

Oxygen equilibrium and kinetics in $\text{PrBaCo}_2\text{O}_{5+\delta}$

C. FRONTERA¹, A. CANEIRO², A.E. CARRILLO¹, J. ORÓ-SOLÉ¹, J.L. GARCÍA-MUÑOZ¹

¹Institut de Ciència de Materials de Barcelona, CSIC

Campus universitario de Bellaterra, E-08.193, Cerdanyola, España.

²Centro Atómico de Bariloche, 8400 San Carlos de Bariloche, Argentina.

By means of in-situ thermo-gravimetry analysis (TGA) we have studied the dependence on temperature of the equilibrium oxygen content (δ) in $\text{PrBaCo}_2\text{O}_{5+\delta}$ cobaltite under different atmospheres or oxygen partial pressure. We have also characterized the kinetics of δ changes at different temperatures. The equilibrium studies have permitted us to prepare samples with the desired values of δ , a crucial step to correctly characterize the interesting family of layered "112" cobalt oxides. Kinetic studies reveal that oxygen diffusion and surface reactivity starts at low temperatures (200°C) in these compounds.

Keywords: Cobalt oxides, termogravimetry análisis, oxygen content determination, oxygen diffusion.

Equilibrio y cinética del oxígeno en $\text{PrBaCo}_2\text{O}_{5+\delta}$

Mediante medidas de análisis termogravimétrico hemos estudiado la dependencia en la temperatura del contenido de oxígeno (δ) en cobaltitas $\text{PrBaCo}_2\text{O}_{5+\delta}$ bajo diferentes atmósferas y diferentes presiones parciales de oxígeno. Por otra parte, hemos caracterizado la cinética de los cambios de δ a diferentes temperaturas. Los estudios en equilibrio nos han permitido preparar muestras con valores deseados de δ . Esto es crucial poder estudiar convenientemente esta familia de óxidos de cobalto con estructura "112" laminar. Los estudios de la cinética revelan que la difusión de oxígeno en el interior de las muestras, así como la reactividad en la superficie, empieza a temperaturas relativamente bajas (200°C).

Palabras clave: Óxidos de cobalto, análisis por termogravimetría, determinación del contenido de oxígeno, difusión de oxígeno.

1. INTRODUCTION

Layered "112" cobaltites ($\text{RBaCo}_2\text{O}_{5+\delta}$, $\text{R} \equiv$ rare-earth, $0 \leq \delta \leq 1$) present very interesting properties that have made them the subject of a growing research activity. From the intriguing features reported by Troyanchuck et al. (1) on " $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ " (a metal-insulator and two magnetic transitions) a vivid interest on these compounds has surged. Maignan et al. (2) established that the structure of these compounds is characterized by two features: (i) Ba and R ions do not form a solid solution at the A position of the perovskite structure but order in alternating (0 0 1) layers; and (ii) the oxygen vacancies, present in these compounds as in many doped cobaltites, locate at the Ln layers and have a great tendency to form ordered patterns. This results in a coexistence of Co ions in octahedra (CoO_6) and pyramidal (CoO_5) environments in an ordered manner. Moreover Maignan et al. (2) showed that different heat treatments, under appropriate atmospheres, can easily change δ and evidenced that the magnetic and transport properties are highly dependent on the oxygen content. In fact δ controls the nominal valence of Co ions that varies from $3.5+$ (50% of Co^{3+} and 50% of Co^{4+}) for $\delta=1$ to $2.5+$ (50% of Co^{3+} and 50% of Co^{2+}) for $\delta=0$ passing through 100% of Co^{3+} for $\delta = 0.5$. In accordance with this, different interesting properties have been reported for different oxygen contents. For $\delta=0$ (50% of Co^{3+} and 50% of Co^{2+}) charge ordering between Co^{3+} and Co^{2+} has been reported (3,4). For $\delta=0.5$ (100% of Co^{3+}) a metal-insulator transition is shown independently of the rare earth (2). This transition has been ascribed to a sudden spin state change of Co in octahedral place (5). Recent thermopower

measurements indicate that this spin state transition produces a blocking of the charge carriers due to "spin blockade" mechanism (6).

The dependence of the properties of these cobaltites on the oxygen contents makes of great interest the knowledge of methods to tailor δ precisely. In this context, different heat treatments under different atmospheres have been used to vary the oxygen content of polycrystalline $\text{NdBaCo}_2\text{O}_{5+\delta}$ (within the range $0 \leq \delta \leq 0.69$) (7) and in single crystals of $\text{GdBaCo}_2\text{O}_{5+\delta}$ (within the range $0 \leq \delta \leq 0.77$) (8). In order to extend these studies and to get a general method, we present here two sets of "in situ" thermo-gravimetry analysis (TGA) studies of $\text{PrBaCo}_2\text{O}_{5+\delta}$. The first one has been done under different atmospheres and varying the temperature. These measurements evidence that oxygen can be exchanged at surface and move easily through PrO_δ planes at temperatures above $T \approx 200^\circ\text{C}$. In order to gain insight on these capabilities that can make these compounds interesting as mixed conductors at relatively low temperature, we have studied the kinetics of the oxygen gain/loss after quick heating/cooling under pure O_2 atmosphere.

The second set of ATG measurements has been done at fixed temperature and varying the oxygen partial pressure. With the aid of this second set of measurements, it becomes possible to plan the adequate heat treatments to get the desired δ for this rare earth. To illustrate this, we have prepared two samples with rational oxygen content $\delta \approx \frac{1}{2}$ and $\delta \approx \frac{3}{4}$. In

addition, we have tried to open as wide as possible the δ range

by preparing a sample with a quite low oxygen content, $\delta \approx 0.17$, and a sample with $\delta \approx 0.17$ by means of moderately high oxygen pressure.

2. EXPERIMENTAL DETAILS

The initial polycrystalline sample has been synthesized by solid state reaction in air. High purity oxides (Pr_6O_{11} , Co_3O_4) and carbonates (BaCO_3) were mixed at stoichiometric ratios. After two decarbonating treatments at 900°C with intermediate grinding, the resulting product were pressed into a pellet at 10 Tm, finally fired at 1100°C during 12 h in air, and cooled down to RT at $100^\circ\text{C}/\text{h}$. The quality of the product obtained was tested by X-ray diffraction. This revealed that the sample obtained is a single phase and that no impurities are detected with this technique. The oxygen content of this "as-synthesized" sample was found to be $\delta=0.763(3)$.

For the first type of studies, small portions of the "as-synthesized" compound were measured by TGA up to 800°C in pure O_2 , air, and pure Ar atmospheres using a Perkin Elmer (model TGA-7) thermo-gravimetric analyzer. First, we have slowly heated the samples up to 800°C while measuring the mass change. In addition, we have performed long time annealing processes at different temperatures reached after quick heating/cooling in order to study the isothermal variation of the sample weight as a function of time and to obtain a most reliable value of δ in equilibrium at the annealing temperatures.

The second set of measurements was done by isothermal annealing of small portions of the sample under controlled oxygen partial pressure (P_{O_2}). By TGA (9) we have found the equilibrium value of δ as a function of T and P_{O_2} in $\text{PrBaCo}_2\text{O}_{5+\delta}$ within the range and $10^{-5}\text{ atm} \leq P_{\text{O}_2} \leq 1\text{ atm}$

With these measurements we have determined the conditions to obtain samples with controlled oxygen content. These compounds were obtained by annealing the as-prepared sample at the appropriate temperatures under the appropriate oxygen partial pressure during 24 hours and quenching them to liquid nitrogen temperature. The absolute oxygen content of the precursor and prepared samples was checked by reduction in dry $10\%\text{H}_2/\text{Ar}$ mixture at 1000°C assuming Co, Pr_2O_3 , and BaO as final products. The so determined values of δ were close (within ± 0.004) to those corresponding to the equilibrium P_{O_2} measurements.

3. RESULTS AND DISCUSSION

3.1 Heat treatments under different atmospheres.

Figure 1 shows the evolution of δ under O_2 atmosphere (solid line) and under air (dashed line) when the sample is slowly heated at a rate of $1^\circ\text{C}/\text{min}$. In order to compare the values of δ obtained during the slow heating with those corresponding to the equilibrium we have performed a second set of measurements at constant temperature of about 3 h (achieved after a quick heating). We have observed that after the initial 40 min no more variation of δ is detected. The obtained values are also depicted in Fig. 1 as crossed circles. The coincidence between both sets of values is remarkable. This indicates that $\delta(T)$ dependence obtained by slow heating is very near the equilibrium one.

Some features evidenced in Fig. 1 must be discussed. It

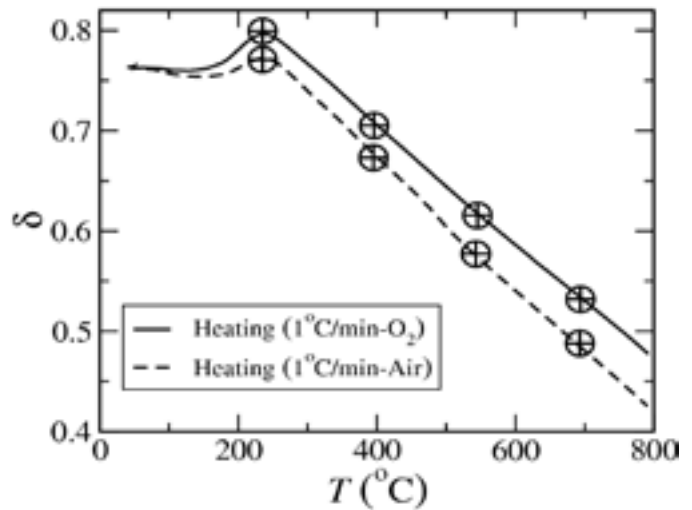


Fig. 1- Measure of δ as a function of temperature during a slow heating ($1^\circ\text{C}/\text{min}$) under pure O_2 (solid line) and in Air (dashed line). The cross centred circles show the values of δ obtained after a long (3 h) annealing at corresponding temperatures.

can be appreciated that, when heating, a certain oxygen gain is achieved from about 175°C - 200°C and that a maximum is achieved at about 240°C . To make possible this oxygen gain two different subprocesses must take place. The first one is the absorption of oxygen at the surface of the material (governed by the chemical surface reactivity) and the second is diffusion toward the bulk of the absorbed oxygen (governed by the diffusion coefficient). The enlargement of δ depicted in Fig. 1 evidences that the oxygen can be absorbed and can diffuse in PrO_3 planes at relatively low temperatures. It is also evidenced that in order to get a large value of δ one must anneal under O_2 and that it has no sense to heat above 240°C . These temperatures are smaller than (but not far from) those reported for $\text{YBaCo}_2\text{O}_{5+\delta}$ where oxygen mobility has been detected at about 230°C (10).

We have tried to obtain curves similar to those shown in

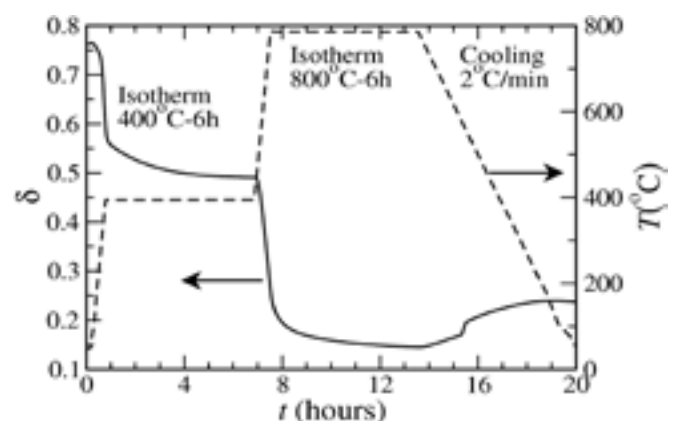


Fig. 2- Measure of δ (left axis, solid line) as a function of time for the depicted temperature profile (right axis, dashed line) under pure Ar atmosphere.

Fig. 1 under pure Ar atmosphere by heating at the same velocity 1°C/min. However, we have failed in obtaining δ values near equilibrium. The reason must be that, in Ar atmosphere, the time needed to equilibrate the samples is much longer than in air or in O₂ atmospheres. In order to guess how δ depends on the temperature under Ar atmosphere we have performed a different thermal study consisting on six parts: (i) annealing during 10 min at 40°C; (ii) a rapid heating (10°C/min) to 400°C; (iii) annealing at 400°C during 6 h; (iv) rapid heating (10°C/min) to 800°C; (v) annealing at 800°C during 6 h; and (vi) slow cooling (-2°C/min) to RT. Figure 2 shows the time evolution of δ, and the temperature profile during this heat treatment under pure Ar atmosphere. At both 400°C and 800°C the time needed for equilibration is quite long. From this figure, it can be appreciated that the oxygen content can be reduced to about δ=0.15 at , although it increases again up to δ ≈ 0.25 during the cooling down process.

3.2 Kinetics of oxygen changes

Relaxation toward equilibrium has been used to obtain information about diffusion coefficient (D) and/or chemical surface reaction coefficient (K) in single crystals with parallelepiped shape where an analytical solution of the diffusion equation exists (8). In powder samples the situation is different as far as the shape and size of the grains is not known precisely. In spite of this difficulty, previous works have studied the kinetics of oxygen change in powder samples by assuming that grains are spheres of average radius R (11) With these hypothesis, when the oxygen content is limited by the diffusion coefficient D, the variation of δ must follow:

$$\frac{\delta - \delta_e}{\delta_0 - \delta_e} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 \pi^2 \frac{Dt}{R^2}\right) \quad [1]$$

Where δ_e and δ₀ are the equilibrium and initial values of δ respectively. The decay towards equilibrium in this expression is given by the characteristic time $\frac{R^2}{D\pi^2}$. We have tried to fit

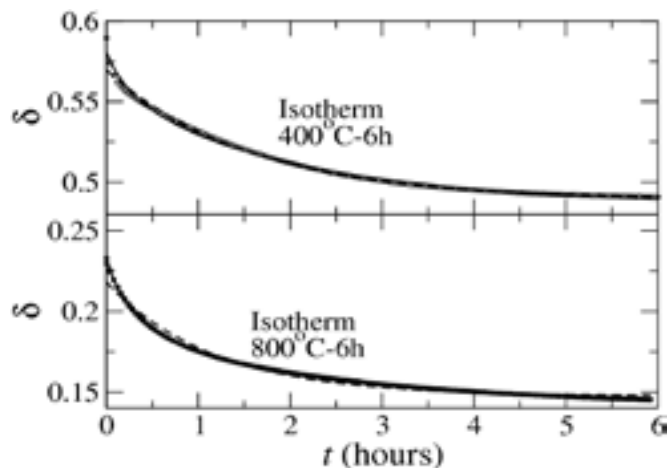


Fig. 3- Decay towards equilibrium of the oxygen content at 400 and 800°C under pure Ar. The solid and dashed lines show the best fit of equations [1] and [2] to experimental data (circles).

this expression to data in Fig. 2 and to data used for obtaining equilibrium points in Fig. 1. Results are shown in Figs. 3 and 4 respectively as solid lines. From Fig. 3, it can be realized that [1] fits well data obtained at 800°C but fails in reproducing data at 400°C, indicating that at lower temperatures and under Ar atmosphere the surface reactivity is also relevant for the kinetics of the process.

It is also worth to consider that Taskin et al. (8) have also studied the kinetics of oxygen change on GdBaCo₂O_{5+δ} powder samples. These authors report that the relaxation toward equilibrium can be well described using a single exponential:

$$\frac{\delta - \delta_e}{\delta_0 - \delta_e} = \exp\left(-\frac{t}{\tau}\right) \quad [2]$$

This type of decay indicates that the effect that governs the process is the oxygen interchange at the surface. We have tested to describe data in Figs. 3 and 4 by means of equation [2]. The best fits to this expression are shown as dashed lines. It is important to remark that fits done using equation [1] have the same number of free (refined) parameters that those using equation [2]. It can be appreciated that, in most of the cases experimental data are not well reproduced by this expression. This means that bulk diffusion is more relevant than surface exchange in PrBaCo₂O_{5+δ} at least at high temperature, and opens the question on how K and D depend on the size of the rare earth in LnBaCo₂O_{5+δ} family.

The unique case where expression [2] reproduces data better than expression [1] corresponds to the annealing under O₂ atmosphere at 235°C. This can be due to two different facts. As diffusion in the bulk will depend on temperature, it can happen that at low temperature the diffusion is slow and

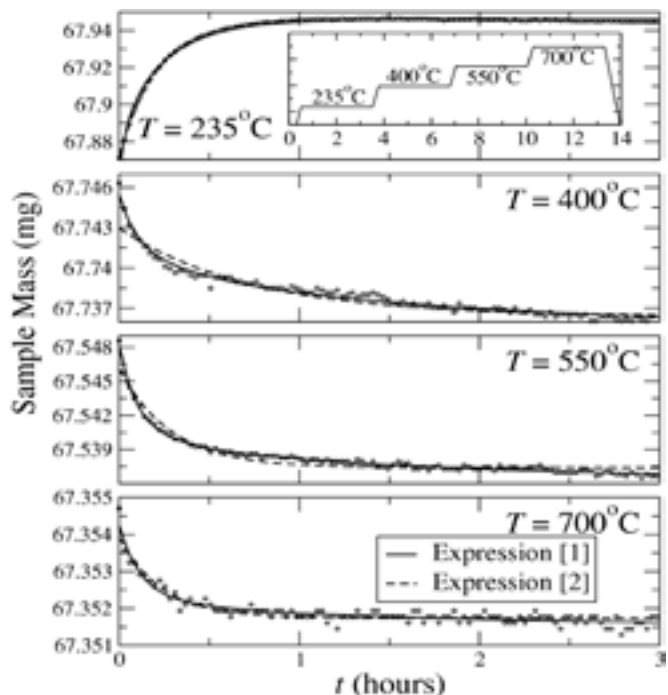


Fig. 4- Decay towards equilibrium of the sample mass at 235, 400, 550 and 700°C under pure O₂. The solid and dashed lines show the best fit of equations [1] and [2] to experimental data (circles). Inset in upper panel shows the temperature profile of the heat treatment.

surface reactivity becomes the limiting factor of the kinetics. This cannot be concluded at all and a second explanation arises: data at 235°C corresponds to an absorption process while all other to desorption processes.

3.3 P_{O_2} - T dependence of δ and oxygen tailoring

A second set of measurements has been done by measuring the weight variations when varying the oxygen partial pressure, P_{O_2} , at constant temperature. The P_{O_2} - T dependence of δ obtained by this way is depicted in Fig. 5. This figure shows the equilibrium value of the oxygen content $5+\delta$ as a function of P_{O_2} . All isotherms were reproducible upon oxidation (reduction) and subsequent reduction (oxidation). Therefore, they must be considered stable equilibrium states of the $\text{PrBaCo}_2\text{O}_{5+\delta}$ material. The equilibrium times were a few minutes for the high T and P_{O_2} range and some hours, and eventually up to two days, for low T and P_{O_2} values.

Results displayed in Fig. 5 have been used to prepare samples with different oxygen contents. For the first three samples the target oxygen levels were $\delta=0.17$, 0.5, and 0.75. These have been done by annealing the samples under appropriate conditions and, afterward, quenching them from each temperature and pressure to liquid nitrogen.

According to Fig. 3, $\delta=0.17$ can be found on isotherm at an oxygen partial pressure $P_{O_2}=5.0710^{-4}$. To get this composition, we have annealed the sample under these conditions during 36 h but the oxygen content found after this first treatment was $\delta=0.25$. To correct this, we performed a second treatment under the same conditions during 48 h more and determined a final oxygen content $\delta=0.176(6)$. A similar procedure were followed for $\delta=0.5$ and $\delta=0.75$ samples. We first searched on Fig. 5 for the appropriate conditions, that is 600°C and $P_{O_2}=5.55$

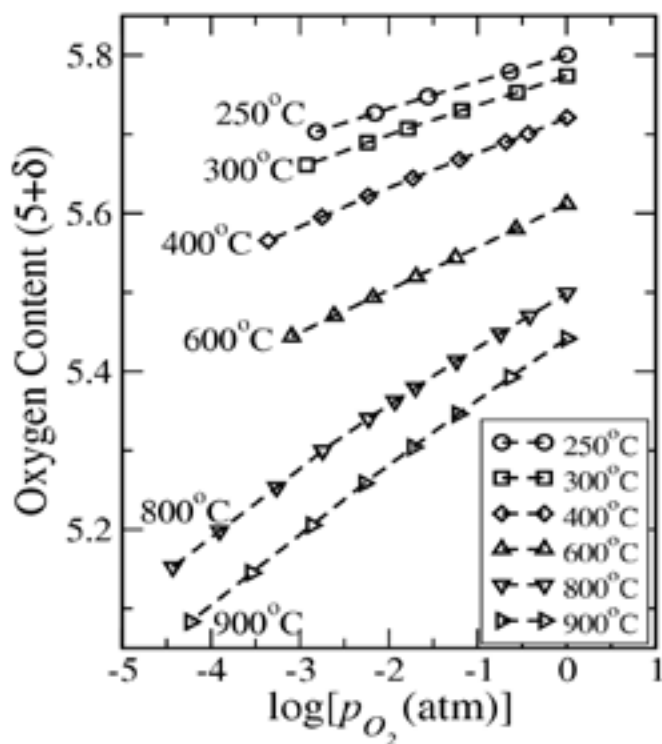


Fig. 5- Isothermal variation of the oxygen content as a function of the oxygen partial pressure P_{O_2} .

10^{-3} atm for $\delta=0.5$ and 250°C and $P_{O_2}=3.2810^{-2}$ for $\delta=0.75$, and performed the prescribed treatments during 36h. The final oxygen content determined was $\delta=0.519(7)$, and $\delta=0.74(1)$.

The objective for the fourth sample has been to increase as much as possible the oxygen content. For this, we have used high oxygen pressure ($P_{O_2}=180$ atm). We first heated the sample at 1°C/min up to 216°C. After 48 h we cooled it down to 190°C at the same rate and stay there during 10 h. We finally cooled the sample down to RT at 1°C/min. The oxygen content was determined to be $\delta=0.87(1)$.

4. CONCLUSIONS AND SUMMARY

$\text{LnBaCo}_2\text{O}_{5+\delta}$ family is the subject of intense research in order to understand its complex and rich phase diagram. In spite of the fact that oxygen content is a key parameter in this phase diagram, detailed investigations to determine the synthesis paths to precisely control δ are scarce or even lacking. The same can be said concerning studies of the specific behaviour of oxygen kinetics and oxygen diffusion, and/or the tendency of oxygen vacancies to form ordered patterns in the LnO_8 planes. With the objective of gaining insight on some of these questions, we have performed, by means of thermogravimetry measurements, a detailed research on the system $\text{PrBaCo}_2\text{O}_{5+\delta}$. We have first determined the dependence of the oxygen content upon temperature for different annealing atmospheres: air, O_2 and pure Ar. This has been achieved following two procedures (i) long time annealing at selected temperatures in the interval RT-800°C and (ii) slow continuous heating. From type (i) measurements, we have realized that annealing times of about 2 hour in air or O_2 atmospheres are enough to bring the system to the equilibrium (in the present case: powder polycrystalline samples of about 0.1 g) thus indicating that the kinetics of the oxygen exchange is rather fast. From the comparison of type (i) and type (ii) measurements, slow continuous heating treatments (1°C/min) can be used to establish the continuous δ - T dependence in air or O_2 atmospheres. Following this procedure, a maximum in the oxygen content is found at $T \approx 240^\circ\text{C}$, and, remarkably, oxygen intercalation starts (on heating) at $T \approx 175-200^\circ\text{C}$. Consequently, we can asses that oxygen diffuses within the PrO_8 planes and starts overcoming the surface energy barrier at unexpectedly low temperatures.

This can be of interest for the field of mixed conductors. It is known that electrical resistivity of these compounds is low ($\sim 10^{-3}\Omega\cdot\text{cm}$ in polycrystalline samples). We have tried to gain insight in these aspects by studying the kinetics of the oxygen absorption/desorption. Data supports that kinetics at the low temperatures is determined by the surface exchange barrier (kinetics of oxygen exchange at the surface of the grains) but at high temperatures the bulk oxygen diffusion governs the kinetics. This indicates that the temperature when the oxygen starts to go into the sample (175-200°C) is determined by the surface exchange barrier rather than from diffusion in the bulk.

The temperature dependence of the equilibrium oxygen content for different oxygen partial pressures was established for $\text{PrBaCo}_2\text{O}_{5+\delta}$ in the interval $5 \cdot 10^{-4}$ atm to 180 atm. This measurements permitted us to precisely determine the annealing temperatures, P_{O_2} , and times, to prepare four different samples having the desired stoichiometry. In particular we prepared polycrystalline samples with fractional values $\delta=\frac{1}{2}$ and $\delta=\frac{3}{4}$. The other two corresponded to stoichiometries near

the extremes of low and high oxygenation (0.176 and 0.869). Although a large variation of the oxygen content was achieved in the Pr layered "112" crystal structure, highly oxygenated samples can only be obtained using relatively high partial oxygen pressures. Using $p_{\text{O}_2} = 180$ atm we obtained a maximum oxygen content of $\delta = 0.87(1)$ annealing the material at 190°C.

ACKNOWLEDGMENTS

Financial support by the spanish MEC (MAT2003-07483-C02-02) and Generalitat de Catalunya (2001SGR-00334, PICS2005-14) projects is thanked. C.F. acknowledges financial support from MEC (Spain).

BIBLIOGRAPHY

1. I.O. Troyanchuk, N.V. Kasper, D.D. Khalyavin, H. Szymczak, R. Szymczak, M. Baran, "Phase Transitions in the $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ Perovskite" *Phys. Rev. Lett.* 80 (15), 3380-3383 1998.
2. 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 (2), 247-260 1999.
3. T. Vogt, P. M. Woodward, P. Karen, B.A. Hunter, P. Henning, A.R. Moodenbaugh, "Low to High Spin-State Transition Induced by Charge Ordering in Antiferromagnetic YBaCo_2O_5 " *Phys. Rev. Lett.* 84 (13), 2969-2972 2000.
4. E. Suard, F. Fauth, V. Caignaert, I. Mirebeau, G. Baldinozzi, "Charge ordering in the layered Co-based perovskite $\text{HoBaCo}_2\text{O}_5$ " *Phys. Rev. B* 61 (18), R11871- R11874 2000.
5. C. Frontera, J.L. García-Muñoz, A. Llobet, M.A.G. Aranda, "Selective spin-state switch and metal-insulator transition in $\text{GdBaCo}_2\text{O}_{5.5}$ " *Phys. Rev. B* 65 (18), 180405R 2002.
6. A. Maignan, V. Caignaert, B. Raveau, D. Khomskii, G. Sawatzky, "Thermoelectric Power of $\text{HoBaCo}_2\text{O}_{5.5}$: Possible Evidence of the Spin Blockade in Cobaltites" *Phys. Rev. Lett.* 93 (2), 026401 2004.
7. J. C. Burley, J.F. Mitchell, S. Short, D. Miller, Y. Tang, "Structural and Magnetic Chemistry of $\text{NdBaCo}_2\text{O}_{5.8}$ " *J. Solid State Chem.* 170 (2), 339-350 2003.
8. A.A. Taskin, A. N. Lavro, Y. Ando, "Transport and magnetic properties of $\text{GdBaCo}_2\text{O}_{5+x}$ single crystals: A cobalt oxide with square-lattice CoO_2 planes over a wide range of electron and hole doping" *Phys. Rev. B* 71 (13), 134414 2005.
9. A. Caneiro, P. Bavdaz, J. Fouletier, J.P. Abriata, "Adaptation of an Electrochemical System for Measurement and Regulation of Oxygen Partial Pressure to a Symmetrical Thermogravimetric Analysis System Developed Using a Cahn 1000 Electrobalance" *Rev. Sci. Instrum.* 53 (7), 1072-1075 1982.
10. D. Akahoshi, Y. Ueda, "Magnetic and MI Transitions in $\text{YBaCo}_2\text{O}_{5+x}$ ($0 \leq x \leq 0.5$)" *J. Phys. Soc. Japan* 68 (3), 736-739 1999.
11. F. Prado, A. Caneiro, A. Serquis, J. Briatico, "Thermogravimetric Study of the Reduction Step in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1.01}\text{O}_y$ as a Function of the Oxygen Partial Pressure" *Solid State Comm.* 94 (1), 75 1995.

Recibido: 15.07.05

Aceptado: 26.01.06

