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Oxygen diffusion in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ observed by resistivity measurements

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Abstract. *In situ* resistivity measurements have been used to monitor the oxygen uptake and removal for the ceramic system $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ (YPBCO) in the temperature range 300–1000 K. The study of the out-diffusion of oxygen was performed by annealing the oxygenated samples in ambient air at constant heating rates. We found that, independently of x , the oxygen concentration $O_{7-\delta}$ is preserved up to 600 K, and that oxygen diffuses out of the oxides at temperatures higher than 600 K. However, the rate of oxygen removal from $PrBa_2Cu_3O_{7-\delta}$ (PBCO) is greatly reduced as compared to the rate for pure $YBa_2Cu_3O_{7-\delta}$ (YBCO), and decreases with increasing x in YPBCO. The study of the in-diffusion of oxygen was performed by annealing the deoxygenated samples in ambient air at constant heating rates. We found that, independently of x , the oxygen uptake takes place in the temperature range 550–750 K, where the in-diffusion rate depends slightly on the Pr concentration. The observed resistivity change $\Delta\rho(\delta)$ for all of the YPBCO samples as they interchange oxygen with the gas phase indicates that the number of majority carriers in the oxides is mainly controlled by the oxygen content δ and seems to be independent of the Pr concentration, at least for $x \leq 0.5$.

1. Introduction

It is well known that partial substitution of Pr for Y in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ (YPBCO) causes marked changes in both normal-state conducting and superconducting properties. An interesting property of YPBCO is the decrease in T_c with Pr concentration, and the lack of superconductivity for $x \geq 0.55$ [1, 2]. For $x \geq 0.5$, $\delta \simeq 0$, and below room temperature, the resistivity (ρ) increases with decreasing temperature, and such increases in $\rho(T)$ are seen even for superconducting samples ($0.35 < x < 0.45$). For large oxygen deficiencies and with varying Pr content, the material is found to be a semiconductor with a single activation energy ($\Delta = d(\ln \rho)/d(1/T)$). However, for a high oxygen deficiency and below room temperature, PBCO shows a strong deviation from linearity when the resistivity data are plotted as $\ln \rho$ versus $1/T$, and the data cannot be fitted at all with a single thermally activated mechanism. Fisher *et al* [3] have suggested that the conductivity in PBCO is due to variable-range hopping.

Fisher *et al* [3] have also studied the high-temperature resistivity of YPBCO with varying Pr and oxygen contents. They found that all of the $\rho(T)$ curves showed identical behaviour above 800 K when the samples were kept under ambient oxygen and equilibrium conditions. Below 800 K, the curves deviate from the YBCO behaviour, with PBCO showing the most dramatic departures.

It is also well established that the cuprates readily exchange oxygen with the gas phase at processing and annealing temperatures, typically in the range 500–1200 K. These redox

reactions usually lead to large excursions in carrier density, such as the one evident for YBCO [4]. Many approaches, some direct [5, 6] and others indirect [7–10], have been made to examine the redox or oxygen diffusion kinetics for oxides. In particular, Tu *et al* [7] have used *in situ* resistivity measurements to monitor the diffusion of oxygen in and out of the ceramic oxide YBCO over the temperature range 300–1000 K. We have also followed this approach in studying oxygen diffusion in YPBCO with several concentrations of Pr ($0 \leq x \leq 1$), by comparing the kinetics of oxygen uptake or removal in these oxides with the kinetics for pure YBCO.

2. Experimental procedure

All of the samples of the system $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($0 \leq x \leq 1$) were prepared by the conventional ceramic method, following the same procedure as described in reference [11], with several regrinding and refiring schedules to improve homogeneity. X-ray diffraction patterns showed that all of the samples were essentially single phase. The powders were pressed into pellets and thermally treated in ambient oxygen for a maximum oxygen content, that is, with $\delta \simeq 0$. The as-prepared samples showed low-temperature resistivities that were essentially identical to previous results for $0 \leq x \leq 1$ [2]. In fact, the superconducting samples with $x \leq 0.5$ showed that the transition temperature (T_c) decreased with increasing x .

In order to reduce the oxygen content ($O_{7-\delta}$) of the samples and prepare them for resistivity measurements during in-diffusion of oxygen, they were annealed at 1213 K in air for 14 hours and quenched into liquid nitrogen.

The resistivities of all of the samples were measured in air using the four-contact van der Pauw method [12] with a sinusoidal applied current. Ohmic behaviour of the contacts was obtained by pressing fine platinum pins against the border of the front face of the samples, which were disk-shaped pellets 10 mm in diameter and 1.0 mm thick. A Hewlett–Packard Model 4274A Multifrequency LCR meter controlled by an HP900 computer was used to measure the resistance of the sample for each four-point configuration required by the technique, at a frequency of 1 kHz and amplitude of 0.1 V. Our resistivity probe was designed to allow air at ambient pressure to flow around the whole sample at all times. The probe was positioned in a temperature-controlled vertical tube furnace. Both isothermal and ramping (at a constant heating rate) modes of annealing were used.

The weight change of the oxides in ambient air due to the oxygen uptake or removal was also monitored by thermogravimetric analysis (TG), using a balance with a microgram sensitivity, and samples with approximately 100 mg weight.

Initially there was concern that the pores between the grains of the prepared samples could introduce experimental artifacts due to inhomogeneities in the oxygen content (the densities of the samples were in the range 80–90% of the theoretical density). However, probably because the oxygen diffusion study was carried out in a relatively high-temperature region, 600 to 800 K, the measured resistivity changes due to variation in oxygen for different samples are very consistent, and appear to be independent of the sample density. Therefore, we assumed that any such inhomogeneities are relatively too small to be of significance for the present study. Furthermore, previous tracer diffusion measurements of oxygen in 123 oxides at high temperatures [5, 13] have shown that the diffusion coefficients are identical in polycrystalline samples having distinct porosity density (80–90%).

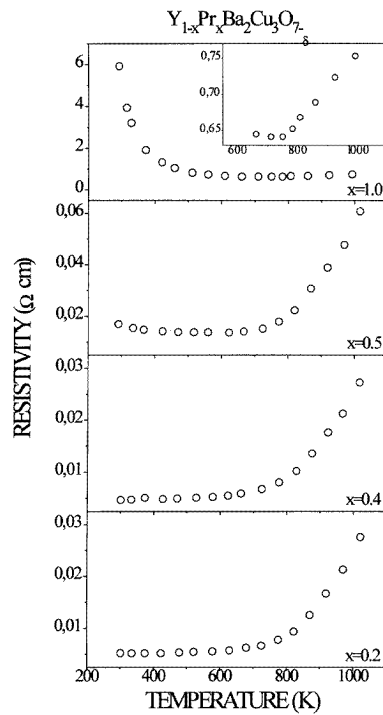


Figure 1. A set of first heating resistivity curves $\rho(T)$ for fully oxygenated YPBCO samples ($\delta \simeq 0$) with varying Pr concentrations x for a constant rate of 2 K min^{-1} in ambient air. The inset shows the data on an amplified scale for $x = 1$, in the temperature range 600–1000 K.

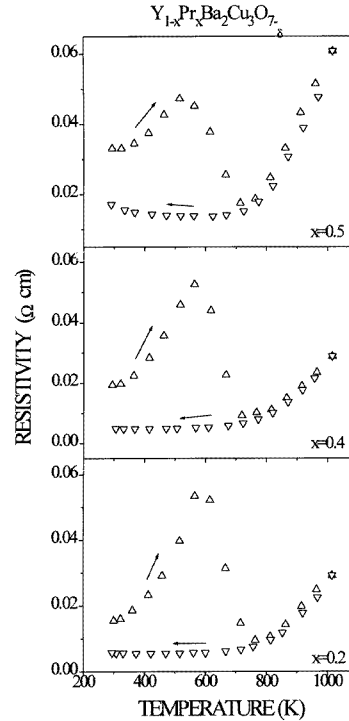


Figure 2. A set of first heating resistivity curves for several deoxygenated YPBCO samples with varying Pr concentrations x for a constant rate of 2 K min^{-1} in ambient air, for $x \leq 0.5$.

3. Results and discussion

Figure 1 shows the high-temperature resistivities of several YPBCO samples with varying Pr contents and low oxygen deficiencies ($\delta \simeq 0$). The data were taken at a constant heating rate of 2 K min^{-1} starting from room temperature up to 1000 K in air. The data clearly show that the addition of Pr causes marked changes in both the magnitude and the temperature dependence of the resistivity. For $x \leq 0.4$, a slight linear increase (metallic behaviour) from room temperature to about 600 K is observed; however, for $x > 0.4$ and in the same temperature range, the resistivity decreases as for a thermally activated transport (semiconducting behaviour) with a single activation energy. Table 1 gives the activation energy Δ as calculated from the slope of the resistivity data plotted as $\ln \rho$ versus $1/T$ in the temperature range 300–600 K. Above 600 K, all of the plots for various x show that the resistivities increase nonlinearly, and the increase shows a more pronounced upward bend for lower Pr concentrations. The average slope of the portion of the curves for $\ln \rho$ versus $1/T$ from 750 to 1000 K is also given in table 1.

The weight change of the oxides in air measured by thermogravimetric analysis revealed that the oxygen content ($\delta \simeq 0$) is preserved up to approximately 600 K, and that oxygen diffuses out of the oxides at temperatures higher than 650 K. The TG curves for heating

Table 1. The activation energy, Δ , for the resistivity $\rho(T)$ of YPBCO as calculated from the slope of $\ln \rho$ versus $1/T$ over the temperature range 300–600 K, and the average slope of the portion of the same plots from 750 to 1000 K.

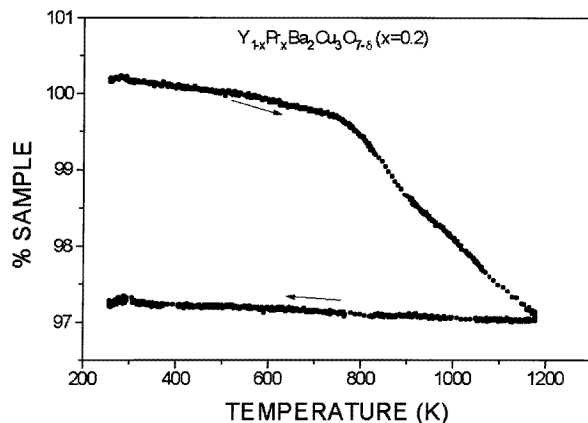
$Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$	Activation energy Δ (eV),	
	300 < T < 600 K	Average slope (eV), 750 < T < 1000 K
$x = 0.2$		-0.3598
$x = 0.4$		-0.3510
$x = 0.5$	0.0108	-0.3426
$x = 1.0$	0.1106	-0.3340

and cooling in air show that the oxygen stoichiometry is actually reversible. Therefore, the temperature behaviour of the resistivity for various Pr concentrations, shown in figure 1, could be explained following the TG profile of the weight change of the samples in air; that is, the temperature variation of the resistivity up to approximately 600 K follows the normal behaviour (either a metallic or a semiconducting behaviour according to the Pr concentration of the corresponding YPBCO sample) with constant $\delta \simeq 0$ oxygen content and distribution in the crystal lattice. Moreover, the observed deviation of the resistivity above 600 K, $\Delta\rho$, from the normal behaviour below 600 K is caused by the loss of oxygen at a fixed annealing temperature, T . On the other hand, we have found that the ρ versus T curves, for heating rates up to 5 K min^{-1} in air, overlap each other closely over the whole temperature range, indicating that the chosen heating rate of 2 K min^{-1} is slow enough for a uniform change of δ , and, hence, for $d\rho/dt$ being proportional to $d\delta/dt$, provided that the heating rate, dT/dt , is sufficiently small [7–11]. Thus, the out-diffusion rate of oxygen, $d\delta/dt$, leaving the sample (grains) at a constant heating rate, dT/dt , is proportional to the temperature derivative of the curve $\rho(T, t)$, as shown in figure 1 for various concentrations x (the heating rate of 2 K min^{-1} is sufficiently slow for $d\rho/dt \simeq 0$). Therefore, from the various curves we conclude that samples with lower Pr concentrations show a faster out-diffusion rate above 600 K. We also notice that a portion of the $\rho(T)$ data from 750 to 1000 K can be fitted with an $\exp(-E/k_B T)$ -type function (see table 1).

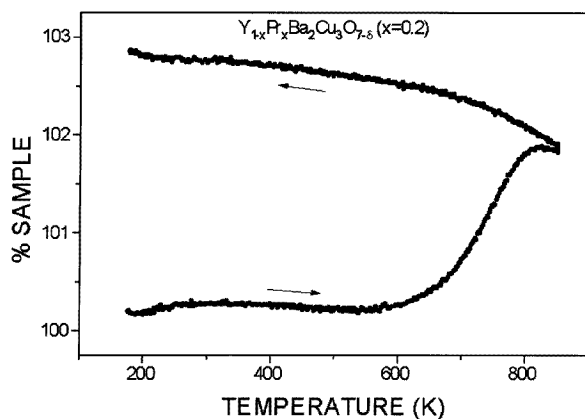
Figure 2 shows the resistivities of several YPBCO samples that were previously annealed at 1213 K in air and quenched into liquid nitrogen. The data were also taken at a constant heating rate of 2 K min^{-1} in air, from room temperature up to 1000 K. As the temperature was increased, the resistivity first increased monotonically, but at around 340 K it showed an upward bend. It reached a maximum at around 550 K, then turned downward and decreased to a minimum at around 750 K. Beyond the minimum, the resistivity increased again. On the subsequent cooling run, the resistivity data followed the same line as that taken on the heating run, down to approximately 750 K, and below this temperature $\rho(T)$ departed from the curve for the first heating run, and it followed the normal heating curve for the corresponding Pr concentration and oxygen content $\delta \simeq 0$. On subsequent thermal cycles (heating and cooling), $\rho(T)$ followed the cooling curve shown in figure 2.

Although the oxygen-deficient sample is thought to be in a nonequilibrium state at room temperature, the behaviour of the first heating $\rho(T)$ curve for the deoxygenated samples for various concentrations x clearly reveals some interesting characteristics of the oxygen in-diffusion into the oxides. The weight change measured by TG revealed that the oxygen concentration is preserved up to 550 K, and that the drop of resistivity above 550 K is due to oxygen absorption. Thus, the initial increase of the resistivity up to a maximum value near 600 K indicates that it is not due to oxygen uptake, but to the dominance of a particular

mechanism that causes an increase of the resistivity with increasing temperature. This behaviour might be due to an increasing disordering of the oxygen defects that strongly reduces the mobility of the charge carriers. The occurrence of the maximum marks the dominance of the increase of carriers (so the resistivity goes down) as a result of indiffusion of oxygen into the oxide. At the minimum, the oxide is saturated with oxygen; hence from this point the resistivity follows the corresponding heating curve for the x and $\delta \simeq 0$ contents.



(a)



(b)

Figure 3. TG curves for heating and cooling runs of YPBCO with $x = 0.2$ for (a) a fully oxygenated sample in nitrogen, for a rate of 40 K min^{-1} , and (b) a deoxygenated sample in air, for a rate of 10 K min^{-1} .

Figure 3 shows two representative TG curves for heating and cooling runs for YPBCO with $x = 0.2$ for (a) a fully oxygenated sample in nitrogen, and (b) a deoxygenated sample in air.

Finally, the bend observed in all of the curves near 340 K for various x -values may reveal a phase transition that, in the case of YBCO, Tu *et al* [7] attributed to an order-disorder transition of oxygen vacancies in the O(1) and O(5) sites in the CuO layers.

4. Conclusions

By comparing *in situ* resistivity measurements of $\rho(T)$ for YPBCO for various Pr concentration to those for pure YBCO [7], during the diffusion of oxygen in and out of the ceramic samples, we have found that the change in resistivity, $\Delta\rho$, as the oxide exchanges oxygen with the ambient air, shows common features for these oxides. On heating a fully oxygenated YPBCO sample in ambient air at a rate of 2 K min^{-1} , the oxygen concentration in the CuO layers, or the number of carriers (holes) in the CuO_2 conduction planes, is preserved up to 600 K, and oxygen diffuses out of the oxide at temperatures higher than 600 K. On heating the deoxygenated YPBCO samples, in ambient air at a rate of 2 K min^{-1} , oxygen starts to diffuse into the CuO layers of the oxide above 550 K.

However, by comparing $d\rho/dT$ at a constant heating rate of 2 K min^{-1} , we found that the rate of oxygen removal in ambient air from a fully oxygenated sample which takes place above 600 K decreases with increasing x , while the rate of oxygen uptake by a deoxygenated sample in ambient air which takes place over the 550–750 K temperature range depends slightly on x .

For all of the deoxygenated YPBCO samples, independently of the Pr concentrations, an upward bend was observed in $\rho(T)$ on heating near 340 K, similar to that observed for pure YBCO, which was attributed to an order–disorder transition of oxygen vacancies.

The observed resistivity change $\Delta\rho(\delta)$ for all of the YPBCO samples as they interchange oxygen with the gas phase indicates, at least qualitatively, that the number of majority carriers in the oxides is mainly controlled by the oxygen content δ , and seems to be independent of the Pr concentration, at least for $x \leq 0.5$.

Acknowledgments

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