

The preparation and processing of bulk superconducting ceramic $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$

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We report the development of a reaction technique which yields ceramic $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ with macroscopically uniform concentrations of Ce and O. Under appropriate argon annealing conditions, samples exhibiting bulk superconductivity as gauged by resistive transition width and diamagnetic shielding are obtained. In addition, metallic behavior, indicated by positive $d\rho/dT$ above T_c , is obtained for the normal state.

Early in 1989, Tokura *et al.*¹ reported the synthesis of superconducting Ce-doped $\text{Nd}_2\text{CuO}_{4-y}$ with an onset $T_c = 20\text{--}24$ K. What made this material unusual was that the excess charge per unit cell available for conduction was negative, whereas in all previously known high- T_c compounds this quantity was positive. Their discovery was rapidly followed by disclosures of other related compounds,² and the growth of single crystals as well.^{3,4} One of the principal distinguishing features 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 former high- T_c compounds. This is an important question, and the discovery of substantially different physical behavior between the two carrier systems could impact theoretical issues regarding the mechanism of high temperature superconductivity. One interpretation of the upturn in ρ vs T observed before onset of superconductivity attributes this behavior to exceedingly strong magnetic impurity scattering arising from the Nd moments.⁵ However, it is more likely, as will be apparent from the work presented in this paper, that both nonzero resistance below T_c and nonlinear temperature dependence above arise from a combination of compositional inhomogeneities and structural irregular-

ities, and there is little intrinsic difference in the electrical properties of n-type and p-type materials, other than a change in carrier sign. 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,⁶ whereas single crystals, although homogeneous with respect to Ce, appear to possess variations in oxygen and copper content⁴ which lead to local structural modifications in the form of superlattices.⁷ It is important to be able to make these new compounds with uniform elemental distributions in order to study significant physical questions such as the dependence of superconducting properties on dopant and carrier concentration. In this paper, we report a preparation and processing technique for $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ which yields ceramic samples uniform in both cerium and oxygen concentrations, to the limit detectable by electron beam microprobe, and which exhibit zero resistance, a narrow (≈ 1 K) resistive transition width, nearly complete diamagnetic shielding, and an almost linear resistivity versus temperature dependence in the normal state.

The n-type ceramics, typified by $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$, have been prepared using solid state reaction methods essentially identical to those employed for the p-type materials; namely, appropriate molar amounts of Nd_2O_3 , CuO, and CeO_2 are mixed, ground, and reacted below their melting point for varying lengths of time. Following calcination, it is necessary to vigorously reduce and quench the product in an inert environment before superconductivity can be made to occur.¹⁻⁴ The main difficulty in obtaining homogeneous cerium distribution in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ by these techniques is that 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

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long reaction times (5–10 days) at usual furnace temperatures ($\approx 1050^\circ\text{C}$). Attempts to accelerate Ce diffusion by calcining at higher temperatures ($>1100^\circ\text{C}$) results in a partially melted product.

Our approach to circumventing these difficulties is to use a two-step procedure where a stable Nd–Ce–oxide is first formed in a high temperature solid state reaction, followed by grinding the resultant product, mixing with Nd_2O_3 and CuO , and firing the new mixture at lower temperatures. Lastly, this final product is reduced in argon and rapidly quenched. The details of the method follow:

(1) We form the known compound⁸ $\text{NdCeO}_{3.5}$ by grinding and mixing the proper molar amounts of Nd_2O_3 and CeO_2 , followed by reaction in a Coors alumina crucible at 1400°C for at least 48 h in air. This assures the complete reaction of all CeO_2 .

(2) The product is then reground and mixed with molar amounts of additional Nd_2O_3 as well as CuO computed to achieve a target composition of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$.

(3) This mixture is fired at 980°C for 24 h in flowing oxygen.

(4) The product is then reground, pelletized, and sintered at 1050°C , with several repetitions, for a total period of at least 48 h, again in flowing oxygen.

(5) An anneal in flowing argon, spectroscopic grade, in a quartz tube tightly sealed against air back-flow, is performed with the sample held at 980°C for at least 24 h.

(6) Lastly, the sample is rapidly quenched (≈ 30 s) to room temperature while held in argon.

Powder x-ray diffraction confirmed the resulting material to be the $\text{Nd}_2\text{CuO}_{4-y}$ structure.⁹ Subsequent electron beam microprobe analyses of the pellet samples, both on the surface and in cross section, indicate some minor phases, mostly NdCe_2O_x , quantitatively present to the order of 1–2%, with a very uniform concentration of Nd, Ce, and O throughout the remaining bulk. The general sample uniformity can be seen in Fig. 1 where we compare backscattered electron images taken on a sample prepared using the conventional solid state reaction⁶ of Nd_2O_3 , CeO_2 , and CuO [Fig. 1(a)] with that on a sample made by the technique described here [Fig. 1(b)]. The variations from elemental concentration target values throughout the sample shown in Fig. 1(b), as determined by electron beam microprobe (spatial analyzing resolution approximately one micron), were 1.3%, 5.7%, and 1.5% for Nd, Ce, and O, respectively. This uniformity is greatly superior to ceramic samples obtained from the usual one-step approach, both by ourselves⁶ and others,⁴ where perhaps only 50% of the sample attains near-target composition with yet a 15–20% variation in Ce concentration still remaining.

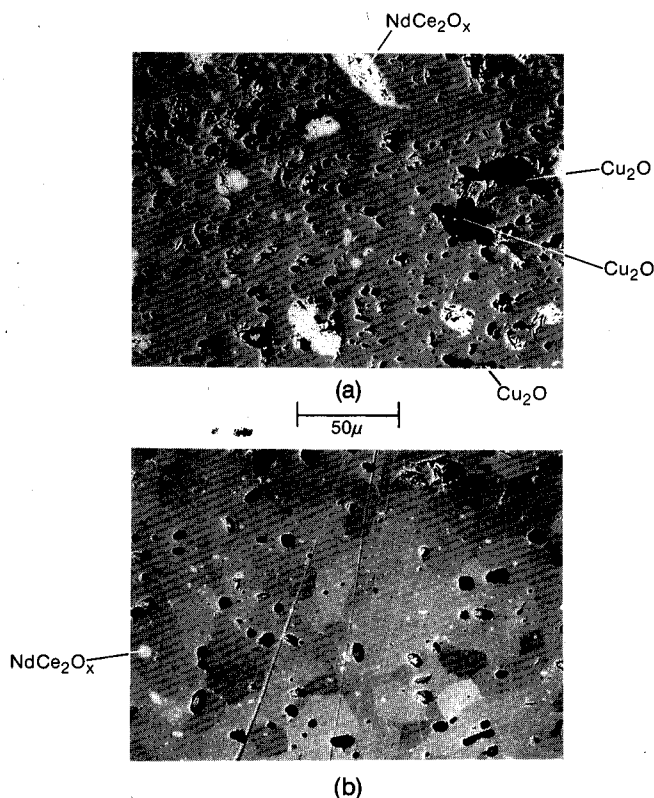


FIG. 1. Backscattered electron images of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ prepared by differing techniques. (a) Conventional solid state reaction methods.^{1,6} (b) Method of present paper. In both images, the small black spots are due to surface pitting, not phase or impurity inclusions. The gray areas are $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$; however, in (a) x varies considerably and some regions are nearly undoped with Ce, while in (b) x is 0.15 with a standard deviation of about 5%.

The thermoelectric power of samples made this way is extremely small ($\approx 1 \mu\text{V}/\text{K}$) with negative sign all the way down to T_c , in general agreement with our earlier results⁶ on less homogeneous $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ samples. The temperature dependence of the resistivity, shown in Fig. 2, and its overall low magnitude, indicates the bulk nature of the superconductivity in the sample. A sharp onset at 21 K with zero resistance at 18 K is observed, with the major portion of the transition possessing a width less than 1 K. Moreover, the temperature dependence in the normal state is essentially linear with only the slightest indication of curvature, very unlike all previously reported results on ceramic material in which only activated behavior appeared. Different regions of this same sample gave nearly identical results. However, the presence of a small "foot" just above zero resistance shows that these samples still contain small amounts of inhomogeneity as well as intergranular contacts. Nevertheless, comparing our results to those obtained on single crystals^{3,4} gives us encouragement that our ceramic samples are of equal or better quality. Taking into account the large anisotropy in resistivity observed between the

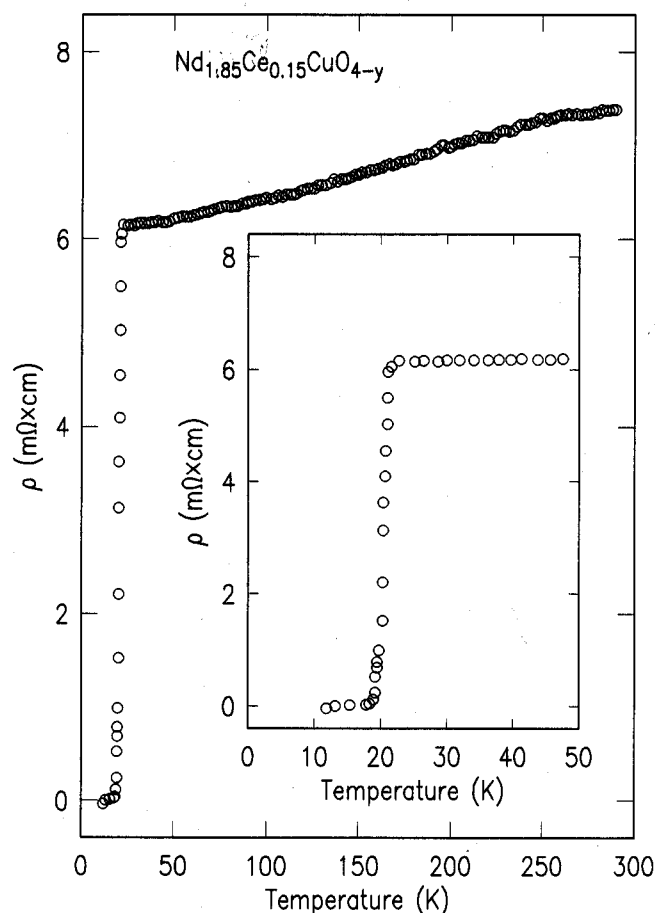


FIG. 2. Resistivity versus temperature of a $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ sample prepared by the procedures described in the text. Inset shows low temperature details.

c-direction and the a-b plane in crystals,³ which, suitably averaged, and the effects of intergranular contacts, could account for the remaining factor of 10 in overall resistivity between our results in Fig. 2 and ρ_{ab} in single crystals. The question of whether the temperature dependence of the normal state resistivity is intrinsically linear remains open. The differential between ρ_{300} and ρ_{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 have reason to believe oxygen reduction may be more macroscopically uniform than in crystals and thus the data of Fig. 2 may indeed be the harbinger to eventual observance of a linear ρ 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 Nd 214 family induced on processing is radically different from that in the La 214 materials,⁷ involving several sets of superlattices which may be related to local oxygen occupation. We are presently studying the equilibrium conditions under

which oxygen is removed from the Nd 214 structure and whether that knowledge can be used to establish more uniform vacancy concentration and hence more intrinsic transport behavior in these n -type materials.

The high quality of the superconducting state in the argon annealed samples made by our synthesis procedure, already indicated by the sharpness of the resistive transition, is further underscored by the large amount of diamagnetic shielding observed in ac susceptibility. Figure 3 shows the absolute ac susceptibility of the sample of Fig. 2 as a function of temperature. The measurement was calibrated using a $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ standard which has essentially complete shielding at 4.2 K. The departure from theoretical density due to voids introduced by powdering was taken into account for both sample and standard. It is seen that χ_{ac} has a low temperature saturation near 65% of ideal diamagnetism.

In summary, we report the development of a reaction technique which yields ceramic $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ with macroscopically uniform concentrations of Ce and O, and which exhibits bulk superconductivity as gauged by resistive transition width and diamagnetic shielding. In addition, metallic behavior, indicated by positive

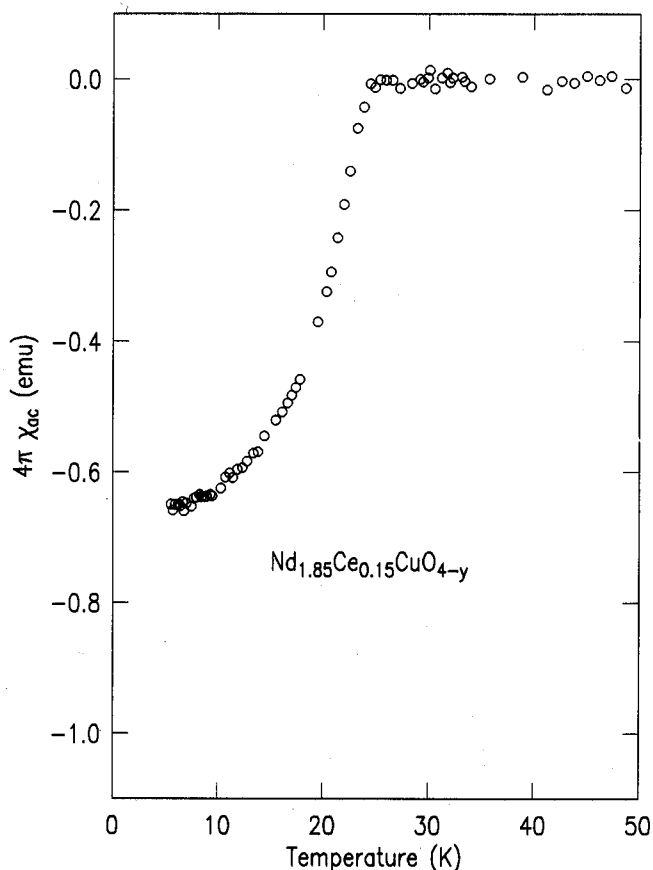


FIG. 3. χ_{ac} , ac susceptibility, versus temperature for sample shown in Fig. 2. Absolute susceptibility obtained by calibration to $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ standard.

dp/dT above T_c , is obtained for the normal state. Unresolved issues include microstructural properties and the dependence of electronic properties on Ce and oxygen concentration. Both areas are under current investigation.

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