

Carbon dioxide gas sensing properties of ordered oxygen deficient perovskite $\text{LnBaCo}_2\text{O}_{5+\delta}$ ($\text{Ln} = \text{La}, \text{Eu}$)



L. Gómez^a, V. Galeano^a, R. Parra^b, C.R. Michel^c, C. Paucar^a, O. Morán^{a,*}

^a Universidad Nacional de Colombia, Campus Medellín, Facultad de Ciencias, Departamento de Física, Laboratorio de Cerámicos y Vítreos, Medellín, Colombia

^b Instituto de Investigaciones en Ciencia y Tecnología de Materiales (INTEMA), CONICET - UNMdP, Mar del Plata B7608FDQ, Argentina

^c Departamento de Física, Universidad de Guadalajara CUCEI, Guadalajara 44410, Jalisco, México

ARTICLE INFO

Article history:

Received 23 April 2015

Received in revised form 8 July 2015

Accepted 18 July 2015

Available online 21 July 2015

Keywords:

$\text{LnBaCo}_2\text{O}_{5+\delta}$

Gas sensors

Impedance

ABSTRACT

Polycrystalline samples of layered cobaltites $\text{LnBaCo}_2\text{O}_{5+\delta}$ ($\text{Ln} = \text{La}, \text{Eu}$) were synthesized by standard solid state reaction. Structural, magnetic and carbon dioxide gas sensing properties of the samples were carefully investigated. The polycrystalline $\text{LnBaCo}_2\text{O}_{5+\delta}$ samples showed typical sequences of magnetic transitions according to the nonstoichiometric oxygen (δ) content. Well-defined hysteresis loops were observed at different temperatures (270 K for $\text{EuBaCo}_2\text{O}_{5+\delta}$), which supports the existence of a ferromagnetic order in the samples. Thick films were prepared with the as-prepared powders for the gas sensing evaluation. Considerable response to CO_2 gas was measured for the first time on sensors based on $\text{LnBaCo}_2\text{O}_{5+\delta}$ powders. The resistance of the sensors increases with an increase of CO_2 concentration, with dry air as base gas. The gas sensing response of the sensors is fast and shows good reproducibility. The $\text{EuBaCo}_2\text{O}_{5+\delta}$, and $\text{LaBaCo}_2\text{O}_{5+\delta}$ cobaltites show distinct behavior upon increase in the CO_2 concentration, which might be associated with the value of δ for each system. The probable carbon dioxide gas sensing mechanism of the studied cobaltites is discussed.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

It is widely known that carbon dioxide (CO_2) is the primary greenhouse gas emitted through human activities. The increase of the CO_2 concentration in the atmosphere since the industrial revolution has played a critical role in global warming and climate change. The concern of global warming has motivated intense research on the detection, capture and storage of CO_2 . Moreover, the detection of CO_2 can be used in many other fields such as air-quality monitoring, agricultural production, clean energy technologies, engine exhausts and chemical industry. Various concepts of CO_2 sensors have been proposed, which are based on the variation of diverse physicochemical parameters. In this regard, infrared [1], capacitive [2], resistive [3] and surface acoustic wave [4] sensors have successfully been tested by various research groups around the world. Particularly, the resistive CO_2 sensor is based on a change in the electrical conductance of semiconductors upon exposure to CO_2 in air. Some composite-type oxides such as CuO-BaTiO_3 [5], CuO-SnO_2 [6], or LaCl_3 -doped SnO_2 [7] have shown resistive responses to CO_2 gas. Similarly, single-phase oxides such as

BaCeO_3 [8], GdCoO_3 [9], nanocrystalline $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ [10], LaOCl [11], or $\text{Nd}_2\text{O}_2\text{CO}_3$ [12] also exhibit considerable resistive response to CO_2 gas. Recently, the novel cobalt oxides series $\text{LnBaCo}_2\text{O}_{5+\delta}$ ($\text{Ln} = \text{Lanthanide or Y}$) have been subject of a variety of studies due to the existence of fascinating magnetic, electrical and magnetotransport properties such as an exceptionally high magnetoresistance [13]. The $\text{LnBaCo}_2\text{O}_{5+\delta}$ compounds have a 112-type structure, that is, an oxygen-deficient and A-site ordered perovskite. Thus, these challenging materials have a wide range of oxygen nonstoichiometry, and the attractive electromagnetic and structural properties depend on the oxygen nonstoichiometry [14]. Concretely, the appealing phenomena depend on the valence and spin states of the Co ions [15]. The valence state of the Co ions is determined by the oxygen content δ ($0 \leq \delta \leq 1$). All the Co ions are expected to be trivalent when $\delta = 0.5$. Here, one half of the cobalt occupy octahedral sites (CoO_6) while the other half possesses square pyramidal symmetry (CoO_5) forming alternating oxygen rich and oxygen deficient *a-c* layers along the *b* axis [16]. For $0.0 < \delta < 0.5$ and $0.5 < \delta < 1.0$, divalent and tetravalent Co ions coexist with trivalent Co ions, respectively. When $\delta = 0$ and $\delta = 1$, the cobalt environment appears to be exclusively pyramidal ($\delta = 0$) or octahedral ($\delta = 1$). Hence, $\text{LnBaCo}_2\text{O}_{5+\delta}$ features a very flexible structure which can either uptake ($\delta > 0$) or release oxygen ($\delta < 0$) depending on the experimental conditions of synthesis

* Corresponding author.

E-mail address: omoran@unal.edu.co (O. Morán).

(temperature and oxygen-partial-pressure) and size of the lanthanide [17]. $\text{LnBaCo}_2\text{O}_{5+\delta}$ can accommodate excess-oxygen atoms in the $\text{Ln}(\text{O})_\delta$ layer and the oxygen nonstoichiometry (the oxygen content δ) is attributed to the occupancy rate of oxygen sites in $\text{Ln}(\text{O})_\delta$ layer [14]. The maximum value of δ is dependent on the size of Ln^{3+} and increases with an increase in the size of Ln^{3+} . For instance, for Pr, $\delta = 0.7$, and for Ho, $\delta = 0.3$, when the compounds are synthesized in air [16]. Since the overlap between the transition-metal d orbital and oxygen 2p orbital is strongly influenced by the average radius of ions on the Ln site, the d–2p interaction will play a decisive role in determining the magnetic properties of these compounds. Apart from the basic physical aspects, the technical aspects of these cobaltites should not be overlooked. Certainly, the high ionic and electronic conductivities and the catalytic and electrocatalytic properties of cobalt-containing compounds make them promising materials for the development of electrochemical devices such as cathodes in solid-state fuel cells, membranes for oxygen separation, and a variety of sensors [18].

The sensitivity of oxide-based gas sensors is determined via a distinctive change of their resistance in the presence of gases. One of the most important evaluation indexes of gas sensors is sensitivity. A high sensitivity sensor could detect small amounts of leakage of toxic gases and thus avoid poisoning incidents. At present, SnO_2 , ZnO , WO_3 and TiO_2 are the main gas sensitive materials [19,20]. Although theoretical studies on the sensing behavior of the lanthanum cobaltite p-type system have been recently reported [21], the gas sensing properties of $\text{LnBaCo}_2\text{O}_{5+\delta}$ cobaltites have not been experimentally assessed up till now. In this work, results of the synthesis, magnetic properties and gas sensing characterization of $\text{EuBaCo}_2\text{O}_{5+\delta}$ and $\text{LaBaCo}_2\text{O}_{5+\delta}$ are reported for the first time.

2. Experimental

Polycrystalline $\text{LnBaCo}_2\text{O}_{5+\delta}$ (Ln = Eu, La) samples were obtained by standard solid state reaction. Stoichiometric quantities of La_2O_3 , BaCO_3 , Eu_2O_3 and Co_2O_3 reactants were mixed together and calcined at 1170 K for 12 h to achieve decarbonization. The resulting powder was slowly heated in air ($\sim 5^\circ\text{C}/\text{min}$) up to 1270 K for 24 h. X-ray diffraction patterns of compounds were registered with a Panalytical X'Pert Pro MPD diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm). The composition of the powders was determined by energy dispersive X-ray spectroscopy (EDS). Surface morphology was performed by scanning electron microscopy (SEM), using a JEOL JSM-6490 E-beam microscope. The magnetic properties were studied by using a vibrating sample magnetometer (Quantum Design). For the gas sensing characterization, $\text{LnBaCo}_2\text{O}_{5+\delta}$ was dispersed in EtOH, using an ultrasonic bath. The resulting suspension was deposited into an alumina ring, which was fixed to an alumina substrate by means of gold wires (99.9%, Aldrich). The suspension

within the alumina ring was heated at 600°C for 5 h in order to consolidate the powder and improve the contact between particles. The gold wires had diameter of 0.25 mm, and were used as electrical contacts. The films were circular, with diameter 1 cm and thickness ~ 1 mm. Fig. 1(a) shows a drawing of the sensor device [22]. The latter was introduced into an alumina tube, which was located inside a programmable temperature tube-type furnace. The test gas was extra dry CO_2 (99.8%). A mass flow control system (MKS Instruments, 647C) was used to deliver the gas through the alumina tube. Fig. 1(b) displays a scheme of the experimental setup used for the gas sensing characterization [22]. The gas sensing response in the experiment was defined as R_g/R_a , where R_g and R_a are the resistances measured under CO_2 gas (in the background of dry air) and dry air, respectively.

3. Results and discussion

XRD measurements on the $\text{EuBaCo}_2\text{O}_{5+\delta}$ samples [Fig. 2(a)] show that the compound can be indexed to an orthorhombic structure with lattice parameters (obtained by Rietveld analysis) $a = 3.92$ Å, $b = 3.88$ Å and $c = 7.53$ Å ($Pmmm$ space group). This result is in accordance with that reported by M.M. Seikh et al. [23] and particularly with that reported by S. Roy et al., who used a similar synthesis procedure to prepare their samples [24]. The encountered phase is described by the tetragonal superstructure $a_p \times 2a_p \times 2a_p$ (a_p being the cell parameter of the cubic perovskite) [25]. For the $\text{LaBaCo}_2\text{O}_{5+\delta}$ system [Fig. 2(b)], the analysis of the results and the definition of a type of structure or superstructure are much more complex. As mentioned in the introduction, the $\text{LnBaCo}_2\text{O}_{5+\delta}$ systems possess a layered crystal structure which consists of layers $[\text{LnO}_\delta]$ - $[\text{CoO}_2]$ - $[\text{BaO}]$ - $[\text{CoO}_2]$ alternating along the c axis. The ordering of Ln^{3+} and Ba^{2+} ions is favorable if the size difference is large between the cations as occurs for Eu ions [26]. Hence, smaller size Ln^{3+} cations easily form a layered structure. In contrast, for La^{3+} ions the size difference with Ba^{2+} is smaller and, as a result, the disordered cubic perovskite [24] is more stable and special conditions are required in order to synthesize the 112-type layered structure. The XRD patterns of the disordered $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ and ordered $\text{LaBaCo}_2\text{O}_{5+\delta}$ phases are very similar and they can be indexed as a simple perovskite using the same space group and the same structural parameters [26]. Measurements on $\text{LaBaCo}_2\text{O}_{5+\delta}$ samples obtained by solid state reaction show a cubic structure (space group $Pm\bar{3}m$). This result excludes the possibility of obtaining a cation ordering between LaO/BaO layers for samples synthesized by this route because the La/Ba ordering involves a slight deformation of the perovskite sublattice with a dilatation of the a_p parameter within the LaO/BaO layers and a compression along the LaO/BaO layers stacking direction [26]. The room-temperature X-ray diffraction pattern of the $\text{LaBaCo}_2\text{O}_{5+\delta}$ sample [Fig. 2(b)]

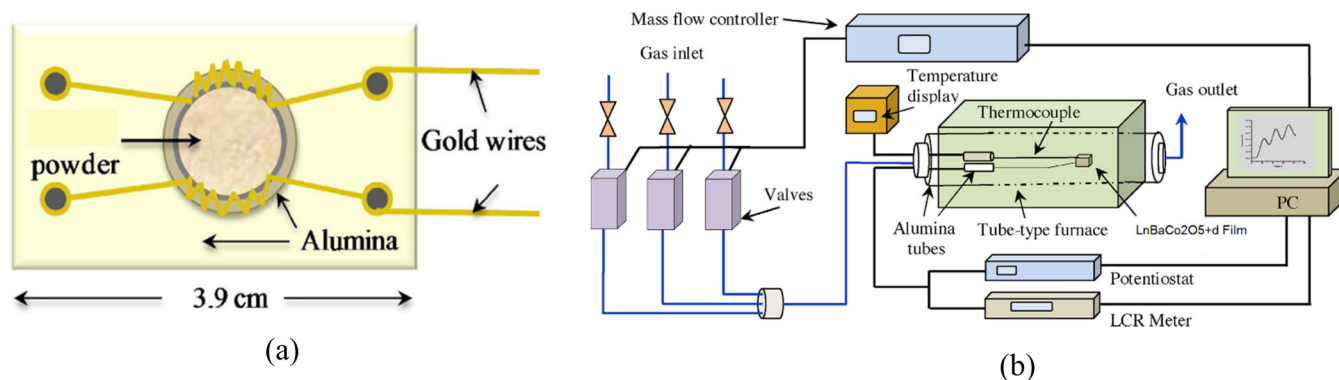


Fig. 1. (a) Drawing of the device and (B) scheme of the experimental setup used in the gas sensing characterization [18].

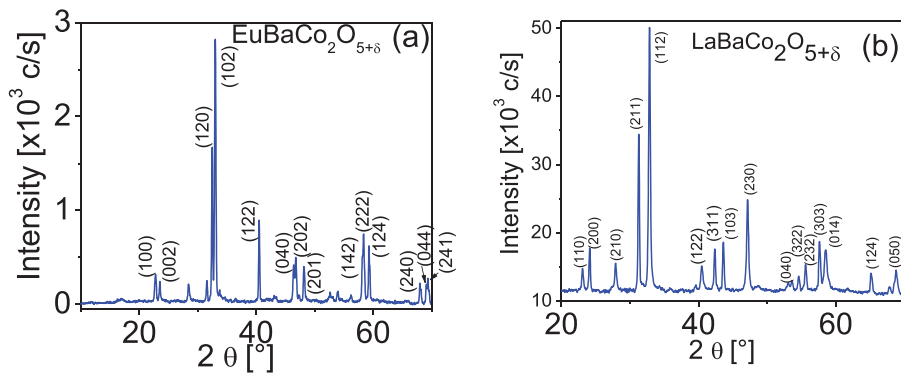


Fig. 2. XRD patterns of $\text{EuBaCo}_2\text{O}_{5+\delta}$ (a) and $\text{LaBaCo}_2\text{O}_{5+\delta}$ (b) samples synthesized by solid state reaction.

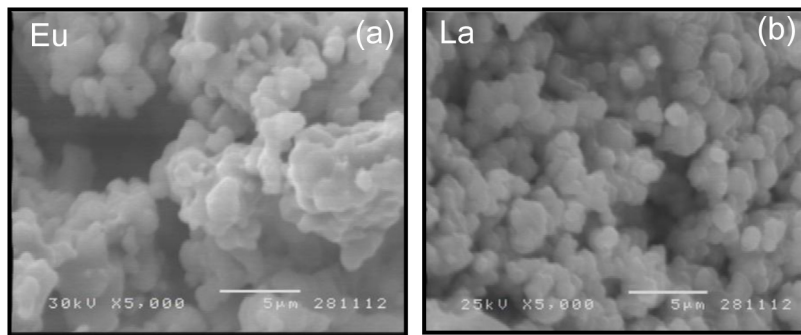


Fig. 3. Typical surface SEM images of the $\text{EuBaCo}_2\text{O}_{5+\delta}$ (a) and $\text{LaBaCo}_2\text{O}_{5+\delta}$ (b) powders used to fabricate the CO_2 sensors.

suggests a trigonal structure with space group $R3c$. However, a better definition of these structures requires the use of more powerful characterization techniques such as neutron diffraction or high-resolution transmission electron microscopy.

Fig. 3 shows the SEM micrographs of the $\text{EuBaCo}_2\text{O}_{5+\delta}$ (a) and $\text{LaBaCo}_2\text{O}_{5+\delta}$ (b) samples used in the present study. We can observe microcrystalline structure with similar particle morphologies with mean crystallite sizes of about $1 \mu\text{m}$ regardless of their specific Ln^{3+} ion.

Fig. 4 shows the dependence of magnetization on temperature for $\text{LnBaCo}_2\text{O}_{5+\delta}$ ($\text{Ln}=\text{La}, \text{Eu}$) polycrystalline samples. The Eu sample [Fig. 4(a)] shows paramagnetic-ferromagnetic-antiferromagnetic transitions (PM-FM-AFM) in a narrow temperature range ($\sim 40 \text{ K}$) around $\sim 250 \text{ K}$ which is typical for the Eu-compound with a $\delta \approx 5.48$ [27]. In turn, the $M(H)$ dependence recorded at 205 K [inset to Fig. 4(a)] clearly shows a ferromagnetic

component in the sample. The $M(T)$ and $M(H)$ dependences for the $\text{LaBaCo}_2\text{O}_{5+\delta}$ are shown in Fig. 4(b). The $M(T)$ of the La-based cobaltite is typical for ferromagnetic ordering with $T_C \sim 200 \text{ K}$. Note that the system remains ferromagnetic in the whole temperature range below 200 K . La-based cobaltites with $\delta = 0.5$ feature a transition to a ferromagnetic state at $T_C \approx 320 \text{ K}$ [26]. The reduced transition temperature suggests that the oxygen concentration in the La-based cobaltite deviates from the parent composition $\delta = 0.5$. The trend of the $M(T)$ curve shown in Fig. 4(b) is similar to that reported in Ref. [25] for the same compound. Hence, the amount of oxygen excess should be lower than 0.3 . In turn, it is important to note that measurements of the dependence of the resistivity of polycrystalline $\text{EuBaCo}_2\text{O}_{5.5}$ samples on temperature have showed a sudden increase of the resistivity by about one order of magnitude around 71°C [23]. Such feature has been associated with a metal-insulator (or semiconductor-semiconductor) transition,

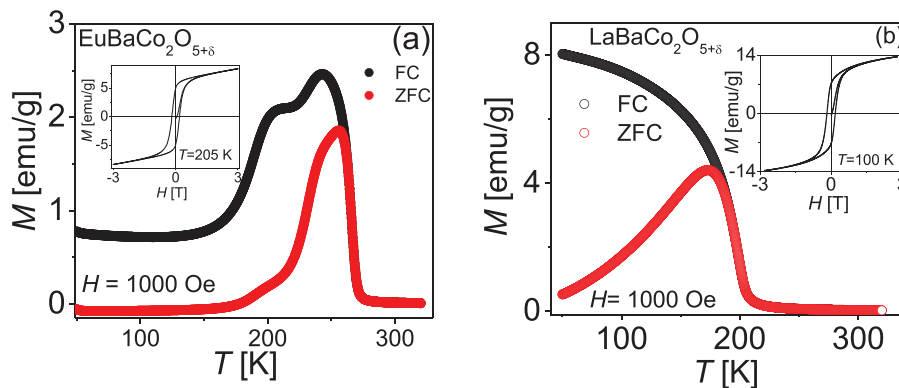


Fig. 4. Temperature dependence of the magnetization in ZFC and FC modes for $\text{EuBaCo}_2\text{O}_{5+\delta}$ (a) and $\text{LaBaCo}_2\text{O}_{5+\delta}$ (b) samples synthesized in air by solid state reaction. The data were recorded under warming condition in a field of 1000 Oe . Inset to (a): Field dependence of the magnetization of the $\text{EuBaCo}_2\text{O}_{5+\delta}$ sample measured at 272 K . Inset to (b): Magnetization as a function of the magnetic field at 100 K for the $\text{LaBaCo}_2\text{O}_{5+\delta}$ sample.

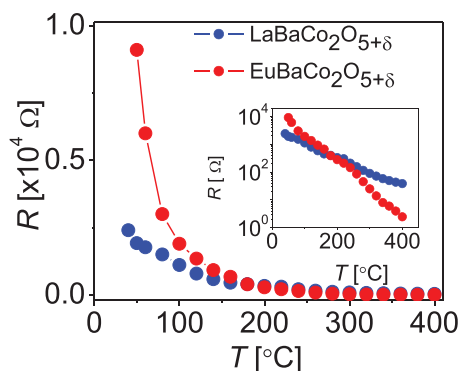


Fig. 5. Dependence of electrical resistance (R) on temperature for $\text{EuBaCo}_2\text{O}_{5+\delta}$ and $\text{LaBaCo}_2\text{O}_{5+\delta}$ samples. Inset: $R(T)$ dependence plotted on semi-logarithmic scale.

characteristic of this family of compounds [16]. Below 71°C , the resistivity of the compound showed a semiconductor-like behavior. Deviation from the ideal value ($\delta=0.5$) leads to a suppression of the transition. Thus, it seems that there exists an optimal carrier doping for the appearance of the metal–insulator transition that coincides approximately with the $\text{O}_{5.5}$ stoichiometry, characteristic of cobalt 3^+ valence [16]. For the $\text{LaBaCo}_2\text{O}_{5.5}$, a significant change in slope corresponding to the semiconductor–semiconductor transition around 52°C has been reported [26]. For the Eu- and La-based sensors, the temperature dependence of the electrical resistance (R) was measured at temperatures above room temperature in congruence with the gas sensing characterization of the compounds. The $R(T)$ dependence for $\text{EuBaCo}_2\text{O}_{5+\delta}$ and $\text{LaBaCo}_2\text{O}_{5+\delta}$ samples is shown in Fig. 5. With decreasing temperature the resistance increases for both compounds mimicking a semiconductor-like behavior. Note that for $T > 200^\circ\text{C}$, the resistance of the $\text{LaBaCo}_2\text{O}_{5+\delta}$ sample is higher than that of the counterpart $\text{EuBaCo}_2\text{O}_{5+\delta}$ (inset to Fig. 5).

As previously mentioned mixed ionic/electronic conducting materials have deserved much attention in the last years due to their potential applications in various novel devices such as ultrasensitive chemical sensors. In order to improve the performance of those devices, the mixed ionic/electronic conducting materials should meet the requirements of both high oxygen diffusivity and great enhancement of surface exchange rate [28]. The two conditions have been found in oxygen deficient perovskite cobaltites $\text{LnBaCo}_2\text{O}_{5+\delta}$ [28]. Generally speaking, the nature of the A-site cations in $\text{LnACo}_2\text{O}_{5+\delta}$ (A = alkaline earth element) compounds, specially their size, and their distributions (ordered or disordered) may have a great influence on the mixed conductivity. The A cation average valence favors a compensating population of oxygen vacancies at low oxygen partial pressures leading then to high ionic conductivity. In this regard, remarkable enhancement of the oxygen diffusivity has been observed in A-site ordered $\text{GdBaCo}_2\text{O}_{5.5+\delta}$ [29].

Moreover, it was reported that A-site ordered $\text{PrBaCo}_2\text{O}_{5.5+\delta}$ has unusual rapid oxygen transport kinetics at temperatures ranging between 300 and 500°C [30]. The layered perovskite $\text{LaBaCo}_2\text{O}_{5.5+\delta}$ features some distinctive properties such as the weakest tendency to A-site ordering and smallest oxygen nonstoichiometry as a consequence of the small difference between the radii of La^{3+} and Ba^{2+} [31]. Kinetic phenomena were investigated in as-grown ($\text{LaBaCo}_2\text{O}_{5+\delta}$) films grown on LaAlO_3 substrates by pulse laser deposition technique [32]. Novel effects observed in these films such as extraordinary sensitivity to reducing-oxidizing environment and their exceedingly fast surface exchange rate make these oxides promising candidates for ultrasensitive chemical gas sensors.

The high crystallinity of the polycrystalline $\text{LnBaCo}_2\text{O}_{5+\delta}$ samples along with their relative uniform distribution of crystallite size makes them suitable for gas sensing characterization. The gas response of $\text{LnBaCo}_2\text{O}_{5+\delta}$ films was evaluated by recording the variation of the magnitude of impedance ($|Z|$) with time. Previous works have showed that reliable gas response may be registered in the frequency range $100\text{ Hz}–100\text{ kHz}$ [33]. Fig. 6 shows the dynamic gas-sensing characteristics of Eu- and La-based sensor exposed to different CO_2 concentrations (50 , 100 , 200 and 400 ppm) in the background of dry air. The data were recorded at a frequency of 1 kHz and operating temperature of 300°C . Exposures were carried out in an on-and-off process. A sharp increase of $|Z|$ in CO_2 followed by a return of $|Z|$ to its original value upon introduction of air is clearly observed in this plot. The value of $R_g/R_a > 1$, found for all CO_2 concentrations, implies that the resistance of the sensor in a CO_2 atmosphere is higher than in air at the same temperature. Moreover, it is observed that the R_g/R_a ratio slightly increases with the increase of the CO_2 concentration. By comparing the slopes of the curves registered in CO_2 and air, it is evident that the gas response in CO_2 is slower than in air. An appealing feature of the $|Z|$ vs. time curve (Fig. 6) is the low intensity of the noise (Flicker noise) at the low applied frequency. The response time (which is defined as the time needed to reach 90% of saturation) and recovery time (defined as the needed to recover to 10% of the original resistance) are important properties of gas sensors [10]. In the present case, the response time is difficult to estimate because the curves do not reach a saturated value of impedance. Nevertheless, the response of the sensor is instantaneous although the stabilization could take about 10 min . The average variation of $|Z|$, caused by the introduction of CO_2 , was about $0.2\ \Omega$ for both sensors at a frequency of 1 kHz and at the indicated operation temperatures. The ability of the $\text{LnBaCo}_2\text{O}_{5+\delta}$ cobaltites to detect changes in the concentration of CO_2 was tested by evaluating the sensitivity of the device defined as the ratio between the average resistance under CO_2 (R_g) and dry air (R_a). Fig. 7 shows the variation of the R_g/R_a ratio with the CO_2 concentration where quantitative detection of this gas can be noticed. The R_g/R_a versus CO_2 concentration curves show a growing, nonlinear trend for the two sensors although with pronounced

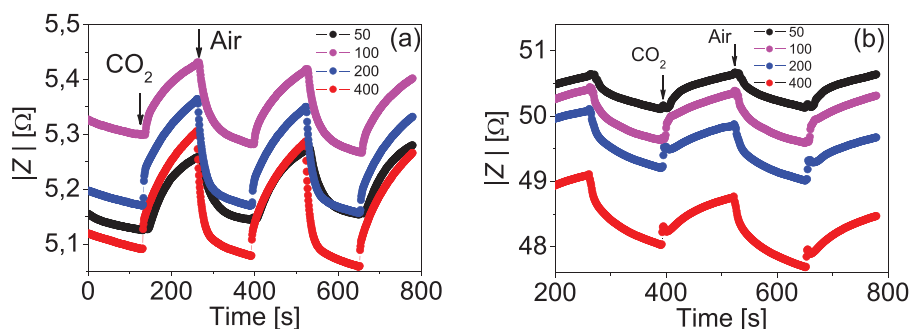


Fig. 6. Dynamic gas-sensing characteristics of $\text{EuBaCo}_2\text{O}_{5+\delta}$ (a) and $\text{LaBaCo}_2\text{O}_{5+\delta}$ (b) based sensors exposed to CO_2 gas with different concentrations in the background of dry air at 300°C .

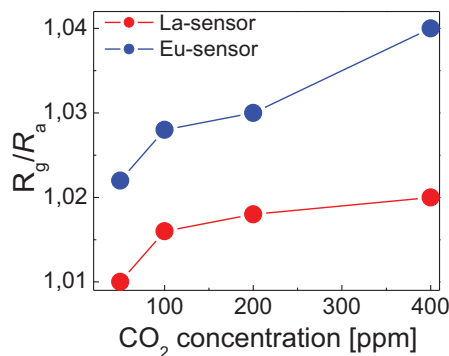


Fig. 7. R_g/R_a ratio as a function of the CO_2 concentration for Eu-based and La-based sensors.

tendency to saturation in case of the $\text{LaBaCo}_2\text{O}_{5+\delta}$ -based sensor. The achieved experimental results clearly show that the $\text{LnBaCo}_2\text{O}_{5+\delta}$ cobaltites-based sensors exhibit considerable response to CO_2 gas. The increase in film resistance upon exposure to CO_2 indicates that the $\text{LnBaCo}_2\text{O}_{5+\delta}$ films are p-type semiconductors. Some sensors based on single-phase p-type semiconductors such as LaOCl [36], and In_2Te_3 [34] have also displayed a similar effect. In addition, the resistance of composite oxide films of La_2O_3 - BaTiO_3 and ZrO_2 - BaTiO_3 also increased upon exposure to CO_2 gas [5]. The mechanism of gas detection by means of these systems is based on reactions occurring at the surface, which modify the surface-oxygen concentration. It has been suggested that, upon CO_2 adsorption, electrons from CO_2 molecules combine with holes (carriers) of the conduction band of perovskites reducing the conductivity [9]. Based on density functional theory investigations, it was shown that carbon dioxide acts as a donor leading to a decrease in the hole concentration, which is responsible for the observed increase in electrical resistance of perovskites exposed to CO_2 gas [21]. An attempt to give an incontrovertible explanation for the CO_2 sensing function of the concerned cobaltites is far away from being trivial. Nevertheless, a plausible approximation to the problem would take into account the fact that in dry air, oxygen adsorbs on the surface of $\text{LnBaCo}_2\text{O}_{5+\delta}$ cobaltites. The oxygen species can capture electrons from the $\text{LnBaCo}_2\text{O}_{5+\delta}$, that is a p-type semiconductor, leading to an increase in the hole concentration and a decrease in the value of $|Z|$ on the grain surface. The oxygen adsorbed on the surface of the semiconductor may then be involved in the sensing process of CO_2 in dry air. The increase in the value of $|Z|$, caused by the introduction of CO_2 , can be explained by the chemisorption of CO_2 , or reaction with oxygen species previously adsorbed. Probably, one free-terminal oxygen atom of an oxygen molecule (pre-adsorbed on the surface of the semiconductor) is able to adsorb CO_2 [10]. Here, the $\text{LnBaCo}_2\text{O}_{5+\delta}$ semiconductor would play a role of catalyst for the interaction between CO_2 and atomic oxygen. The surface carbonation will decrease the dielectric constant of the film (κ) according to the equation $|Z| = [R^2 + (1/\kappa\omega C_0)^2]^{1/2}$, where R represents the electrical resistance, ω the angular frequency and C_0 is the capacitance in air [35,36]. Hence, it is evident that the explanation of the gas response of $\text{LnBaCo}_2\text{O}_{5+\delta}$ requires not only related calculations of electronic structure, but also molecular dynamics simulations.

4. Conclusions

Polycrystalline $\text{LnBaCo}_2\text{O}_{5+\delta}$ ($\text{Ln} = \text{Eu}, \text{La}$) samples were fabricated by standard solid-state reaction. The XRD patterns showed distinct structures for the Eu-based and La-based cobaltites. Results of magnetic measurements performed on both systems suggested that the oxygen content in the samples deviated from the value $\delta \approx 0.5$. The $\text{LnBaCo}_2\text{O}_{5+\delta}$ films exhibited a quantitative detection

of CO_2 as verified by the increasing impedance when CO_2 gas was introduced. The variation of the sensitivity with the CO_2 concentration was different for the Eu-based and La-based cobaltites, which is, probably related with the distinct oxygen content in the sublattices of both compounds. The CO_2 gas sensing properties in dry air for $\text{LnBaCo}_2\text{O}_{5+\delta}$ were shown for the first time. However, the operating mechanism is still not clear and needs more experimental and theoretical work.

Acknowledgments

This work was supported by Universidad Nacional de Colombia, Sede Medellín. V.G acknowledges the financial support of the “Dirección Nacional de Investigaciones” of the Universidad Nacional de Colombia, Campus Medellín.

References

- [1] M.I. Baraton, FT-IR surface study of nanosized ceramic materials used as gas sensors, *Sens. Actuators B: Chem.* 31 (1996) 33.
- [2] T. Ishihara, K. Kometani, M. Hashida, Y. Takita, Application of mixed oxide capacitor to the selective carbon dioxide sensor, *J. Electrochem. Soc.* 138 (1991) 173.
- [3] S.A. Waghuley, S.M. Yenorkar, S.S. Yawale, S.P. Yawale, Application of chemically synthesized conducting polymer-polypyrrole as a carbon dioxide gas sensor, *Sens. Actuators B: Chem.* 128 (2008) 366.
- [4] M.S. Nieuwenhuizen, A.J. Nederlof, A SAW gas sensor for carbon dioxide and water. Preliminary experiments, *Sens. Actuators B: Chem.* 2 (1990) 97.
- [5] A. Haeusler, J.U. Meyer, A novel thick film conductive type CO_2 sensor, *Sens. Actuators B: Chem.* 34 (1996) 388.
- [6] J.C. Xu, G.W. Hunter, D. Lukco, C.C. Liu, B.J. Ward, Novel carbon dioxide microsensor based on tin oxide nanomaterial doped with copper oxide, *IEEE Sens. J.* 9 (2009) 235.
- [7] D.H. Kim, J.Y. Yoon, H.C. Park, K.H. Kim, CO_2 -sensing characteristics of SnO_2 thick film by coating lanthanum oxide, *Sens. Actuators B: Chem.* 62 (2000) 61.
- [8] T. Hibino, H. Iwahara, CO_2 sensors using BaCeO_3 -based ceramics, *Sens. Actuators B: Chem.* 13–14 (1993) 483.
- [9] C.R. Michel, A.H. Martínez, F. Huerta-Villalpando, J.P. Morán-Lázaro, Carbon dioxide gas sensing behavior of nanostructured GdCoO_3 prepared by a solution-polymerization method, *J. Alloys Compd.* 484 (2009) 605.
- [10] K. Fan, H. Qin, L. Wang, L. Ju, J. Hu, CO_2 gas sensors based on $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ nanocrystalline powders, *Sens. Actuators B: Chem.* 177 (2013) 265.
- [11] A. Marsal, G. Dezanneau, A. Cornet, J.R. Morante, A new CO_2 gas sensing material, *Sens. Actuators B: Chem.* 95 (2003) 266.
- [12] I. Djerdj, A. Haensch, D. Koziej, S. Pokhrel, N. Barsan, U. Weimar, M. Niederberger, Neodymium dioxide carbonate as a sensing layer for chemoresistive CO_2 sensing, *Chem. Mater.* 21 (2009) 5375.
- [13] C. Martin, A. Maignan, D. Pelloquin, N. Nguyen, R. Raveau, Magnetoresistance in the oxygen deficient $\text{LnBaCo}_2\text{O}_{5.4}$ ($\text{Ln} = \text{Eu}, \text{Gd}$) phases, *Appl. Phys. Lett.* 71 (1997) 1421.
- [14] D. Akahoshi, Y. Ueda, Oxygen nonstoichiometry, structures, and physical properties of $\text{YBaCo}_2\text{O}_{5+x}$ ($0.00 \leq x \leq 0.52$), *J. Solid State Chem.* 156 (2001) 355.
- [15] D.D. Khalyavin, S.N. Barilo, S.V. Shiryayev, G.L. Bychkov, I.O. Troyanchuk, A. Furrer, P. Allenspach, H. Szymczak, R. Szymczak, Anisotropic magnetic, magnetoresistance, and electrotransport properties of $\text{GdBaCo}_2\text{O}_{5.5}$ single crystals, *Phys. Rev. B* 67 (2003), 214421.
- [16] A. Maignan, C. Martin, D. Pelloquin, N. Nguyen, B. Raveau, Structural and magnetic studies of ordered oxygen-deficient perovskites $\text{LnBaCo}_2\text{O}_{5+\delta}$, closely related to the “112” structure, *J. Solid State Chem.* 142 (1999) 247.
- [17] E.L. Rautama, P. Boullay, A.K. Kundu, V. Caignaert, V. Pralong, M. Karppinen, B. Raveau, Cationic ordering and microstructural effects in the ferromagnetic perovskite $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$: Impact upon magnetotransport properties, *Chem. Mater.* 20 (2008) 2742.
- [18] V.I. Gatal'skaya, H. Dabkowska, P. Dube, J.E. Greedan, S.V. Shiryayev, Magnetic properties of single crystals of a new cobaltite $\text{TbBaCo}_4\text{O}_{7+x}$, *Phys. Solid State* 49 (2007) 1125.
- [19] S.M. Kanan, O.M. El-Kadri, I.A. Abu-Yousef, M.C. Kanan, Semiconducting metal oxide based sensors for selective gas pollutant detection, *Sensors* 9 (2009) 8158.
- [20] (a) C. Wang, L. Yin, L. Zhang, D. Xiang, R. Gao, Metal oxide gas sensors: sensitivity and influencing factors, *Sensor* 10 (2010) 2088; (b) Z. Wen, L. Tian-mo, Hydrogen sensing characteristics and mechanism of nanosize TiO_2 dope with metallic ions, *Physica B* 405 (2010) 564.
- [21] C. Shi, H. Qin, L. Li, Y. Chen, L. Ju, J. Hu, CO_2 sensing characteristics and mechanism for LaCoO_3 predicted by density function theory, *Appl. Surf. Sci.* 327 (2015) 168.
- [22] C.R. Michel, A.H. Martínez-Preciado, R. Parra, C.M. Aldao, M.A. Ponce, Novel CO_2 and CO gas sensor based on nanostructured Sm_2O_3 hollow microspheres, *Sens. Actuators B: Chem.* 202 (2014) 1220.

- [23] Md. Motin Seikh, V. Caignaert, V. Pralong, Ch. Simon, B. Raveau, Expansion of ferromagnetism by calcium doping in the ordered oxygen deficient perovskite $\text{EuBaCo}_2\text{O}_{5.50 \pm \delta}$, *J. Physics: Condens. Matter* 20 (2008) 015212.
- [24] S. Roy, I.S. Dubenko, M. Khan, E.M. Condon, J. Craig, N. Ali, W. Liu, B.S. Mitchell, Magnetic properties of perovskite-derived air-synthesized $\text{RBaCo}_2\text{O}_{5+\delta}$ ($\text{R}=\text{La-Ho}$) compounds, *Phys. Rev. B* 71 (2005) 024419.
- [25] Md. Motin Seikh, Ch. Simon, V. Caignaert, V. Pralong, M.B. Lepetit, S. Boudin, B. Raveau, New magnetic transitions in the ordered oxygen-deficient perovskite $\text{LnBaCo}_2\text{O}_{5.50+\delta}$, *Chem. Mater.* 20 (2008) 231.
- [26] A.K. Kundu, B. Raveau, V. Caignaert, E.-L. Rautama, V. Pralong, Electron transport and thermoelectric properties of layered perovskite $\text{LaBaCo}_2\text{O}_{5.5}$, *J. Phys.: Condens. Matter* 21 (2009) 056007.
- [27] B. Raveau, Md. Motin Seikh, V. Pralong, V. Caignaert, Ordered oxygen deficient '112' perovskites, $\text{LnBaCo}_2\text{O}_{5.50+\delta}$: complex magnetism and transport properties, *Bull. Mater. Sci.* 32 (2009) 305.
- [28] Y.L. Yang, C.L. Cheng, S.Y. Cheng, C.W. Chu, A.J. Jacobson, Impedance studies of oxygen exchange on dense thin film electrodes of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-d}$, *J. Electrochem. Soc.* 147 (2000) 4001.
- [29] A.A. Taskin, A.N. Lavrov, A. Yoichi, Achieving fast oxygen diffusion in perovskites by cation ordering, *Appl. Phys. Lett.* 86 (2005) 091910.
- [30] G. Kim, S. Wang, A.J. Jacobson, L. Reimus, P. Brodersen, C.A. Mims, Rapid oxygen ion diffusion and surface exchange kinetics in $\text{PrBaCo}_2\text{O}_{5+x}$ with a perovskite related structure and ordered A cations, *J. Mater. Chem.* 17 (2007) 2500.
- [31] F. Fauth, E. Suard, V. Caignaert, B. Domengès, I. Mirebeau, L. Keller, Interplay of structural, magnetic and transport properties in the layered Co-based perovskite $\text{LnBaCo}_2\text{O}_5$ ($\text{Ln}=\text{Tb, Dy Ho}$), *Eur. Phys. J.* 21 (2001) 163.
- [32] J. Liu, M. Liu, G. Collins, C. Chen, X. Jiang, W. Gong, A.J. Jacobson, J. He, J. Jiang, E.I. Meletis, Epitaxial nature and transport properties in $(\text{LaBa})\text{Co}_2\text{O}_{5+\delta}$ thin films, *Chem. Mater.* 22 (2010) 799.
- [33] C.R. Michel, A.H. Martínez-Preciado, J.P. Morán-Lázaro, Effect of the frequency on the gas sensing response of CoSb_2O_6 prepared by a colloidal method, *Sens. Actuators B: Chem.* 140 (2009) 149.
- [34] R.R. Desai, D. Lakshminarayana, P.B. Patel, C.J. Panchal, Indium sesquiteroxide (In_2Te_3) thin film gas sensor for detection of carbon dioxide, *Sens. Actuators B: Chem.* 107 (2005) 523.
- [35] D. Halliday, R. Resnick, J. Walker, *Fundamentals of Physics*, Wiley, New York, 2001.
- [36] C.R. Michel, A.H. Martínez-Preciado, N.L. López-Contreras, CO_2 and CO gas sensing properties of submicron CoSb_2O_6 wires prepared by a colloidal method, *Sens. Lett.* 10 (2012) 8.

Biographies

Leandro Gómez obtained his M.Sc. in Chemistry from Universidad Nacional de Colombia, Campus Medellín in 2014. His research interests include the synthesis of inorganic nanomaterials, particularly cobaltites, using wet-chemistry methods.

Velkis Galeano obtained her degree in Physics Engineering in 2013. She is working on her master project in the Physics Department of the Universidad Nacional de Colombia, Campus Medellín. Her research interests include the growing and characterization of cobaltites thin films.

Rodrigo Parra has a Doctorate degree in Materials Science from Universidad Nacional de Mar del Plata, Argentina (2006). Since 2008, he is assistant professor–researcher of CONICET-Instituto de Investigaciones en Ciencia y Tecnología de Materiales (INTEMA), Mar del Plata. His work focuses on the synthesis and characterization of nanostructured ceramics.

Carlos R. Michel obtained a master's degree in manufacturing engineering in the ITESM Cam-pus Monterrey, México, in 1992, and his Ph.D. in Materials Science in 1997 from the Universitat Autònoma de Barcelona/Institut de Ciència de Materials de Barcelona, Spain. He is professor–researcher in the Centro Universitario de Ciencias Exactas e Ingenierías (CUCEI) of the Universidad de Guadalajara, México. His main interests are focused on the preparation of inorganic oxides, through several synthesis methods, and their potential application as environmental gas sensor materials.

Carlos Paucar obtained his M.Sc. degree in Chemistry from Universidad de Antioquia, Colombia. He is candidate to a Doctor in Chemistry from the Universidad del País Vasco (Spain). He is assistant professor–researcher in the Chemistry Department of the Universidad Nacional de Colombia, Campus Medellín. His research interests include the synthesis of inorganic nanomaterials using diverse synthesis methods.

Oswaldo Morán has a Doctorate degree in Physics from the Technical University of Karlsruhe, Federal Republic of Germany (2002). In 2006, he joined the Physics Department of the Universidad Nacional de Colombia, Campus Medellín. His work focuses on the synthesis and characterization of novel oxides, particularly in thin film form.