1. Introduction

Currently, solid oxide fuel cells (SOFCs) are one of the most promising electrochemical devices developed for energy conversion [1]. These devices, however, may present complex problems such as electrode degradation and interfacial reactions between the electrolyte and the electrodes due to their high operating temperatures, above 1000 °C [2]. To avoid these problems, it is desirable to operate SOFCs at temperatures between 500 °C–800 °C [2, 3], known as ‘intermediate-temperature solid-oxide fuel cells’ (IT-SOFCs). Nonetheless, intermediate temperatures affect the performance of the cathode, which is responsible for catalyzing the reduction of O₂(δ−) to oxide ions (O²−). As the temperature decreases, the cathode presents a significant drop of its electrochemical response, thus decreasing the energy density of the device. One of the main improvements required for the commercialization of IT-SOFCs is the development of new mixed ionic-electronic conductors (MIECs) that confer a better performance at intermediate temperatures [4–6]. MIEC materials provide not only the electrons for the reduction of oxygen but also the ionic conduction required to ensure the transport of the formed oxide ions [7]. This allows the oxygen reduction reaction to take place on the entire surface of the electrode, unlike conventional electronic conductors in which the reaction occurs only on the triple points [electrolyte/electrode/gas] [7]. Pioneer research on MIEC cathodes for IT-SOFCs is focused on the search of perovskite-type structures that combine high tolerance to oxygen vacancies, electronic conductivity and electrochemical activity for oxygen reduction [4, 8, 9].

SrCoO₃₋ₓδ-based perovskites are promising candidates to fulfill this role because they are MIECs with high ionic conductivity [10–14]. Particularly, the cubic-3C phase of SrCoO₃₋ₓδ is of great interest as it offers high O²−-conductivity due to its corner-linked octahedral network while the cubic structure vacancies allow for an oxygen permeation flux [15–17]. Unfortunately, this phase is not stable at temperatures lower than 900 °C and suffers a transition to a dielectric hexagonal-2H phase [16].
Nevertheless, the high-temperature cubic phase can be retained at lower temperatures, and even at room temperature, by partially doping the cobalt site with other transition metal cations (usually tetra-, penta- or hexavalent). The inclusion of a highly charged cation at the octahedral position induces electrostatic repulsion effects that destabilize the octahedral face-sharing configuration present in the 2H hexagonal phase [18]. Hence, the phase transition can be avoided by generating a solid solution of the type SrCo_{1−x}M_{x}O_{3−δ} where the incorporation of M^{n+} cations stabilizes the new phase. In this framework, there are several articles analyzing the effect of partial substitutions of cobalt by Ti^{4+} [3], V^{5+} [3], Nb^{5+} [17], Sb^{5+} [18], Mo^{6+} [19] or Ta^{5+} [20] ions, in which the stabilization of the cubic phase at room temperature is reported.

Particularly, the incorporation of Nb^{5+} and Ta^{5+} ions at the Co positions in the SrCo_{1−x}M_{x}O_{3−δ} system was recently reported by Cascos et al [21] and Chen et al [20], showing that these ions promote the stabilization of a tetragonal superstructure and cubic phase, respectively. However, these materials were synthesized by methods that employed high temperatures, generating crystallite sizes on a micrometric scale [17, 20, 21]. No wet chemistry method for the synthesis of cubic Nb/Ta-doped SrCoO_{3−δ} perovskites has been reported to date. Based on this context, the present study is focused on the synthesis of cubic SrCo_{0.90}M_{0.10}O_{3−δ} perovskites (with M = Nb^{5+} and Ta^{5+}), using temperatures lower than those already reported in the above-mentioned works. Specifically, a tartrate-decomposition sol-gel method was employed. The materials developed in this work were characterized with x-ray powder diffraction, thermal gravimetric analysis, spectroscopic and microscopic measurements.

2. Materials and methods

SrCo_{0.90}M_{0.10}O_{3−δ} (M = Nb, Ta) powders were prepared from metal nitrates of analytical grade with Nb_{2}O_{5(s)} or Ta_{2}O_{5(s)} as precursors of the doping ions. A dissolution treatment was necessary to synthesize the samples because the oxides of niobium and tantalum are insoluble in water, even with small aggregates of HNO_{3(ac)}

Hydrofluoric acid (48%–51% W/V), ammonia (28%–30% W/V), hydrogen peroxide (30% W/V) and (NH_{4})_{2}C_{2}O_{4} · H_{2}O_{(s)} were used in order to carry out the dissolution process of niobium and tantalum oxides.

2.1. Nb_{2}O_{5(s)} and Ta_{2}O_{5(s)} dissolution

The dissolution of M_{2}O_{5(s)} (M = Nb and Ta) was achieved via the formation of a soluble complex of the corresponding metallic tartrates [22]. The M_{2}O_{5(s)} oxide was dissolved in HF 48%–51% W/V under a heated water bath with stirring. When the complete dissolution of the oxide was reached, the heating was halted and a solution of ammonium oxalate was added to regulate pH. The precipitation of a hydrated oxide was then produced by the continuous dripping of ammonia into the solution, under an ice bath. The precipitate was filtered and washed with ammonia solution to ensure the complete elimination of fluorine. Finally, the required quantity of hydrated oxide was dissolved with tartaric acid and continuous additions of hydrogen peroxide.
under heating with constant stirring, until complete dissolution (yellow colored for niobium and white for tantalum). A complete summary of the procedure is detailed in figure 1.

### 2.2. Sol-gel synthesis

The synthesis of samples was carried out using the sol-gel method. Stoichiometric quantities of the strontium and cobalt nitrates were dissolved along with the appropriate amount of Nb/Ta tartrate solution. Solid tartaric acid (a complexing agent) was added in a molar ratio equivalent to twice the total cations, and ethylene glycol (a polymerization agent) in a 1:3 ratio in relation to tartaric acid. The resulting solutions were thermally treated, with magnetic stirring, until the formation of a vermilion precursor gel. The resulting gel was treated following a three-stage procedure: 100 °C for 2 h (to evaporate the remaining water), 300 °C for 3 h and 600 °C for 12 h (to eliminate nitrates and remains of organic matter through the formation of CO₂(g) and NO₂(g)). The resulting black precursor was calcined in air atmosphere for 36 h (48 h for Ta-doped sample) in subsequent heat treatments at increasing temperatures until the highest degree of purity was achieved. The final calcination temperatures were of 975 °C and 1075 °C for the Nb-doped and Ta-doped samples, respectively. Two samples of each composition were synthesized, demonstrating the versatility and good reproducibility of the method.

### 2.3. Characterization

The structural characterization of the products was carried out by x-ray powder diffraction (XRPD) using a PANalytical x-ray diffractometer model X’Pert Pro with PIXcel detector (40 kV, 40 mA) with a graphite
monochromator, in Bragg-Brentano reflection geometry with CuKα radiation (\(\lambda = 1.5418 \text{ Å}\)). The 2\(\theta\) range was of 15°–100° in steps of 0.02°. The refinement of the crystal structures was performed by the Rietveld method \[23\] using the FULLPROF program \[24\]. A pseudo-Voigt shape function was used.

Infrared spectroscopy with Fourier transform (FT-IR) studies were also carried out using a Brüker IFS-28 FT-IR spectrometer, in the range between 4000–400 cm\(^{-1}\), with a spectral resolution of 2 cm\(^{-1}\). Furthermore, Raman spectroscopy was used to probe the symmetry of the crystal structure of synthesized samples. Raman spectra were obtained with a HORIBA spectrometer model LabRAM HR 800, using a green laser of \(\lambda = 514.5 \text{ nm}\) and a power of 4 mW with diffraction grating of 600 lines mm\(^{-1}\).

Thermogravimetric analyses were carried out to determine the oxygen vacancies (\(\delta\)) in the samples with a Shimadzu DTG-60 device in air flow up to 900 °C, using a heating rate of 10 °C min\(^{-1}\) with \(\alpha\)-alumina as reference and crucible material \[21, 25\]. The morphology of the samples was observed by field-emission scanning electron microscopy (FE-SEM) images using a Zeiss Sigma FE-SEM microscope.

3. Results and discussion

3.1. XRPD analysis

Figure 2 shows XRPD patterns at room temperature for the (a) SrCo\(_{0.90}\)Nb\(_{0.10}\)O\(_{3-\delta}\) sample synthesized at 900 °C, 950 °C and 975 °C, and (b) SrCo\(_{0.90}\)Ta\(_{0.10}\)O\(_{3-\delta}\) sample heat-treated at 1000 °C, 1050 °C and 1075 °C. For the Nb-doped sample calcined at 900 °C, it was observed that the main phase correlated to a cubic perovskite-type one with the presence of an orthorhombic (brownmillerite) phase (ICSD #162239) \[26\] and a hexagonal phase (ICSD #427011) \[27\], and a rhombohedral phase (ICSD #81312) as impurities. In addition, the small peak present at \(\sim 31°\) in 2\(\theta\), is probably due to a residue of Co\(_3\)O\(_4\) (ICSD #27497). A decrease of the intensity of the peaks corresponding to these secondary phases was seen with successive thermal treatments until a final heating step of 975 °C, where the sample exhibited a single-phase perovskite. In the case of the SrCo\(_{0.90}\)Ta\(_{0.10}\)O\(_{3-\delta}\) sample, it was necessary to raise the calcination temperature to 1075 °C to increase its purity.

Rietveld analysis of XRPD data for both final samples (SrCo\(_{0.90}\)Nb\(_{0.10}\)O\(_{3-\delta}\) calcined at 975 °C and SrCo\(_{0.90}\)Ta\(_{0.10}\)O\(_{3-\delta}\) calcined at 1075 °C) was performed using the crystal structure data reported in the ICSD.
Inorganic Crystal Structure Database database. For these refinements, tetragonal P4\(/\)mmm (ICSD #238964) and cubic Pm-3m (ICSD #190750) models with similar structure to those reported in literature \([17, 20, 21]\) were used. Knowledge of the crystal structure of these materials is important to understand their potential application as an IT-SOFC cathode. It is important to determine the distribution of oxygen vacancies or the spatial dispositions of the atoms in the crystal lattice, as they are directly related to the electrochemical performance. A tetragonal crystal superstructure would locate the oxygen vacancies on a single plane of \((\text{Co}/\text{M})\text{O}_6\) octahedra \([17, 21]\), whereas the cubic phase would have the vacancies distributed homogeneously throughout the material, thus increasing its ionic conductivity in all directions \([16]\).

Both models would explain all peaks present in the XRPD patterns of both samples. However, the tetragonal model assigns a peak (centered on \(\sim 25.6^\circ\) in 2\(\theta\)) which was not detected in the experimental pattern, indicating that this structural model is inadequate for these samples. Further discrepancies can be seen in the amplified range near \(\sim 68.5^\circ\) in 2\(\theta\) shown in figure 3. Here it can be observed that the cubic model better fits the experimental data, suggesting two overlapping peaks rather than an asymmetric peak. Thus, the Rietveld analysis confirms that the main diffraction peaks can be well indexed according to a cubic perovskite structure with Pm-3m space group. Therefore, these results show that the sol-gel method reported in the present work (tartrate-precursor decomposition) successfully lowered the calcination temperature by 225 \(^\circ\)C for the Nb-doped sample and by 125 \(^\circ\)C for the Ta-doped sample, with respect to traditional solid-state syntheses of these materials \([20, 28]\).

Rietveld refinements of XRPD patterns at RT for both samples are presented in figure 4. The \(a\) parameters of the Nb-doped and Ta-doped samples resulted of 3.8726(2) \(\AA\) and 3.8762(1) \(\AA\), respectively. No impurity phases were detected in the SrCo\(_{0.90}\)Nb\(_{0.10}\)O\(_{3-\delta}\) sample while the SrCo\(_{0.90}\)Ta\(_{0.10}\)O\(_{3-\delta}\) sample was obtained with a small impurity of a tetragonal phase (ICSD #028918), shown in the second group of Bragg’s reflections.
information obtained from these Rietveld refinements, a representation of the structural arrangement of the ions in the crystal lattice was generated by the Vesta 3.1.8 program \[29\] as presented in figure 4 \(\text{see inset}\). It can be observed in this figure that the \((\text{Co}/\text{M})_6\) octahedra are joined through their vertices, creating a compact packed lattice in which Sr\(^{2+}\) ions are placed between octahedra.

3.2. FT-IR and Raman spectroscopy
To complement the XRPD study, FT-IR analysis of \(\text{SrCo}_{0.90}\text{Nb}_{0.10}\text{O}_{3-\delta}\) and \(\text{SrCo}_{0.90}\text{Ta}_{0.10}\text{O}_{3-\delta}\) samples was also carried out. Perovskite-type oxides have an intense band at \(\sim 600\ \text{cm}^{-1}\), attributed to the asymmetric M–O stretch of the MO\(_6\) octahedra, where M represents the transition metal \[30\]. The spectra obtained for these samples are presented in figure 5, bounded between 400 and 4000 cm\(^{-1}\). It can be observed in this figure that both samples presented an intense band centered at 580 cm\(^{-1}\), which is due to the stretching vibrations of the MO\(_6\) octahedra. The small absorption peaks around 2343 cm\(^{-1}\), 2847 cm\(^{-1}\) and 2921 cm\(^{-1}\) present in the Ta-doped sample are due to CO\(_2\) molecules present in air and to the symmetric and antisymmetric stretching of C–H bonds, respectively. It should be pointed out here that the presence of such bands has not been considered as contamination of the sample, but may be related to residual organic matter. A broad absorption band at \(\sim 3400\ \text{cm}^{-1}\) is attributed to the hydroxyl (–OH) group of H\(_2\)O, indicating the existence of water absorbed on the surface of the sample.

\textbf{Figure 5.} FT-IR spectra for (a) \(\text{SrCo}_{0.90}\text{Nb}_{0.10}\text{O}_{3-\delta}\) and (b) \(\text{SrCo}_{0.90}\text{Ta}_{0.10}\text{O}_{3-\delta}\). The intense band at \(\sim 580\ \text{cm}^{-1}\) is characteristic of Perovskite-type oxides. \textit{Inset:} Raman spectra for \(\text{SrCo}_{0.90}\text{Ta}_{0.10}\text{O}_{3-\delta}\).

\textbf{Figure 6.} TGA curves for \(\text{SrCo}_{0.90}\text{Nb}_{0.10}\text{O}_{3-\delta}\) (bold) and \(\text{SrCo}_{0.90}\text{Ta}_{0.10}\text{O}_{3-\delta}\) (dashed) in air flow.
Additionally, a Raman analysis was performed to revalidate that the samples present a cubic phase. Using a group theory analysis, Sacchetti et al predicted that a cubic structure of solids of similar composition should not have any active modes in Raman [31]. In this framework, Zhu et al reported that a tetragonal P4/mmm structure of Nb-doped strontium cobaltite samples exhibit six active modes in Raman while a cubic Pm-3m one does not present any active mode [28]. The spectrum obtained is presented in figure 5 (see inset), bounded between 400 and 3500 cm$^{-1}$. Analyzing this spectrum, the lack of active phonon peaks confirmed that the samples present a cubic structure. Weak signals observed at $\sim$650 cm$^{-1}$ are attributed [31] to Raman prohibited modes that are activated by disorder in the crystal lattice, or by second order Raman scattering, and not by the presence of a significant tetragonal phase.

Figure 7. FE-SEM images with decreasing magnifications for the samples obtained after the final calcination treatment: (a)–(d) SrCo$_{0.90}$Nb$_{0.10}$O$_{2.85}$ calcined at 975°C and (e)–(h) SrCo$_{0.90}$Ta$_{0.10}$O$_{2.85}$ calcined at 1075°C.
3.3. Thermal gravimetric analysis
The TGA curves obtained for these samples are shown in figure 6. A pronounced and continuous loss of mass was observed for temperatures higher than 350 °C, for both samples. A weight loss equivalent to 1.19% and 1.17% is seen for SrCo$_{0.90}$Nb$_{0.10}$O$_{3-\delta}$ and SrCo$_{0.90}$Ta$_{0.10}$O$_{3-\delta}$, respectively, at 850 °C. No thermodynamic process was present in the differential thermic analysis (DTA) (not shown), as such the weight change is completely attributed to oxygen loss. Consequently, an oxygen non-stoichiometry of $\delta = 0.15$ was calculated for both samples. This allowed the chemical formulas to be rewritten as: SrCo$_{0.90}$Nb$_{0.10}$O$_{2.85}$ and SrCo$_{0.90}$Ta$_{0.10}$O$_{2.85}$. Assuming an oxidation state of $5^+$ for Nb and Ta cations in the structure, an average oxidation state of $3.56^+$ was obtained for Co cations in both samples. These analyses indicated that, under IT-SOFC working conditions, the materials are oxygen deficient improving the movement of O$^{2-}$ through these MIEC oxides [17]. After the thermogravimetric analysis, the XRPD patterns of the residual solids were measured and resulted indistinguishable from the starting patterns. This confirms no decomposition or phase transitions after heating in air, and suggests a complete reversibility of the absorption-desorption oxygen process.

3.4. Microstructural analysis
The morphology of the samples obtained after the final calcination treatment was analyzed by FE-SEM, as shown in figure 7. Micrometric particles of approximately 2 μm can be observed in both cases. Furthermore, a nanometric dendritic habit can be seen evenly distributed over the whole surface of each sample, with an average grain size less than 100 nm.

Previous solid state syntheses of these materials have resulted in similar micrometric-sized particles [20, 28], although none have been reported to exhibit a superficial nanometric habit. This is to be expected, as this method of synthesis is known to yield products with higher particle size and low surface area [32]. However, wet chemistry routes of synthesis, like the sol-gel method, are known not only to reduce calcination temperature but also to produce nanomaterials [32]. Therefore, the novel nano-morphology observed is attributed to the tartrate-precursor decomposition sol-gel method employed.

A mixed nano-micro surface brings forth a new prospect for the construction of IT-SOFC electrodes. This new nano-component could give the electrode a high density of defects (grain edges, polyoriented edges, punctual defects, etc) and greater surface area which could lead to an improvement of previously measured electrochemical properties [5, 6, 28, 32].

4. Conclusions
In summary, the incorporation of Nb$^{5+}$/Ta$^{5+}$ as dopant ions allowed the stabilization of a Pm-3m cubic phase in SrCo$_{0.90}$M$_{0.10}$O$_{2.85}$ perovskites. The use of the tartrate-precursor decomposition sol-gel method successfully lowered the synthesis temperature by 225 °C for the Nb-doped sample and 125 °C for the Ta-doped sample. Unlike the morphology reported for samples synthesized by the solid-state method, this method presented micrometric particles along with a novel surface nanometric dendritic habit. This change in morphology is tied to an increase in the surface/volume ratio that could prove useful in a SOFC electrode. To the best of our knowledge, this marks the first instance that a doped cubic phase SrCoO$_3$ perovskite with mixed nano-micro morphology has been synthesized by a wet chemistry method.

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References
[1] Kendall K and Kendall M 2016 High-Temperature Solid Oxide Fuel Cells for the 21st Century: Fundamentals, Design and Applications 2nd Edn (Cambridge, MA, USA: Academic) 2015 pp 1–24
[2] Schrodi N, Bucher E, Egger A, Kreiml P, Teichert C, Hschen T and Sitte W 2015 Long-term stability of the IT-SOFC cathode materials La$_0.6$Sr$_0.4$CoO$_{3-\delta}$ and La$_2$NiO$_{4+\delta}$ against combined chromium and silicon poisoning Solid State Ion. 276 62–71
[3] Cascos V, Troncoso L and Alonso J A 2015 New families of \( \text{M}^{\text{III}} \)-doped \( \text{SrCo}_{x-\delta}\text{M}_\text{O}_3 \) perovskites performing as cathodes in solid-oxide fuel cells Inter. J. Hydr. Energy 40 134

[4] Jun A, Kim J, Shin J and Kim G 2016 Perovskite as a cathode material: a review of its role in solid-oxide fuel cell technology ChemElectroChem 3 311–30

[5] Mejía Gómez A E, Sacanell I, Leyva A G and Lamas D G 2016 Performance of \( \text{La}_\alpha\text{Sr}_\beta\text{Co}_{1-\gamma}\text{Fe}_\gamma\text{O}_3 \) for \( \gamma = 0.2, 0.3 \) and 0.8 nanostructured cathodes for intermediate-temperature solid-oxide fuel cells: influence of microstructure and composition Ceram. Int. 42 3145–53

[6] Mejía Gómez A E, Lamas D G, Leyva A G and Sacanell J 2019 Nanostructured \( \text{La}_\alpha\text{Sr}_\beta\text{Co}_{1-\gamma}\text{O}_3 \) as cathode for solid oxide fuel cells Ceram. Int. 45 14182–7

[7] Aguadero A et al 2012 Materials development for intermediate-temperature solid oxide electrochemical devices J. Mater. Sci. 47 3925–48

[8] Zhu X, Zhai L, Gao X, Li A and An H 2018 A novel cathode material \( \text{Pr}_\alpha\text{Sr}_\beta\text{Co}_\gamma\text{Fe}_\delta\text{O}_3 \) for intermediate temperate solid oxide fuel cell Mater. Res. Express 5 26307

[9] Themmozhi N, Sasi Kumar S, Sonai S and Saravanan R 2017 Electronic structure and chemical bonding in \( \text{La}_\alpha\text{Sr}_\beta\text{Mn}_\gamma\text{O}_3 \) perovskite ceramics Mater. Res. Express 4 046103

[10] Nagai T, Ito W and Sakon T R 2007 Relationship between cation substitution and stability of perovskite structure in \( \text{SrCo}_\gamma\text{O}_3 \) J. Solid State Chem. 179 362–9

[11] Deng Z Q, Liu W, Chen C S, Liu H and Yang W S 2004 Germanium and iron Co-substituted \( \text{SrCo}_{2.5}\text{Ge}_\delta\text{O}_3 \) as solid oxygen electrodes J. Eur. Ceram. Soc. 24 1059–64

[12] Zeng P, Ran R, Chen Z, Zhou W, Gu H, Shao Z and Liu S 2008 Efficient stabilization of cubic perovskite \( \text{SrCo}_{2+\delta}\text{O}_3 \) by B-site low concentration scandium doping combined with sol–gel synthesis J. Alloys Compd. 455 465–70

[13] Jiang S P 2019 Development of lanthanum strontium cobalt ferrite perovskite electrodes of solid oxide fuel cells—a review Int. J. Hydrogen Energy 44 7448–93

[14] Wang Z, Yang Z, Song Y, Xiao J, Jiang F and Zhou W 2018 Alkaline metal doped strontium cobalt ferrite perovskites as cathodes for intermediate-temperature solid oxide fuel cells Int. J. Hydrogen Energy 43 13420–9

[15] Deng Z Q, Yang W S, Liu W and Chen C S 2006 Relationship between cation substitution and stability of perovskite structure in \( \text{SrCo}_3\text{O}_4 \) based mixed conductors Solid State Ion. 177 3433–44

[16] De la Calle C, Aguadero A, Alonso J A and Fernández-Díaz M T 2008 Correlation between reconstructive phase transitions and phase transformations in mixed-conducting oxides J. Solid State Chem. 179 362–9

[17] De la Calle C, Aguadero A, Alonso J A and Fernández-Díaz M T 2008 Relationship between reconstructive phase transitions and transport properties from \( \text{SrCo}_{2+\delta}\text{O}_3 \) brownmillerite: a neutron diffraction study Solid State Sci. 10 1924–35

[18] Cascos V, Martínez-Coronado R and Alonso J A 2014 New Nb-doped \( \text{SrCo}_{1-\delta}\text{Nb}_\gamma\text{O}_3 \) perovskites performing as cathodes in solid-oxide fuel cells Inter. J. Hydr. Energy 39 14349–54

[19] Agudo, Alonso J A, Pérez-Cell D, Del Calle C, Fernández-Díaz M T and Goodenough J B 2010 \( \text{SrCo}_{0.95}\text{Sb}_{0.05}\text{O}_3 \) as cathode material for high power density solid oxide fuel cells Chem. Mater. 22 789–98.

[20] Wang R, Jin F, Ta L and He T 2015 \( \text{SrCo}_x\text{MoO}_{3-\delta}\text{O}_3 \) as cathode materials for \( \text{LaGaO}_3 \)-based intermediate-temperature solid oxide fuel cells Solid State Ion. 288 32–35

[21] Chen X, Huang L, Wei Y and Wang H 2011 Tantulum stabilized \( \text{SrCo}_{2+\delta}\text{O}_3 \) perovskite membrane for oxygen separation J. Membrane Science 368 159–64

[22] Cascos V, Alonso J A and Fernández-Díaz M T 2016 \( \text{Nb}^{\text{IV}} \)-doped \( \text{SrCo}_{2+\delta}\text{O}_3 \) perovskites as potential cathodes for solid-oxide fuel cells Materials 9 579

[23] Fuertes V C, Blanco M C, Franco D G, De Paoli J M, Sánchez R D and Carbonio R E 2011 Influence of the B-site ordering on the magnetic properties of the new \( \text{La}_\alpha\text{Co}_\delta\text{Mn}_\gamma\text{O}_3 \) double-perovskites with M = Nb or Ta Mater. Res. Bull. 46 62–9

[24] Rietveld H M 1969 A profile refinement method for nuclear and magnetic structures J. Appl. Crystallogr. 2 65

[25] Rodríguez-Carvajal J 1993 Recent advances in magnetic structure determination by neutron powder diffraction Physica B: Physics of Condensed Matter 192 53–69

[26] Wang J, Jiang L, Xiong X, Zhang C, Jin X, Lei L, Huang K and Broad A 2016 Stability investigation of Nb-doped \( \text{SrCo}_{2+\delta}\text{O}_3 \) as a reversible oxygen electrode for intermediate-temperature solid oxide fuel cells J. Electrochem. Soc. 163 F891–8

[27] Muñoz A, del Calle C, Alonso J A, Botta P M, Pardo V, Baldomir D and Rivas J 2008 Crystallographic and magnetic structure of \( \text{SrCo}_{2+\delta}\text{O}_3 \) brownmillerite: neutron study coupled with band-structure calculations Phys. Rev. B 78 035404

[28] Zhao Q, Darriet J, Whangbo M H, Ye L, Stockhouse C and zur Loye H-C 2011 Intriguing interconnections among phase transition, magnetic moment, and valence disproportionation in 2H-perovskite related oxides J. Am. Chem. Soc. 133 20981–94

[29] Zhu Y, Lin Y, Shen X, Sunarso J, Zhou W, Jiang S, Su D, Chen F and Shao Z 2014 Influence of crystal structure on the electrochemical performance of A-site-deficient \( \text{Sr}_1-x\text{Nd}_x\text{Co}_{1-\delta}\text{O}_3 \) perovskite cathodes J. Power Sources 250 40865–72

[30] Momma K and Izumi F 2011 VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data J. Appl. Crystallogr. 44 1272–6

[31] Pecchi G, Campos C and Peña O 2009 Thermal stability against reduction of \( \text{LaMn}_{1-x}\text{Co}_x\text{O}_3 \) perovskites Mater. Res. Bull. 44 846

[32] Sacchetti A, Baldini M, Postorino P, Martin C and Maignment A 2006 Raman spectroscopy on cubic and hexagonal \( \text{SrMn}_3\text{O}_7 \), J. Raman Spectrosc. 37 591–6

[33] Mos A and Aparicio M 2015 Sol-gel materials for batteries and fuel cells The Sol-gel Handbook ed D Levy and M Zayat (Weinheim, Germany: Wiley)VCH Verlag GmbH & Co. KGaA pp 1071–117