Sintering induced impurity phase in $La_{1.8}Sr_{0.2}CuO_{4-\delta}$

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Abstract

Microestructural changes induced by prolonged heat treatment of $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ are reported. Experimental evidence of the formation of an impurity phase during sintering of $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ is presented.

The high T_c superconducting oxide $La_{2-x}Sr_xCuO_{4-\delta}$ has been the subject of extensive academic research partially because it allows significant changes of oxygen content keeping constant its K_2NiF_4-type structure[1]. Experiment demonstrates that the stoichiometry deviation, δ, has a relevant influence on the normal and superconducting properties of this oxide[2]. However, the values of δ measured by different authors show a large dispersion[3] which makes it difficult to establish quantitative correlations between δ and other physicochemical properties. In particular, oxygen contents higher than the stoichiometric value of 4.0 ($\delta<0$) have been reported for samples with $0.15<x<0.20$ by several authors[4]. Recently, a thermogravimetric study of δ as a function of oxygen partial pressure (P_{O_2}) performed in our laboratory for $La_{1.8}Sr_{0.2}CuO_{4-\delta}$[5] indicates that the negative δ values can be related to the presence in the sample of the impurity phase $La_{8-x}Sr_xCu_8O_{20-\varepsilon}$. We also notice that, although the impurity phase could be detected thermogravimetrically, its concentration levels were lower than the detection limit of conventional x-ray powder diffraction (XRD) techniques.

Thermogravimetric measurements are usually performed using finely divided samples, but many other physical properties must be measured on high density, sintered samples. Accordingly, the aim of this work is to investigate the incidence of the sintering process on the formation of the impurity phase $La_{8-x}Sr_xCu_8O_{20-\varepsilon}$ in nominal $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ samples.

The thermogravimetric equipment as well as the solid state ZrO_2-based electrochemical system for control and measurement of P_{O_2} used in this work have been described in detail elsewhere[6]. Estimated errors are ±1% in P_{O_2} and $\pm 2 \times 10^{-4}$ in the oxygen content. Starting materials for sample preparation were La_2O_3, $SrCO_3$ and 99.99 % Cu, the first two being thermogravimetrically analized before use to assess the amount of volatile impurities they contained[7]. $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ powder samples were prepared by means of the citrate based "liquid mix" technique[8]. XRD of the powders showed only the K_2NiF_4-type structure. According to our previous experience[5], the powder was succesively treated with pure oxygen and pure argon at 900°C in order to reduce the amount of $La_{8-x}Sr_xCu_8O_{20-\varepsilon}$ impurity phase that may have formed during sample preparation, in concentrations lower than the XRD detection level. Dense pellets were prepared by sintering the obtained powder at 900°C in a nitrogen atmosphere during 18 hours, and then reoxidizing in oxygen at the same temperature for 2 hours. The absolute oxygen content of the samples was determined by the usual dry hydrogen reduction method. The well known superconducting transition near 36 K was verified by means of electrical resistivity measurements. Additional characterization of the samples included scanning electron microscopy (SEM) and electron probe microanalysis (EPMA).

Curve A in Fig. 1 shows the equilibrium data points for P_{O_2} vs. oxygen content at 900°C, for nominal $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ in powder form. This curve shows a small plateau at around 4×10^{-3} atmospheres (atm.) whose existence we related in a previous

work[6] to the decomposition of the impurity phase $La_{6.25}Sr_{1.75}Cu_8O_{20-\varepsilon}$, which is present in very small amounts and under the form of intergrown microdomains. The corresponding decomposition reaction is assumed to be of the general type

$$2\ ABO_{3-z} \text{ -----> } A_2BO_4 + BO_{1/2} + \left[\frac{3}{4} - z\right] O_2 \quad (1)$$

Therefore the existence of the plateau can be approximately described by the reaction

$$La_{6.25}Sr_{1.75}Cu_8O_{20} \text{ --> } 4\ La_{1.56}Sr_{0.44}CuO_4 + 4\ CuO_{1/2} + O_2 \quad (2)$$

which accounts for the mass loss of the sample through the formation of gaseous O_2. Since the plateau shown by curve A in Fig. 1 represents essentially this mass loss, we can estimate using reaction (2) the amount of $La_{6.25}Sr_{1.75}Cu_8O_{20-\varepsilon}$ present in our sample. The value obtained is 2.4 wt.%, which is lower than the detection limits of our conventional XRD technique.

The sintered samples showed x-ray diffractograms free of reflections corresponding to the $La_{8-x}Sr_xCu_8O_{20-\varepsilon}$ structure. One of these sintered samples was chosen for heat treatment at 900°C during 10 days, under pure oxygen, within the thermobalance. No mass change was observed. Following, the same sample was analized by means of XRD, SEM, EPMA and thermogravimetry. The XRD analysis showed a small peak at approximately 32.9 degrees which does not belong to the characteristic spectra of the K_2NiF_4-type structure but can be adscribed to the $La_{8-x}Sr_xCu_8O_{20-\varepsilon}$ structure[9]. In

agreement with this result, polished sections of the sample observed through SEM clearly indicated the presence of regions corresponding to a minority phase, as shown by the micrographs in Fig. 2. These regions were found to be inhomogeneously distributed through the sample and localized near the pores. EPMA of lanthanum and copper performed both on the matrix and the minority phase rendered the relative ratios expected for the compositions $La_{2-x}Sr_xCuO_{4-\delta}$ and $La_{8-x}Sr_xCu_8O_{20-\varepsilon}$, respectively. Regarding the thermogravimetric measurements, curve B in Fig. 1 shows the equilibrium data points for P_{O_2} vs. oxygen content at 900°C for the same chosen sintered sample, which has been previously crushed. A significant enhancement of the plateau at $4x10^{-3}$ atm. can be observed. The amount of $La_{6.25}Sr_{1.75}Cu_8O_{20-\varepsilon}$ now estimated from this plateau using again reaction (2) is 5.0 wt.%, which agrees with estimations also made from the XRD and SEM results.

The other sintered samples have shown the same behaviour as the one described above. For them, the impurity $La_{8-x}Sr_xCu_8O_{20-\varepsilon}$ phase was always easily detected by means of thermogravimetric analysis and, in some cases, through XRD.

Clearly, solid state sintering is responsible for the enhanced formation of the $La_{8-x}Sr_xCu_8O_{20-\varepsilon}$ impurity phase. This can be understood considering that the sintering process of the multicomponent $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ oxide powder implies component fluxes and mass rearrengements throughout the sample, the driving force being provided by the excess surface free energy associated to the surface area of the powder[10]. Thus, during the sintering process there are transitory cationic inhomogeneities in the sample due to the difference in diffusion coefficients, which

finally result in its trapping in the particular (metaestable) states for which the cationic inhomogeneities correspond to the $La_{8-x}Sr_xCu_8O_{20-\varepsilon}$ microdomains. In fact, this picture agrees with the conclusions reached in a previous paper by the authors[5].

We conclude :

1) Attemps to produce $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ single phase powders, free of $La_{8-x}Sr_xCu_8O_{20-\varepsilon}$, have been successful only in a few cases. Mostly, we have obtained powders that seem to be single phase through XRD but where the P_{O_2} vs oxygen content measurements show the existence of a small plateau of variable width at $4x10^{-3}$ atm.. This is indicative of the presence of some $La_{8-x}Sr_xCu_8O_{20-\varepsilon}$ impurity phase. The amount of $La_{8-x}Sr_xCu_8O_{20-\varepsilon}$ can be reduced upon cycling the sample in P_{O_2} across the plateau characteristic pressure. Enough cycles in P_{O_2} can cause the dissaparence of the plateau and lead to the formation of the K_2NiF_4-type single phase.

2) Attemps to produce sintered $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ samples free of $La_{8-x}Sr_xCu_8O_{20-\varepsilon}$ have failed, even using single phase powders without the characteristic thermogravimetric plateau as departure material. It seems well proved that the sintering process induces the formation of the $La_{8-x}Sr_xCu_8O_{20-\varepsilon}$ impurity phase up to concetration levels that can be easily detected by thermogravimetry and, in some cases, XRD.

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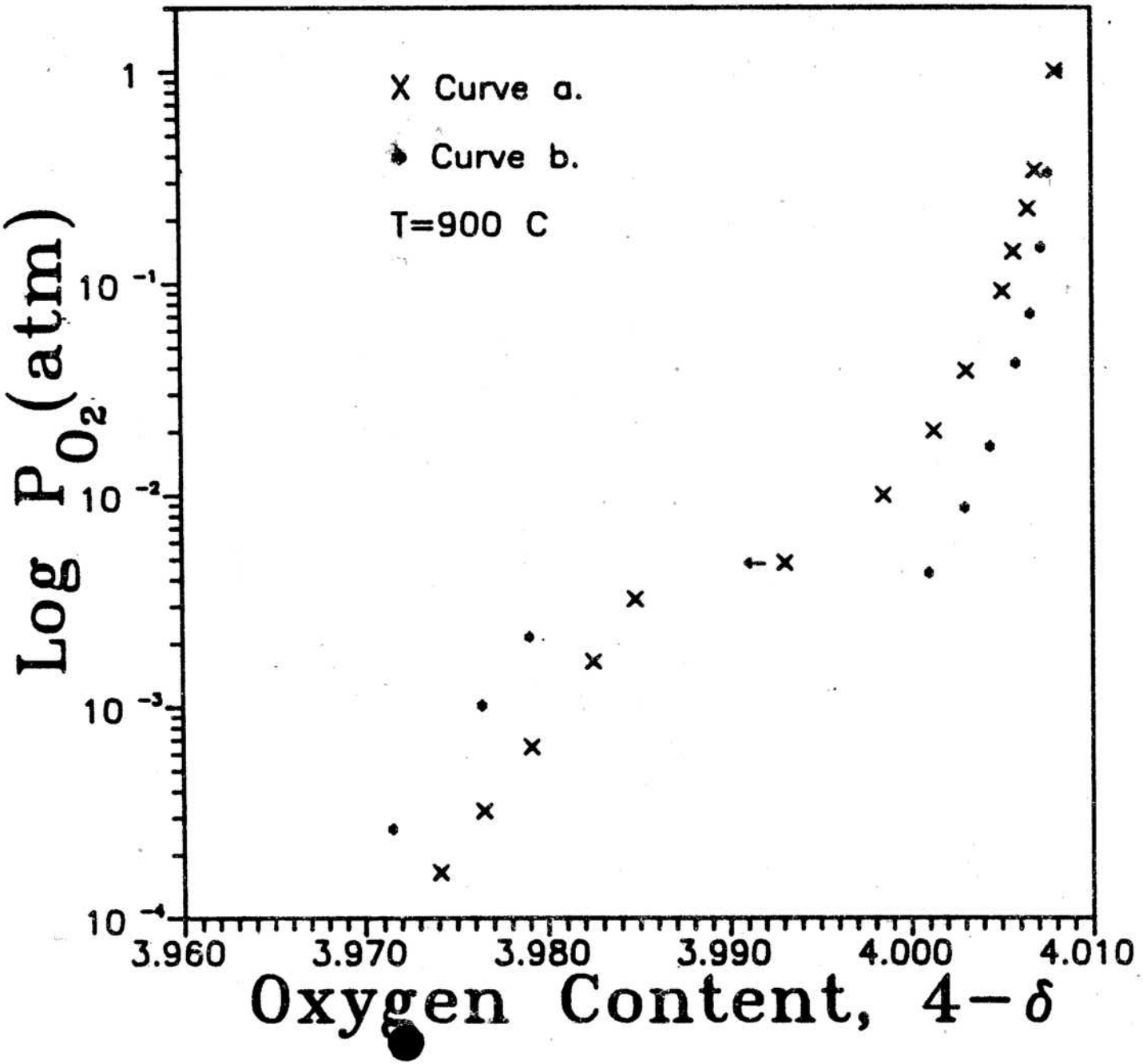
FIGURE CAPTIONS

Figure 1. Plot of $\log_{10} P_{O_2}$ as a function of oxygen content, $4-\delta$. Curve a corresponds to powder sample and curve b represents the isotherm for the same sample after anneling. Arrows indicate unstable, drifting data points.

Figure 2. SEM micrographs showing the formation of two phases of different composition over a polished section of the sintered sample. a) Secondary electron image. b) Backscattered electron image.


X Curve a.
Curve b.
T=900 C
Log P_{O_2}(atm)
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
3.960
3.970
3.980
3.990
4.000
4.010
Oxygen Content, $4-\delta$