

# Crystallographic, microstructural and magnetic properties of polycrystalline $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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## Abstract

In this work we report on an extensive study devoted to obtaining phase pure  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$  polycrystalline sintered samples. We have prepared samples by a polymeric precursors routine. Several synthesis routes with different heat treatments and atmosphere conditions were performed followed by x-ray diffraction in conjunction with Rietveld refinement, Scanning electron microscopy and x-ray photoelectron spectroscopy analysis. Magnetic measurements show an antiferromagnetic transition at low temperatures and paramagnetic behaviour for temperatures above 11 K.

## 1. Introduction

Since the discovery of high-temperature superconductivity (HTS) by Bednorz and Müller in 1986 [1], there has been an enormous theoretical effort to understand both the origin and the mechanism of this remarkable property. In this context the study of superconductivity and magnetism in  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (PBCO) has been a very controversial issue in the last decade. Even though superconductivity was reported in thin films and single crystals [2, 3], the phenomenon in polycrystalline systems has been reported only recently [4, 5].

Considerable efforts have been made in order to establish the role of Cu and Pr in PBCO magnetically ordered and superconducting phases. Nevertheless, this remains an open question [6–8]. In this scenario the study of the  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$

system is decisive, once the co-existence of superconductivity and magnetic ordering might correlate superconductivity in copper oxides to the crystal structure instead of to the Cu–O planes [9]. This could also impose restrictions on the validity of charge reservoir models to explain superconductivity [10].

It is well known that in  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , the Pr ions are responsible for a strong paramagnetic signal [7], being predominantly in the  $\text{Pr}^{3+}$  state. There are two types of  $\text{Pr}^{3+}$  site: the first is found when  $\text{Pr}^{3+}$  occupies its expected place, i.e. in the vicinity of the Cu–O planes, and the second is found when  $\text{Pr}^{3+}$  is on Ba sites. One theory claims that the latter situation prevents Cooper pairs from being formed, as a consequence of additional scattering of holes by the  $\text{Pr}^{3+}$  exchange [2].

Naturally, the study of these properties in polycrystalline specimens requires good quality samples. Some researchers have reported that polycrystalline samples prepared by a solid-

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state reaction technique show up to 5% of BaCuO<sub>2</sub>, among other impurity phases, according to the phase diagram for the PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> family [4, 11]. To prevent this problem we used a chemical route to prepare samples that show no secondary phases. This route is the modified polymeric precursors method, also known as the Pechini method [12], which is recognized as a suitable way to produce excellent polycrystalline ceramic samples [13].

This paper describes the results of a systematic study devoted to understand the influence of different atmospheric conditions during the synthesis of polycrystalline samples of PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub>. The study also aims to comprehend connections between the microstructure and the physical properties of the samples prepared.

## 2. Results and discussion

### 2.1. Synthesis

The polymeric precursor was prepared using a modified polymeric precursor route, based on the Pechini method. A stoichiometric amount of BaCO<sub>3</sub> was dissolved in an aqueous citric acid solution, to which CuO dissolved in HNO<sub>3</sub> was added. To this solution was added Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O. The mixed metallic citrate solution had a ratio of citric acid:metal of 3:1 (on a molar basis). Ethylene glycol was added to this solution, to obtain a citric acid:ethylene glycol ratio of 60:40 (mass ratio). The resulting blue solution was neutralized to pH ~ 7 with ethylene diamine. This solution was turned into a gel, and subsequently decomposed to a solid by heating at 400 °C. No phase segregation was observed during the polymerization step. The resulting powder was separated in different groups of samples. The first group was heat treated at 850 °C for 12 h in air with several intermediate grindings, in order to prevent undesirable phase formations of BaCuO<sub>2</sub> and Pr<sub>6</sub>O<sub>11</sub> [11]. Then, samples were pressed into pellets and sintered under different conditions at 900 °C for 12 h in air or O<sub>2</sub> atmosphere. A second group was also heat treated at 850 °C for 12 h in an Ar flux with several intermediary grindings in order avoid the undesirable phases. Some of these samples were sintered in Ar flux at 900 °C for 12 h using heating and cooling rates of 2 °C min<sup>-1</sup>. The use of a reducing atmosphere during synthesis was for two reasons, not only did it prevent the appearance of superoxide phases, such as Pr<sub>6</sub>O<sub>11</sub>, but it also prevented the occupancy of oxygen in the anti-chain site position O(5).

The value of δ was determined for each sample using thermogravimetry–differential thermo-analysis (TG–DTA) Netzsch STA409, in conjunction with mass spectroscopy (MS). For the samples prepared in air, the value of δ was about 0.2, for those prepared in O<sub>2</sub> flux, δ was about 0.0. The samples prepared in an Ar flux had δ around 0.7. These are characteristic values, similar to those found by other authors [11, 14].

### 2.2. Crystallographic analysis

Crystallographic phases were followed by x-ray diffraction (XRD) using a Siemens D5000 diffractometer and the phase purity and structural characteristics of samples synthesized in an argon atmosphere were confirmed by Rietveld refinement [15]. The Rietveld analyses were performed with the aid of

the FULLPROF suite of programs of x-ray powder diffraction data [16], obtained using Cu Kα radiation with a Seifert Scintag PAD-II diffractometer (2θ range, 20° to 100°).

Some of the samples were selected for the study in which only PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> and BaCuO<sub>2</sub> phases were detected. No traces of Pr<sub>6</sub>O<sub>11</sub> were found from the refinements in samples treated in the Ar flux. The refinement of the BaCuO<sub>2</sub> phase was performed with the oxygen positions fixed [17] due to the low percentage of this phase in the sample. The quantitative analysis was performed following Brindley criteria [18], using the equation

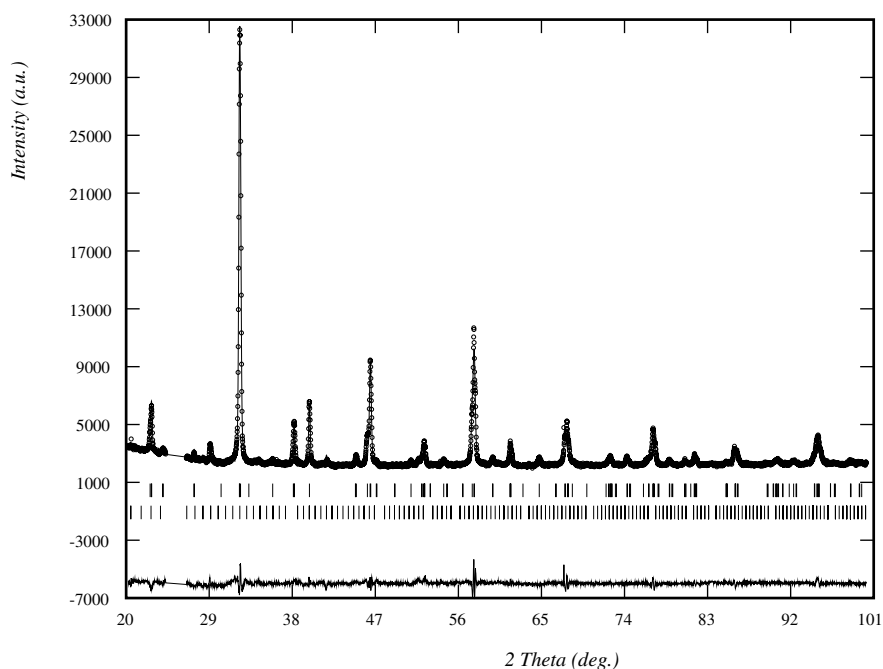
$$W_j = \{S_j Z_j M_j V_j / t_j\} / \sum_i \{S_i Z_i M_i V_i / t_i\} \quad (1)$$

where  $W_j$  is the weight fraction of phase  $j$ ,  $S_j$  is the scale factor of phase  $j$ ,  $Z_j$  is the number of formula units per unit cell for phase  $j$ ,  $M_j$  is the mass of the formula unit,  $V_j$  is the unit cell volume and  $t_j$  is the Brindley particle absorption contrast factor for phase  $j$  defined as

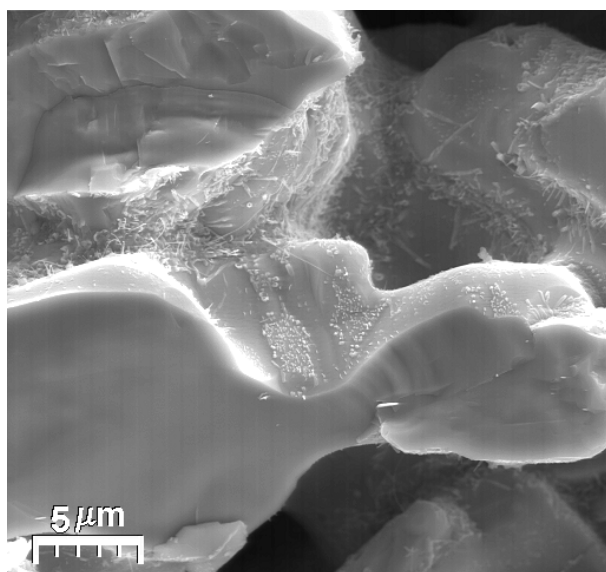
$$t_j = (1/V_j) \int \exp\{-(\mu_j - \mu_i)x\} dV_j. \quad (2)$$

Here  $V_j$  is the volume of a particle of phase  $j$ ,  $\mu_j$  is the particle linear absorption coefficient,  $\mu_i$  is the mean linear absorption coefficient of the solid material of the powder and  $x$  is the path of the radiation in the particle of phase  $j$  when reflected by the volume element  $dV_j$ . The  $t_j$  parameter accounts for microabsorption effects and is very important for a mixture of powders with very different linear absorption coefficients. This is true for the case of PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> and BaCuO<sub>2</sub>, with  $\mu = 144.05$  and  $126.38$  mm<sup>-1</sup>, respectively. Due to the majority of the PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> phase, the linear absorption coefficient of the mixture was assumed to be the same as that of pure Pr-123. Consequently, the weight fraction for each phase was found assuming a  $t_j$  range of 5.2–5.4. The Rietveld plot is seen in figure 1 and the calculated values are shown in table 1.

The results achieved in this crystallographic analysis allow for some important conclusions. The argon flux atmosphere during the synthesis prevented the formation of the PrBaO<sub>3</sub> phase and substantially diminished the occurrence of the BaCuO<sub>2</sub> phase, both considered ordinarily as secondary undesirable phases. It is also important to examine the  $c$ -axis length obtained, since it is one piece of evidence of Pr occupancy on the Ba site. Flux grown single crystals have a  $c$ -axis length of about 11.71 Å, whereas it is claimed that superconducting single crystals have  $c$ -axis of 11.76 Å [3]. The value obtained for the  $c$ -axis for samples prepared under Ar flux, of approximately 11.80 Å (somewhat above the value for single crystals), can be taken as evidence of lower incidence of Pr on the Ba site. The refinement of mixed occupancy Pr(Ba) in both sites led to a single occupancy without mixing in portions. Due to the low x-ray scattering atomic factor of oxygen in comparison to those of Pr, Ba and Cu, it is difficult to determine the occupancy of the O(5) position ( $x = 0.5$ ,  $y = 0.5$ ,  $z = 0.5$ ). When refinement is performed in order to determine the O(5) occupancy the converged value was 0.00(5).



**Figure 1.** Observed x-ray diffraction intensities (circles) for  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  at room temperature and calculated intensities (full curve) obtained from Rietveld fits. The upper and lower tick marks correspond to the Pr-123 and the  $\text{BaCuO}_2$  phases, respectively. The excluded region ( $24.10^\circ$ – $26.30^\circ$ ) avoided the signal from the container without a significant loss of signal from any of the phases involved (including  $\text{Pr}_6\text{O}_{11}$ ).

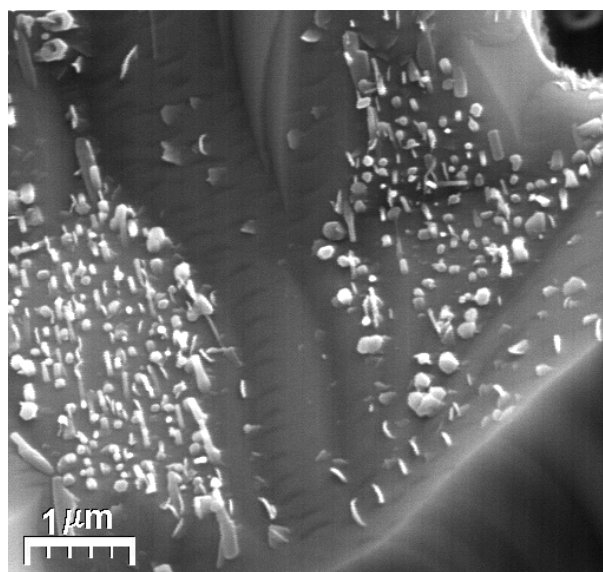


**Figure 2.** SEM image for the sample prepared in an  $\text{O}_2$ -rich atmosphere (see the higher-magnification image in figure 3).

### 2.3. Microstructural studies

This part of the study was performed by scanning electron microscopy (SEM), using a Zeiss microscope, model 940, in conjunction with x-ray energy dispersive spectrometry (EDS) using a Prisma-PGT x-ray energy dispersion spectrometer. It confirms the deep influence of the microstructure on the quality of the samples, notably when one is seeking polycrystalline samples of  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$  that are clean and free from impurities.

Initially, we managed to establish the correlation between the disappearance of undesirable secondary phases



**Figure 3.** SEM image showing a detailed view of the sample prepared in an  $\text{O}_2$  rich atmosphere.

through thermal treatments and the effects on the microstructure. These heat treatments were performed using a reducing atmosphere (Ar), as described above. As can be observed in figure 2, the sample prepared in an  $\text{O}_2$ -rich atmosphere presents small agglomerates on the grain surface. These structures were identified as secondary phases of  $\text{Pr}_6\text{O}_{11}$  and  $\text{Ba}_2\text{CuO}_3$ , found in the Rietveld refinement calculations. Figure 3 shows a detailed view of the superficial agglomerates. The existence of two types of structures can be identified: one of them, in smaller amounts, presents a needle form, whereas the other has a round shape and is more abundant.

**Table 1.** Structural parameters derived from the Rietveld refinements of PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> (a) and BaCuO<sub>2</sub> (b) at room temperature (space groups *Pmmm* and *Im3m*, respectively).

Position	X	Y	Z
Pr	0.5	0.5	0
Ba	0.5	0.5	0.1894(2)
Cu(1)	0	0	0
Cu(2)	0	0	0.3516(5)
O(1)	0	0	0.163(2)
O(2)	0.5	0	0.362(6)
O(3)	0	0.5	0.373(5)
O(4)	0.5	0	0

Lattice constants:  $a = 3.90574(3) \text{ \AA}$ ,  
 $c = 11.80355(5) \text{ \AA}$ .

Cell volume:  $180.304(2) \text{ \AA}^3$ .

Fraction (%): 97.9(7).

Bragg *R*-factor: 5.18.

(b)

Position	X	Y	Z
Cu(1)	0.126(2)	0.626(2)	0.25
Cu(2)	0	0.161(6)	0.161(6)
Cu(3)	0.291(7)	0	0
Cu(4)	0.38(2)	0	0
Ba(1)	0	0.140(2)	0.332(2)
Ba(2)	0	0.329(2)	0.329(2)
Ba(3)	0.151(2)	0.151(2)	0.151(2)
O(1)	0.0741	0.0741	0.1859
O(2)	0.1432	0.1432	0.3494
O(3)	0.2662	0.2662	0.0845
O(4)	0.25	0	0.5
O(5)	0.3348	0	0
O(6)	0	0.1052	0.4497

Lattice constants:  $a = 18.3742(2) \text{ \AA}$ .

Cell volume:  $6203.3(1) \text{ \AA}^3$ .

Fraction (%): 2.1(2).

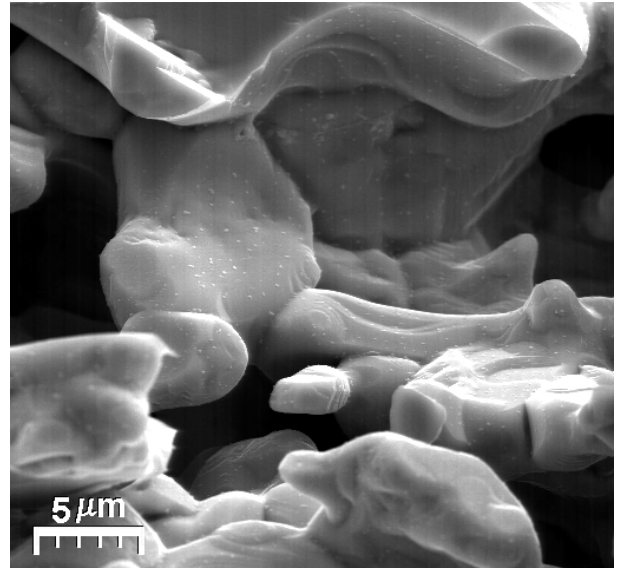
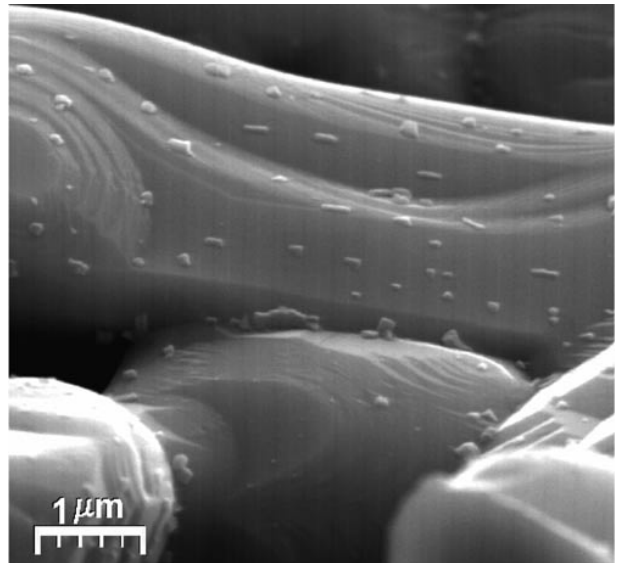
Bragg *R*-factor: 57.3.

$R_p$  and  $R_{wp}$  (with all non-excluded points):  
 3.04 and 4.06, respectively.

With the objective of contrasting the occurrence of these agglomerates, the sample prepared under a reducing Ar-rich atmosphere was studied by SEM using the same conditions. The result can be seen in figures 4 and 5. It can be observed that the Ar flux treatment prevents the formation of these agglomerates on the grain surface.

Comparing figures 3 and 5, we observe that the needle structures are no longer formed upon the argon-rich atmosphere treatments, so these structures may be associated with the Pr<sub>6</sub>O<sub>11</sub> phase, which did not appear in the XRD associated with Rietveld refinement results. As the Ba<sub>2</sub>CuO<sub>3</sub> phase is still present in the samples prepared under an argon-rich atmosphere, it is associated with the round structure, still visible in figure 5.

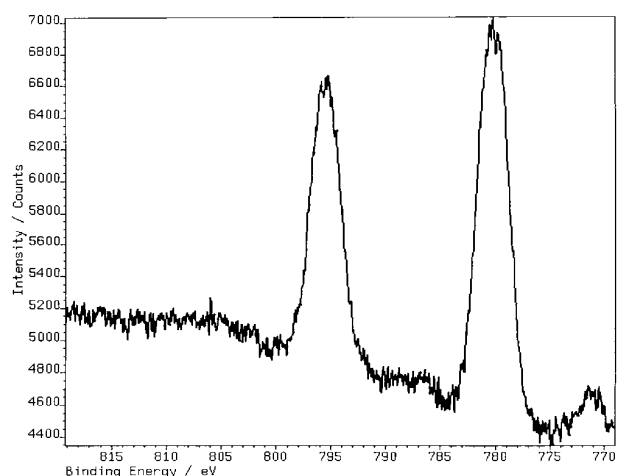
These microstructural studies, along with the crystallographic analysis, are evidence that the phase purity in polycrystalline samples of PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> is thoroughly related to crystallographic phase stability and microstructural features. In fact, during the synthesis, the formation of Pr<sub>6</sub>O<sub>11</sub> and Ba<sub>2</sub>CuO<sub>3</sub> phases leads to the formation of a non-stoichiometric, and, consequently, non-pure phase of PBCO.

**Figure 4.** SEM image for the sample prepared in an Ar-rich atmosphere (see the higher-magnification image in figure 5).**Figure 5.** SEM image showing a detailed vision of the sample prepared in an Ar-rich atmosphere.

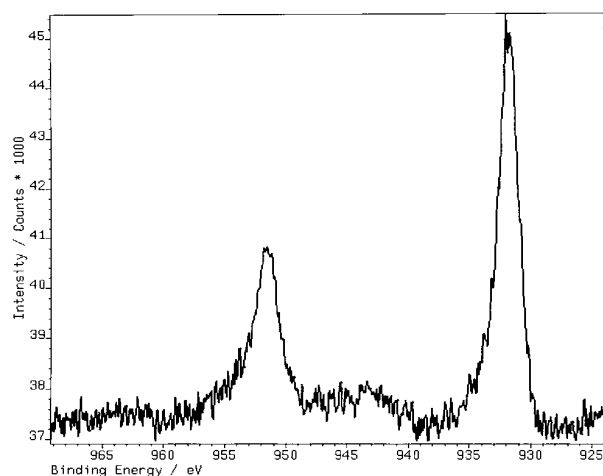
#### 2.4. XPS spectra

X-ray photoelectron spectroscopy (XPS) analysis was performed in ultra-high vacuum (low  $10^{-7}$  Pa range) using a KRATOS XSAM HS spectrometer, with a Mg *Kα* ( $h\nu = 1253.6 \text{ eV}$ ) x-ray source operating at 15 mA and 15 kV. The high-resolution spectra were obtained with an analyser pass energy of 20 eV. The binding energies were referred to adventitious carbon 1s line set at 284.8 eV. The Shirley background and a least-squares routine were used for peak fitting.

The exact valence value of Pr in the PBCO compound is still an open question [19, 20]. Studies show that the state of the Pr is a mix between Pr<sup>3+</sup> and Pr<sup>4+</sup>, depending on its crystallographic position. Another important point is that the possible variations in the state of the Pr valence could also



**Figure 6.** Ba 3d XPS spectrum of the Ar-treated sample.

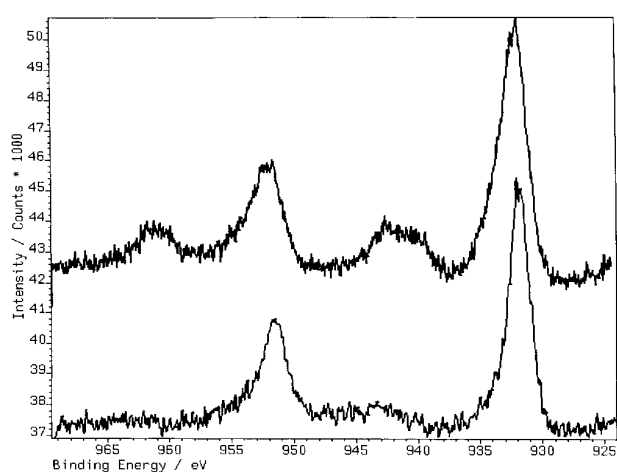


**Figure 7.** Cu 2p XPS spectrum of the Ar-treated sample.

cause variations in the valence of the Cu, which, in turn, constitutes a fundamental fact for the occurrence (or not) of superconductivity.

The region from 770 to 810 eV, related to the Ba 3d orbital, is commonly used to confirm the sample quality. Our results, for the Ar-treated sample, in agreement with the literature [20], can be observed in figure 6 and exhibit the state Ba 3d<sub>5/2</sub> of larger intensity with binding energy of 780 eV, and the other peak, with smaller intensity, related to the state Ba 3d<sub>3/2</sub> of 795 eV.

Continuing the study of the XPS spectrum for PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  polycrystalline samples prepared in an argon atmosphere, the region of energy between 925 and 965 eV is shown in figure 7. In this region the signals related to the orbitals Cu 2p and Pr 3d can be found. The spectrum of PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  prepared in Ar shows peaks related to Cu<sup>+</sup> (Cu<sub>2</sub>O) and Cu<sup>2+</sup> (CuO), as can be seen in figure 7. The peaks were analysed according to average indexation for the oxides of transition metals [21]. The main peak, at 932 eV, is the Cu2p<sub>3/2</sub>, with the Cu2p<sub>1/2</sub> at 951.5 eV, but associated to the Cu<sup>+</sup> character [21]. It is also possible to identify a small contribution of peaks due to Cu<sup>2+</sup>, at 934 and 955 eV.



**Figure 8.** Cu 2p XPS spectra of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  (upper curve) and PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  (lower curve) samples.

The Cu 2p spectrum indicates that PBCO Ar-treated samples are more evidently Cu<sup>+</sup> character. In order to improve this analysis, figure 8 shows a comparative Cu 2p spectra between YBCO and PBCO samples prepared under the same conditions. In the Cu 2p spectrum, the existence of satellite peaks at 940 and 950 eV is an indication of the existence of Cu<sup>2+</sup> specimens. As can be observed, the non-existence of satellite peaks indicate a predominance of Cu<sup>+</sup> character for PBCO polycrystalline samples, according to previous results [22] in the literature. It is well known that the Cu<sup>+</sup> ions are located only in the chains, while the Cu<sup>2+</sup> ions are positioned in the Cu–O planes, indicating that PBCO has intrinsically more Cu<sup>+</sup> in the chains of Cu when compared with other compounds of the 123-family [23].

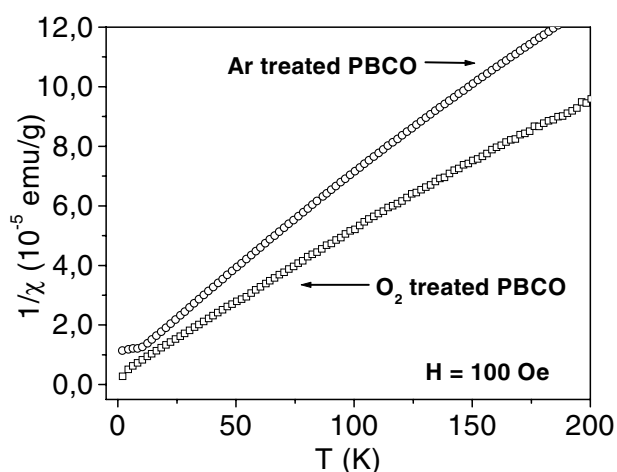
Also noticeable is the absence of a peak corresponding to Pr 3d<sub>5/2</sub> at 930 eV, associated with the valence Pr<sup>4+</sup>, as can be appreciated from figure 7. The occurrence of this peak would be clear evidence of the mixed valence of the ions of Pr. Another indication of Pr<sup>4+</sup> is the occurrence of a structure at 966 eV [20].

## 2.5. Magnetic measurements

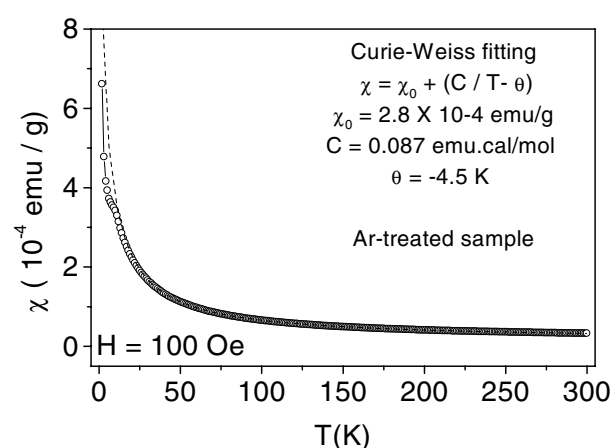
We also performed dc magnetic susceptibility versus temperature measurements,  $\chi(T)$ , using a SQUID magnetometer (Quantum Design, MPMS-5S), employing the zero-field-cooling (ZFC) and the field-cooled-cooling (FCC) procedures, as described elsewhere [4, 5].

A comparative measurement between the sample prepared under oxygen and that prepared under an argon atmosphere is shown in figure 9. These results show that the sample prepared under Ar flux presents a clear antiferromagnetic transition close to 11 K. This study strengthens the evidence for the presence of Pr<sup>3+</sup>.

For both samples,  $\chi(T)$  shows Curie–Weiss (CW) behaviour. Using the CW law modified to include a residual constant,  $\chi = \chi_0 + C/(\theta + T)$ , we calculated for the Ar-treated sample,  $\chi_0 = 2.8 \times 10^{-4}$  emu g<sup>-1</sup>,  $C = 0.087$  emu cal mol<sup>-1</sup> and  $\theta = -4.5$  K. Figure 10 shows the experimental data and the CW fitting, which deviate from each other below the Néel temperature. To emphasize the fact that the magnetic



**Figure 9.** Inverse magnetic susceptibility versus temperature measurements for the PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  polycrystalline samples in an applied field  $H = 100$  Oe.



**Figure 10.** Magnetic susceptibility versus temperature for PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  polycrystalline sample prepared under Ar flux for an applied field  $H = 100$  Oe.

response of the samples is different from a sample with purely paramagnetic Pr ions, the CW background was subtracted from the  $\chi(T)$  results [4, 5].

From the normal properties of Pr-123, measured at temperatures higher than  $T = 200$  K, we have also calculated the effective magnetic moment,  $\mu_{eff} = 2.75 \mu_B$ , a value that further confirms the Pr-123 stoichiometry and, furthermore, that the samples are rich in Pr occupying its own site [24, 25].

### 3. Conclusions

In short, we have used the modified polymeric precursors method to produce polycrystalline samples of PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub> . From this study it has become evident that an Ar flux is

indispensable to produce samples free from secondary phases, which is in contrast with the widely accepted concept that heat treatments with O<sub>2</sub> flux are necessary to improve the quality of samples of the 123-family.

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