Oxygen behavior in $Nd_{2-x}Ce_xCuO_{4-\delta}$ observed by resistivity measurements

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We present *in situ* resistivity measurements of the high-temperature phase behavior associated with oxygen variation of the ceramic system $Nd_{2-x}Ce_xCuO_{4-\delta}$ (NCCO) when annealed in ambient air. We observed a resistivity anomaly around 550 K in all deoxygenated samples prepared by rapid cooling into liquid N2, which is smaller for higher Ce content. We attribute this anomaly to oxygen in-diffusion, which is less with increasing x. The implications of these results on the role of the oxygen vacancies to establish a metallic phase in NCCO are discussed.

Keywords: T'-type cuprates; oxygen diffusion

Presentamos medidas de resistividad *in situ* del comportamiento de fases a altas temperaturas asociado con la variación de oxígeno del sistema cerámico $Nd_{2-x}Ce_xCuO_{4-\delta}$ (NCCO) cuando se templa en aire. Observamos una anomalía en la resistividad alrededor de 550 K en todas las muestras desoxigenadas preparadas por rápido enfriamiento en N2 líquido, la cual es menor para altos contenidos de Ce. Atribuimos la anomalía a la difusión de oxígeno hacia el interior de la muestra, la cual es menor a medida que crece x. Se discuten las implicaciones de este resultado en el papel que juegan las vacancias de oxígeno en el establecimiento de la fase metálica en NCCO.

Descriptores: Cupratos tipo T'; difusión de oxígeno

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1. Introduction

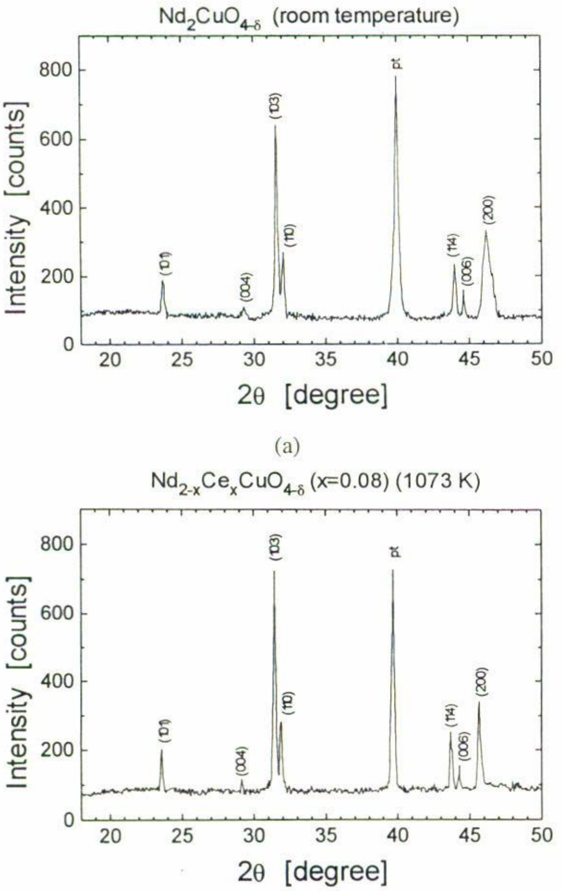
The T'-type system $Nd_{2-x}Ce_xCuO_{4-\delta}$ can be prepared in the range of Ce content $0 \leq x \leq 0.2$ at ambient pressure. Although oxygenated samples show semiconducting n-type behavior, superconductivity with the highest T_c near 24 K appears after reduction annealing for $x = 0.14$–0.18 [1–3]. Various experimental works have been done [4–7] to study the influence of the Ce- doping and the reduction of oxygen content on establishing a metallic phase in NCCO. It is evident from those results that critical levels of carriers and oxygen vacancies are essential for the T'-type cuprates to exhibit superconductivity. Kawashima *et al.* [4] using thermogravimetry, dc susceptibility and X-ray diffraction show that for $x = 0.15$ or 0.16 a lesser amount of oxygen defects was needed to realize superconductivity compared with the case $x = 0.14$ suggesting that introduction of oxygen defects works to add carriers (electrons) to the system. Alp *et al.* [5] using X-ray absorption spectroscopy show that the Ce ions add carriers (electrons) to the CuO_2 planes. Takayama *et al.* [6] using neutron powder diffraction suggests that the oxygen defects are introduced at least to the sites within the CuO_2 layer. However, the reduction process and the role of oxygen defects (vacancies) thus created have not been adequately understood so far [7].

In the present study, we prepared sample with $x = 0$, 0.08, 0.12, 0.16 and investigated in detail the variation of oxygen content in the temperature range 300–1000 K by *in situ* resistivity measurements. We believe, the resistivity change, $\Delta\rho(T)$, between the oxidized and reduced phases of NCCO in the normal state may provide information on carrier doping due the occupancy on the oxygen sites.

2. Experimental

The $Nd_{2-x}Ce_xCuO_{4-\delta}$ samples ($x = 0$, 0.08, 0.12, and 0.16) were prepared by solid state reaction [8] at 1223 K in air using Nd_2O_3, CeO_2 and CuO as starting reagents with several regrinding and refiring schedules to improve homogeneity. The powders were pressed into pellets and thermally treated in air. To get samples with the minimum oxygen content, they were equally reduced at 1213 K in air for 14 hours, then quenched into liquid nitrogen. X-ray diffraction patterns showed that all the samples were essentially single phase and the lines are indexed on the basis of tetragonal structure with the lattice parameters of pure Nd_2CuO_4 [9] (see Fig. 1).

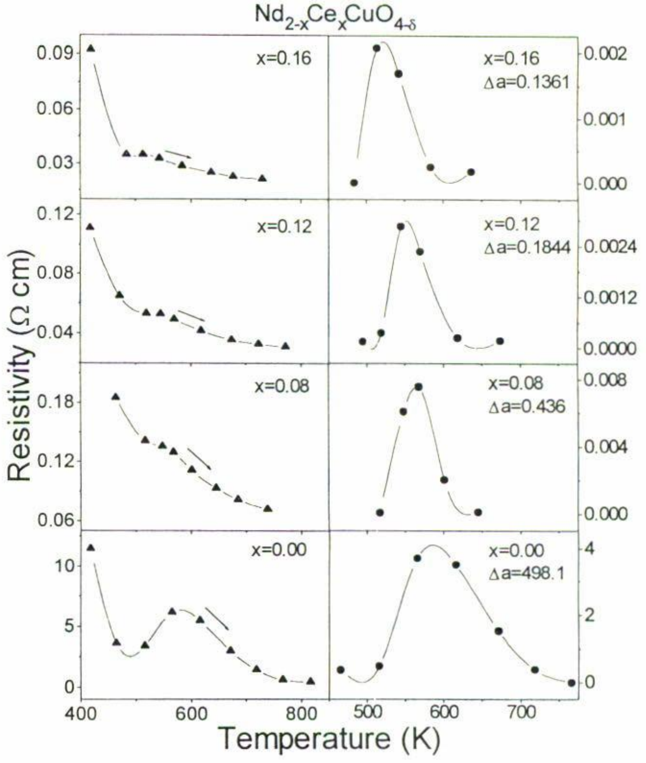
The resistivity of all the samples was measured in air using the four contact van der Pauw method [10] with a sinusoidal applied current. Ohmic behavior of the contacts were obtained by pressing fine platinum pins against the border of the front face of the samples, which were disk-shape pellets of 10 mm in diameter and 1.0 mm thickness. A Hewlett-Packard Model 4274A Multifrequency LCR meter controlled by a 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



(a)

(b)

FIGURE 1. Powder X-ray diffraction patterns of representative samples of $Nd_2CuO_{4-\delta}$ at room temperature (a) and of doped sample $Nd_{2-x}Ce_xCuO_{4-\delta}$ with $x = 0.08$ at 1073 K (b).



(a) (b)

FIGURE 2. A set of first sweep heating resistivity curves of several equally reduced samples of $Nd_{2-x}Ce_xCuO_{4-\delta}$ with varying Ce contents, x, at a constant rate of 2 K/min in ambient air: a) Total $\rho(T)$ in the 400–800 K temperature range; b) resistivity change, $\Delta\rho(T)$ between de reduced and normal curves (see Fig. 3) in the 500–700 K temperature range.

TABLE I. Area Δa of the peak shown in Fig. 2b as a function of Ce concentration

Ce concentration (x)	Peak area, Δa (Ω cm K)
0.00	498.1
0.08	0.436
0.12	0.1844
0.16	0.1361

probe was positioned in a temperature-controlled vertical tube furnace. Constant ramping modes (heating and cooling) of annealing were used.

3. Results and discussion

The powder X-ray diffraction patterns of representative samples of Nd_2CuO_4 ($x = 0$) at room temperature (a) and doped sample with $x = 0.08$ taken at 1073 K (b) are shown in Fig. 1. Both patterns are perfect reproduction of the powder pattern reported by Singh *et al.* [9], confirming that the samples are a single phase with the tetragonal structure of pure Nd_2CuO_4.

Figure 2a shows the high-temperature resistivity in the 400–800 K temperature range of several $Nd_{2-x}Ce_xCuO_{4-\delta}$ samples with varying Ce contents, which were previously annealed at 1213 K in air and quenched into liquid nitrogen. The data were taken at a constant heating rate of 2 K/min in air, from room temperature up to 1000 K. Figure 2b shows on an amplified scale the variation of the resistivity with respect to the base line of the observed peak anomaly. The area (Δa) of the peak as a function of Ce concentration was then calculated (see Table I). Figure 3 shows the resistivity data for two representative samples (Ce contents of $x = 0$ and $x = 0.16$) taken on the first heating run (data points marked by solid upward triangles, the subsequent cooling run (points market by solid downward triangles), the second heating run (points marked by open circles) and the second cooling run (points marked by open squares). The data clearly show that the addition of Ce marked changes in both the magnitude and the temperature dependence of the resistivity on the first heating run (see Fig. 2). As the temperature was increased, the resistivity first decreased, indicating a semiconducting behavior, but around 500 K it showed an upward bend. Beyond

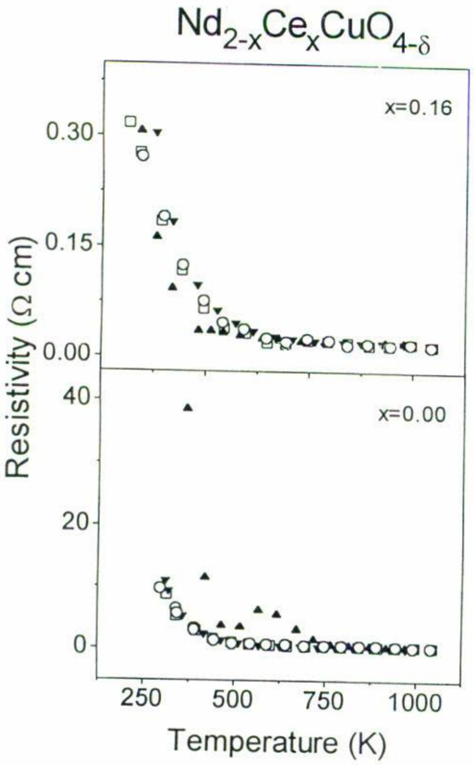


FIGURE 3. Resistivity data, $\rho(T)$, of two representatives $Nd_{2-x}Ce_xCuO_{4-\delta}$ samples with varying Ce concentrations: a) for $x = 0.16$ and b) $x = 0.0$ at a constant rate of 2 K/min in ambient air. On the first heating run (solid uptriangles), on the subsequent cooling run (solid downtriangles), on the second heating run (open circles) and the second cooling run (open squares).

approximately 550 K, the resistivity decreased again, but above 700 K it leveled to a constant value. On the subsequent cooling runs, the resistivity data did not show any anomaly around 500 K: it followed the same line down to approximately 700 K, and below this temperature the resistivity departed from the first heating run with a similar semiconducting behavior. On subsequent thermal cycles (heating and cooling) $\rho(T)$ followed the first cooling curve (see Fig. 3).

The observed behavior of the first heating $\rho(T)$ curves of as-prepared deoxygenated samples (reduced at the same temperature (1213 K) to secure identical oxygen deficient) for various Ce concentrations clearly reveals some interesting characteristics of their exchange of oxygen with the gas phase. Thus, all the samples showed a semiconducting behavior but the resistivity decreased with Ce-doping indicating that it creates carriers (electrons) by the Ce^{4+} substitution on the Nd^{3+} sites (Notice the drastic reduction of the resistivity scale as x increases in Figs. 2 and 3). The occurrence of the upward bend of ρ(T) around 500 K marks the dominance of the decrease of carriers (so the resistivity goes up) as a result of in-diffusion of oxygen into the oxide. In other words, we are claiming that the in-diffusion rate of oxygen, $d\delta/dt$, entering the sample (grains) at constant heating rate, dT/dt, is proportional to the temperature derivative of the curve $\rho(T, t)$ as shown in Fig. 4 for various x concentrations (the heating rate of 2 K/min is sufficiently slow for $\partial\rho/\partial t \approx 0$). Therefore, from the resistivity change, $\Delta\rho(T)$, between the reduced and normal oxygen content phases of NCCO above room temperature (Fig. 2b) we conclude that samples with lower Ce-doping show higher oxygen in-diffusion in the 500–550 K temperature range. When the sample is saturated with oxygen at a particular temperature or the partial oxygen pressure of the gas phase (ambient air) is in equilibrium with the compound, the resistivity follows the corresponding temperature variation for the x and fully oxidized phase.

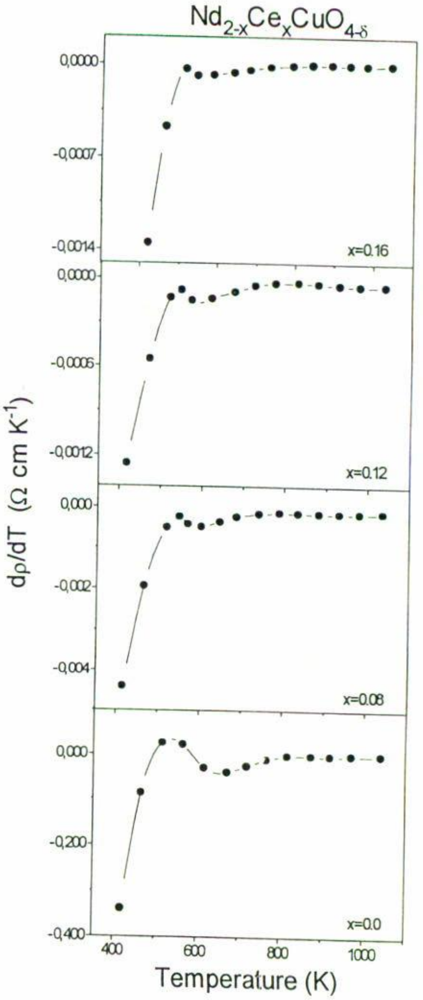


FIGURE 4. Temperature derivative of the first heating resistivity data, $d\rho/dT$ *vs.* T, for various x concentrations of NCCO.

4. Conclusions

By comparing *in situ* resistivity measurements $\rho(T)$ in the semiconducting phase of NCCO for various Ce concentration, we found that the temperature variation of the resistivity as the samples exchanges oxygen with the ambient air, shows common features for these oxides. On heating a deoxygenated sample in ambient air at a moderate rate (2 K/min) the oxygen concentration is preserved up to approximately 500 K where oxygen starts to diffuse into those energetically available empty sites of the corresponding oxide. By comparing $d\rho/dt$ for equally reduced samples with various Ce content, we found that the rate of oxygen uptake decreases with increasing x. Our results then reveal that establishing critical levels of oxygen-vacancy doping in NCCO requires a good control of low partial oxygen pressures in equilibrium with the sample mainly above 500 K. Moreover, *in situ* resistivity experiments when these oxides are thermally treated are shown to be a simple tool to monitor their carrier doping due to variations of oxygen content.

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