

# Pulsed reactive crossed beam laser ablation of $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ using $^{18}\text{O}$ Where does the oxygen come from?

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## Abstract

The composition of thin perovskite films, especially the oxygen content, is a crucial parameter which influences many physical properties, such as conductivity and catalytic activity. Films produced by pulsed laser deposition are normally annealed in an oxygen atmosphere after deposition to achieve a desired oxygen content. In pulsed reactive crossed beam laser ablation, no annealing step is necessary, but a fundamental question regarding this deposition technique is still open: where does the oxygen in the films come from?

There are three possibilities, i.e. from the target, from the gas background, or from the gas pulse. To answer this question two experiments were performed:  $^{18}\text{O}_2$  was used during the deposition process as background gas with  $^{16}\text{O}$  anions in the target and  $^{16}\text{O}_2$  gas pulse, and a  $^{18}\text{O}_2$  gas pulse with  $^{16}\text{O}$  from the target and background. These experiments revealed that the quantification of the oxygen origin is only possible, when no oxygen exchange occurs at the deposition temperature. The films are characterized after deposition by elastic recoil detection analysis (ERDA) to determine the  $^{16}\text{O}/^{18}\text{O}$  ratio. Experiments with different oxidizing species in the gas pulse ( $\text{N}_2\text{O}$  and  $\text{O}_2$ ) confirm that the oxidizing potential ( $\text{N}_2\text{O} > \text{O}_2$ ) as well as the number of molecules are important.

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## 1. Introduction

In laser evaporation processes, film growth occurs during a short period of time after each laser pulse. During the time interval between the pulses, no matter is transferred from the target to the film. However, structural rearrangements can occur in the film during this period of time, as well as oxygen incorporation, loss and oxygen exchange. The pulsed laser deposition process thus appears as a sequential process with growth steps, separated by annealing-like steps of about 100 ms for a deposition rate of 10 Hz.

In general, there are three main sources for the oxygen incorporation during the deposition process with pulsed laser deposition: (i) from the oxygen background either after a

chemical reaction in the gas phase with species emitted from the target or directly at the film surface during the growth; (ii) from the oxygen background during the time interval between laser pulses, via direct film oxidation, and/or an exchange process between oxygen atoms that are already incorporated in the film and those coming from the ambient gas; (iii) directly from the target by laser ablation [1].

For pulsed reactive crossed beam laser ablation (PRCLA), an additional way to incorporate oxygen has to be considered. The oxygen from the gas pulse, which may very likely exist in the form of oxygen molecules or atomic oxygen after collisions in the gas phase, will react at the film surface.

Many studies related to  $^{18}\text{O}$  exchange are concentrated on calculations of the shift of magnetism and resistivity when  $^{16}\text{O}$  is exchanged for  $^{18}\text{O}$  [2,3]. After the development of PLD as a promising method to grow high Tc films, such as YBCO, it was analyzed how much oxygen is originating from the target and how much from the background gas [4,5]. The degree of

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oxygen saturation in the films and the influence of the oxygen pressure on the film properties are still important problems to be solved to optimize technological deposition conditions. To answer these questions, several experiments of oxygen exchange, i.e. from  $^{16}\text{O}$  to  $^{18}\text{O}$ , during deposition were performed by different groups [1,4,6]. The main information obtained from these studies indicates the oxygen source, i.e. target or oxygen ambient, and the process of oxygen incorporation into the films. The results are still controversial and strongly dependent on the materials being deposited.

The main question we try to answer with our studies is: from where does the oxygen originate in grown film when using PRCLA?  $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$  thin films were deposited by PRCLA using  $^{18}\text{O}$  as a background gas or in the gas pulse in order to analyze the role of the gas pulse on the oxygen content of the films. This perovskite compound has been selected due its application as electrocatalyst in rechargeable Zn–air batteries [7] and because the growth and film properties has been studied in detail previously [8]. The role of the gas pulse was also tested using different gases in the synchronized pulse, i.e.  $\text{O}_2$  and  $\text{N}_2\text{O}$ .

## 2. Experimental

$\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$  thin films were deposited on  $\text{MgO}(1\ 0\ 0)$  substrates. All films were grown at 923 K. A KrF excimer laser ( $\lambda = 248$  nm, 17 ns pulse length, 21,000 pulses), with a laser fluence of  $7.6\ \text{J cm}^{-2}$  and a repetition rate of 10 Hz was used for the ablation process. The target material (i.e. rod) was located at a distance of 4.5 cm from the substrate. Two oxidizing sources were used during the experiments: a synchronized  $\text{N}_2\text{O}$  or  $\text{O}_2$  pulse (99.999% purity, pulse length of 400  $\mu\text{s}$ , backing pressure = 200 kPa) and oxygen from a leak valve to provide an additional background pressure of  $\approx 8 \times 10^{-2}$  Pa during the deposition. The time delay between the gas pulse and the laser pulse was optimized for the maximum interaction between the ablation plasma and the gas pulse. Details about the procedure have been described elsewhere [9]. The influence of the number of molecules in the gas pulse was tested by varying the gas pulse pressure between 100 and 300 kPa for  $\text{O}_2$  and  $\text{N}_2\text{O}$  in the gas pulse. Two experiments with the  $^{18}\text{O}_2$  isotope were performed: the background gas  $^{16}\text{O}_2$  was exchanged for  $^{18}\text{O}_2$  at a pressure of  $8 \times 10^{-2}$  Pa and  $^{16}\text{O}_2$  in the gas pulse with a pressure of 200 kPa; the other experiment was performed with  $^{18}\text{O}_2$  as gas pulse with a pressure of 200 kPa and  $^{16}\text{O}_2$  as background gas with a pressure of  $8 \times 10^{-2}$  Pa. The samples were measured by heavy ion elastic recoil detection analysis (HIERDA) [10,11] to quantify the amount of  $^{18}\text{O}$  present in the films. Twelve mega-electron-volt  $^{127}\text{I}$  ions were used as projectile beam and the scattering angle was  $35^\circ$ . The data was analyzed by the DataFurnace computer code [12].

## 3. Results and discussion

### 3.1. PRCLA using $^{16}\text{O}_2$ as background and/or gas pulse source

Several experiments using  $^{16}\text{O}_2$  were performed prior to the experiments with  $^{18}\text{O}$ -isotope. The aim of these experiments

Table 1

Stoichiometry of the LCCO films produced with different gas pulse pressures and gases. The error of the measurement is  $\pm 5\%$

Gas pulse pressure (bar)	Stoichiometry for $^{16}\text{O}$ as gas pulse + $\text{O}_2$ background	Stoichiometry for $\text{N}_2\text{O}$ as gas pulse + $\text{O}_2$ background
1.0	$\text{La}_{0.65}\text{Ca}_{0.35}\text{Co}_{0.86}\text{O}_{2.48}$	$\text{La}_{0.65}\text{Ca}_{0.35}\text{Co}_{0.9}\text{O}_{2.7}$
1.5	$\text{La}_{0.65}\text{Ca}_{0.35}\text{Co}_{0.88}\text{O}_{2.51}$	$\text{La}_{0.66}\text{Ca}_{0.34}\text{Co}_{0.96}\text{O}_{2.72}$
2.0	$\text{La}_{0.68}\text{Ca}_{0.32}\text{Co}_{0.91}\text{O}_{2.6}$	$\text{La}_{0.64}\text{Ca}_{0.36}\text{Co}_{0.87}\text{O}_{2.8}$
2.5	$\text{La}_{0.68}\text{Ca}_{0.32}\text{Co}_{0.91}\text{O}_{2.72}$	$\text{La}_{0.68}\text{Ca}_{0.32}\text{Co}_{0.97}\text{O}_{2.82}$
3.0	$\text{La}_{0.68}\text{Ca}_{0.32}\text{Co}_{0.97}\text{O}_{2.82}$	$\text{La}_{0.7}\text{Ca}_{0.3}\text{Co}_{0.99}\text{O}_{2.88}$

was to analyze the amount of oxygen incorporated in the film as a function of the pressure when  $^{16}\text{O}_2$  was applied as gas pulse instead of  $\text{N}_2\text{O}$ . In all experiments, oxygen was used as the background gas in the chamber.

The oxygen incorporation in the growing film takes place continuously. The presence of only one oxidizing source, i.e. background or gas pulse always produces films with lower oxygen contents. The films produced in the presence of only the oxygen background have higher oxygen contents than the films produced only using the  $\text{N}_2\text{O}$  gas pulse and a pressure in the chamber of  $8 \times 10^{-4}$  Pa. For this set of experiments, several films were produced using the “standard” oxygen background pressure ( $8 \times 10^{-2}$  Pa) while two gases ( $\text{O}_2$  or  $\text{N}_2\text{O}$ ) with different pressures were used for the gas pulse. The film compositions as a function of the gas pulse pressure for  $^{16}\text{O}_2$  and  $\text{N}_2\text{O}$  gas pulses are summarized in Table 1 and are shown graphically for the oxygen content in Fig. 1.

The amount of the metals (La, Ca, Co) is almost constant, while an increase in the oxygen content of the films can be observed for both gas pulses when the pressure of the gas pulse is increased. This result can be rationalized in the following way. An increase of the gas pulse pressure corresponds to a larger amount of gas molecules which will collide with the plasma plume, forming atomic and excited state species, which can be easily incorporated in the film. The amount of oxygen

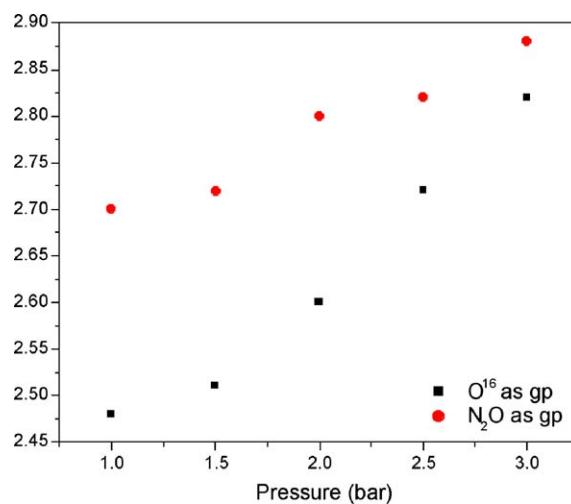


Fig. 1. Oxygen stoichiometry index of LCCO films as a function of pressure for  $\text{O}_2$  and  $\text{N}_2\text{O}$  gas pulses, respectively, with a constant oxygen background of  $8 \times 10^{-2}$  Pa.

present in the film is always higher for any given pressure when  $N_2O$  is used as a gas pulse instead of  $O_2$ . The differences in oxygen content between films grown with the different gases in the gas pulse become smaller as the film composition approach the stoichiometric composition of  $AA'BO_3$ . Because the contribution of the oxygen background is constant in both cases, the only explanation of the observed result is the oxidizing nature of the gas pulse. The interaction of the plume with the gas pulse ( $O_2$  or  $N_2O$ ) plays a crucial role in producing the atomic oxygen required for the growth of the film. The origin of the atomic oxygen, primarily in the vicinity of the target, is due to the dissociation of  $N_2O$  or  $O_2$  by collisional fragmentation with the plasma or electron-impact [13]. The effectiveness of  $O_2$  as an oxidizing agent is limited due to its higher dissociation energy (5.11 eV) compared to the lower value for  $N_2O$  (1.67 eV) [13]. The amount of atomic oxygen in the instantaneous flux of species arriving at the substrate is smaller when  $O_2$  is used as a gas pulse than in the case of  $N_2O$ . This amount is not high enough to satisfy the kinetic requirements during the deposition from each pulse, yielding films with lower oxygen content. Nevertheless, the oxygen non-stoichiometry can be minimized when the gas pulse pressure is increased, as shown in Fig. 1. This result indicates that the amount of the atomic oxygen in the instantaneous flux can be directly controlled by adjusting the pressure of the gas pulse.

### 3.2. PRCLA using $^{18}O_2$ as the background or gas pulse source

The role of the different oxygen sources in the growth process is quite well understood, but the main question to answer is to quantify the oxygen origin, i.e. the amount from the background and from the gas pulse. Therefore, experiments were performed using  $^{18}O$ -isotope as background gas with  $^{16}O$  from the gas pulse and the target, and with  $^{18}O_2$  as gas pulse and  $^{16}O$ -isotope as background gas and from the target. The cooling of the grown films was performed according to a procedure which has been established to yield the highest oxygen content, i.e. a fast cooling with the open chamber [14,15].

The ERDA spectra for LCCO films grown with  $^{18}O$  as gas pulse (Fig. 2a) and background (Fig. 2b) are presented in Fig. 2.

The spectra in Fig. 2 confirm that all expected elements are present in the film and no contaminations are introduced. When the film was grown using  $^{18}O_2$  as a background it was possible to observe in the film the presence of  $^{18}O$  from the background and  $^{16}O$  from the target and the gas pulse. On the other hand, when  $^{18}O_2$  was used as a gas pulse it was not possible to detect any  $^{18}O$  in the resulting film by HIERDA. This observation is shown in Fig. 3, where the oxygen yields are plotted as a function of the atomic mass, with  $^{18}O$  as background in Fig. 3a and as gas pulse in Fig. 3b.

The results presented in Figs. 2 and 3 indicate that no isotopic oxygen from the gas pulse was incorporated into the films during the growth. This result is very surprising, as the experiments with the different pressures of the gas pulse (see Fig. 1) clearly indicate that oxygen also originates from the gas pulse. We reexamined therefore our experimental approach,

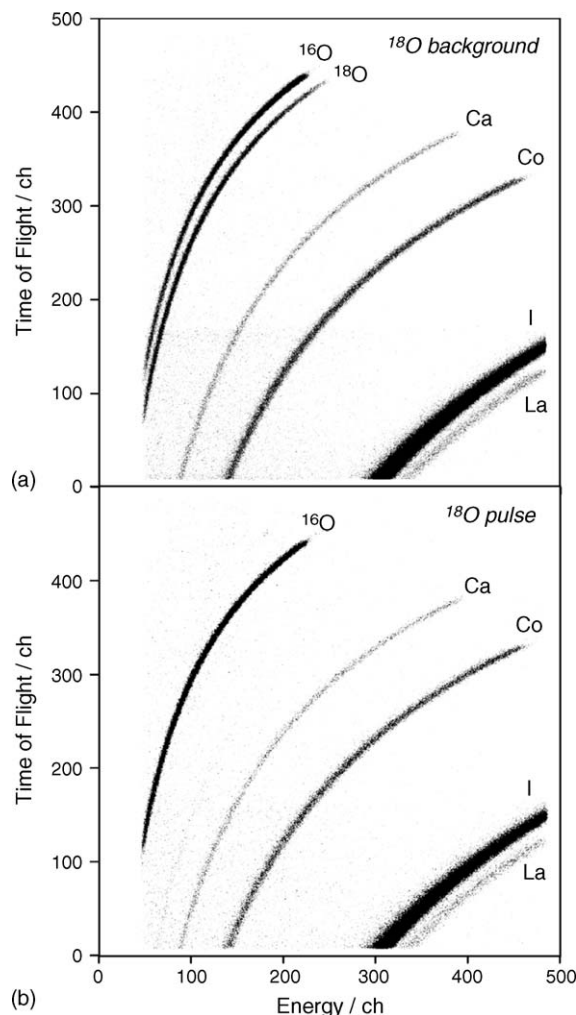


Fig. 2. ERDA spectra of LCCO films grown with  $^{18}O_2$  as background (a) and gas pulse (b).

and had to realize that the films incorporate oxygen when the particles arrive on the substrate and between the laser pulses.

The standard cooling procedure will result additionally in an exchange of  $^{18}O$  in the film by the  $^{16}O$  from the air at the high temperatures when the cooling starts. The above described results show that the amount of oxygen incorporated in the film is higher when only the background pressure is used compared to experiments where only the gas pulse was applied. This clearly indicates that the amount of oxygen which originates from the background is larger compared to the amount from the gas pulse. However, Fig. 3 shows obviously, that the amount of  $^{18}O$  present in the sample is larger in the case of the background than for the gas pulse as isotope source, which corroborates our previous observations. To solve this controversy, one has to take into account that after deposition the films were cooled in air and that a back-exchange process ( $^{18}O \rightarrow ^{16}O$ ) can influence the actual isotope balance in the grown films.

After realizing this problem several new questions came up. Is this  $^{18}O \rightarrow ^{16}O$  exchange homogeneous within the film thickness? Are the films stable in air with the time? We therefore measured the  $^{18}O$ -content of the film deposited using  $^{18}O_2$  as a background gas as a function of the depth and repeated the

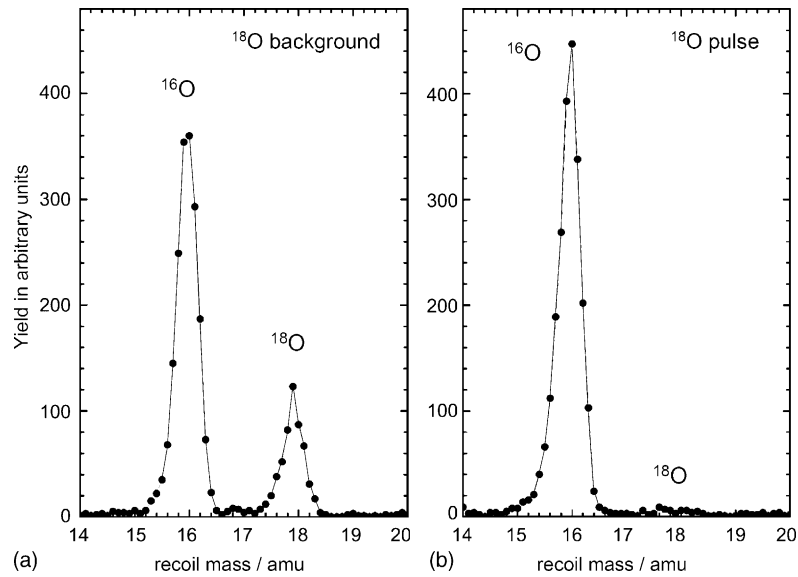


Fig. 3. Plot of the oxygen 16/18 yield for the LCCO films for  $^{18}\text{O}_2$  as background (a) and gas pulse (b).

measurements after a storage time of 6 weeks at room temperature in air. The results are presented in Fig. 4, with the original measurements in Fig. 4a and the measurements after storage in Fig. 4b.

The data in Fig. 4 show clearly that the percentage of  $^{18}\text{O}$  is not constant through the thickness of the film. Close to the surface the amount is  $\approx 10\%$  compared to the  $\approx 50\%$  close to the interface with the substrate. The solid line in Fig. 4 is a trendline which is the same in both graphs. The  $^{18}\text{O}$  to  $^{16}\text{O}$  ratio did not

significantly change between the two measurements except for a possible slight decrease of  $^{18}\text{O}$  in the first few nm of the stored sample. The total amount of oxygen ( $^{16}\text{O} + ^{18}\text{O}$ ) was found to be constant throughout the whole film in both measurements. This result indicates that the  $^{18}\text{O}$  incorporated in the film during the growth process was exchanged for  $^{16}\text{O}$  during the cooling. The variation of the  $^{18}\text{O}$ -content through the film presents a rather complex behavior which could, e.g. be fitted by an exponential or two linear functions (included as dotted lines in Fig. 4a). The origin of this complex variation of the isotope content is not yet clear, but may be related to backexchange processes during cooling and film growth. From the comparison between the measurements after 6 weeks no clear differences are observed, indicating that the  $^{18}\text{O} \rightarrow ^{16}\text{O}$  exchange takes place only at higher temperatures.

The next step was therefore to identify at which temperature the  $^{18}\text{O} \rightarrow ^{16}\text{O}$  exchange in LCCO takes place. For these experiments, target material was pulverized and milled until a fine powder was obtained to ensure that the identical perovskite is applied in the PLD and exchange experiments. The first experiments to determine the oxygen content of the target material were thermogravimetric hydrogen reduction (TG/ $\text{H}_2$ ), where the LCCO material was reduced in an atmosphere of 5% of  $\text{H}_2$  in He according to the following reaction:

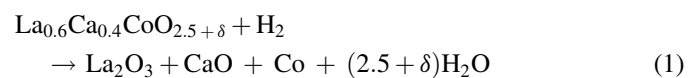


Fig. 5 shows a typical thermogravimetry curve obtained during the hydrogen reduction of the LCCO target material. Calculations of the oxygen content based on the weight change of 11.62% recorded between 473 and 1193 K give an oxygen stoichiometry value of  $2.77 \pm 0.02$  for the starting material. The other information which can be obtained from this plot is that the reduction process takes place in three steps as indicated by the mass spectrometry measurements of the  $m/e = 18$  signal

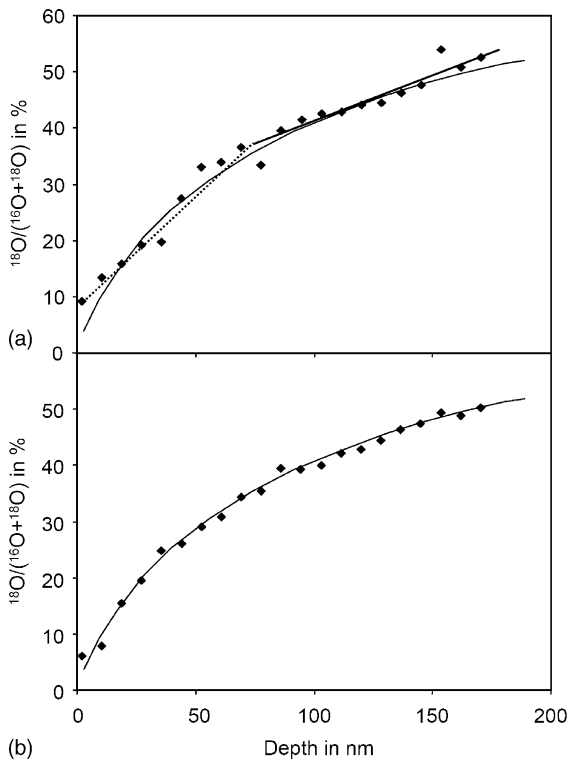


Fig. 4. Plot of the  $^{18}\text{O}$  content in LCCO films as a function of the film depth without (a) and with a storage time of 6 weeks (b).

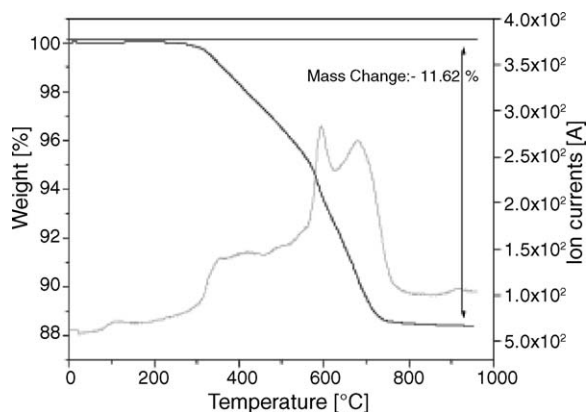


Fig. 5. Thermogravimetric curve obtained during the hydrogen reduction of the LCCO target material. The dotted gray line shows the mass spectrometric signal for evolving water (see Eq. (1)).

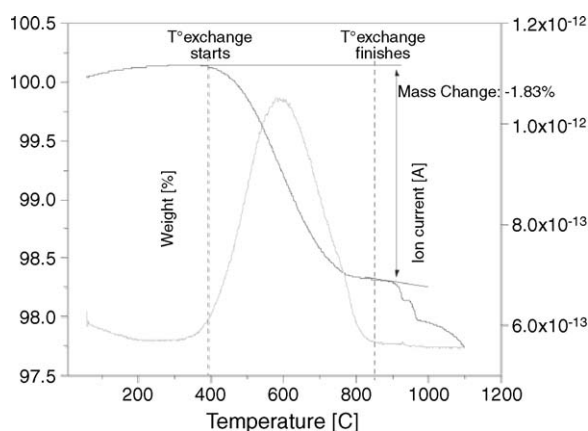


Fig. 6. Thermogravimetric curve of the  $^{18}\text{O} \rightarrow ^{16}\text{O}$  backexchange in a LCCO sample. The dotted line shows the mass spectrometric signal for the  $^{18}\text{O}^{16}\text{O}$  molecules created during the oxygen isotope backexchange.

(water). From these data we can conclude that the target material is already oxygen understoichiometric.

In order to identify the temperature at which the oxygen in the structure becomes mobile and the isotope exchange is possible a back exchange ( $^{18}\text{O} \rightarrow ^{16}\text{O}$ ) process was performed on the thermobalance. First a LCCO sample was substituted with  $^{18}\text{O}$  by reacting at 973 K for 10h. This “ $^{18}\text{O}$ -sample” is then heated from 298 to 1273 K in a flow of 50%  $^{16}\text{O}_2$  in He on the thermobalance. Fig. 6 shows a thermogravimetry curve obtained during this exchange process. Calculations of the oxygen content based on the weight change recorded between 673 and 1123 K indicate a mass change of 1.83%, which correspond to an  $^{18}\text{O}$ -content in the sample of 68% assuming the previously estimated oxygen stoichiometry ( $2.77 \pm 0.02$ ). The gray line is the spectrometric signal of the mass of 34 corresponding to the mixed  $\text{O}_2$  ( $^{16}\text{O}^{18}\text{O}$ ) molecule, which is produced during the exchange process. The plot indicates that the oxygen exchange takes place between 673 and 1123 K. This value confirms that during the deposition temperature of 923 K one part of the  $^{18}\text{O}$  is exchanged for  $^{16}\text{O}$ , but also that during the cooling, until 673 K are reached,  $^{18}\text{O}$  is continuously exchanged for  $^{16}\text{O}$  from the air.

## 4. Conclusions

The data reveal that a higher oxygen content can be obtained in the films when  $\text{N}_2\text{O}$  is used as gas pulse compared to  $\text{O}_2$  which can be explained by the lower dissociation energy of  $\text{N}_2\text{O}$ . An increase of the gas pulse pressure, i.e. a larger amount of molecules in the gas pulse, results also in a higher oxygen content of the films. The difference between  $\text{N}_2\text{O}$  and  $\text{O}_2$  become smaller as the films approach the stoichiometric composition of  $\text{AA}'\text{BO}_3$ . From the isotopic experiments we can conclude that it is only possible to detect  $^{18}\text{O}$  when  $^{18}\text{O}_2$  is used as a background gas. When the  $^{18}\text{O}_2$  is used as a gas pulse it was not possible to detect  $^{18}\text{O}$  in the film. This result is difficult to understand when the experiments, with the different pressures of the gas pulse are considered. These data showed that oxygen also originates from the gas pulse, although in a lower yield than for the background gas. A detailed analysis of the data and possible processes suggest that the small amount of  $^{18}\text{O}$  from the gas pulse which is incorporated during the deposition process is exchanged with  $^{16}\text{O}$  from the air during the cooling procedure. The thermogravimetric analysis of the oxygen exchange process shows that it would only be possible to obtain quantitative data of the oxygen origin during PLD or PRCLA when the films are deposited at low temperatures, i.e. below the exchange temperature for oxygen. This temperature has to be determined for each material if isotope experiments are performed.

It was therefore not possible to determine quantitatively the amount of oxygen originating from the gas pulse and from the background gas due to the exchange process during the film growth and cooling.

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