoire Léon Brillouin (CEA-CNRS), Gif sur Yvette, France.
Schmidt, M., & Campbell, S. (2002). J. Phys. Chem. Solids, 63, 2085–2092.
Sehlin, S., Anderson, H. & Sparlin, D. (1995). Phys. Rev. B, 52, 11681–11689.
Setevich, C., Mogni, L., Caneiro, A., & Prado, F. (2012). J. Electrochem. Soc., 159, B73–B80.
Stephens, P. W. (1999). *J. Appl. Cryst.* **32**, 281–289.
Streule, S., Podlesnyak, A., Pomjakushina, E., Conder, K., Sheptyakov, D., Medarde, M. & Mesot, J. (2006b). *Physica B*, **378–380**, 539–540.
Streule, S., Podlesnyak, A., Sheptyakov, D., Pomjakushina, E., Stingaciu, M., Conder, K., Medarde, M., Patrakeev, M. V., Leonidov, I. A., Kozhevnikov, V. L. & Mesot, J. (2006a). *Phys. Rev. B*, **73**, 094203.
Suntsov, A., Leonidov, I., Patrakeev, M. & Kozhevnikov, V. (2011). *J. Solid State Chem.* **184**, 1951–1955.
Tai, L., Nasrallah, M. M., Anderson, H. U., Sparlin, D. M. & Sehlin, S. R. (1995). *Solid State Ionics*, **86**, 273–783.
Tarancón, A., Marrero-López, D., Peña-Martinez, J., Ruiz-Morales, J. C. & Nuñez, P. (2008). *Solid State Ionics*, **179**, 611–618.
Tarancón, A., Skinner, S., Chater, R., Hernández-Ramirez, F. & Kilner, J. (2007). *J. Mater. Chem.*, **17**, 3175–3181.
Taskin, A. A., Lavrov, A. N. & Ando, Y. (2005). *Appl. Phys. Lett.*, **86**, 091910.
Teraoka, Y., Zhang, H., Okamoto, K. & Yamazoe, N. (1988). *Mater. Res. Bull.*, **23**, 51–58.
Zhang, K., Ge, L., Ran, R., Shao, Z. & Liu, S. (2008). *Acta Mater.*, **56**, 4876–4889.
Zhou, W., Ran, R. & Shao, Z. (2009). *J. Power Sources*, **192**, 231–246.