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Study of \( LnBaCo_2O_{6-\delta} \) (Ln = Pr, Nd, Sm and Gd) double perovskites as new cathode material for IT-SOFC

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Abstract. Oxides with double perovskites structures of general composition \( LnBaCo_2O_{6-\delta} \) (Ln = rare earth, \( 0 \leq \delta \leq 1 \)) were synthesized by solid state reaction with the purpose to evaluate new materials to be used as cathodes in intermediate temperature solid oxide fuel cell (IT-SOFC). A preliminary study about electrochemical properties was performed by impedance spectroscopy between 500 and 800 \( \degree \)C under atmosphere of pure \( O_2 \). Symmetrical cells were obtained by spray deposition of \( LnBaCo_2O_{6-\delta} \) (Ln = Pr, Nd, Sm and Gd) at both sides of a dense ceramic electrolyte. The impedance spectroscopy measurements as a function of temperatures show a hysteresis loop which could be associated to a tetragonal/orthorhombic phase transition. The existence of this transition was corroborated by high temperature X-Ray diffraction and Differential Scanning Calorimetry measurements.

1. Introduction

Layered cobaltites with general formula \( LnBaCo_2O_{6-\delta} \) (Ln = rare earth, \( 0 \leq \delta \leq 1 \)) have been extensively studied due to their attractive magnetic and transport properties at low temperatures (below 150 \( \degree \)C) [1, 2, 3]. These cobaltites present two main structural features [3, 4]: The first one is the perfect order in alternating (0 0 1) layers of the Ln and Ba ions due to great differences between the ionic radii of them. The second structural feature is due to the fact that the oxygen vacancies are located at the Ln layers with a great tendency to form ordered patterns. This results in an order coexistence of Co ions in octahedral (CoO6) and pyramidal (CoO5) environments. Then, the magnetic and transport properties are highly dependent on the oxygen content.

At high temperatures cobaltites are interesting due to their high mixed conductivity. This property make these materials attractive for applications as gas sensors, oxidation catalysts, or materials for fuel cells. In the last years, the trend to low the operating temperature of Solid Oxide Fuel Cells (SOFCs) to the intermediate temperature range (500-700 \( \degree \)C) has become one of the main SOFC research goals. In this range of temperatures, the contribution of the cathode to the total resistance of the cell usually becomes the dominant contribution. This is due to the high activation energy associated to the oxygen reduction reaction taking place in the cathode side.

Recent studies demonstrated that layered cobaltites, \( LnBaCo_2O_{6-\delta} \) with Ln = Gd and Pr [5, 6], could be identified as a potential cathode materials for intermediate-temperature
SOFC (IT-SOFC) due to their excellent oxygen transport properties, i.e. high oxygen surface exchange coefficient, reasonable oxide ionic diffusivity and high electronic conductivity. However, an order-disorder phase transition recently reported for these compound around 500 °C [6, 7] could affect the electrochemical performances of this family of compounds. This order-disorder phase transition involves a rearrangement of oxygen vacancies going from the low-temperature one-dimensional distribution alternating filled and empty chains of oxygen along the *a* axis (orthorhombic symmetry O, P*m*mm space group) to the high-temperature two-dimensional distribution of vacancies in (0 0 1) layers, i.e. in the LnOx plane (tetragonal symmetry T, P4/mmm space group).

In this work we present preliminary results of the effect of Ln cation (Ln = Pr, Nd, Sm, Gd) on the structural and electrochemical properties of \( \text{LnBaCo}_2\text{O}_{6-\delta} \) compounds. The electrochemical performance was evaluated by means of impedance spectroscopy while the phase transition was investigated by high temperature X-ray diffraction (HT-XRD) and differential scanning calorimetry (DSC).

2. Experimental

\( \text{LnBaCo}_2\text{O}_{6-\delta} \) (Ln = Pr, Nd, Sm and Gd) compounds were obtained by solid state reaction at 1100 °C using stoichiometric amounts of lantanides oxides, \( \text{Co}_3\text{O}_4 \) and \( \text{BaCO}_3 \). The presence of single-phase materials was verified in the four samples by room temperature XRD using a Philips PW1700 diffractometer with \( \text{CuK}_\alpha \) radiation and a graphite monochromator. The samples display Orthorhombic (P*m*mm) or retain the high temperature Tetragonal (P4/mmm) symmetry depending on the cooling rates. Figure 1 shows the typical diffraction patterns of these compound for both symmetries.

![Figure 1. Characteristic XRD diagram of tetragonal and orthorhombic phases.](image)

Symmetrical \( \text{LnBaCo}_2\text{O}_{6-\delta}/\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-x}/\text{LnBaCo}_2\text{O}_{6-\delta} \) cells were prepared by spray deposition of double perovskites paint on both sides of the \( \text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-x} \) (CGO) dense
Figure 2. Arrhenius plot for the total electrode resistance of polarization $R_P$ by $LnBaCo_2O_{6-\delta}$ (Ln = Pr, Nd, Sm and Gd) between 500-800 °C.

electrolyte. Then, these films were sintered at 1000 °C for 1 h. The structural characterization of the as-prepared film was performed by XRD before and after the electrochemical measurements. No significant differences were found between them. The uniform morphology and composition of as-deposited electrode films were checked after the electrochemical measurements using scanning electron microscope (SEM, Philips 515) and energy dispersive spectroscopy (EDS, Genesis 2000).

The electrochemical characterization was performed by Electrochemical Impedance Spectroscopy (EIS) measurements under pure $O_2$ atmosphere at temperatures (T) from 500 to 800 °C using a frequency response analyzer (FRA) coupled to an AUTOLAB potenciostat. Measurements were performed increasing and decreasing T in the 1 MHz-0.1 Hz frequency range with null voltage bias. The amplitude of the applied voltage signal was 10 mV.

The HT-XRD studies were carried out using an Anton Paar camera coupled to the diffractometer. The measurement were performed from room temperature to 900 °C between $20 \leq 2\theta \leq 80$ ° under static air.

The thermal behavior of the samples was studied using a differential scanning calorimeter (Modulated DSC 2910 TA Instruments). Measurements were done under air atmospheres at a heating rate of 5 °C/min between room temperature and 550 °C.

3. Results and Discussions

3.1. Electrochemical characterization

The EIS data shown in fig 2 indicate an hysteretic behavior of the electrode polarization resistances $R_P$ vs. T above 500 °C. These results disagree with that observed by Tarancón el al. [6], who found hysteresis in their electrical conductivity measurements but not in the impedance measurements performed in air between 400 and 800 °C. We assume that this behavior should be associated to the order-disorder phase transition since our XRD data after EIS measurements show no differences with those obtained before, excluding chemical reactivity.
between electrode/electrolyte. Despite the increase in the polarization resistance, these $R_P$ values are lower than those of mostly conventional cathode materials and decrease as the ionic radii of Ln increases: $R_P^{Pr} \leq R_P^{Nd} \leq R_P^{Sm} \leq R_P^{Gd}$.

3.2. HT-XRD study

The change of symmetry from orthorhombic Pmmm to tetragonal P4/mmm was followed through the splitting of the peak around $2\theta = 22.5^\circ$ (see figure 3). We selected these peaks in order to avoid the diffraction peak of Pt holder at $2\theta \sim 47^\circ$. This transition takes place at 350-400, $\sim 400$, 375-400 and around 450-500 °C for Ln = Pr, Nd, Sm, and Gd, respectively. For Pr compound we found a transition temperature different to that reported by Streule et al. [7] (503 °C). However, in that case the transition was study in a sample prepared with an oxygen content of $6 - \delta \simeq 5.48$ and the NPD measurements were carried out under Ar atmosphere in order to maintain the $6 - \delta$ value constant. By other hand, we found for the Gd compound a similar transition temperature than that reported by Tarancón et al. [6] under comparable experimental conditions.

![Figure 3. High temperature XRD evolution with T showing the orthorhombic-tetragonal (O/T) phase transition for LnBaCo$_{2}$O$_{6-\delta}$ (Ln = Pr, Nd, Sm and Gd).](image)

However, previous studies performed at room temperature in samples with different oxygen content indicate that the order-disorder phase transition depends on the oxygen stoichiometry. Thus, at $6 - \delta < 5.45$, GdBaCo$_{2}$O$_{6-\delta}$ exhibits tetragonal symmetry while above it ($5.45 \leq 6 - \delta \leq 5.60$) becomes orthorhombic [2]. Therefore, it seems that this phase transition can
be achieved either, by controlling temperature or oxygen content. With this in mind, it seems reasonable to observe a different behavior between our EIS measurements and those of Tarancón et al [6]. Our measurements were performed under pure $O_2$, then it is reasonable to expect for our samples a higher oxygen content than that of Tarancón’s sample. Therefore, the stability of the orthorhombic symmetry should be shifted to higher temperatures and hampering the electrochemical performance.

3.3. Thermal analysis

In figure 4 are shown the heat flows as a function of T obtained for 5 °C/min heating rate for $LnBaCo_2O_{6-\delta}$ ($Ln = Pr, Nd, Sm and Gd$) compounds.

The DSC measurements didn’t show the O/T transition observed by HT-XRD for Pr and Nd samples (see fig. 4). Besides, the transition temperatures for Sm sample (512-508 °C) is higher than that of Gd sample (476-468 °C). This results disagree with those observed by HT-XRD. This disagreement may be related to different experimental conditions between DSC and HT-XRD. DSC is a dynamic technique while our HT-XRD data are collected at constant temperatures.

The enthalpy change associated to the O/T transition are $\Delta H = 0.85$ and 3.78 J/g for Sm and Gd compounds, respectively. The value obtained for Gd compound is in agreement with that of Tarancón et al. (3.9 J/g) [6]. The $\Delta H$ values decreases as we move right to left in periodic table (Sm and Gd samples). Therefore, it should be expected lower $\Delta H$ values for Nd and Pr samples, with the consequent decrease of the peak until it disappears. Thus, this fact will explain the lack of the DSC peak for Nd and Pr samples.

Besides, we want to emphasize that this order-disorder transitions seems to depend on thermal history of the samples. Thus, if samples are fast cooled, it’s possible to retain the tetragonal phase at room temperature and, a subsequent fast heating avoid the orthorhombic
phase formation. We think that these behaviors indicate a kinetics effect over the O/T transition which is related not only with the oxygen content and temperature, but also to the oxygen diffusion inside of each materials.

4. Conclusion
The HT-XRD and DSC studies show an order-disorder phase transition (O/T) at temperatures around 500 °C that strongly depends on the thermal history and the oxygen content of the samples.

The $R_P$ values vary according to $PrBaCo_2O_{6-δ} \leq NdBaCo_2O_{6-δ} < SmBaCo_2O_{6-δ} < GdBaCo_2O_{6-δ}$. Then, the ionic radii of Ln seems to play a role for improving the electrochemical properties. However, the $R_P$ values show a hysteresis loop that could be associated to the O/T transitions and could compromise the electrochemical performance in SOFC applications.

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