



Crystal structure and compositional effects on the electrical and electrochemical properties of $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ $0 \leq x \leq 2$ oxides for use as air electrodes in solid oxide fuel cells

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Daniel Muñoz-Gil^a, Esteban Urones-Garrote^b, Domingo Pérez-Coll^c, Ulises Amador^d and Susana García-Martín^{a*}

The effects of Co substitution by Mn in the crystal structure, oxygen content, thermal stability and expansion and electrical properties of the $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ $0 \leq x \leq 2$ oxides are reported. Composites of $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ - $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ (70 : 30 wt%) are used as cathode materials and the electrochemical behaviour is presented. Layered-type ordering of Ba and Gd cations in the perovskite structure occurs in the whole system when the materials are prepared in argon but only for compositions in the range corresponding to $x < 1.4$ when the materials are prepared in air. The oxygen content increases with increasing the Mn content, making thermal stability to improve and thermal expansion to decrease. However, lowering of the dc conductivity and increasing of electrode polarization resistances are observed by Mn substitution for Co. Cation ordering of the Gd and Ba atoms seems to affect the electrochemical properties of the materials.

Introduction

$\text{GdBaCo}_2\text{O}_{5+\delta}$ is a layered-type perovskite with potential applications as air-electrode for Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs) due to its electrical behavior and high catalytic activity for the oxygen reduction.¹⁻³ From the point of view of the electrical properties, it is a p-type electronic conductor also presenting oxygen-anion conductivity associated to its non-stoichiometric anion sublattice. In this context, layered-type ordering of Gd and Ba in the crystal structure of $\text{GdBaCo}_2\text{O}_{5+\delta}$ seems to be crucial to the location of the anion vacancies within the Gd-O layers, creating very high ion-conducting planes.^{4,5} All these aspects contribute to the low electrode polarization resistances measured in symmetrical cells using this oxide as the electrodes.¹⁻³ However, despite the mentioned good qualities, $\text{GdBaCo}_2\text{O}_{5+\delta}$ shows an important number of inconveniences for being used as air electrode in IT-SOFCs: in addition to the high cost of Co-based materials, this oxide is not thermally stable because suffers from variation of the oxygen content on heating and presents very high thermal expansion coefficients (TECs) associated to oxygen loss and spin transitions of trivalent cobalt.⁶⁻⁹

Substitution of Co by M= Ni, Fe or Cu in $\text{GdBaCo}_{2-x}\text{M}_x\text{O}_{5+\delta}$ systems has proven to increase thermal stability and decrease TECs, though in general, higher electrode polarization resistances are measured in cells fabricated with these electrode-materials.¹⁰⁻¹⁴ In this context, studies of the effects of Mn-doping on the properties of the $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ system have not yet been reported, though in the case of the $\text{NdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ oxides, good chemical compatibility with $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.90}$ (CGO) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$ (LSGM) electrolytes and low TECs have been determined.¹⁵ However, layered-type ordering of Nd and Ba atoms is only achieved in this system for x values in the range $0 \leq x \leq 1$, unless reducing conditions are used in the synthesis.¹⁵⁻¹⁷ This is because ordering in the A cation-sublattice of the layered-perovskite structure ($\text{AA}'\text{B}_2\text{O}_3$) is not only assisted by differences between the ionic radii and oxidation states of the A and A' atoms but also depends on the B-type cation, which highly affects the oxygen content too. In fact, whereas A-cation ordering occurs in Co-based perovskites, ordering in Mn-based perovskites requires a more complicated process and therefore, modification of the properties by the A-cation ordering in these materials can be controlled by the preparation method. Thus, layered ordering of Gd and Ba in $\text{GdBaMnFeO}_{5+\delta}$ is achieved by using a reducing atmosphere in the first step of the synthesis.^{18, 19} Besides, it has clearly been demonstrated the improvement of electrochemical performance of ordered $\text{GdBaMnFeO}_{5+\delta}$ oxide as air electrode in symmetrical cells using CGO as electrolyte in comparison with the disorder $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ material.¹⁸ However, $\text{GdBaMnFeO}_{5+\delta}$ showed higher electrode polarization resistances in comparison to analogous Co-based phases.^{3,12} This feature reinforces the interest in Co-based compositions, which, nevertheless, requires further effort to overcome their limitations for practical applications. In addition to

^a Departamento de Química Inorgánica. Facultad de C.C. Químicas, Universidad Complutense, 28040-Madrid, Spain.

^b Centro Nacional de Microscopía Electrónica, Universidad Complutense, 28040-Madrid, Spain

^c Instituto de Cerámica y Vidrio, CSIC, Cantoblanco, 28049 Madrid, Spain

^d Universidad San Pablo-CEU, CEU Universities, Facultad de Farmacia, Departamento de Química y Bioquímica, Urbanización Montepríncipe, Boadilla del Monte, E-28668, Madrid, Spain

* Electronic Supplementary Information (ESI) available:
See DOI: 10.1039/x0xx00000x

the improvements expected both in thermal stability and TECs, substitution of Mn for Co generally extends the redox stability of the material; in this sense, PrBaMn₂O_{6-δ} has shown high redox stability under reducing conditions and high tolerance to carbon coking and H₂S poisoning, proving a good electrochemical performance not only as anode in SOFCs using hydrocarbon fuels but also in SOECs (solid oxide electrolysis cells).^{20,21}

Taking into account all these results and considering that Gd/Ba-compounds seem to present increased oxygen-vacancy concentrations compared to other REBaCo₂O_{5+δ} layered-perovskites with lower size difference between RE and Ba,²² which also can enhance the oxygen-anion conductivity, we have studied the influence on the crystal structure and properties of the Co substitution by Mn in the system GdBaCo_{2-x}Mn_xO_{5+δ}. We report in this article the influence of the preparation conditions on the ordering of Gd and Ba ions in the structure. We also compare results of the electrode polarization resistances of symmetrical cells using ordered or disordered oxides of the system in the electrodes, finding that layered-type compounds show better electrochemical performance.

Experimental section

GdBaCo_{2-x}Mn_xO_{5+δ} 0 ≤ x ≤ 2 oxides have been prepared from stoichiometric amounts of Gd₂O₃ (Sigma Aldrich, 99.99%), BaCO₃ (Sigma Aldrich, 99.99%), Co₂O₃ (Sigma Aldrich, 99.99%) and Mn₂O₃ (Sigma Aldrich, 99.99%). Gd₂O₃ was heated at 1173 K prior to weighing. These starting compounds were mixed and heated at 1173 K during 12 hours for decomposition of the BaCO₃ in air or under a gas flow of argon (purity ≥ 99.999). After this first thermal treatment, the samples were re-ground and pelletized and finally heated at 1473 or at 1773 K (those with higher Mn contents) during 48 hours. The thermal treatment was carried out twice with intermediate ground in all the samples and in the two different atmospheres (air and argon). The compounds were quickly cooled to room temperature.

Crystalline phase identification was carried out by powder X-ray diffraction (PXRD) using a PANalytical X'PERT PRO MPD diffractometer with CuKα₁ (λ = 1.5406 Å) radiation and X'PERT PEAPD software. The patterns were taken at step mode with a step size equal to 0.02 (2θ degrees) and time per step equal to 10 s. X-ray diffraction patterns at different temperatures in the 298–1173 K range were taken every 50 K in air after stabilization for 30 min, applying a heating/cooling rate of 2 K min⁻¹ on Multi-Purpose PANalytical X'Pert PRO MPD diffractometer equipped with an Anton Paar HTK2000 camera.

LeBail fitting (without structural model) of the XRD patterns was performed to obtain the lattice parameters and symmetries (S.G.) of the phases in every sample using the Fullprof software.^{23,24}

The oxygen content of the compounds was determined by redox titration.²⁵ A 50 mg sample and an excess of FeSO₄·7H₂O (ca. 120 to 180 mg) were dissolved in 20 mL of HCl, 75 ml of distilled water and 5 ml of phosphoric acid (the titrations were carry out under an Ar atmosphere for preventing oxidation). As a result, the species (Co, Mn) were reduced to divalent ions and the stoichiometric amount of trivalent iron was formed. The rest of Fe²⁺ was titrated with a 5.10⁻³ M solution of K₂Cr₂O₇ (ca. 12–22 ml are required). Two drops of a

0.01 M solution of tris (5,6-dimethyl-1,10 phenanthroline) iron (II) sulfate were used as indicator; the end-point was detected visually as the solution changes from red to a yellow-green colour. Thermogravimetric analyses (TGA) were carried out dynamically applying a heating/cooling rate of 2 K min⁻¹ in flowing (2 ml/min) air or oxygen streams to evaluate oxygen stoichiometry stability of the samples from 298 K to 1173 K in an SDT Q600 thermogravimetric analyser.

In addition to the PXRD, the crystal structures of the materials were analysed by combination of selected-area electron diffraction (SAED), high-resolution transmission electron microscopy (HRTEM), high-angle annular dark field (HAADF) and annular bright field (ABF) scanning TEM (STEM) and electron energy-loss spectroscopy (EELS). For TEM studies the compounds were ground in n-butyl alcohol and ultrasonically dispersed. A few drops of the resulting suspension were deposited on a carbon-coated grid. SAED, HRTEM and EELS experiments were performed with a JEOL JEM 3000F microscope operating at 300 kV (double tilt ±20°) (point resolution 0.17 nm), fitted with a X-Ray energy dispersive spectroscopy (XEDS) microanalysis system (OXFORD INCA) and ENFINA spectrometer with an energy resolution of 1.3 eV. The atomic ratio of the metals was determined by XEDS analyses finding good agreement between analytical and nominal composition in all the crystals. Average oxidation state of Mn atoms of the oxide was determined by EELS.²⁶ When necessary, plural-scattering effects were removed with a Fourier-ratio deconvolution method.²⁶ The spectra were acquired in diffraction mode, with a dispersion of 0.1 eV/channel, a collection angle β ~ 5.3 mrad and an acquisition time of 2 s. The HAADF and ABF STEM experiments and EELS mapping were performed on an ARM200cF microscope, fitted with a condenser lens aberration corrector (point resolution in STEM mode of 0.08 nm) and GIF Quantum-ER spectrometer. HAADF images were acquired with an inner acceptance angle of 90 mrad and ABF ones with a collection angle of 11 mrad. EELS mapping was performed with a collection semi-angle β ~ 30 mrad, 0.5 eV/channel dispersion and collection time for each spectrum of 0.09 seconds. Gd-M_{4,5}, Ba-M_{4,5}, Co-L_{2,3} and Mn-L_{2,3} edge signals were chosen for mapping.

The electrical characterization was performed by d.c. four probe methodology. 99% Densified rectangular bars were prepared by sintering at 1473 or 1773 K (depending on the composition) and four electrodes were prepared by attaching Pt wires with Pt paste and firing at 1223 K for 1 hour. A potentiostat/galvanostat (Autolab PGStat302N) equipment was employed to produce the current flow through the sample by means of the external electrodes and also to read the voltage difference between the inner electrodes. The resistances of the samples were determined from the slopes of the linear I-V curves in the temperature range of 423–1223 K.

Area specific resistance (ASR) values associated with the electrode polarization processes in air were determined from complex impedance spectra obtained by AC impedance spectroscopy on symmetrical two-electrode configuration cells at different temperatures. The high-frequency offset in the impedance spectra is associated to the electrolyte resistance, whereas the difference between the high and low frequency intercepts on the real axis (Z') is associated to all the resistive processes taking place at the electrodes. Electrolyte

pellets of 10 mm diameter and 1.2 mm thickness of commercial $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ (CGO) powder (Fuel Cells Materials) were prepared with 99% of density by pressing the powder at 250 MPa and sintering in air at 1673 K for 12 hours. Slurries prepared using $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$:CGO composites (70:30 wt%) with a commercial organic vehicle (Decoflux™) were deposited onto both surfaces of the CGO electrolyte pellets and then fired at 1173 K for 3 h in air (heating/cooling rate of 2,5 K min⁻¹). The experimental procedure was carefully followed by SEM for the preparation of the different systems in order to minimize microstructural differences and corresponding effects on the later electrochemical behavior. Silver paste and mesh were used as current collectors on both sides of the pellets. The impedance measurements were carried out using a frequency response analyzer Solartron 1255A with a dielectric interface 1296. Measurements were performed in air on heating and cooling cycles between 723 K and 923 K, in a frequency range of 0.1 Hz to 1 MHz and an excitation voltage of 50 mV.

Results and Discussion

Fig. 1 shows the PXRD patterns of $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ with $x = 0.2$ and 1.8 synthesised in air. The pattern of $\text{GdBaCo}_{1.8}\text{Mn}_{0.2}\text{O}_{5+\delta}$ is indexed using tetragonal S.G. P4/mmm and unit cell $a_p \times a_p \times 2a_p$ (a_p refers to the lattice parameter of the cubic perovskite). On the contrary, the pattern of $\text{GdBaCo}_{0.2}\text{Mn}_{1.8}\text{O}_{5+\delta}$ is indexed as a cubic disordered perovskite (S.G. Pm3m; $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_{2.5+\delta}$). The patterns of all the compounds prepared in argon are similar to the one of $\text{GdBaCo}_{1.8}\text{Mn}_{0.2}\text{O}_{5+\delta}$ in Fig. 1a. The PXRD results indicate that under argon atmosphere single-phase samples can be obtained for the whole compositional range, $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ $0 \leq x \leq 2$, whereas in air the $x = 0$ member cannot be prepared; thus, single-phase $\text{GdBaCo}_2\text{O}_{5+\delta}$ is only obtained in argon atmosphere.³ Layered-type ordered perovskites, with tetragonal symmetry S.G. P4/mmm and

unit cell $a_p \times a_p \times 2a_p$, are obtained when the synthesis proceeds in argon flow for the whole compositional range. However, when the materials are prepared in air, ordering of Ba and Gd only occurs for compositions in the range $0 < x < 1.4$ (for $x > 1.4$ cubic disordered perovskites with S.G. Pm3m are obtained). The compositional range of ordered oxides is wider than that observed in the analogous Nd-system,¹⁵⁻¹⁷ probably due to the larger size difference between Gd and Ba in comparison to Nd and Ba.

The thermal stability of the materials was studied by TGA (Fig. S1, Supplementary Information). Table 1 collects the δ values of different oxides after preparation and after the first heating/cooling cycle. Although the materials prepared in Ar have slightly lower oxygen content after the first heating-cooling cycle, the oxygen content does not seem to strongly depend on the conditions of synthesis, unlike the crystal structure. The oxygen content in $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ increases as the substitution of Co by Mn does. The air-prepared oxides suffer significant oxidation on heating from room temperature up to about 723K; above 723 K loss of oxygen occurs (Fig. S1a,b). On cooling, the materials oxidise but the second heating-cooling cycle is reversible and consists of only two processes (loss of oxygen on heating above 723 K and uptake of oxygen on cooling). The oxidation of the compounds during the initial heating is probably related to the instability of the as prepared phase due to the fast cooling on preparation and also occurs in the $\text{NdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ oxides.^{3,15} The oxides prepared in argon show lower variations of oxygen content on heating-cooling cycles (Table 1 and Fig. S1c,d). Notice that variations of the oxygen content with temperature are clearly lower with increasing the Mn content. This agrees with previous results reported in systems such as $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Co}_{1-y}\text{Mn}_y\text{O}_{3-\delta}$ ²⁷ or $\text{NdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ ¹⁵ and suggests a stronger binding of oxygen in oxides with higher Mn contents.

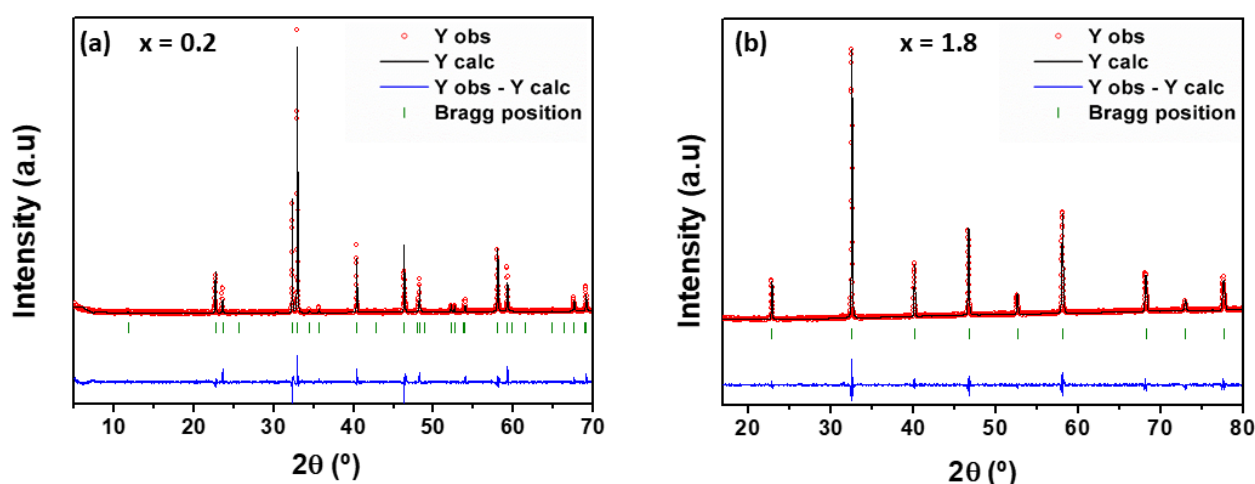


Figure 1. Room temperature PXRD patterns (red points) of two oxides of the system $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ prepared in air, $x=0.2$ (a) and $x=1.8$ (b). Profile fitting has been carried out with (a) $P4/mmm$ space group and $a_p \times a_p \times 2a_p$ unit cell and (b) $Pm3m$ space group and $a_p \times a_p \times a_p$ unit cell. Calculated patterns correspond to black line, and their difference with the experimental ones is indicated in blue at the bottom of each panel.

Table 1. Oxygen content (given as δ values in the general formulae $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$) obtained for the as prepared samples (from redox titration) and during heating-cooling processes in air for different values of x in the system $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ prepared in air and argon.

| Composition | Samples prepared in Air | | | Samples prepared in Argon | | |
|---|---------------------------|-------------------|---|---------------------------|-------------------|---|
| | δ (RT) as prepared | δ (1173 K) | δ (RT) after heating/cooling cycle | δ (RT) as prepared | δ (1173 K) | δ (RT) after heating/cooling cycle |
| $\text{GdBaCo}_{1.8}\text{Mn}_{0.2}\text{O}_{5+\delta}$ | 0.10(2) | 0.27 | 0.48 | 0.12(2) | 0.18 | 0.45 |
| $\text{GdBaCo}_{1.4}\text{Mn}_{0.6}\text{O}_{5+\delta}$ | 0.22(4) | 0.35 | 0.56 | 0.20(4) | 0.20 | 0.48 |
| $\text{GdBaCoMnO}_{5+\delta}$ | 0.39(2) | 0.53 | 0.80 | 0.40(4) | 0.41 | 0.68 |
| $\text{GdBaCo}_{0.6}\text{Mn}_{1.4}\text{O}_{5+\delta}$ | 0.57(4) | 0.80 | 1.00 | 0.64(4) | 0.70 | 0.87 |
| $\text{GdBaCo}_{0.2}\text{Mn}_{1.8}\text{O}_{5+\delta}$ | 0.76(3) | 0.85 | 0.96 | 0.74(4) | 0.70 | 0.75 |
| $\text{GdBaMn}_2\text{O}_{5+\delta}$ | 0.85(3) | 0.92 | 0.95 | 0.75(3) | 0.60 | 0.75 |

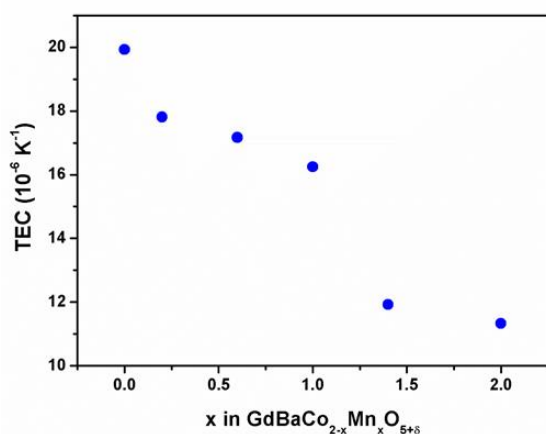


Figure 2. TEC values of the oxides of the $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ system calculated in the range of temperatures $575 \text{ K} < T < 1200 \text{ K}$

Therefore, the sample without cobalt presents a very stable value of δ as a function of temperature after the first heating/cooling cycle (Fig. S1 b, d), indicating a very stable value of the average oxidation state of Mn. This behaviour suggests that the changes in the oxygen content for Mn-Co-based samples during heating/cooling processes are mainly related to variations in the oxidation state of Co.

Fig. 2 shows the TEC values of the oxides of the $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ system calculated in the range of temperatures $575 \text{ K} < T < 1200 \text{ K}$. TEC values were determined from the variation of their unit cell volume with temperature (Fig. S2) and unit cell volumes were determined from the PXRD patterns taken from room temperature up to 1173 K (Fig. S3). TEC values significantly decrease with increasing Mn content, as it happens in other systems such as $\text{NdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ ¹⁵ and $\text{SmSrCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ ²⁸ and expected of the lowering of oxygen loss with temperature and the lower fraction of Co^{3+} , which diminishes the effect associated to the spin state transition.

The crystal structure of the $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ oxides has been confirmed by SAED and HRTEM (Fig. S4). The SAED patterns and corresponding HRTEM images, of the compounds with $0 \leq x < 2$ prepared in argon and the compounds with $0 < x < 1.4$ prepared in air are characteristic of layered-type perovskite.^{3,12} In $\text{GdBaMn}_2\text{O}_{5.75}$, modulation of the crystal structure due to $\text{Mn}^{3+}/\text{Mn}^{4+}$ charge ordering has been reported.²⁹ The results of the materials prepared in air with composition corresponding to $1.4 \leq x \leq 2$ are characteristic of perovskite structure, as not ordering of Gd and Ba atoms occurs. A more detailed study of the crystal structure of $\text{GdBaCoMnO}_{5+\delta}$ has been carried out by means of STEM and EELS in order to confirm the Ba and Gd ordering and to determine the location of the Co and Mn atoms and the anion vacancies. Fig. 3 displays the HAADF-STEM image and corresponding FFT along the $[100]_p$ zone axis, intensity

line profiles and EELS mapping. The FFT of the image indicates a modulation of the crystal structure of the cubic perovskite along the $[001]_p$ direction corresponding to $c \sim 2a_p$.

The contrast differences observed in the image, in agreement with the modulation and confirmed by the intensity line profile run along $[001]_p$ on a row of columns of A-type atoms (Ba and Gd), indicate layered-type ordering of cations. The EELS mapping demonstrates that Gd and Ba are distributed in the alternating $(001)_p$ -layers and that Co and Mn are located at random within the B positions of the perovskite-type structure. When the line intensity profile is taken on columns of Co/Mn atoms along the $[001]_p$ direction, two alternated distances (0.34 nm and 0.42 nm) between these atoms are detected. Displacement of consecutive Co/Mn atoms towards the Gd-O layers is causing the alternation of these two Co/Mn-Co/Mn distances. Therefore, a combination of both compositional and displace-type two-fold modulations of the crystal structure occurs along the $[001]_p$ direction.

Fig. 4 shows the ABF and HAADF-STEM images of the $[100]_p$ zone axis for comparison. The intensity line profile run along $[001]_p$ on the rows of Gd/O/Ba/O columns in the BF image reveals two alternating Gd-O/Ba-O distances. Oxygens are drawn closer to the Gd positions (0.17 nm) than to the Ba positions (0.21 nm). Moreover, the intensity profile along (CoMn)/O columns indicates lower concentration of oxygen atoms in the Gd-O layers. This agrees with a lower contrast at the anion sites of the Gd-O layers. Therefore, we confirm that the anion vacancies are located at the Gd-O layers.

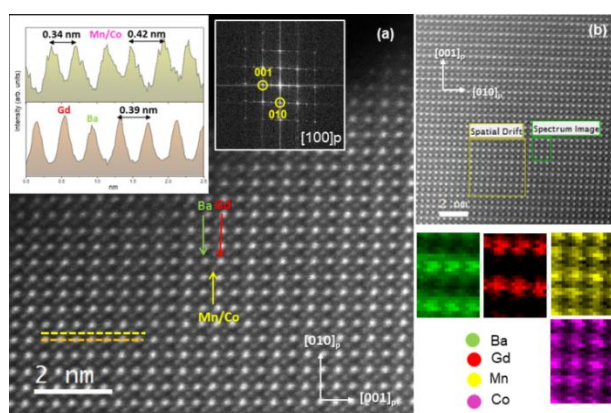


Figure 3. (a) HAADF-STEM image of a $\text{GdBaCoMnO}_{5+\delta}$ crystal along the $[100]_p$ orientation. The corresponding FFT is included as an inset. The intensity line-profiles along the Gd/Ba (orange line on the image) and along the Mn/Co (yellow line on the image) positions are displayed on the left top corner. (b) EELS maps from a crystal along the $[100]_p$ orientation.

Figure 5 shows the temperature dependence of the d.c. conductivity of different oxides of the $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ system prepared in air. The samples were heated at 1173 K for 12 h to equilibrate the oxygen content before starting the measurements on cooling.

The electrical behavior and conductivity values of the materials prepared in Ar are similar to those of the oxides with the same composition but prepared in air. For the compounds with $x=0.2$ and 0.6, the conductivity increases with temperature up to $\sim 723\text{--}773\text{K}$ and then decreases, as it is expected for the p-type electronic character of these materials (Fig. S5) and the loss of oxygen above 723 K (loss of electron hole species when oxygen vacancy content increases). However, the oxides with $x \geq 1$ present a different electrical behavior: the conductivity continuously increases with temperature and decreasing is not detected despite oxygen losses also occur above 723 K. Similar trends have previously been observed for $\text{SmSrCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ ²⁸ and $\text{NdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$,¹⁵ suggesting a change in the conduction mechanism by Mn substitution of Co. Moreover, comparison of the conductivity values at a fixed temperature with the Mn content (Fig. 6 at 923 K) indicates that the substitution of Co by Mn produces a monotonous decrease of conductivity for contents of Mn corresponding to $x \leq 1.2$ followed by a slight increase of conductivity for higher contents of Mn, which is also consistent with a change in the conduction mechanism. This variation of the conductivity with the composition seems to be characteristic of the Co/Mn systems.^{15, 30}

The electrical properties of $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ might be associated to a polaron hopping mechanism ascribed to electron hole transfer between $(\text{Co,Mn})^{4+}$ and $(\text{Co,Mn})^{3+}$ sites. It has been previously outlined that exists a preferential electrical compensation by the formation of Mn^{4+} instead of the formation of Co^{4+} , which also coexists with different degrees of oxygen vacancies depending on the level of doping.^{27, 28, 30}

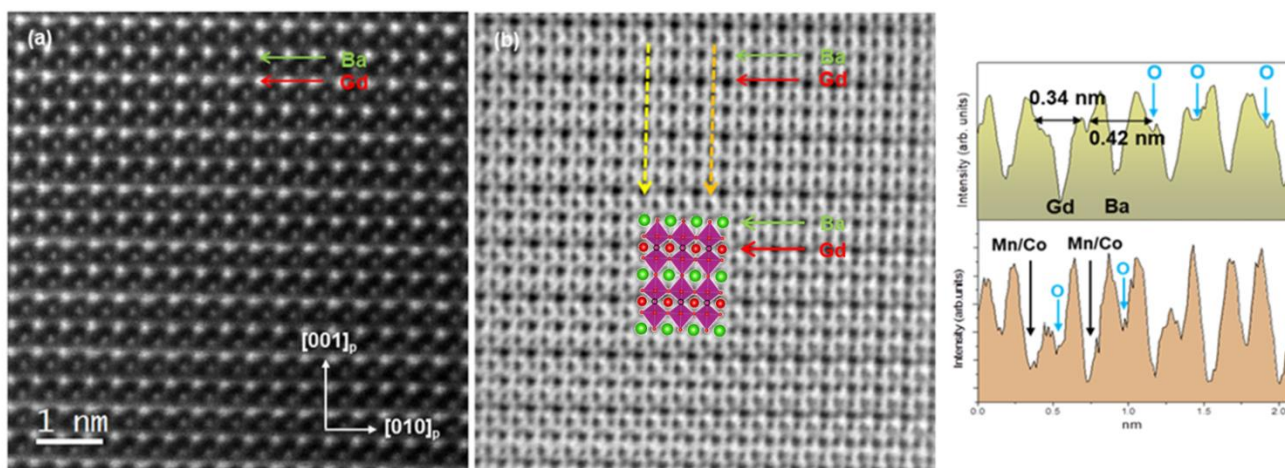


Figure 4. (a) HAADF-STEM and (b) ABF-STEM images of a $\text{GdBaCoMnO}_{5+\delta}$ crystal along the $[100]_p$ orientation. The intensity line-profile (top right) along the $[001]_p$ direction on the Ba/O/Gd/O positions (yellow line on the ABF image) reveals that oxygen columns are closer to Gd than to Ba. The intensity line profile on the (CoMn)/O positions (orange line on the ABF image) suggests that oxygen vacancies are concentrated in the Gd-O layers. The columns of oxygen atoms containing these vacancies, within the Gd-O planes, are indicated with black circles.

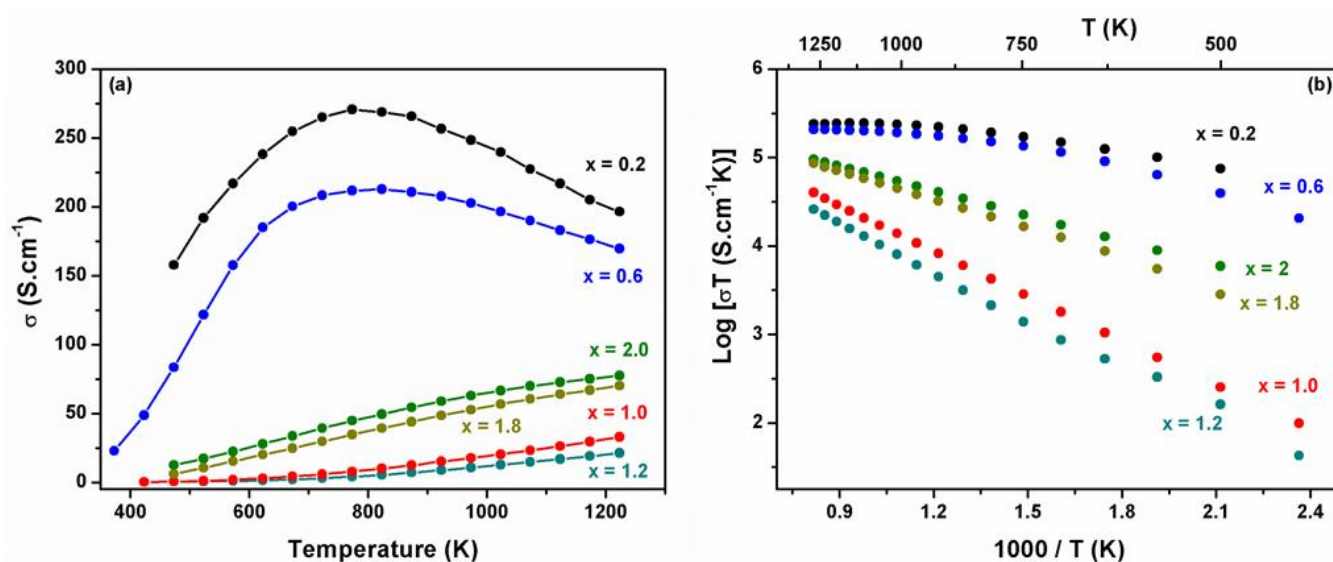


Figure 5. (a) Temperature dependence of conductivity measured in air and (b) Arrhenius representation of the total conductivity measured in air of $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ oxides with $x = 0.2, 0.6, 1.0, 1.2, 1.8$ and 2.0 prepared in air.

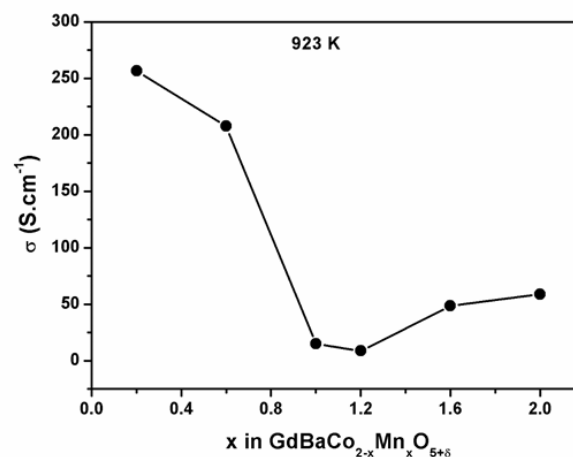
When small contents of Mn ($x=0.2$) are introduced by substitution of the Co species, the main oxidation state of Mn is close to 4+ according to our EELS results. Given that the presence of Mn^{3+} is very low for the lower contents of Mn, the electrical conduction may occur mainly by adjacent Co^{4+}/Co^{3+} sites and the Mn^{4+} ions have the effect of acting as hole traps, decreasing the electronic conductivity in comparison to $BaGdCo_2O_{5+\delta}$.

Kostoglou et al. reported that the transition rate between two adjacent cobalt sites is higher than between two adjacent manganese sites, which implies that cobalt sites are the preferred movement for holes, producing high values of conductivity and low activation energies for low contents of Mn.³⁰

Therefore, an increase in the Mn content produces a decrease of the electrical conductivity by a simple decrease of the concentration of the dominating conducting species. At this point, it is worth mentioning that in $GdBaMn_2O_{5+\delta}$, the average oxidation state of Mn was reported to be 3.28, which confirmed that the material has Mn^{4+}/Mn^{3+} species.²⁸

Taking into account that Mn^{4+} is more stable than Co^{4+} , reduction of Co^{4+} to Co^{3+} is expected when Co is substituted by Mn in this system, eliminating Co^{4+}/Co^{3+} pairs. Therefore, high Mn concentration produces enough contents of Mn^{3+} for the movement of the electron holes to take place through adjacent Mn

Figure 6. Variation of conductivity measured in air for $GdBaCo_{2-x}Mn_xO_{5+\delta}$ as a function of manganese content (x) at 923 K.



components of the symmetrical cell, was evaluated also by scanning electron microscopy (SEM). Fig S7 shows a scanning electron microscopy (SEM) image of a cross-section of one of the cells after impedance measurements, which confirms a good adhesion between electrode and electrolyte without apparent interdiffusion between the components. Homogeneous distribution of CGO and GBCM as cathode-composite constituents is also observed.

The electrochemical behavior of the $GdBaCo_{2-x}Mn_xO_{5+\delta}$ oxides prepared either in air or in argon was evaluated by complex impedance spectroscopy measurements in symmetrical cells using these materials as the electrodes, as it is explained in the experimental section. Fig. 7a shows impedance diagrams at 923 K of cells using different materials prepared in air as electrodes. The spectra were displaced to the origin of the Z' axis in order to remove the ohmic contribution and to compare different electrode processes.

As a general aspect, the electrode performance is harmed as the Mn content increases, which agrees well with the results previously reported for relative Co/Mn systems.^{15, 28, 31, 32} The area-specific-electrode-polarization resistance (ASR) is clearly lower for the samples with lower contents of Mn, $x \leq 0.6$ (Fig. 7b), corresponding to samples with higher electronic conductivity (Fig. 5) and lower oxygen content (Table 1). It is important to note that the decrease of the electronic conductivity in more than one order of magnitude for $x=1$ in comparison to $x=0.6$ only produces the deterioration of the electrode performance by a factor of 2, which points to the oxygen vacancy concentration as the key factor for the oxygen electrochemical reaction. For higher Mn contents ($x \geq 1.4$), the ASR increases (Fig. 7b), despite having similar or even higher values of electronic conductivities. Table 1 shows that these compositions possess low contents of oxygen deficiency, which diminishes as the Mn concentration increases, concomitant with the increasing of ASR, supporting that the oxygen content might be the dominant factor in the electrode performance.

Fig. 8a and b show impedance diagrams at 923 K of cells assembled with electrodes corresponding to $GdBaCo_{2-x}Mn_xO_{5+\delta}$ oxides ($x = 0, 0.6$ and 2.0) prepared either in air or in argon. For low contents of Mn, the samples have similar ASR values independent on the synthesis conditions of the material, however, for high Mn contents, the compositions prepared in argon show lower ASR values than those corresponding to compositions prepared in air. Taking into account

sites, given that the transition rate for Mn^{4+}/Mn^{3+} sites is considerably higher than that of Mn^{4+}/Co^{3+} sites.³⁰ Once the dominant conduction-mechanism consists of polaron-hopping between Mn^{4+} and Mn^{3+} sites ($x > 1$), the conductivity increases with increasing the amount of Mn^{4+}/Mn^{3+} species. It is important to note that the loss of oxygen in samples with $x \geq 1$ for $T > 723$ K is not expected to produce a decrease of the concentration of active holes for the electrical conduction. The oxidation states of Mn are generally very stable with temperature, suggesting that the oxygen loss may be associated to changes in the oxidation state of Co species. As a consequence, the concentration of electronic-conducting species, associated to Mn^{4+}/Mn^{3+} pairs, should not be considerably affected by temperature, which is consistent with the behaviour observed for the samples with higher contents of Mn (Fig. 6).

The chemical compatibility of the oxides with the electrolyte (CGO) was determined prior to the study of their electrochemical properties in symmetrical cells. The PXRD patterns of the composites $GdBaCo_{2-x}Mn_xO_{5+\delta}$:CGO (70 : 30 wt%) heated at 1173 K for 12 hours only show reflections corresponding to the material under study and CGO (Fig S6 shows one example), suggesting that reaction between these two compounds does not occur or that in case of reaction the fraction of the new phase(s) is below the detection limit of XRD. Electrolyte/Electrodes quality of contact, in addition with possible formation of new phases in the surface of contact between

that all the compositions prepared in argon present ordering of Gd and Ba cations in the crystal structure, which only exists for $0 < x < 1.4$ in the samples prepared in air, these results demonstrate that the cells with electrodes using oxides presenting cation ordering have similar ASR values no depending on the synthesis conditions of the

material. However, the cells using layered-perovskites in the electrodes present significantly lower ASR values than those using compounds of the same composition but with the Ba and Gd atoms statistically distributed within the structure.

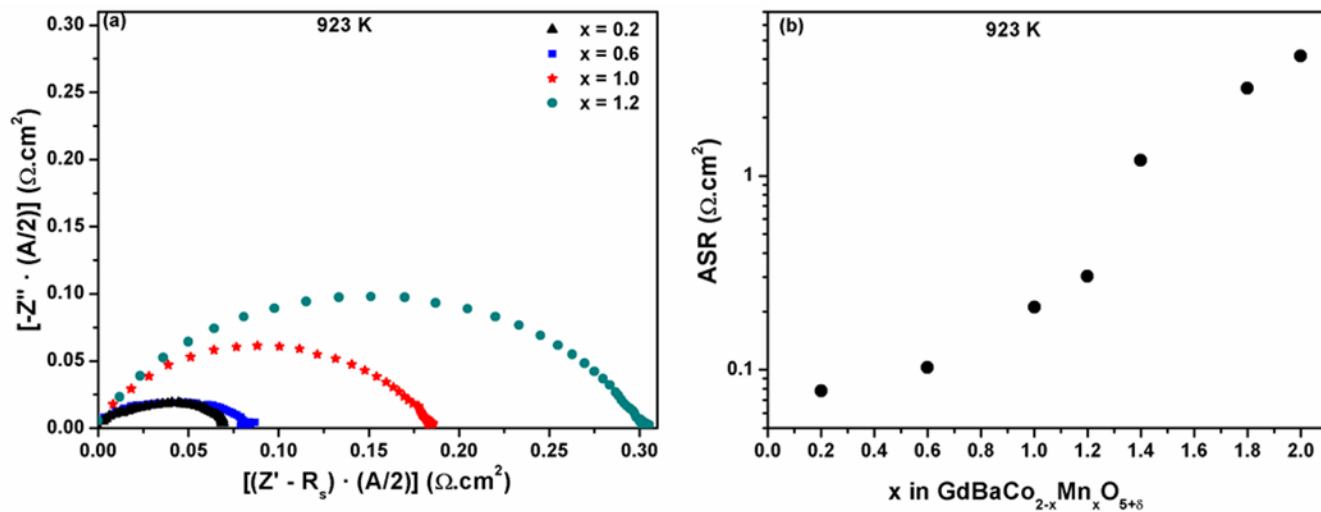


Figure 7. (a) Impedance spectra of symmetrical cells using $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ prepared in air with $x = 0.2, 0.6, 1.0$ and 1.2 . (b) Variation of ASR values for $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ prepared in air as a function of manganese content at 923 K .

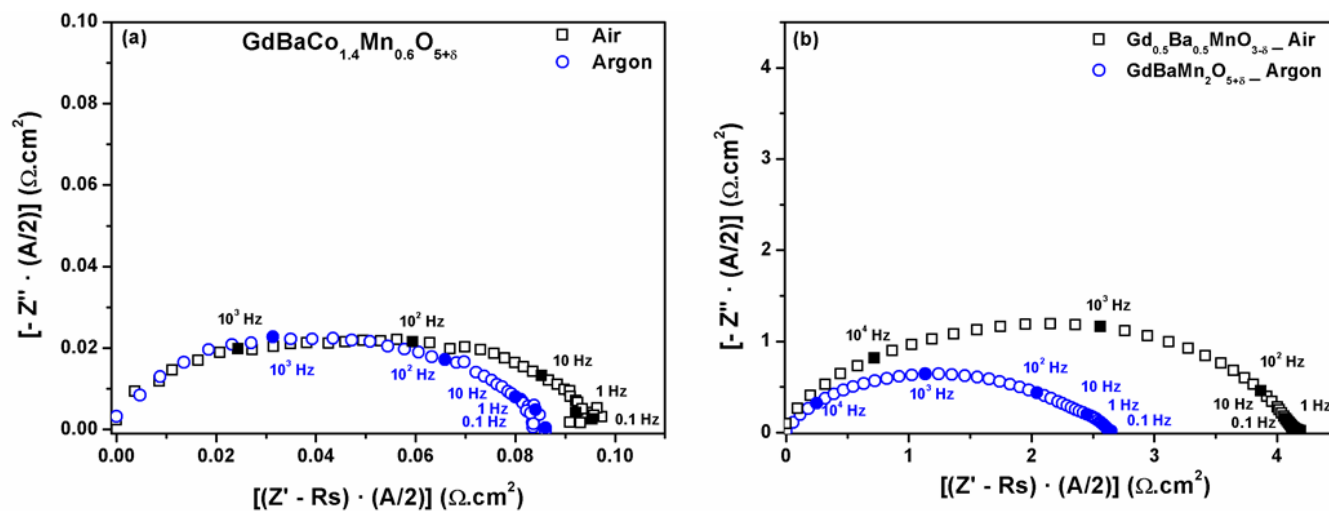


Figure 8. Impedance spectra of symmetrical cells $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}:\text{CGO} / \text{CGO} / \text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}:\text{CGO}$ at 923 K in air. a) $x = 0.6$ prepared in air and argon; b) $x = 2.0$ prepared in air and argon.

Table 2. ASR values at 923 K of symmetrical cells with different oxides of the system $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ prepared in air and argon.

| Composition | ASR ($\Omega\cdot\text{cm}^2$) at 923 K | |
|-------------|--|---------------------------|
| | Samples prepared in Air | Samples prepared in Argon |
| | | |

| | | |
|--|-------|-------|
| GdBaCo_{1.8}Mn_{0.2}O_{5+δ} | 0.078 | 0.075 |
| GdBaCo_{1.4}Mn_{0.6}O_{5+δ} | 0.095 | 0.082 |
| GdBaCoMnO_{5+δ} | 0.210 | 0.187 |
| GdBaCo_{0.6}Mn_{1.4}O_{5+δ} | 1.10 | 1.09 |
| GdBaCo_{0.2}Mn_{1.8}O_{5+δ} | 2.65 | 1.36 |
| GdBaMn₂O_{5+δ} | 4.13 | 2.89 |

Therefore, the GdBaCo_{2-x}Mn_xO_{5+δ} system seems to be a new example of experimental evidence of the better electrochemical properties of layered- perovskites compare to those of perovskites with random location of the A-cations and therefore random location of the oxygen vacancies. Table 2 summarizes the ASR values of all the cells measured at 923 K. Values lower than 0.15 Ω.cm² are found for cells with electrodes using GdBaCo_{2-x}Mn_xO_{5+δ} oxides with $x < 1.0$, indicating good behavior of these materials as air-electrodes in IT-SOFCs, although optimization of the cell construction is essential for the application of the materials.

Conclusions

Materials of the GdBaCo_{2-x}Mn_xO_{5+δ} $0 \leq x \leq 2$ system have been synthesized under different conditions (in air or argon atmospheres) highly impacting on the Gd/Ba cation ordering of the crystal structure. Layered-type ordering of Gd and Ba in the perovskite-type structure occurs in the whole range of composition of the system when the materials are prepared in argon. However, layered-perovskites are formed in air only for compositions corresponding to $x < 1.4$. A 2-fold modulation associated to correlated displacements of consecutive Co/Mn atoms towards the Gd-O layers is observed in GdBaCoMnO_{5+δ} in addition to the layered cation-ordering.

These materials are p-type conductors and the dc conductivity results indicate a change in the conduction mechanism in the system from $x > 1$. The polaron hopping mechanism ascribed to electron hole transfer between M⁴⁺/M³⁺ sites (M = Co, Mn) depends on the concentration of Co and Mn in the oxide. The conductivity decreases by substitution of Mn for Co because the electron-hole transition rate is higher between Co⁴⁺/Co³⁺ sites than between Mn⁴⁺/Mn³⁺ sites.

Electrochemical studies on symmetrical cells using these materials as electrodes reveal that substitution of Mn for Co, in the GdBaCo_{2-x}Mn_xO_{5+δ} $0 \leq x \leq 2$ system, increases the ASR values probably due to the decreasing of the anion vacancies. On the contrary, TEC values decrease with increasing the Mn content. Layered-type ordering of the Gd and Ba atoms seems to affect the electrochemical properties of these materials in such a way that materials with ordering show lower ASR values than those with similar composition but the A cations statistically distributed, which implies that the oxygen vacancies are also located at random. Some of these oxides give ASR values lower than 0.15 Ω.cm² at 923 K, indicating their promising good behaviour as air electrodes in IT-SOFCs by optimizing the cell.

Acknowledgements

This work has been supported by MINECO with Projects MAT2013-46452-C4-4-R, MAT2016-78362-C4-1-R, MAT2016-78362-C4-4-R, ENE2015-66183-R and CM with project MATERYENER3CM-S2013/MIT-2753. U.A. also thanks the Universidad San Pablo for financial support. S. García-Martín thanks Prof. West for his unique teaching on solid state chemistry during her post-doc time at the University of Aberdeen.

References

- 1 A. Chang, S.J. Skinner, J.A. Kilner, *Solid State Ionics*, 2006, **177**, 2009-2011.
- 2 A. Tarancón, S. J. Skinner, R. J. Chater, F. Hernández-Ramírez, J. A. Kilner, *J. Mater. Chem.*, 2007, **17**, 3175-3181.
- 3 D. Muñoz-Gil, D. Pérez-Coll, J. Peña-Martínez, S. García-Martín, *J. Power Sources*, 2014, **263**, 90-97.
- 4 A.A. Taskin, A. N. Lavrov, Y. Ando, *Prog. Solid State Chem.*, 2007, **35**, 481-490.
- 5 D. Parfitt, A. Chroneos, A. Tarancón, J. A. Kilner, *J. Mater. Chem.*, 2011, **21**, 2183-2186.
- 6 A. Tarancón, D. Marrero-López, J. Peña-Martínez, J.C. Ruiz-Morales, P. Núñez, *Solid State Ionics*, 2008, **179**, 611-618.
- 7 L. Moggi, F. Prado, C. Jiménez, Alberto Caneiro, *Solid State Ionics*, 2013, **240**, 19-28.
- 8 K. R. Zhdanov, M. Yu. Kameneva, L. P. Kozeeva, A. N. Lavrov, *Physics of the Solid State*, 2010, **52**, 1688-1693.
- 9 S. Roy, M. Khan, Y. Q. Guo, J. Craig, N. Ali, *Phys. Rev. B.*, 2002, **65**, 064437-5.
- 10 R. Pelosato, G. Cordaro, D. Stucchi, C. Cristiani, G. Dotelli, *Journal of Power Sources*, 2015, **298**, 46-67.
- 11 B. Wei, Z. Lu, D. Jia, X. Huang, Y. Zhang, W. Su *International J. of Hydrogen Energy*, 2010, **35**, 3775-3782.
- 12 D. Muñoz-Gil, D. Pérez-Coll, E. Urones-Garrote, U. Amador, S. García-Martín, *J. Mater. Chem. A*, 2017, **5**, 12550-12556.
- 13 D. A. Medvedev, T. A. Zhuravleva, A. A. Murashkina, V. S. Sergeeva, B. D. Russ. *J. Phys. Chem.*, 2010, **84**, 1623-1627.
- 14 Y. N. Kim, A. Manthiran, *J. Electrochem. Soc.*, 2011, **158**, B276-B282.
- 15 T. Broux, M. Bahout, J.M. Hanlon, O. Hernandez, S. Paofai, A. Berenov, S.J. Skinner, *J. Mater. Chem. A*, 2014, **2**, 17015-17023.
- 16 O. L. Pineda, Z. L. Moreno, P. Roussel, K. Świerczek, G. H. Gauthier, *Solid State Ionics*, 2016, **288**, 61-67.
- 17 F. Tonus, M. Bahout, V. Dorcet, G. H. Gauthier, S. Paofai, R. I. Smith, S. J. Skinner *J. Mater. Chem. A*, 2016, **4**, 11635-11647.
- 18 D. Muñoz-Gil, D. Ávila-Brandé, E. Urones-Garrote and S. García-Martín, *Dalt. Trans.*, 2015, **44**, 10867-10874.
- 19 S. García-Martín, K. Manabe, E. Urones-Garrote, D. Ávila-Brandé, N. Ichikawa, Y. Shimakawa, *Inorg. Chem.* 2017, **56**, 1412-1417.
- 20 S. Sengodan, S. Choi, A. Jun, T. Ho Shin, Y.W. Ju., H. Y. Jeong, J. Shin, J. T. S. Irvine, G. Kim, *Nature Mater.*, 2015, **14**, 205-209.

- 21 T. H. Shin, J. H. Myung, M. Verbraeken, G. Kim, J. T. S. Irvine, *Faraday Discuss.*, 2015, **182**, 227–239.
- 22 Y. N. Kim, A. Manthiran, *J. Mater. Chem. A*, 2015, **3**, 24195–24210.
- 23 A. Le Bail, H. Duroy, J.L. Fourquet, *Materials Research Bulletin*, 1988, **23**, 447–452.
- 24 J. Rodríguez-Carvajal, *Phys. B*, 1993, **192**, 55–69.
- 25 J. C. Pérez Flores, C. Ritter, D. Pérez-Coll, G. C. Mather, F. García-Alvarado and U. Amador, *J. Mater. Chem.*, 2011, **21**, 13195.
- 26 H. K. Schmid and W. Mader, *Micron*, 2006, **37**, 426–432.
- 27 K.T. Lee, A. Manthiram, *Journal of Power Sources*, 2006, **158**, 1202–1208.
- 28 Y. Wang, X. Zhao, S. Lü, X. Meng, Y. Zhang, B. Yu, X. Li, Y. Sui, J. Yang, C. Fu, Y. Ji, *Ceramics International*, 2014, **40**, 11343–11350.
- 29 D. Ávila-Brandé, G. King, E. Urones-Garrote, Subakti, A. Llobet, S. García-Martín, *Adv. Funct. Mater.*, 2014, **24**, 2510–2517.
- 30 G.Ch. Kostoglou, P. Fertis, Ch. Ftikos, *Solid State Ionics*, 1999, **118**, 241–249.
- 31 H. Lv, B-Y. Zhao, Y-J. Wu, G. Sun, G. Chen, K. Ao Hu, *Materials Research Bulletin*, 2007, **42**, 1999–2012.
- 32 M.B. Phillipps, N.M. Sammes, O. Yamamoto, *Solid State Ionics*, 1999, **123**, 131–138.

Crystal structure and compositional effects on the electrical and electrochemical properties of $\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ $0 \leq x \leq 2$ oxides for use as air electrodes in solid oxide fuel cells

Daniel Muñoz-Gil, Esteban Urones-Garrote, Domingo Pérez-Coll, Ulises Amador and Susana García-Martín

$\text{GdBaCo}_{2-x}\text{Mn}_x\text{O}_{5+\delta}$ is a new system in the family of layered-perovskites which evidence better electrochemical properties when there is layered-type ordering between the Gd and Ba cations than for the materials with random location of these cations.

