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SYNTHESIS, TRANSPORT AND MICROSTRUCTURAL PROPERTIES OF
 $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$



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SYNTHESIS, TRANSPORT AND MICROSTRUCTURAL PROPERTIES OF $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$

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ABSTRACT

The n-type superconductor, $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$, has been prepared by solid state reaction and solution precursor techniques under various conditions and characterized by means of X-ray diffraction, magnetic susceptibility, electrical resistivity and SEM measurements. Samples prepared by solution method displayed higher normal state resistance but better superconducting volume fractions than those prepared by conventional ceramic techniques. In addition, the solution precursor technique reduces the sintering temperature from 1150°C (used for solid-state route) to 1000°C in achieving the superconducting phase. The solution-route yields particles with relatively uniform size distribution, but poor connectivity between the grains. In contrast, the solid state preparations yield well connected grains but with a larger distribution of sizes. The observed differences in the superconducting properties of samples prepared by different techniques have been attributed to the differences in their microstructure.

INTRODUCTION

With the discovery of electron doped superconductivity in the cuprate compounds ($T_c^{\text{onset}} \sim 24$ K) [1], mechanisms that related the occurrence of high-temperature superconductivity to the presence of holes in Cu-O layers were extended to electrons as well. Single crystals of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ prepared from CuO rich fluxes showed T_c^{onset} around 22.5 K [2]. The single crystal and the polycrystalline forms of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ differ in their temperature dependence of normal state electrical resistivity. The single crystal specimens exhibit metallic behavior between T_c and room temperature, while the polycrystalline analogs always show semiconducting behavior [3]. The differences in the normal state properties of single crystal and polycrystalline samples could be related to differences in their microstructures. Samples prepared by conventional high temperature ceramic techniques often suffer from inhomogeneities and require relatively high temperatures for the formation of single phases due to diffusion constraints. On the other hand, solution routes provide excellent microscopic mixing of component ions and thus are considered superior to the ceramic techniques. In this report, we examine the influence of the method of preparation on the microstructure and the superconducting properties of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ and also the effect of sintering temperature on the formation and properties of the superconducting phase.

EXPERIMENTAL

Superconducting compositions of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ have been prepared by two different

methods. In the solid state route, samples were prepared by a method previously described [1]. In the solution method, stoichiometric amounts of Nd_2O_3 , $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich, 99.999%) and CuO were dissolved in a minimum amount of dilute nitric acid and the resultant solution was heated to dryness at $\sim 120^\circ\text{C}$. The dried mixture of nitrates was decomposed at 500°C for 10 hours in air and sintered at various temperatures from 1000°C to 1150°C . The final products were annealed in Ar atmosphere at 960°C for 10 hours and slow cooled to room temperature. X-ray powder diffraction patterns of the samples were recorded in a SCINTAG PAD V diffractometer. The d.c. electrical resistivity were measured on brick shaped specimens in a DE 201 cryostat (APD company) by four probe method between 10 and 300 K. Magnetic susceptibility of samples was measured in a SQUID magnetometer (Quantum Design) in the temperature region 2 ~ 300 K at applied magnetic fields 25 ~ 50 G. Brick shaped specimens of similar dimension were used in the magnetic measurements. Volume fractions of the superconducting phase were estimated from the magnetization measurements and pycnometrical measurements of density. No correction for the demagnetization and paramagnetic contribution from Nd^{3+} was applied. Scanning electron micrographs and energy dispersive x-ray spectra were obtained on an Amray 1400 SEM.

RESULTS AND DISCUSSION

A. Sintering Temperature

We examined the effect of sintering temperature on the superconducting properties of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4.8}$ composition. In the synthesis of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4.8}$ by conventional solid state technique, it is necessary to sinter the samples above 1100°C in order to facilitate the dissolution of Ce^{4+} ions into the structure. However, we find that, when the samples are prepared by solution routes, single phase specimens could be prepared at temperatures $\sim 1000^\circ\text{C}$, as revealed from the diffraction studies. Further, we have compared the superconducting properties of the samples from solution and solid state methods, that were sintered at 1000°C . Superconductivity was observed only on the samples prepared via the solution routes, while the samples from solid state method remained paramagnetic down to 2 K. It is evident from these studies that solution methods have a definite advantage over the the conventional ceramic techniques, in that the processing temperatures could be lowered without losing the superconducting characteristics.

B. Transport Properties

Single phase $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4.8}$ could be prepared by solid state and solution techniques without any detectable impurities. There was no difference in the cell parameters of the samples prepared by these two synthetic procedures. Fig. 1 compares the temperature dependence of the electrical resistivity of the samples, prepared by both methods. It is evident that regardless of the method of preparation, the samples always displayed semiconducting behavior between T_c and room temperature. However, the sample prepared from the solution precursor technique has a higher normal state resistivity ($7 \times 10^{-2} \Omega \cdot \text{cm}$ at 300 K) than the value obtained for the solid state analogs ($1.5 \times 10^{-2} \Omega \cdot \text{cm}$ at 300 K). Nevertheless, both the samples showed sharp superconducting onsets ~ 25 K. In Fig. 2 we compare the magnetic susceptibilities of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4.8}$ prepared by solid-state and solution routes, measured at an applied magnetic field of 25 G. The transition temperatures inferred from the magnetization studies are in good

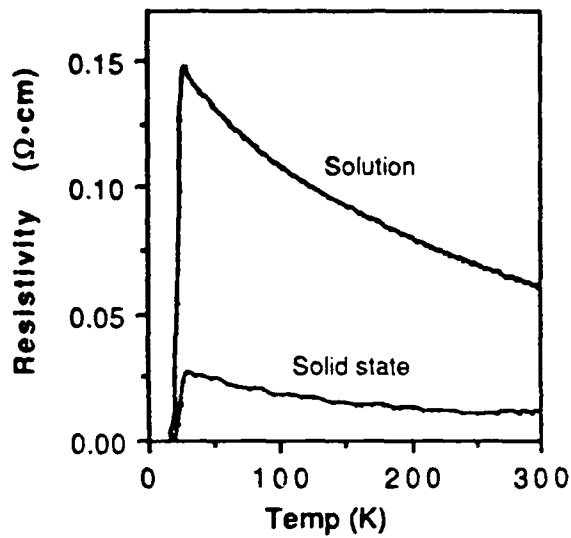


Fig.1 Electrical resistivity as a function of temperature for $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ prepared by two different methods.

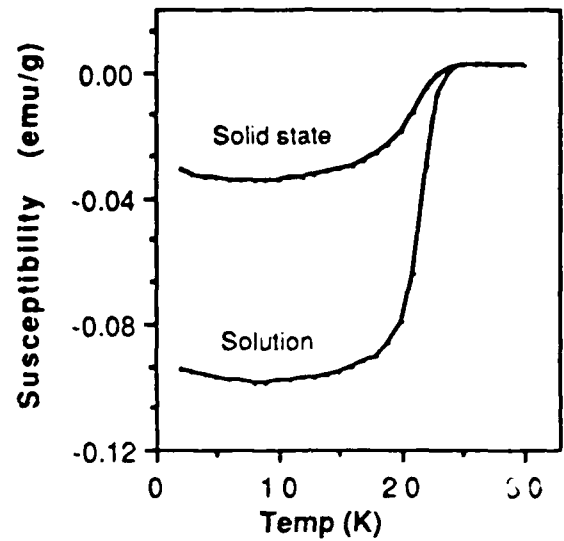


Fig.2 Comparison of magnetic susceptibility of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ prepared by solid state and solution methods.

agreement with the T_c from the electrical resistivity measurements. In addition, we find that the samples from the solution techniques exhibited larger Meissner fractions as compared to the solid-state samples.



Fig.3 SEM micrographs of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ prepared by a) solid state and b) solution precursor techniques

C. Microstructural Properties

In order to understand the differences in both the normal state and superconducting properties of samples prepared by different methods, we have investigated their microstructural properties by SEM. The scanning electron micrographs are presented in Fig. 3. The microstructure of samples prepared by solid-state method consists of plate-like grains of 2-20 μm with a broad distribution of grain size. In contrast, we find that the samples from the solution precursor methods display relatively uniform size of particles ($\sim 15 \mu\text{m}$) with narrow range of particle size distribution. Also, it is evident from these micrographs, that the solution based samples exhibit loose surface texture, with average pore diameter $\sim 5 \mu\text{m}$. In the solid state samples, despite irregular grain size distribution, it appears that the porosity is much smaller than in the solution samples. The relatively higher normal state conductivity of solid state samples compared to the solution based samples is consistent with the observed differences in their microstructures. We attribute the relatively larger Meissner fraction of the superconducting phase derived from the solution routes to: a) more uniform particle size distribution, b) higher interface area between the grains and c) possibly better compositional homogeneity within grains.

CONCLUSIONS

Samples of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ were prepared by solid state and solution precursor techniques and their superconducting properties were compared. Samples prepared by solution method displayed higher normal state resistance and superior Meissner fractions than the samples prepared by solid state method. The differences in the normal state and superconducting properties of the samples prepared by different methods have been correlated with their microstructures.

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