

# THE EFFECTS OF SYNTHESIS AND REDUCTION PROCESSING ON THE PHYSICAL PROPERTIES OF CERAMIC



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Following the discovery of "n-type" superconductivity in  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$  many reports appeared describing the transport properties of this phase as significantly different from its "p-type" predecessors. These reports typically found a negative slope in the temperature dependence of the resistivity throughout the normal state in ceramic samples, which was interpreted by some as evidence for anomalously strong magnetic scattering of the electron carriers. We believe this behavior is not intrinsic and arises from large inhomogeneities in Ce concentration, and in oxygen vacancies as well, the presence of the latter being a necessary condition for superconductivity. The method of sample synthesis and attendant reduction is thus critical to the observed electronic properties of this material, both in the superconducting and normal state. In this paper we describe a technique for preparing  $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$  with uniform Ce concentration, which is then reduced by precisely controlling the oxygen content using oxygen coulometric titration. We discuss the conditions leading to samples that exhibit more intrinsic behavior, as indicated by a sharp, narrow resistive transition at  $T_c$ , positive  $\partial\rho/\partial T$  above and nearly complete diamagnetic shielding.

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## I. Introduction

Recently, Tokura, et al<sup>1</sup> reported the synthesis of superconducting Ce-doped  $\text{Nd}_2\text{CuO}_{4-y}$  with an onset  $T_C=20-24$  K. What makes this material unusual is that the excess charge per unit cell available for conduction is negative, whereas in all previously known high- $T_C$  compounds this quantity is positive. The number of these "n-type" superconductors has been extended<sup>2</sup> to include thorium-doped  $(\text{Nd},\text{Pr})_2\text{CuO}_{4-y}$  and fluorine-doped  $\text{Nd}_2\text{CuO}_{4-y}$ ,<sup>3,4</sup> with properties similar to their cerium predecessors. Single crystals of  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$  have also been grown and studied.<sup>5,6</sup> Superconductivity in the  $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$  materials exists only in a narrow range of cerium concentration, around  $x \approx 0.15$ , unlike the broad doping range accommodated by their alkaline earth-doped  $\text{La}_2\text{CuO}_{4-y}$  relatives. One distinguishing feature of these new "n-type" materials is that they are much more difficult to prepare with optimal superconducting properties compared to their "p-type" predecessors. For example, both ceramic and single crystal samples often fail to exhibit zero resistance below  $T_C$ . Moreover, all data to date on the normal state resistivity in either ceramics or crystals lack the ubiquitous linear dependence on temperature observed in all "p-type" systems. At present, there is no reason to expect the nature of either the superconducting or normal state in the "n-type" materials to differ substantially from other high- $T_C$  compounds, except for the sign of the charge carriers. This is an important issue, and the discovery of substantially different physical behavior between the two carrier systems could impact theories regarding the mechanism of high temperature superconductivity. One interpretation of the upturn in  $\rho$  vs.  $T$  observed before the onset of superconductivity attributes this behavior to exceedingly strong magnetic impurity scattering arising from the Nd moments.<sup>7</sup> However, from the work presented here, it is more likely that both the non-zero resistance below  $T_C$  and the non-linear temperature dependence above arise from a combination of compositional inhomogeneities and structural irregularities, and there is little intrinsic difference in the electrical properties of "n-type" and "p-type" materials.

We have previously discussed the difficulty of preparing ceramic samples of  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$  with uniform cerium concentration throughout.<sup>8</sup> Similarly, single crystals, although homogeneous with respect to Ce, appear to possess variations in oxygen content that lead to local structural modifications in the form of superlattices.<sup>9</sup> It is important to be able to make these new compounds with uniform elemental distributions to provide reliable experimental data so that significant physical questions such as the dependence of superconducting properties on dopant and carrier concentration can be studied. In this paper, we report the techniques used for obtaining ceramic samples of  $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$  that are microscopically uniform in both cerium and oxygen concentrations, to the limit detectable by electron beam microprobe. We also describe the solid state ionic technique used for precisely controlling their oxygen deficiency. The ceramic samples obtained by this method display narrow resistive transition widths, nearly complete diamagnetic shielding, and an almost linear resistivity vs. temperature dependence in the normal state.

## II. Experimental details

"N-type" ceramics like  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$  are typically prepared using solid-state reaction methods essentially identical to those employed for the "p-type" materials; namely, appropriate molar amounts of  $\text{Nd}_2\text{O}_3$ ,  $\text{CuO}$  and  $\text{CeO}_2$  are mixed, ground and reacted below their melting point for varying lengths of time. However, the post-calcination procedure differs significantly for the former in that it is necessary to reduce and quench the product in a reducing environment before superconductivity can occur. Using these techniques it is difficult to obtain homogeneous cerium and oxygen distributions in ceramic samples of  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ . The energy required to break the strong Ce-O bond results in very slow diffusion of this cation throughout the host  $\text{Nd}_2\text{CuO}_{4-y}$  lattice, even over very long reaction times (5-10 days) at typical furnace temperatures ( $\approx 1050$  C). Attempts to accelerate Ce diffusion by calcining at higher temperatures ( $> 1100$  C) result in a partially melted product. Moreover reducing the samples under such extreme conditions results in an inhomogeneous oxygen distribution. Samples prepared this way will always have variable oxygen contents depending on parameters such as the length and temperature of the reduction process, rate of cooling, initial oxygen concentration, and purity of the reducing gas. In the growth of single crystals, uniform cerium distribution can be attained because the starting materials are dissolved in a CuO-rich flux.<sup>5,6</sup> However, due to the relatively large distances over which oxygen must diffuse in crystals, as compared to finely ground ceramic powder, subsequent oxygen concentration after reduction processing is found to be quite nonuniform.<sup>6,9</sup> In addition, the necessity to use excess CuO in the flux growth approach leads to its entrapment in the crystal lattice and a degradation of superconducting properties.<sup>6</sup>

As a first step to circumvent these difficulties, we begin by using a two-stage procedure to produce a sample that is homogeneous in cerium. First,  $\text{NdCeO}_{3.5}$  is formed in a high-temperature solid-state reaction.<sup>10</sup> In this way it is assured the complete reaction of all  $\text{CeO}_2$ . Next  $\text{NdCeO}_{3.5}$  is ground, mixed with the appropriate amounts of  $\text{Nd}_2\text{O}_3$  and  $\text{CuO}$ , and fired at lower temperatures,<sup>11</sup> under flowing oxygen. It has been found that undergoing this step in flowing oxygen also helps assure complete reaction.<sup>12</sup>

Details of the method are as follows: We form the compound  $\text{NdCeO}_{3.5}$  by grinding and mixing the proper molar amounts of  $\text{Nd}_2\text{O}_3$  and  $\text{CeO}_2$ , then reacting the mixture in a Coors alumina crucible at  $1400$  C for at least 48 hours in air. The product is then ground and mixed with additional  $\text{Nd}_2\text{O}_3$  and  $\text{CuO}$  computed to achieve an overall composition of  $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ . This mixture is fired at  $980$  C for 24 hours in flowing oxygen. The product is then ground, pelletized and sintered at  $1050$  C, with several repetitions, for a total period of at least 48 hours, again in flowing oxygen. The sample is slowly cooled in flowing oxygen to room temperature. Powder x-ray diffraction confirms that the product has the  $\text{Nd}_2\text{CuO}_{4-y}$  'T' structure.<sup>13</sup>

The second step to achieve homogeneous samples is to reduce the resultant material using a coulometric titration technique that precisely controls the amount of oxygen in the sample and allows it to reach thermodynamic equilibrium, with a more homogeneous oxygen distribution.<sup>14,15</sup> The solid-state ionic cell used consists of a closed quartz chamber with two interconnected compartments, as shown in Fig. 1. Each compartment has its own furnace for independent temperature control. One compartment contains the  $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$  sample. A nearby thermocouple monitors the thermal history of the sample including the quenching process. The other compartment houses a yttria-stabilized-zirconia (YSZ) solid electrolyte tube, closed at one end, with porous platinum electrodes deposited on the inner and outer walls at the closed end. The interior of the YSZ tube is exposed to air, to act as an oxygen reference electrode. The YSZ tube serves two purposes. Under open circuit conditions, it acts as an oxygen sensor to monitor the oxygen pressure inside the sealed chamber. Under DC-biased conditions, it serves as an oxygen pump to quantitatively titrate oxygen into or out of the chamber and to maintain a desired level of oxygen pressure within the chamber. The YSZ compartment is operated at a fixed temperature of 850 C to obtain high ionic conductivity and thus rapid oxygen transport.

The following procedure is used to prepare samples with reduced oxygen content:  $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$  starting material is placed in an alumina boat in the chamber, evacuated and heated to 900 C. During the temperature ramp up, oxygen is liberated from the sample but the total oxygen content inside the chamber remains constant. At 900 C, oxygen is then titrated out of the chamber for 2 to 3 days. The sample remains at 900 C for at least one additional day after the desired oxygen content is attained. Note that after each titration, the oxygen partial pressure inside the chamber increases asymptotically to a new equilibrium value. However, even after several days, sometimes there is a persistent small increase in the oxygen pressure in the chamber, indicating that the oxygen concentration within the sample is still not completely uniform. This small increase in oxygen pressure with time does not occur when no sample is present in the chamber, indicating that oxygen evolution from the sample is responsible for this "virtual leak" in the system. Finally, the sample is slowly cooled by stepping down the sample furnace temperature to room temperature at a rate of 20 C per hour.

Subsequent electron beam microprobe analysis of the pellet samples, both on the surface and in cross-section, indicates some minor phases, mostly  $\text{NdCe}_2\text{O}_x$ , qualitatively present to the order of 1-2%, with a very uniform concentration of Nd, Ce and O throughout the remaining bulk. The uniformity is greatly superior to ceramic samples obtained from the usual one-step approach, both by ourselves<sup>8</sup> and others<sup>6</sup>, where perhaps only 50% of the sample attains the target composition, with 15-20% variation in Ce concentration still remaining.

Resistivity, thermopower, and ac susceptibility measurements were subsequently performed to determine the superconducting properties of the low-

## Coulometric Titration

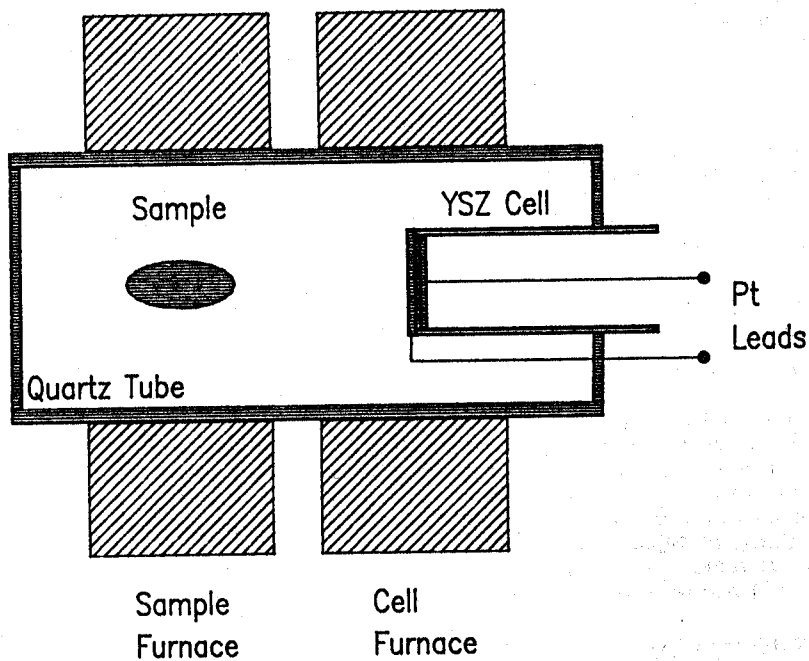


Fig. 1. Schematic representation of the coulometric titration apparatus.

oxygen content samples according to the methods previously described.<sup>8</sup> The results are discussed below.

### III. Results

We find the transport properties of  $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$  to be strongly influenced by the processing conditions. Fig. 2 shows the temperature dependence of the resistivity of a sample prepared according to the method described above. The overall magnitude of the resistivity and its temperature dependence in the normal state is representative of the best ceramic samples published in the literature. The temperature dependence is essentially linear, with only a slight indication of curvature. A sharp onset at 27 K with zero resistance at 21.5 K is observed. The low-temperature diamagnetic shielding fraction was 65% as determined by ac susceptibility and the thermopower was small and negative down to the transition temperature, consistent with our previously reported results.<sup>11</sup> Comparing our results to those obtained on single crystals<sup>5,6</sup> gives us encouragement that our ceramic samples are of equal or better quality. The large anisotropy in resistivity observed between the c-direction and the a-b plane in crystals<sup>5</sup> and the effects of intergranular contacts could account for the factor of 10 difference in overall resistivity between our results and  $\rho_{ab}$  in single crystals. The question of whether the temperature dependence of the normal state resistivity is intrinsically linear remains open. The differential between  $\rho_{300}$  and  $\rho_{21}$  in our samples is too small compared to single crystals to definitely rule out curvature. However, due to the small size of the ceramic crystallite grains and lack of flux inclusions, we believe oxygen in our samples may be more macroscopically uniform than in crystals and thus the data of Fig. 2 may indeed be a harbinger to the observance of a linear  $\rho$  vs. T behavior in n-type high- $T_c$  compounds. It is our opinion that departures from linearity result from subtle effects of microstructure. Evidence is accumulating that the microstructure of the  $\text{Nd}_2\text{CuO}_{4-y}$  family induced by processing is different from that in the  $\text{La}_2\text{CuO}_{4-y}$  materials,<sup>9</sup> involving superlattices that may be related to local oxygen occupation. Since these superlattices extend along a-b plane directions, metallic and insulating regions in series could exist that yield an effective resistor network which could easily show semiconducting tendencies in  $\rho$  vs. T at low temperatures.

Differences in oxygen occupation and ordering may also affect the superconducting state as well. A close inspection of Fig. 2 reveals the presence of two distinct, sharp superconducting transitions in this sample, one with onset at 27 K and the second at 24 K. The observation of such "double" transitions is typical of many of our samples, a behavior we believe is due to small remaining amounts of microscopic inhomogeneities in oxygen concentration. For the sample of Fig. 2, the transition at 27 K is the highest we have ever observed, and, as far as we know, represents the largest  $T_c$  yet reported for cation-doped n-type perovskite superconductors. Interestingly, broad resistive transitions beginning at roughly 27 K have also occasionally been observed in fluorine-doped  $\text{Nd}_2\text{CuO}_{4-y}$ ,<sup>3,4</sup> suggesting that we may well be approaching the upper limit for T'-structure-hosted high temperature superconductors.

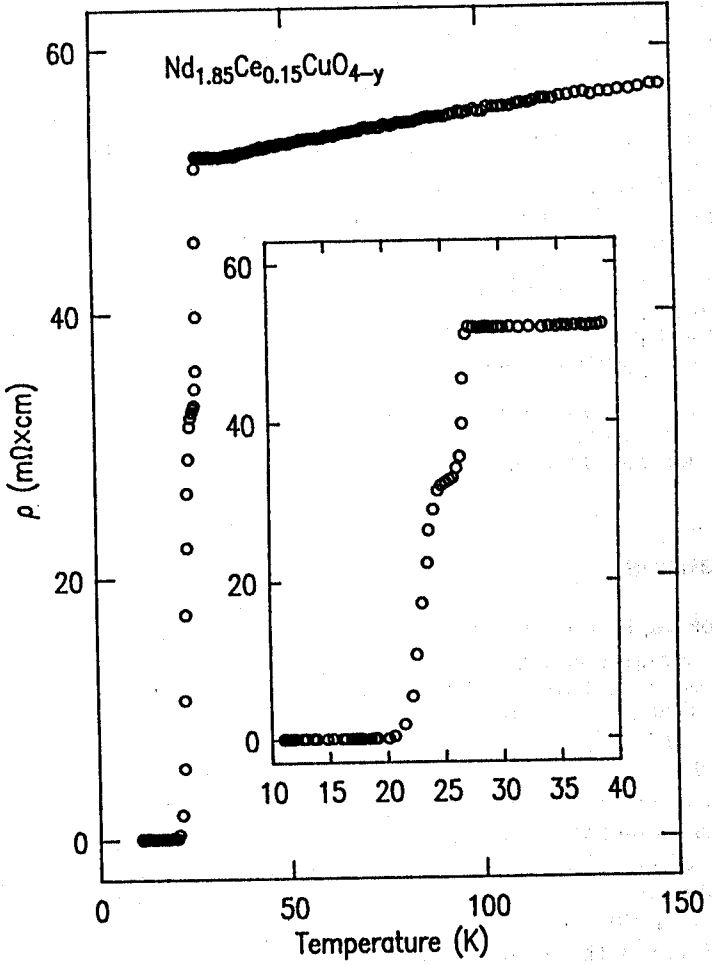


Fig. 2. Temperature dependence of the resistivity of  $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$

## IV. Conclusions

In summary, we report a procedure yielding ceramic  $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$  with macroscopically uniform concentrations of Ce and O within electron-beam-microprobe resolution. We use oxygen coulometric titration as the reduction technique. This method enables us to have complete control of both the thermal history of the sample and its oxygen environment. We obtained samples exhibiting bulk superconductivity as gauged by their resistive transition width and diamagnetic shielding. In addition, metallic behavior, indicated by positive  $d\rho/dT$  above  $T_c$  is obtained for the normal state. However, the fact that two close and distinct transitions are often observed, along with a small increase in the partial oxygen pressure in the chamber even after long equilibration periods, suggests that our samples may not yet be completely equilibrated. Nonetheless, from the point of view of their electronic properties, our samples present the best results for ceramic n-type materials reported to date.

In addition to the equilibrium question, other unresolved issues in this work include microstructural properties and a systematic study of the dependence of transport properties of  $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$  upon its oxygen concentration. Both of these areas are under investigation.

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