

Preparation and General Physical Properties of Polycrystalline $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ Obtained From Sol-Gel Precursors

V. A. Meza, X. Gratens, R. F. Jardim,
Instituto de Física, Universidade de São Paulo
CP 66318, 05315-970, São Paulo, SP, Brazil

and L. Ben-Dor
Department of Inorganic and Analytical Chemistry,
Hebrew University, Jerusalem, 91904, Israel

Received on 28 February, 2002

Polycrystalline samples of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ were prepared through two different routes: (a) mixing Pr_6O_{11} , BaCO_3 , and CuO ; (b) sol-gel precursors. The samples were heat-treated in the temperature range $700 \leq T \leq 930$ °C and under different atmospheres, (Argon and air). Oxidation of these compounds, based on the results of thermogravimetric analysis, TGA, was performed at low temperatures, from 300 to 400 °C, for time intervals as long as 120 h. The crystal structure was determined by measurements of X-ray powder diffraction and revealed that samples heat-treated at 810 °C in Ar and for 130 h have a tetragonal structure with lattice parameters $c \sim 11.88$ Å. Oxygenated $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ samples were found to have an orthorhombic structure with lattice parameter c ranging from 11.72 to 11.75 Å. Electrical resistivity $\rho(T)$ measurements performed on these compounds revealed a semiconductor-like behavior in the temperature range $77 \leq T \leq 300$ K. The magnetic susceptibility $\chi(T)$ data showed a paramagnetic-like behavior from 5 to 300 K and a clear contribution of the crystalline electrical field (CEF) below 150 K. We have also found an antiferromagnetic ordering associated with the Pr sub-lattice at $T_N \sim 17$ K. Evidence of superconductivity was not observed on our samples, in agreement with most of the results reported in the literature.

I Introduction

Recent investigations on members of the family $\text{REBa}_2\text{Cu}_3\text{O}_{7-y}$; RE = rare earth; revealed that only $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ (Pr123) exhibits physical properties similar to conventional insulators [1]. While most of the members of this family display superconductivity below the critical temperature $T_c \sim 90$ K, the Pr123 is an insulator with antiferromagnetic ordering due the Pr sub-lattice below $T_N \sim 15$ K [2,3]. Several theories were put forward in order to explain the reason of this failure such as hole-filling [4], exchange between Pr^{+3} and Ba^{+2} in their sites [5], hybridization between 2p-O and 4f-Pr orbitals [6], and magnetic pair breaking due an intermediary valence state of Pr^{+3} and Pr^{+4} [7]. However, ten years after the discovery of the first member of the family RE123, some results raised important questions about the absence of superconductivity in Pr123. First, Blackstead *et al.* [8] produced thin films of Pr123 that showed a small reduction of the

surface resistance below 90 K, which is an indication of superconductivity in this system at relatively high temperatures. Following their results, Zou *et al.* [9,10] were capable to produce single crystal of Pr123 that showed a clear transition to zero resistivity state and appreciable Meissner effect below 85 K. One of the significant features showed in those Pr123 single crystals was the relatively large lattice parameter $c \sim 11.85$ Å, a length larger than those usually found in the literature for the same compound. Such a larger lattice parameter c results in an appreciable separation of the CuO_2 planes from each other, decreasing possible effects of hybridization between the orbital 2p-O and 4f-Pr [11, 12]. In fact, a slight contraction of the lattice parameter c promotes the non-metallic/non-superconductor character of the Pr123, a structural constraint not observed in other members of this family [13]. The contraction takes place since both Pr^{+3} and Ba^{+2} ions exchange

their original site positions in the Pr123 unit cell due to similar ionic radii. However, an oxidizing environment near the CuO chains can stimulate this exchange and promote a contraction of the lattice parameter c , followed by an orthorhombic-tetragonal transition O-T [5, 14]. Therefore, it seems important to control the absorption of oxygen into the lattice, in order to have a crystal structure with a robust lattice parameter c , which can support superconductivity. Besides, the material should maintain its high quality, that is, a high degree of homogeneity and absence of additional phases [8]. As pointed out by Park *et al.* [14] and followed by Zou *et al.* [9, 10], the first procedure to avoid inhomogeneity and multiphase material is through annealing in inert atmospheres avoiding an oxidizing environment near CuO chains and thus limit a possible exchange between Pr and Ba from their original crystallographic sites. This would result in an increase of the lattice parameter c and consequently obtaining superconductivity below $T_c \sim 90$ K [9, 10].

The aim of this work is to contribute to this discussion by searching for possible interrelations between structure and superconductivity in polycrystalline samples of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ (Pr123). The role of processing conditions was determined by varying the starting materials, sintering temperature, and atmosphere used for heat treatments. This was done in polycrystalline specimens of Pr123 prepared through two different routes: reacting oxides and carbonates and sol-gel precursors. The samples were sintered at different temperatures and under different atmospheres and their properties were characterized by X-ray diffraction analysis, electrical resistivity, and magnetic susceptibility. Our results strongly suggest that $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ is an antiferromagnetic insulator and the absence of superconductivity in this series is briefly discussed.

II Experimental Procedure

Polycrystalline samples of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ were prepared by two different routes: reacting binary oxides and carbonates [15] and through sol-gel precursors [16, 17]. For the latter, appropriate amounts of the nitrates (all from Alfa Aesar with 99.99% purity) $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$, and $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 100 ml of distilled water in a beaker. After complete dissolution of all nitrates, 50% excess of solid citric acid and ethylene glycol were added to the mixture. This solution was placed on a hot plate and stirred magnetically. The solution was heated until it initiates a process of polymerization through a transformation into a green gel which was transferred to an alumina crucible and dried on the hot plate. The crucible was transferred to a muffle furnace, the temperature raised to 400 °C, and kept for two days. For a systematic study of the formation kinetics of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$,

samples obtained from the sol-gel precursor were heat-treated in both air and Ar atmosphere at temperatures ranging from 700 to 820 °C for time intervals as long as 130 h. Similar heat treatments were performed for samples prepared by reacting binary oxides and carbonates.

Thermogravimetric analysis (TGA) of samples heat-treated in Ar was employed in order to obtain the temperature range in which oxygen is absorbed by the samples. Annealing in O_2 atmosphere was performed in the temperature range $300 \leq T \leq 400$ °C. Phase purity, crystal structure, and lattice parameters were obtained by means of powder X-ray diffraction using Cu $K\alpha$ radiation on a Bruker D8 Advanced diffractometer. All samples were measured between $20 \leq 2\theta \leq 80$ ° with angular scanning steps of 0.02 ° for 10 s. The lattice parameters were obtained by the method of least square refinement after the peak positions were corrected using MgO as an internal standard. Electrical resistivity and magnetic measurements were also performed on selected samples. Four-wire resistivity measurements were performed using a Keithley current source model 224 and a Keithley nanovoltmeter model 182. Copper electrical leads were attached on parallelepiped-shaped samples using silver epoxy. Typical excitation currents were ~ 1 mA. Magnetic susceptibility measurements were performed in a Quantum Design SQUID magnetometer. Zero-field-cooled (ZFC) and field-cooled (FC) curves were obtained from 4.2 to 300 K in applied magnetic fields up to 7 T.

III Results and discussion

Formation kinetics of Pr123 sintered in air

In order to follow the formation kinetics of the Pr123 phase, the sol-gel precursor was subjected to heat treatments in air at several temperatures ranging from 700 to 930 °C. The kinetics of the phase formation was accompanied by measurements of X-ray powder diffraction XRD. Typical results of such a kinetic of the phase formation is shown in Fig. 1. This figure displays X-ray patterns of two polycrystalline samples of Pr123. The X-ray pattern of the heat-treated sample at 850 °C for 48 h is displayed in Fig. 1(a). The results show the presence of additional phases as PrBaO_3 and CuO , as the main phases in the diffractogram. The beginning of the Pr123 formation is also observed due to the presence of the Bragg plane (103) of this phase, as indicated by an arrow in Fig. 1(a). Increasing the sintering temperature to 930 °C results in appreciable changes in the material, as shown in Fig. 1(b). This figure displays the X-ray diffractogram for the same sample heat-treated for 60 h at 930 °C. The main Bragg reflections belonging to the Pr123 phase can be identified but there are some peaks belonging to the same additional

phases found in Fig. 1(a). These X-ray results suggest that the temperature and time of sintering were not enough to promote materials with a single-phase character. Furthermore, the atmosphere employed seems to be unsuitable for producing single-phase materials.

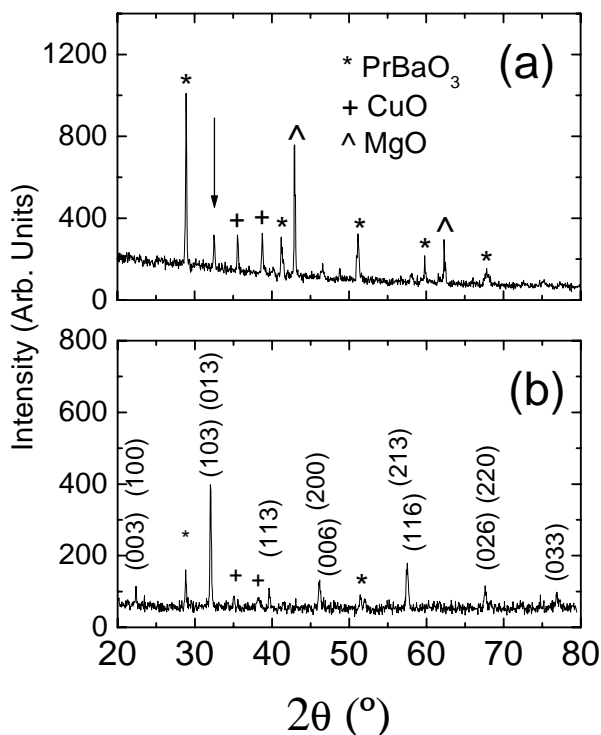


Figure 1. X-ray diagrams of polycrystalline samples of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ prepared from a sol-gel precursor and heat-treated at different conditions in air: (a) 850 °C for 48 h; (b) 930 °C for 60 h. The additional phases PrBaO_3 (*), CuO (+) are marked in the figure. Reflections belonging to MgO (\wedge), used as an internal standard, are also marked. The most intense reflection belonging to the $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ phase is indicated by an arrow in (a).

Although the desired phase Pr123 was obtained, its crystallographic structure was far from that considered as the one that could support superconductivity, based on the arguments raised by Zou *et al.* [10]. In their Pr123 single crystals, both tetragonal and orthorhombic structures were found to have larger lattice parameters $c = 11.85 \text{ \AA}$ and 11.75 \AA , respectively. Such a lattice parameter $c = 11.85 \text{ \AA}$ is much larger than any reported in literature. Our refinements of the lattice parameters revealed materials with a structure essentially tetragonal and shorter lattice parameters $c \sim 11.70 \text{ \AA}$. Therefore, heat treatments in air at 930 °C always resulted in materials with extra phases and lattice parameter c smaller than 11.75 \AA , as shown in Fig. 1(b). These results indicated that the atmosphere employed during the heat-treatment is an important variable for

producing single phase materials with desired crystallographic features. It is also important to note that similar results were found in samples prepared by reacting binary oxides and carbonates. Thus, the kinetics of formation of Pr123 was studied in samples heat-treated in Ar atmosphere, as described below.

Formation kinetics of Pr123 sintered in Ar atmosphere

As observed by Park *et al.* [14] and Zou *et al.* [9,10], to avoid site exchange between Pr^{+3} and Ba^{+2} in the $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ structure, an inert atmosphere must be employed during the sintering process of the material. This, according to these authors, would guarantee the formation of single phase Pr123 with larger lattice parameter c , viz. 11.85 \AA . In order to verify these statements, powders obtained from sol-gel precursors were heat-treated following the same steps as described in the last section, but in an Ar atmosphere. Some of the main results are shown and discussed below.

First, the powder was heat-treated at 700 °C for 48 h and the X-ray diagram of this material is shown in Fig. 2(a). It is clear from the pattern that the material is comprised of several phases such as PrBaO_3 , CuO and BaCO_3 and it was not possible to identify any reflection belonging to the desired Pr123 phase. Increasing sintering temperature to 780 °C for 60 h results in appreciable changes in the XRD diagram of the powder, as shown in Fig. 2(b). The first relevant change is the appearance of well-defined Bragg reflections belonging to the Pr123 phase, as indicated in the figure.

Although the temperature was slightly increased, a heat treatment in an inert atmosphere results in decomposition of the binary compound PrBaO_3 and promotes the formation of the Pr123 phase. This result also indicates that the sol-gel precursor, when properly heat-treated, promotes the formation of the Pr123 phase at temperatures at least 200 °C below the one commonly used in mixture of binary oxides and carbonates [1,2]. Increasing further the sintering temperature to 810 °C results in drastic changes in the XRD diagram of the material, as shown in Fig. 2(c). In samples heat-treated for 35 h, the dominant phase is Pr123 , but reflections belonging to extra phases, such as PrBaO_3 and BaCuO_2 , were still observed. This implies that the sintering time was insufficient to promote single-phase materials. Considering this sintering time, the crystal structure of the sample is essentially tetragonal, as expected for materials subjected to annealing in an inert atmosphere. The calculated lattice parameters a , b , and c were found to be 3.903, 3.901, and 11.73 \AA , respectively.

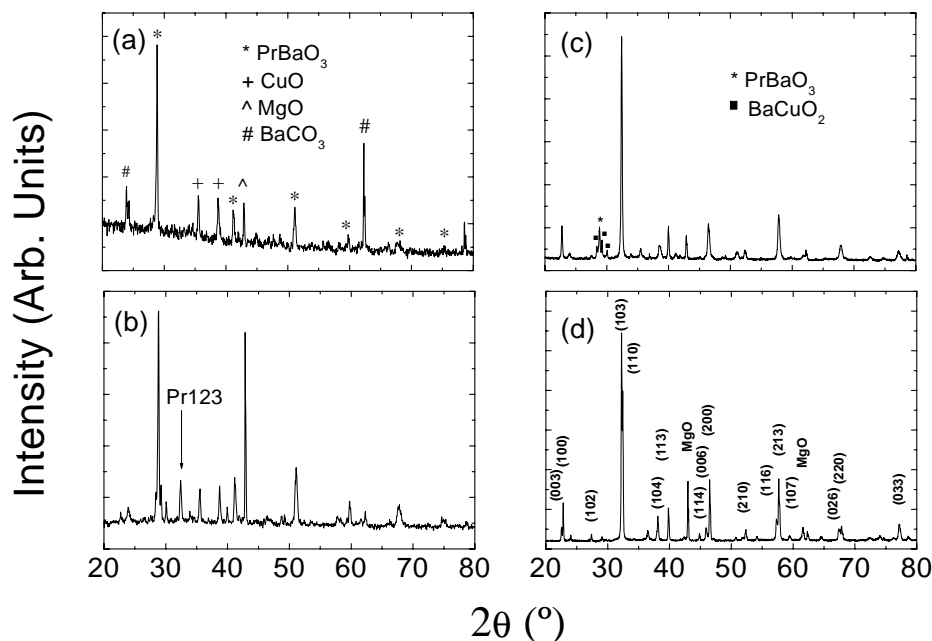


Figure 2. X-ray diagrams of polycrystalline samples of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ heat-treated in Argon atmosphere: (a) 700 °C for 48 h; (b) 780 °C for 60 h; (c) 810 °C for 35 h; and (d) 810 °C for 50 h. The additional phases PrBaO_3 (*), CuO (+), BaCO_3 (#), and BaCuO_2 (■) are marked in the figure. The most intense reflection belonging to the $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ phase is indicated by an arrow in (b). The reflections belonging to the tetragonal $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ phase are indexed in (d).

By maintaining the sintering temperature 810 °C and increasing further the sintering time to 50 h, drastic changes occurs in the material, as shown in the XRD of Fig. 2(d). The most pronounced change observed in this XRD diagram is related to the absence of extra peaks belonging to any additional phase such as PrBaO_3 , BaCuO_2 , or oxides. However, we have observed few extra peaks, with rather low intensities, occurring in the 2θ interval, ranging from 25 to 30 ° of the XRD diagram. An analysis of the peak positions of these reflections revealed that they correspond to Bragg reflections of the tetragonal structure Pr123 phase, as for example the reflection (102) occurring near 27 °. Also, the reflection near 29 ° corresponds to the $\text{Cu}_{k\beta}$ contribution related to the reflections (103) and (110), probably due the high degree of crystallinity of the material obtained.

Although the lattice parameter c is small, increasing sintering time in an inert atmosphere leads to larger c value. Refinement of the lattice parameters performed in Pr123 samples subjected to different annealing times revealed that the lattice parameter c increases appreciably with increasing sintering time from ~ 11.73 Å, for a sample heat-treated for 50 h, to ~ 11.88 Å, for 130 h. This lattice parameter $c \sim 11.88$ Å is similar to the one obtained by Zhou *et al.* [9, 10] in single crystals.

From the above results we concluded that Ar atmosphere plays an important role for producing single-

phase Pr123 compounds and seems to avoid a local oxidizing environment close to CuO chains. This indicates that both Ba^{+2} and Pr^{+3} ions are maintained in their original crystallographic sites, in a crystal structure similar to the one found by Zhou *et al.* [9,10], i. e., a tetragonal structure with large lattice parameter c .

Oxygen absorption by Pr123 at low temperatures

It is well known that members of the family RE123 exhibit superconductivity when the samples are annealed in oxygen at temperatures below ~ 400 °C [10]. Some important features of this annealing process were the tetragonal to orthorhombic transition TO, followed by a contraction of the lattice parameter c , and the occurrence of superconductivity below $T_c \sim 90$ K in compounds with oxygen content of $7 - y \sim 6.93$, for instance, in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ [18]. The optimal annealing temperature can be obtained by performing thermogravimetric analysis (TGA) of the materials in an O_2 environment.

Based on these arguments, TGA measurements in an O_2 atmosphere were performed on powders derived from a sample previously subjected to a heat treatment in Ar at 810 °C for 130 h. These results indicated that the maximum oxygen absorption occurs in a temperature range $300 \leq T \leq 400$ °C [18]. Taking into

account the results obtained in TGA analysis, we have subjected single-phase, tetragonal Pr123 samples to annealing in an O₂ atmosphere in the temperature range $300 \leq T \leq 400$ °C. Two important features observed in these samples can be summarized, as follows: (a) samples annealed at temperatures $T > 400$ °C were found to exhibit additional phases, as inferred from XRD analysis; and (b) appreciable changes in the crystallographic structure of samples annealed in temperatures between 300 and 400 °C were observed using an accurate analysis of specific regions of their XRD diagrams. Changes in the tetragonal structure are summarized in Table 1, which displays the calculated lattice parameters a , b , and c of several Pr123 samples which were subjected to different time intervals and temperatures in an O₂ environment. The data reveal that increasing annealing time results in an increase of the lattice parameter a and a decrease of both lattice parameters b and c in samples annealed at 380 °C. In addition, the lattice parameters a and b start to deviate from those expected in a tetrag-

onal structure $a = b$, after the sample is subjected for a few hours in an O₂ environment. This would be the expected behavior, assuming that increasing annealing time results in more absorption of oxygen in the CuO chains. However, the most important result is related to the behavior of the lattice parameter c . For heat treatments performed at 380 °C, we have observed that annealing for 8 h seems to be enough to promote an appreciable decrease of the lattice parameter c , from 11.88 to 11.73 Å. This annealing temperature of 380 °C was considered too high to avoid this decrease in the lattice parameter c , as indicated by the data shown in Table I. In this stage of the annealing process, the crystal structure of Pr123 reaches an orthorhombic character. In addition, the lattice parameters a and b were found to be unaltered for prolonged annealing times. Thus, other samples from the same batch were annealed at 350 °C.

Table 1: Lattice parameters a , b , and c of the PrBa₂Cu₃O_{7-x} annealed in O₂ atmosphere at different temperatures and time intervals.

Temperature	Time (h)	a (Å)	b (Å)	c (Å)
380 °C	0	3.903(2)	3.904(5)	11.88(1)
380 °C	8	3.929(4)	3.869(5)	11.73(1)
380 °C	10	3.926(5)	3.865(7)	11.69(1)
380 °C	12	3.915(4)	3.877(4)	11.68(1)
350 °C	0	3.903(2)	3.904(5)	11.88(1)
350 °C	10	3.894(4)	3.883(6)	11.75(1)
350 °C	25	3.910(5)	3.886(9)	11.72(1)
350 °C	50	3.924(4)	3.862(4)	11.70(1)
350 °C	80	3.923(5)	3.871(5)	11.72(2)
350 °C	120	3.921(5)	3.867(5)	11.73(2)

The lattice parameters of samples annealed at 350 °C were found to exhibit similar behavior as compared to the ones annealed at 380 °C. This indicates that these samples have a crystal structure which seems to be incompatible with superconducting properties, based on the crystal structure and the arguments given in Refs. 9 and 10. However, it is possible that a small volume fraction of these samples is comprised of superconducting phases. Thus, the occurrence of superconductivity in this series would be inferred from macroscopic measurements, as discussed below.

Transport Properties of Pr123

All superconducting members of the family RE123 exhibit two important features: (i) metallic-like behavior above T_c , or an increasing electrical resistivity $R(T)$ with increasing temperature; and (ii) a transition to the superconducting state below $T_c \sim 90$ K. Within this context, most of the samples of Pr123 exhibit nei-

ther metallic-like nor superconductivity in a large range of temperature [1, 2]. These two features are consistent with the mechanism involving high hybridization of 2p-O and 4f-Pr orbitals, as described elsewhere [6]. Such a mechanism accounts for the non-metallic-like behavior of $R(T)$ above T_c and the absence of superconductivity below T_c . However, experimental results on Pr123 obtained by Blackstead and co-authors [8, 19] suggested that Pr123 is a superconductor with a very small superconducting volume fraction (SVF). It was argued that such a small SVF is hardly detected by conventional techniques as electrical resistivity $R(T)$ and magnetization $M(T)$. Thus, surface resistance R_S measurements, a technique very sensitive to small SVF [20], were employed to detect superconductivity in thin films of Pr123 [19]. In fact, Blackstead and co-authors [8, 19] observed a small decrease in the magnitude of R_S just below 90 K in thin films of Pr123 and attributed such a decrease to the onset of superconductivity in a small SVF, ~ 5 %, of the sample. Considering these

results, we argue that if such a small SVF is related to superconductivity, both transport and magnetic data should reveal changes close to T_c as well. Following this discussion, some granular superconductors, which are comprised of an intimate mixture of superconducting and insulating components, exhibit similar features as conventional superconductors (decrease of $R(T)$ just below T_c and appreciable drop of $M(T)$ at T_c) even when the SVF is rather low. Let us consider, for instance, the electron-doped system $\text{Sm}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$; $x \sim 0.17$; in which changes in both electrical resistivity and magnetization are observed below T_c even when the SVF is rather low, i. e., $\sim 5\%$ [21]. Based on these arguments, if our Pr123 samples have a very small SVF, measurements of $R(T)$ or $M(T)$ would show measurable changes close to T_c . Therefore, we have performed measurements of electrical resistivity in our samples in a large range of temperature and applied magnetic field, as described below.

Starting with the samples subjected to annealing in O_2 at 380°C , their temperature dependence of the normalized electrical resistivity at 300 K, $\rho(T)/\rho(300\text{ K})$, is displayed in Fig. 3 (a). In this figure the $\rho(T)/\rho(300\text{ K})$ data belonging to the pristine sample (sintered in Ar at 810°C for 130 h) is also shown for comparison. A careful inspection of these curves reveals that annealing in O_2 alters the magnitude of the $\rho(T)/\rho(300\text{ K})$ data appreciably. In fact, it seems that annealed samples in O_2 have more charge carriers, which are believed to be introduced by increasing oxygen content of the material. This results in an appreciable decrease of $\rho(T)$, as inferred from the two orders of magnitude drop of $\rho(T)/\rho(300\text{ K})$ at 77 K between the pristine sample and the sample annealed in O_2 for 10 h. However, all samples exhibit a semiconductor-like behavior in the whole range of temperature investigated. In addition, no appreciable changes in the $\rho(T)/\rho(300\text{ K})$ behavior close to 90 K was observed in all samples, suggesting the absence of superconductivity in these Pr123 compounds. All the samples subjected to lower annealing temperature, i. e., 350°C , exhibited similar behavior as shown in Fig. 3(b). Based on these results of temperature dependence of the electrical resistance there is no evidence of superconductivity in all the Pr123 samples investigated.

However, it is possible that the annealing procedure employed for increasing the O_2 content in these samples was not adequate. By checking this particular point, we have prepared a sample of $\text{NdBa}_2\text{Cu}_3\text{O}_{7-y}$ Nd123 following the same steps described above and an additional annealing in O_2 at 350°C for 80 h. We have observed that such a Nd123 sample exhibited zero-state electrical resistivity and appreciable Meissner effect just below $T_c \sim 90\text{ K}$. Therefore, the experimental procedure for preparing these Pr123 can be considered as adequate. Thus, based on the results of electrical resistivity, no evidence of superconductivity,

even in a small volume fraction, was observed in these Pr123 samples. However, it is also possible that magnetic measurements would reveal even a small SVF in these compounds. Therefore, a detailed characterization through magnetization measurements was carried out in the samples mentioned above, as discussed below.

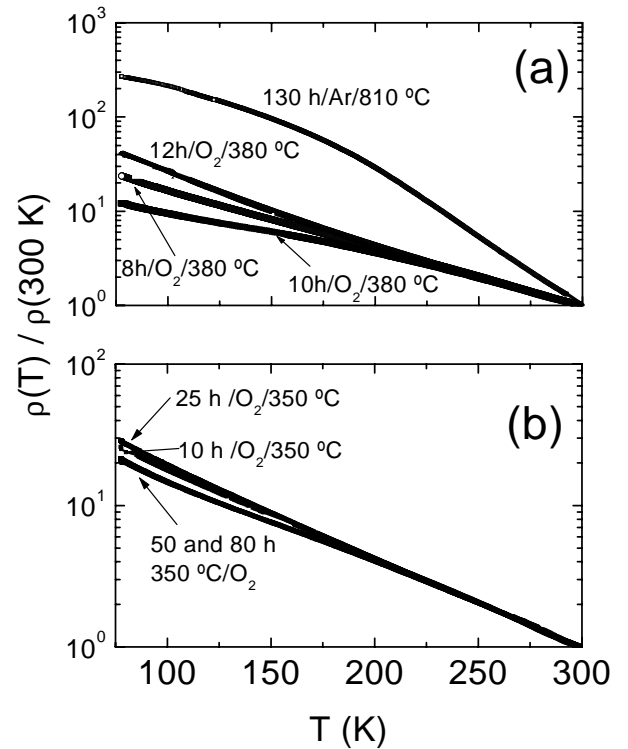


Figure 3. Normalized electrical resistivity curves of Pr123 heat-treated under different conditions: (a) in Ar, 810°C for 130 h and 380°C , in O_2 for 8, 10 and 12 h; (b) 350°C , in O_2 for 10, 25, 50, and 80 h.

Magnetic properties of Pr123

Superconductors display diamagnetism or Meissner effect in temperatures below T_c . The magnitude of this diamagnetic contribution can be considered robust as compared to a paramagnetic material. While $\chi \sim 10^{-5}$ emu for the latter, superconductors reveal a diamagnetic signal about $\chi \sim 10^{-3}$ emu. Therefore, if Pr123 would have a SVF of about 5%, magnetization data would show changes close to 90 K or even at lower temperatures. Thus, we have performed measurements of magnetization in our samples of Pr123 in a large temperature range and under applied magnetic fields up to 7 T. Typical curves obtained from this characterization are shown in Fig. 4.

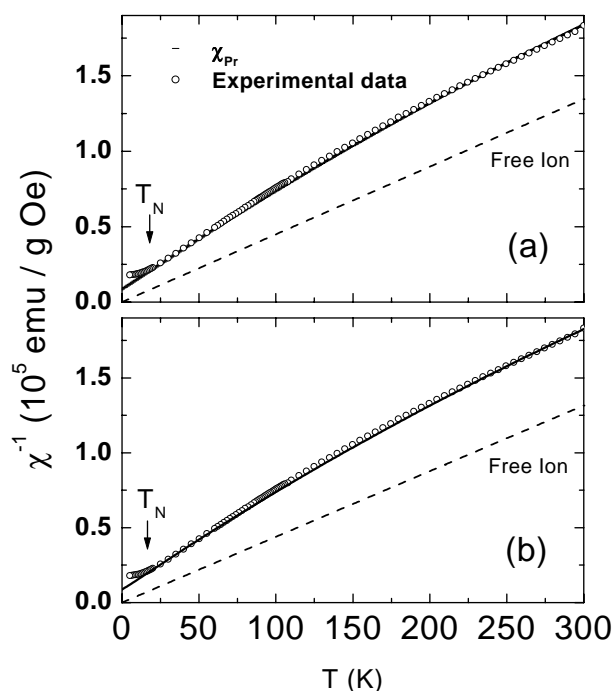


Figure 4. Temperature dependence of χ^{-1} of polycrystalline samples of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ heat-treated under different conditions: (a) 380 °C for 10 h, in O_2 ; b) 810 °C for 130 h, in Ar. The expected Curie behavior for the free ion is represented by dashed lines. The temperature $T_N \sim 17$ K in which Pr^{+3} ions order antiferromagnetically is indicated by arrows. The χ_{Pr} curve is the best result of the simulation of the paramagnetic susceptibility of Pr123 including a contribution of the CEF.

The figure shows the temperature dependence of the inverse of the magnetic susceptibility $\chi^{-1}(T)$ for two selected samples: (a) annealed at 380 °C for 10 h in an O_2 environment (Fig. 4 (a)); and (b) a sample sintered at 810 °C in Ar for 130 h (Fig. 4 (b)). The first sample is considered as the one with the highest oxygen content and the lowest magnitude of $\rho(T)$ at 77 K (see Fig. 3 (a)). The second sample, which was sintered at 810 °C in Ar for 130 h, corresponds to the one with the lowest oxygen content and the highest magnitude of $\rho(T)$ at 77 K (see Fig. 3 (a)). The figure also shows the expected behavior for a simple Curie law susceptibility for the free ion of Pr^{+3} ($J = 4$ and $g_J = 4/5$). The overall magnetic behavior of both samples is similar and experimental curves exhibit a convexity compared to the Curie law trace. In addition, at temperatures close to $T_N \sim 17$ K, a cusp in the $\chi^{-1}(T)$ data was observed and associated with the antiferromagnetic ordering of the Pr sub-lattice. However, no appreciable changes in $\chi^{-1}(T)$ were observed close to 90 K in both samples, suggesting absence of superconductivity in these materials. This is corroborated by the data since, at least for the sample annealed in O_2 , a SVF close to 5% would produce a small change in the behavior of $\chi^{-1}(T)$ close to T_c , due to the appreciable magnitude of its diamag-

netic signal. On the other hand, the observed deviation from the Curie-Weiss law may be associated with the onset of superconductivity. This point requires additional consideration of the magnetic behavior of these RE123 compounds. As far as this point is concerned, it is important to notice that previous works [22-24] have shown that the paramagnetic susceptibility of Pr123 is strongly influenced by the $J = 4$ state splitting due to crystalline electric field (CEF). In order to gain further information of our $\chi^{-1}(T)$ data, the paramagnetic susceptibility of Pr123 was simulated following the procedure made in Ref. 23. The best results of the simulation displayed in Fig. 4 (a) and (b) are for the triplet Γ_3 as a ground state of the system [24]. The crystal field parameters for which the best match of the simulation and the experimental curve is found are similar to those determined in Refs. 22 and 23. Indeed, the CEF effect makes the search for superconductivity in Pr123 more delicate. In any event, our analysis of the $\chi^{-1}(T)$ data suggested the absence of superconductivity in Pr123 and an appreciable contribution of the CEF to the paramagnetic behavior of these compounds.

In summary, we have produced polycrystalline samples of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ through different routes. The samples were subjected to different sintering temperatures and annealing times in both O_2 and Ar environments. From the results of X-ray powder diffraction we have obtained single-phase materials only when the samples are heat-treated in Ar at 810 °C for 130 h. These samples were found to have a tetragonal structure and lattice parameter c as large as 11.88 Å. In addition, we have found that annealing these materials in O_2 at relatively low temperatures ($T < 400$ °C) results in a decrease of the lattice parameter c , driving the system to an orthorhombic structure. Such an annealing in O_2 also resulted in appreciable changes in both transport and magnetic properties of these compounds. However, measurements of electrical resistance and magnetization revealed no evidence of superconductivity in these polycrystalline materials. Also, we have found that a precise description of the magnetic susceptibility data of Pr123 requires an additional contribution of the crystalline electrical field at temperatures below 150 K.

This work was supported by the Brazilian agency Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) under Grant No. 99/10798-0. Two of us V.A.M. and X.G. are FAPESP fellows under Grant Nos. 01/03938-2 and 98/11522-6, respectively, and R.F.J. is a Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) fellow under Grant No. 304647/90-0. L.B-D. acknowledges support from FAPESP under Grant No. 00/07362-5 and from the Sabbatical Fund of the Hebrew University during her stay in São Paulo, where this work was carried out.

References

- [1] J. M. Tarascon, W. R. Mckinnon, L. H. Greene, G. W. Hull, B. G. Bagley, E. M. Vogel, and Y. LePage, *Adv. Ceram. Mat.* **2**, 498 (1987).
- [2] M. B. Maple, C. C. Almasan, C. L Seaman, S. H. Han, K. Yoshiara, M. Buchgeister, L. M. Paulius, B. W. Lee, D. A. Gajewski, R. F. Jardim, C. R. Fincher, Jr., Graciela B. Bhanchet, and R. P. Guertin, *J. Superconductivity* **7**, 97 (1994).
- [3] V. N. Narozhnyi, D. Eckert, K. A. Nenkov, G. Funchs, T. G. Uvarova, and K. H. Müller, *Physica C* **312**, 233 (1999).
- [4] J. J. Neumeier, T. Bjørnholm, M. B. Maple, J. J. Rhyne, and J. A. Gotta, *Physica C* **166**, 191 (1990).
- [5] W. H. Tang and J. Gao, *Physica C* **315**, 66 (1999).
- [6] R. Fehrenbacher and T. M. Rice, *Phys. Rev. Lett.* **70**, 3471 (1993).
- [7] A. A. Abrikosov and L. P. Gor'kov, *Zh. Eksp. Teor. Fiz.* **39**, 1781 (1961).
- [8] H. A. Blackstead, D. B. Chrisey, J. D. Dow, J. S. Horwitz, A. E. Klunzinger, and D. B. Pulling, *Phys. Lett. A* **207**, 109 (1995).
- [9] Z. Zou, K. Oka, T. Ito, and Y. Nishihara, *Jpn. J. Appl. Phys.* **36**, L18 (1997).
- [10] Z. Zou, J. Ye, T. Ito, and Y. Nishihara, *Phys. Rev. Lett.* **80**, 1074 (1998).
- [11] J. Ye Z. Zou, , K. Oka, Y. Nishihara, and T. Matsumoto, *J. Alloys Comp.* **288**, 319 (1999).
- [12] K. Oka, Z. Zou, and J. Ye, *Physica C* **300**, 200 (1998).
- [13] T. A. Vanderah and C. K. Lowe-Ma, *J. Superconductivity* **7**, 107 (1994).
- [14] M. Park, M. J. Kramer, K. W. Dennis, and R. W. Calum, *Physica C* **259**, 43 (1996).
- [15] See, for instance, R. F. Jardim, E. A. Early, and M. B. Maple, *J. Alloys Comp.* **221**, 1 (1995).
- [16] R. F. Jardim, L. Ben-Dor, and M. B. Maple, *J. Alloys Comp.* **199**, 105 (1995).
- [17] M. T. Escote, A. M. L. Silva, J. R. Matos, and R. F. Jardim, *J. Solid State Chem.* **151**, 298 (2000).
- [18] V. A. Meza, L. Ben-Dor, and R. F. Jardim, private communication.
- [19] W. L. Hults, J. C. Cooley, E. J. Peterson, J. L. Smith, H. A. Blackstead, and J. D. Dow, *Intern. J. Mod. Phys. B* **12**, 3278 (1998).
- [20] H. A. Blackstead, R. F. Jardim, D. B. Pulling, A. E. Klunzinger, and P. Beeli, *Phys. Rev. B* **57**, 3683 (1998).
- [21] M. J. R. Sandim, P. A. Suzuki, S. Spagna, S. C. Tripp, R. E. Sager, and R. F. Jardim, *Physica C* **289**, 265 (1997).
- [22] A. T. Boothroyd, S. M. Doyle, and R. Osborn, *Physica C* **217**, 425 (1993).
- [23] Y. Takano, S. I. Yokoyama, and K. Sekizawa, *Physica C* **252**, 61 (1995).
- [24] L. Soderholm, C. -K. Loong, G. L. Goodman, and B. D. Dabrowski, *Phys. Rev. B* **43**, 7923 (1991).