THERMOGRAVIMETRIC INVESTIGATION OF THE OXYGEN CONTENT AS A FUNCTION OF OXYGEN PARTIAL PRESSURE IN $La_{1.8}Sr_{0.2}CuO_y$ AT 1173 K

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Abstract

Thermogravimetric measurements have been performed at 1173 K on $La_{1.8}Sr_{0.2}CuO_{\psi}$ samples with the tetragonal K_2NiF_4-type structure. Depending on the sample preparation method, $La_{1.8}Sr_{0.2}CuO_{\psi}$ can be trapped in metastable states showing a characteristic plateau in P_{O_2} vs. ψ at $P_{O_2} = 5(\pm 2)\times 10^{-3}$ atm. The existence of this plateau is correlative to ψ values larger than $\psi = 4$. Cycling the sample between $P_{O_2} = 1$ to 10^{-6} atm makes the metastable isotherms to evolve slowly towards the true equilibrium one. A possible reason for the appearance of the plateau is discussed in terms of $La_{8-x}Sr_xCu_8O_{20-\varepsilon}$ microdomains.

1. INTRODUCTION

Among the recently discovered high temperature superconducting oxides, the system represented by $La_{2-x}Sr_xCuO_\psi$ is of particular interest for research purposes because it maintains a relatively simple K_2NiF_4-type structure over the wide composition range $0 < x < 1.35$.[1,2] Another possibility, to keep the structure constant while changing composition in this system, is to vary the oxygen content, ψ, by adequated annealing under controlled partial pressure of oxygen, P_{O_2}.[3] Various studies[4,5] showed that the electrical resistivity of $La_{2-x}Sr_xCuO_\psi$ is very sensitive to changes in P_{O_2} and this emphasizes the importance of knowing in detail the dependence of ψ with P_{O_2} as a function of fixed x. However, the data reported in the literature are limited, with values of ψ for P_{O_2} = 1 atmosphere (atm) which in some cases are larger than the stoichiometric value $\psi = 4$, and reach up to about $\psi = 4.05$.[6,7] This led us to investigate more in detall P_{O_2} vs. ψ for the particular case of $La_{1.8}Sr_{0.2}CuO_\psi$, by means of a high precision thermogravimetric equipment developed in our laboratory which was specially designed for equilibrium thermogravimetric measurements of P_{O_2} in oxides.[8] The measurements were carried out isothermically at the convenient working temperature of 1173 K. The results obtained demonstrate the primary importance of an adequate sample preparation and characterization in order to reach reproducible and meaningful results when performing physical measurements on the sample.

Complementary measurements performed in this work were

X-rays powder diffraction and electrical resistivity.

2. EXPERIMENTAL

The construction, details and performance of the experimental equipment used in our thermogravimetric measurements were described in detail elsewhere.[9] In essence, this equipment consists of a symmetrical Cahn 1000 electrobalance coupled to an electrochemical system (pump and oxygen gauge)[9,10] for the measurement and regulation of P_{O_2}. Weight changes can be measured within ± $5x10^{-6}$ gram, so, for our samples of about 1 gram of $La_{1.8}Sr_{0.2}CuO_{\psi}$, it was possible to determine changes in ψ within ± $2x10^{-4}$. The appropriate oxygen atmosphere was obtained by a mixture of argon-oxygen supplied by the electrochemical system, with P_{O_2} values ranging between 10^{-6} and 1 atm. Estimated errors in P_{O_2} were ± 2 %, including systematic errors. Equilibration times at the working temperature varied with P_{O_2}, ranging from 2 hours at 1 atm to 24 hours at 10^{-6} atm. The equilibrium criterion used in this work was "constant sample weight with time, within ± $5x10^{-6}$ gram". This equilibrium criterion was verified over periods of 24 hours.

Raw materials for sample preparation were reagent grade La_2O_3, $SrCO_3$ and 99.99 % pure Cu, the first two provided by Mallinckrodt Chemical Works. La_2O_3 and $SrCO_3$ were thermogravimetrically analized before use in order to assess the amount of volatile impurities they contained, such as H_2O and CO_2, which may be absorbed or chemically bonded to these reactants. In this way we have minimized systematic errors in

cationic compositions which, otherwise, are likely to occur.[11] Our $La_{1.8}Sr_{0.2}CuO_{\psi}$ samples were prepared either by thermal decomposition of nitrates or by the "liquid-mix" technique.[12] The samples obtained are listed in Table 1. La:Sr:Cu cationic ratios for all samples were 1.80:0.20:1.00 except for sample III for which this ratio was 1.82:0.20:1.00 . Cationic compositions are estimated to be correct within ± 0.5 % . Sample IV was in powder form (about 3 μm average size) which helped to reduce equilibration times. X-rays powder analysis performed before the thermogravimetric measurements confirmed the tetragonal K_2NiF_4-type structure for all samples, with no evidence of impurity phases. The well known superconducting transition[5] near 36 K was verified by means of electrical resistivity measurements.

The absolute oxygen content of our samples was determined by reduction in dry hydrogen complemented by iodometric titration.[13] The estimated error in ψ associated to these determinations is ± $2x10^{-3}$.

3. RESULTS AND DISCUSSION

The results of our thermogravimetric measurements, performed at the fixed temperature of 1173 K using the $La_{1.8}Sr_{0.2}CuO_{\psi}$ samples listed in Table 1, are shown in Figures 1 to 4.

Figure 1 corresponds to sample I. Three different parts, AB, BC and CD, are clearly differentiated on the corresponding isotherm. In order to obtain part AB, sample I was first kept 72 hours under P_{O_2} = 1 atm at 1173 K thus obtaining the starting point A whose oxygen content is $\psi(A;I) = 4.033$.

Then, data points corresponding to part AB were measured. Part AB corresponds to a region where P_{O_2} changes rapidly with ψ. When P_{O_2} was lowered below the value $P_{O_2} = 4x10^{-3}$ atm, the sample in part AB became clearly unstable (see Figure 1) and began to reduce continuously moving along the constant P_{O_2} segment BC until (after 1 day equilibration time) part CD was reached. Then, data points on part CD were obtained and the behavior of P_{O_2} as a function of ψ was similar to that in part AB. For P_{O_2} slightly larger than $P_{O_2} = 10^{-2}$ atm the sample in part CD became unstable and started to oxidize back to part AB. Thus, a slight hysteresis exists in the behavior of P_{O_2} vs. ψ (see Figure 1). Part AB was not exactly reached upon oxidation from CD but a new starting point, A', was finally obtained for $P_{O_2} = 1$ atm. It is $\psi(A';I) = 4.023$, which is smaller than the previous $\psi(A;I)$ but still larger than the stoichiometric value $\psi = 4$. It should be noticed that, within the conditions of our experiment, A and A' should be considered metastable states of the $La_{1.8}Sr_{0.2}CuO_{\psi}$ sample which depend on the sample history and preparation method. This consideration is, in principle, extensible to the complete isotherm ABCD.

Figure 2 corresponds to sample II. Three runs were made using this sample and the isotherms observed are similar to that for sample I. In the first run, the starting point A shows $\psi(A;II) = 4.007$, a value significantly smaller than $\psi(A;I)$ and $\psi(A';I)$. The plateau BC occurs at practically the same P_{O_2} as in the case of sample I, but with the oxygen composition width reduced to about one fourth (compare Figures

1 and 2). We estimate $P_{O_2}(BC) = 5(\pm 2)x10^{-3}$ atm. The second isotherm A'B'C'D' was measured after cycling the sample across $P_{O_2}(BC)$. This operation was performed with the sample inside the thermogravimetric equipment using succesively pure oxygen and pure argon, at one atmosphere, for at least four times. The first run isotherm is not reproduced in the second run, but smaller oxygen contents and a diminished width of the plateau, B'C', are observed (see Figure 2). The third run A"B"C"D" was performed after further cycling of the sample across $P_{O_2}(BC)$. This results in some additional reduction of the oxygen contents as well as of the width of the plateau, B"C" (see Figure 2). The composition of the starting point A", obtained after 45 days manipulating the sample at the fixed temperature of 1173 K, is $\psi(A";II) = 3.993$. Thus, compared to sample I, the metastable isotherms shown by sample II are lower in oxygen content and have $P_{O_2} = 1$ atm starting compositions which are closer to the stoichiometric value $\psi = 4$. Sample II clearly displays a systematic evolution of the consecutive isotherms toward smaller ψ values and a correlative decrease in the oxygen composition widths for the plateau BC.

Figure 3 corresponds to sample III. Two runs were made for this sample. The starting point A of the first run shows $\psi(A;III) = 3.990$, a value which is close to $\psi(A";II)$. The plateau BC shown by sample III is very narrow near the resolution limit of our experimental equipment. After several cycles in P_{O_2} across $P_{O_2}(BC)$, a second run A'D' was performed with the result $\psi(A';III) = 3.983$ and, remarkably, the plateau BC has completely disappeared. In addition, further cyclings

of sample III between 1 and 10^{-5} atm do not cause modifications in curve A'D'. Therefore, isotherm A'D' is reproducible, and, consequently, we assume it to represent well the true equilibrium states of the $La_{1.8}Sr_{0.2}CuO_{\psi}$ sample.

Figure 4 corresponds to sample IV. After preparation, this sample was cycled several times in P_{O_2} at high temperatures directly inside the sample preparation furnace (avoiding in this way the rather troublesome procedure of cycling the sample within the thermogravimetric equipment). Thereafter, isotherm AD, with no plateau, was obtained. As expected from our previous observations on sample III, this isotherm was reproducible after additional reductions and oxidations. Hence, curve AD should be taken to represent true equilibrium states and should agree with isotherm A'D' obtained using sample III. However, $\psi(A;IV) = 3.988$ is somewhat larger than $\psi(A';III) = 3.983$. Although inherent errors in the determinations of absolute oxygen contents might contribute to this small discrepancy, departures from cationic stochiometry can also be responsible for it.

From the thermogravimetric results described above it can be concluded that:

(i) For the true equilibrium states of the $La_{1.8}Sr_{0.2}CuO_{\psi}$ samples, at 1173 K and in the range $10^{-5} < P_{O_2} <$ 1atm, P_{O_2} vs. ψ is represented by a clearly smooth curve. Within experimental error, this curve can be taken to be either A'D' in Figure 3 or AD in Figure 4. The oxygen content, ψ, keeps smaller than the stoichiometric value $\psi = 4$ even at $P_{O_2} = 1$ atm. P_{O_2} increases rapidly for ψ approaching $\psi = 4$, a

behaviour which is indicative of oxygen saturation.

(ii) The $La_{1.8}Sr_{0.2}CuO_{\psi}$ samples can be easily trapped in metastable states which constitute isotherms showing a characteristic plateau in P_{O_2} vs. ψ at $P_{O_2} = 5(\pm 2)x10^{-3}$ atm. P_{O_2} cycling through this plateau makes these metastable isotherms to evolve slowly towards the isotherm which corresponds to true equilibrium. The existence of the plateau in the metastable isotherms is correlative with ψ values larger than those corresponding to true equilibrium, including ψ values at $P_{O_2} = 1$ atm which are significantly larger than the stoichiometric one $\psi = 4$. It appears that careful sample preparation and characterization is indeed needed in order to exclude undesirable metastable states from the $La_{1.8}Sr_{0.2}CuO_{\psi}$ samples.

It is of interest to discuss the reasons for the appearance of a plateau in P_{O_2} vs. ψ for the metastable isotherms. Thermodynamically, this plateau resembles that of a first order transition. Thus, we have X-ray analyzed a sample identical to sample II, respectively quenched from what corresponds to parts AB and CD (see Figure 2), finding only the K_2NiF_4-type structure with small differences in lattice parameters. A similar situation occured with respect to sample I. The conclusion is that the presence of the plateau would not be easily detected by means of conventional X-ray techniques

The activation energy for cationic diffusion is certainly much higher than that for oxygen diffusion[14] (which is in agreement with the relatively short oxygen equilibration times observed in our thermogravimetric experiments). Therefore, we

think that the metastable states of the $La_{1.8}Sr_{0.2}CuO_{\psi}$ samples can be attributed to non-equilibrium, practically frozen, cationic configurations. Upon cycling in P_{O_2}, these configurations evolve slowly at 1173 K towards the true equilibrium one.

Although it is difficult to assess the nature of these cationic configurations, it is likely that they are associated with microscopic but strong cationic inhomogeneities produced during sample preparation. Hence, at a local level, tiny microdomains with ionic arrangements characteristic of other phases of the quaternary system La-Sr-Cu-O would exist embbeded in the K_2NiF_4-type matrix. In particular, one of these phases can be the oxygen-deficient copper perovskite $La_{8-x}Sr_xCu_8O_{20-\varepsilon}$.[2,15,16] To test this idea, a $La_{6.75}Sr_{1.25}Cu_8O_z$ sample was prepared in our laboratory using the liquid-mix technique. After X-ray characterization, the isotherm shown in Figure 5 was obtained for this sample. This isotherm indicates that $La_{6.75}Sr_{1.25}Cu_8O_z$ decomposes for P_{O_2} values lower than $4x10^{-3}$ atm. The latter value is very close to that at wich part AB becomes unstable in the case of samples I to III. Therefore, we propose that the P_{O_2} vs. ψ plateau in the metastable isotherms, and the correlative excess in ψ over the true equilibrium values, are related to the existence in the $La_{1.8}Sr_{0.2}CuO_{\psi}$ sample of very small uniformly distributed, intergrowth microdomains of composition close to $La_{6.75}Sr_{1.25}CuO_z$.

To confirm that the proposed cationic inhomogeneities are due to the sample preparation method, a sample was prepared using the standard ceramic route (mechanical mixing of CuO,

La_2O_3 and $SrCO_3$, firing at high temperatures and intermediate grinding). For this sample, the cationic inhomogeneities are expected to be significantly larger than those for samples I to IV. In fact, a cursory thermogravimetric run for this sample confirmed the existence of a large plateau at about $P_{O_2} = 5x10^{-3}$ atm while the absolute oxygen content at $P_{O_2} = 1$ atm and 1173 K was $\psi = 4.06$, well above the stoichiometric value $\psi = 4$.

Finally, let us mention that oxygen contents larger than the stoichiometric value $\psi = 4$ [6] as well as electronic inhomogeneities[17] and the separation of $La_{1.8}Sr_{0.2}CuO_4$ in two K_2NiF_4-type phases which are close in lattice parameters[18], are previously reported in the literature. According to the results presented in this paper, we think that the corresponding samples were probably trapped in metastable states of the kind suggested in the present work.

Work is in progress in our laboratory to measure the true equilibrium oxygen potential as a function of temperature in samples of the $La_{2-x}Sr_xCuO_\psi$ system.

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FIGURE CAPTIONS

Figure 1. Plot of $\log_{10} P_{O_2}$ as a function of oxygen content, y, for sample I, at 1173 K. Point A is the starting point of the first run ABCD. Point A' represents the shift of A after the ABCD run. Filled points and arrows indicate unstable, drifting data points.

Figure 2. Plot of $\log_{10} P_{O_2}$ as a function of oxygen content, y, for the three runs made using sample II, at 1173 K. Points A, A' and A" are the starting points for each of the three runs.

Figure 3. Plot of $\log_{10} P_{O_2}$ as a function of oxygen content, y, for the two runs made using sample III, at 1173 K. A'D' represents true equilibrium states of the sample.

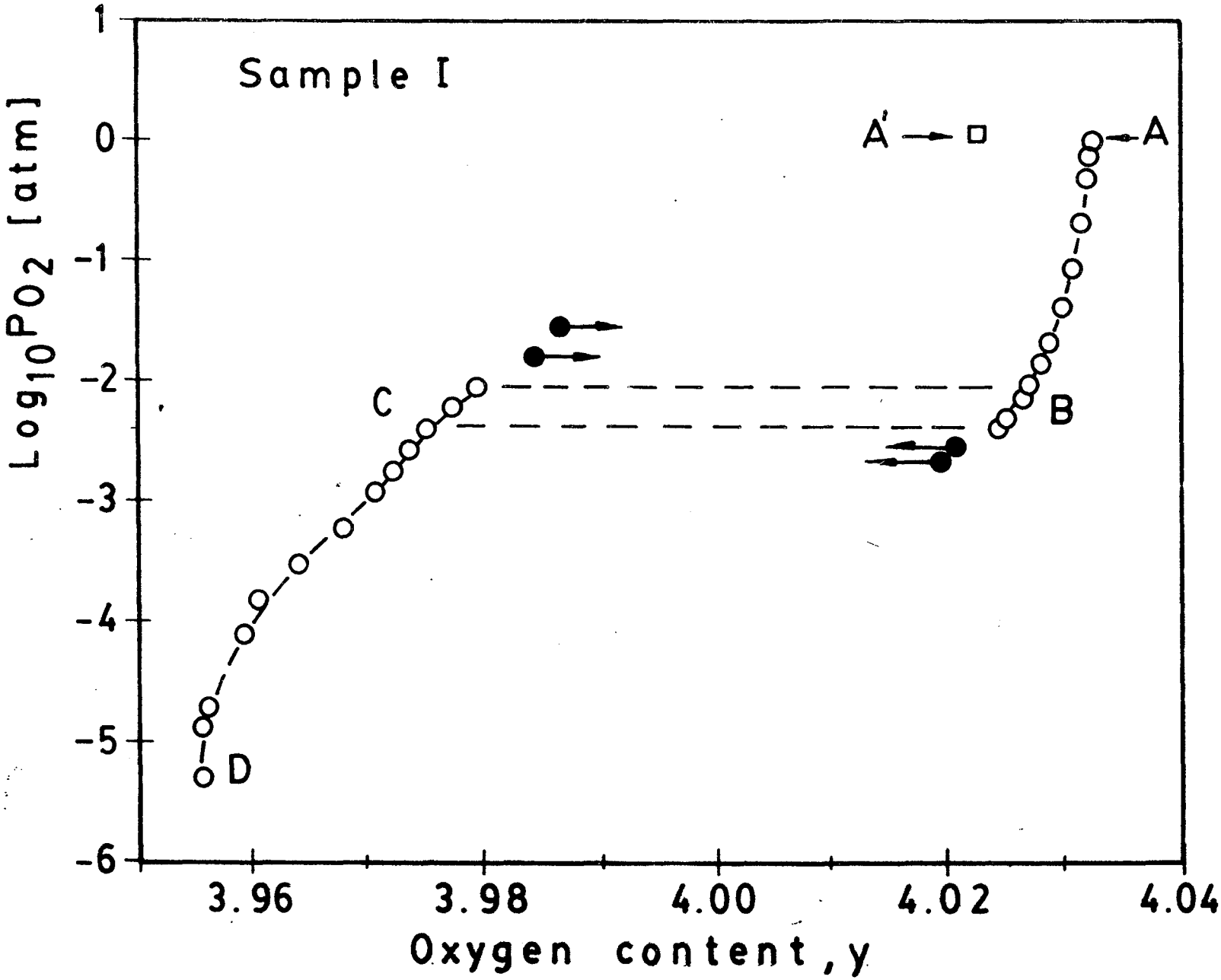
Figure 4. Plot of $\log_{10} P_{O_2}$ as a function of oxygen content, y, for sample IV, at 1173 K. AD represents true equilibrium states of $La_{1.8}Sr_{0.2}CuO_y$.

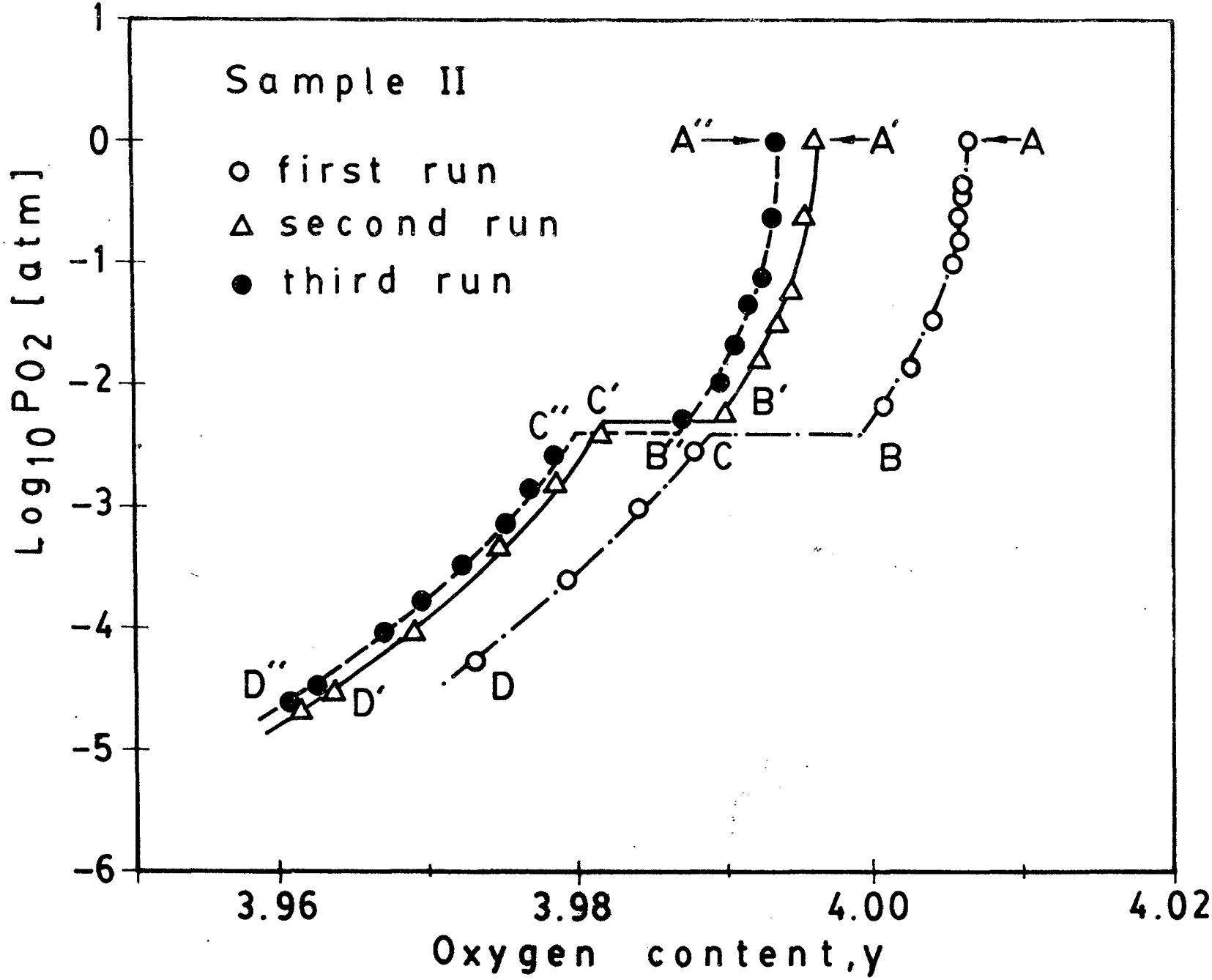
Figure 5. Plot of $\log_{10} P_{O_2}$ as a function of oxygen content, y, for $La_{6.75}Sr_{1.25}Cu_8O_z$, at 1173 K. Filled point and arrow indicates unstable, drifting experimental point. The dashed line indicates decomposition pressure for this sample.

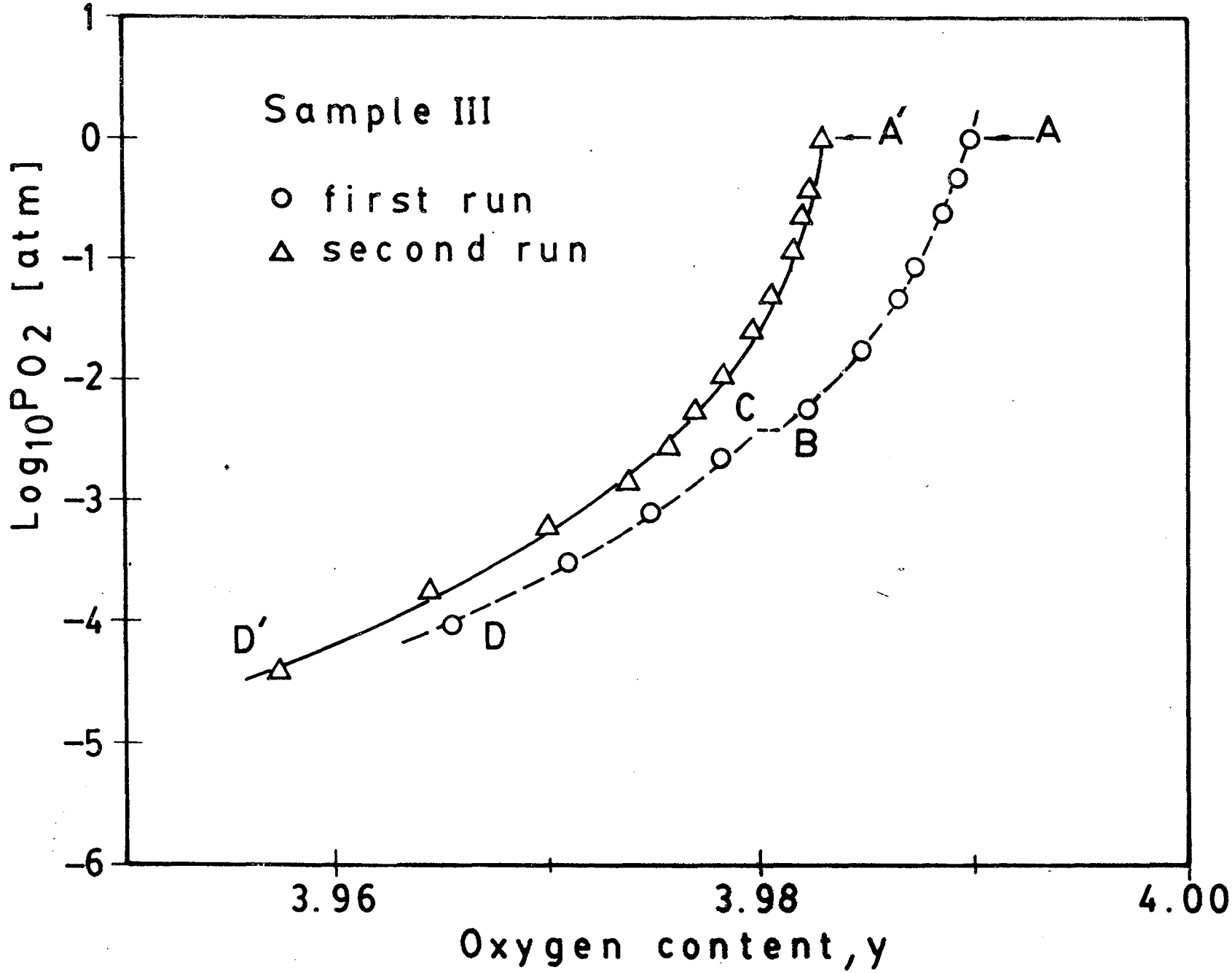
Table 1. $La_{1.8}Sr_{0.2}CuO_{4}$ sample treatment, prior to thermogravimetric measurements.

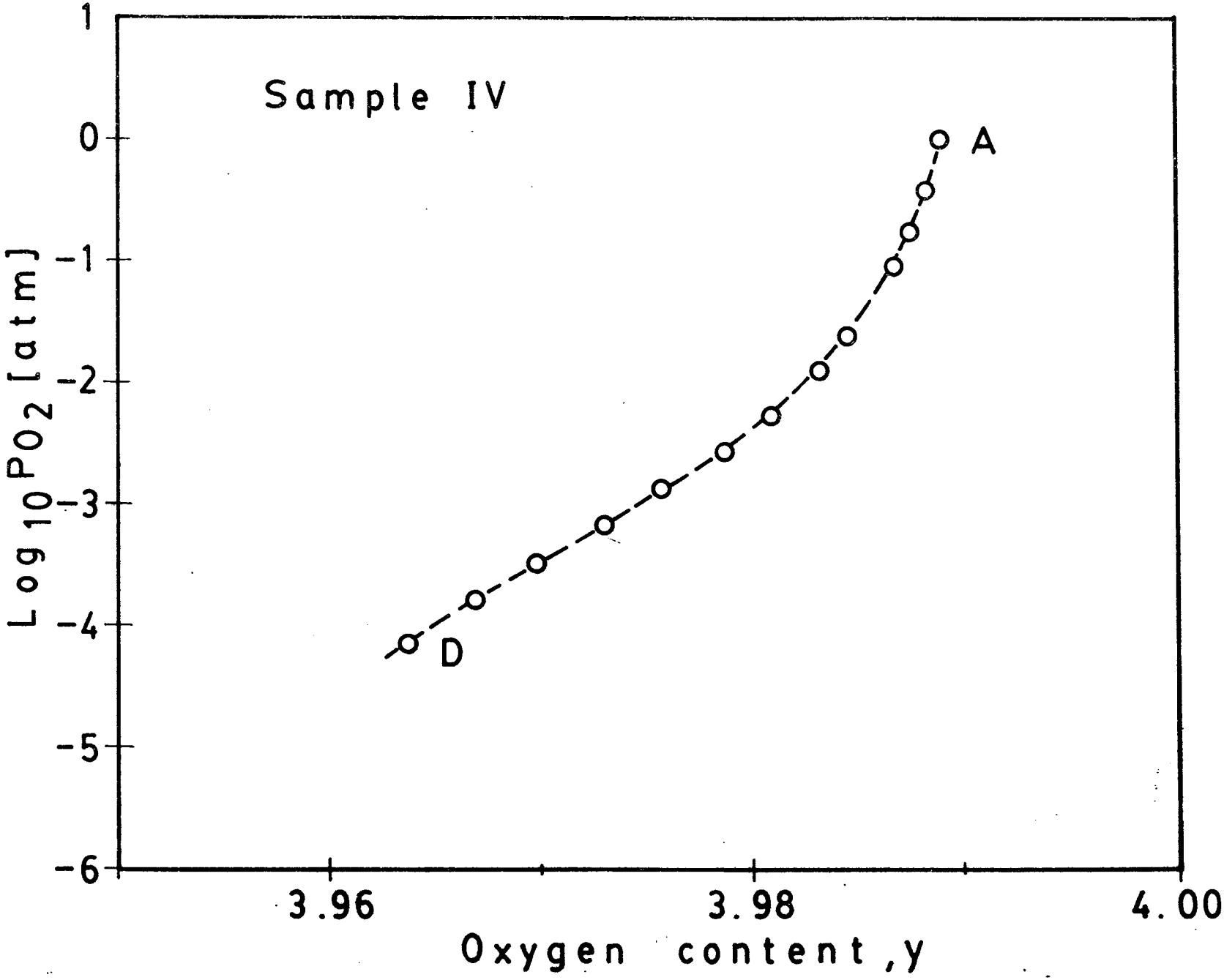
TABLE 1

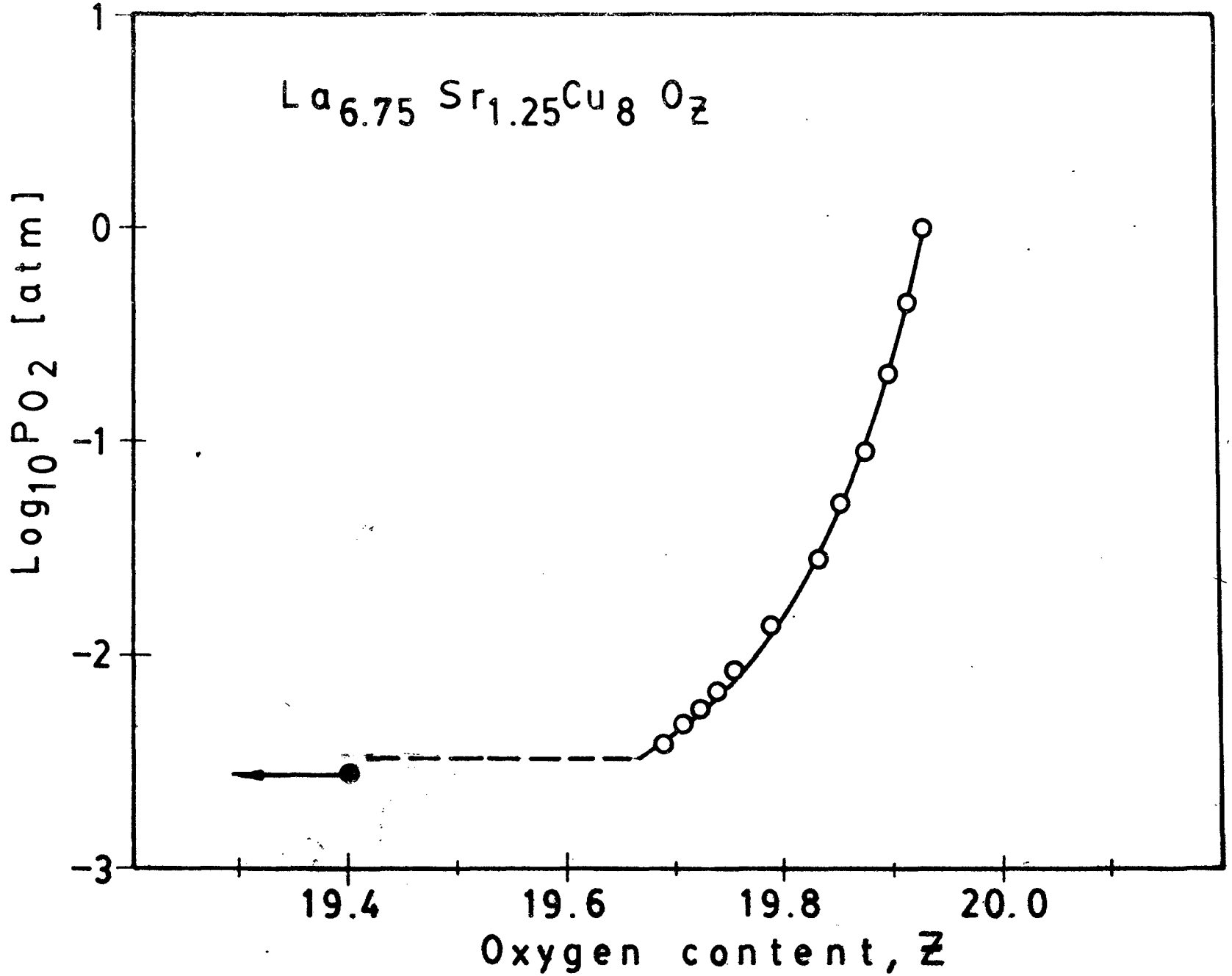
Sample	Preparation method	Heat treatment	Final form
I	Nitrates decomposition	Sintered in air 16 hours at 1323 K.	Crushed pellet
II	Liquid-mix	Powder calcined in air 6 hours at 1173 K. Sintered in air 12 hours at 1323 K.	Crushed pellet
III	Liquid-mix	Powder calcined in air 6 hours at 1173 K. Sintered in air 12 hours at 1323 K.	Crushed pellet
IV	Liquid-mix	Powder calcined in air 6 hours at 1173 K Pure Argon-Pure Oxygen cycling at 1173 K.	Powder


Sample I
A'
A
B
C
D
1
0
-1
-2
-3
-4
-5
-6
$Log_{10}P_{O_2}$ [atm]
3.96
3.98
4.00
4.02
4.04
Oxygen content, y


Sample II
o first run
Δ second run
● third run
A''
A'
A
B'
B
C''
C'
C
B''
D''
D'
D
1
0
-1
-2
-3
-4
-5
-6
Log10PO2 [atm]
3.96
3.98
4.00
4.02
Oxygen content, y


Sample III
o first run
Δ second run
A'
A
C
B
D'
D
1
0
−1
−2
−3
−4
−5
−6
$Log_{10}P_{O_2}$ [atm]
3.96
3.98
4.00
Oxygen content, y


Sample IV
A
D
1
0
-1
-2
-3
-4
-5
-6
Log 10 PO2 [atm]
3.96
3.98
4.00
Oxygen content, y


La6.75 Sr1.25Cu8 Oz
Log10PO2 [atm]
1
0
-1
-2
-3
19.4
19.6
19.8
20.0
Oxygen content, z