

Superconductivity and microstructure of ntype $\text{Ln}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ ($\text{Ln}=\text{Pr}, \text{Sm}, \text{Eu}$) produced under highpressure sintering

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Superconductivity and microstructure of n -type $\text{Ln}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ ($\text{Ln}=\text{Pr}, \text{Sm}, \text{Eu}$) produced under high-pressure sintering

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Using an unconventional reduction method, high-pressure sintering at 6.0 GPa and about 600 °C for 20 min, we have produced high-quality n -type $\text{Ln}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ ($\text{Ln}=\text{Pr}, \text{Sm}, \text{ and Eu}$) superconductors from the as-prepared materials. The samples show higher critical temperatures, higher superconducting phase fractions, and much lower resistances in the normal state than those synthesized by conventional methods. The increase of critical temperature in $\text{Eu}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ is most obvious with an onset temperature T_c^{on} and zero-resistance temperature T_c^0 of 28.4 and 23.3 K, respectively. High-pressure sintering seems to be effective on the modulation of the fine crystal and electronic structures of n -type systems. In particular, metallic resistance versus temperature behaviors in normal states similar to those found in single crystals and epitaxial films are observed in $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ and $\text{Eu}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$, in sharp contrast to the semiconductorlike behaviors in the conventionally prepared samples. From transmission electron microscopy studies, it is found that the compacting and regrowth of the polycrystal under high-pressure sintering greatly improves the weak links at grain boundaries.

The discovery of superconductivity (T_c about 20 K) in an n -type $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ system^{1,2} with a T' structure provides a new angle in the study of high-temperature superconductors (HTSC). Like the p -type counterpart of the LaSrCuO system,³ the highest T_c is realized at a doping level of $x=0.15$ in the n -type compound. By substituting the rare-earth elements, n -type $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ ($\text{Ln}=\text{Pr}, \text{Sm}, \text{ and Eu}$) superconductors were also synthesized.⁴⁻⁷ But their T_c 's are usually below 20 K. Unlike the p -type HTSC, for which annealing in an oxygen-rich atmosphere is necessary, the n -type $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ must be processed in a low PO_2 environment, such as in N_2 , Ar, He, or vacuum, in order to form a superconducting phase. The reduction procedures often leave the n -type polycrystals with a lower superconducting phase fraction and semiconductorlike resistance behavior in normal state. Since the early days of HTSC research, it has been believed that high-pressure sintering may improve the overall qualities of these highly porous ceramic materials. But many experiments have shown that direct (without special atmospheric conditions, such as oxygen pressure) heat treatment under high pressure leads to deterioration of the properties of p -type superconductors.^{8,9} In this letter, we report that from the as-prepared materials high-pressure sintering can produce $\text{Ln}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ ($\text{Ln}=\text{Pr}, \text{Sm}, \text{ and Eu}$) polycrystals with superior qualities which are superconducting and have electrical resistivity behaviors close to those of single crystals or thin films.

High-purity grade Pr_6O_{11} (Sm_2O_3 , or Eu_2O_3), CeO_2 , and CuO fine powders were thoroughly mixed according to the stoichiometric ratio $\text{Ln}:\text{Ce}:\text{Cu}=1.85:0.15:1$ ($\text{Ln}=\text{Pr}$,

$\text{Sm}, \text{ and Eu}$). The starting material was sintered using a conventional solid-state reaction method at the temperature ranging from 1000 to 1050 °C in a muffle furnace in air. The product was ground and pressed into 8-mm-diam and 2-mm-thick pellets. The pellets were calcined in a muffle furnace at 1050 °C for 20 h, then cooled to room temperature inside the furnace. Finally, these nonsuperconducting as-prepared pellets were directly sintered under 6.0 GPa and about 600 °C for 20 min. The pellets were wrapped in silver foil and placed at the center of a thin pyrophyllite tube. The tube was inserted into a graphite furnace which was mounted in a cubic pyrophyllite cell. High pressure was generated by a 3000-ton press equipped with six tungsten carbide anvils. Temperature was measured by a NiCr-NiAl thermocouple mounted near the samples. At the end of each run, the samples were quenched from high temperature by cutting off the furnace power before releasing the high pressure.

Resistivities were measured by the standard four-probe method with the temperature being monitored by a Rh-Fe thermocouple. dc susceptibilities were measured by a dc extracting sample magnetometer, while transmission electron microscopy (TEM) studies were carried out on a Philips EM420.

Figure 1 shows the electrical superconducting transitions of the three samples: $\text{Ln}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ ($\text{Ln}=\text{Pr}, \text{Sm}, \text{ and Eu}$). Their onset temperatures (T_c^{on}) and zero-resistance temperatures (T_c^0) are listed in Table I. Compared with the samples prepared by conventional methods,⁴⁻⁷ the corresponding T_c 's are increased. Using the conventional method in our experiment, it is very difficult

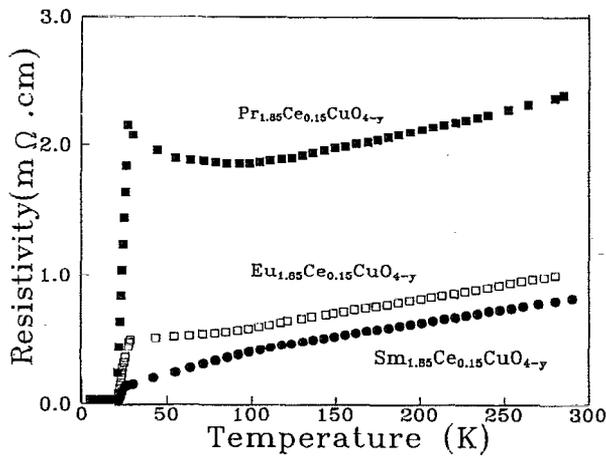


FIG. 1. The temperature dependence of resistivities for the three high-pressure sintered samples.

to reach zero resistance in all three $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ compounds. The increase of T_c for $\text{Eu}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ is most obvious. For the conventionally prepared $\text{Eu}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$, its T_c is only 17 K,⁷ the lowest among $\text{Ln}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ ($\text{Ln}=\text{Pr}, \text{Nd}, \text{Sm}, \text{and Eu}$). Markert *et al.*⁵ argued that if the magnetic factor were taken into account, $\text{Eu}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ should have a higher T_c among the $\text{Ln}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ ($\text{Ln}=\text{Pr}, \text{Nd}, \text{Sm}, \text{and Eu}$) due to the zero magnetic moment of Eu^{3+} . Since the high-pressure sintered $\text{Eu}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ actually shows a higher T_c , the highest T_c^0 in the three samples, the magnetic influence on the superconductivity should not be excluded. From the structure point of view, Eu^{3+} has the smallest ionic radius among Pr^{3+} , Nd^{3+} , Sm^{3+} , and Eu^{3+} ions which can form a stable superconducting T' phase at ambient. It is likely that high-pressure sintering favors an optimal T' structure through modulating the $\text{Ln}-\text{O}$ and $\text{Cu}-\text{O}$ bond length and therefore eliminates the mismatch between the Ln_2O_2 blocks and CuO_2 layers. X-ray diffraction measurements show that in high-pressure sintered samples of $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ ($\text{Ln}=\text{Pr}, \text{Nd}, \text{Sm}, \text{and Eu}$), impurity phases, usually the unreacted CuO and cubic Nd-Ce-O compounds,¹⁰ are considerably suppressed (with the content fraction below 2%), compared with the conventionally prepared samples whose impurity content is usually around 5%. (Details will be published elsewhere.) This effect should be appreciable for small rare-earth elements because high pressure is likely to increase the coordination number of small cations, facilitating the formation of a T' structure, which is in agreement with the report that Ln_2CuO_4 with a T' structure ($\text{Ln}=\text{heavy rare-earth elements such as Tb, Dy, Y, etc.}$) has only been synthesized under high pressure.¹¹⁻¹³ The normal-state resistivi-

TABLE I. Onset temperature T_c^{on} and zero-resistance temperature T_c^0 for the high-pressure sintered samples.

	$\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$	$\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$	$\text{Eu}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$
T_c^{on} (K)	27	26.7	28.4
T_c^0 (K)	17.5	21.8	23.3

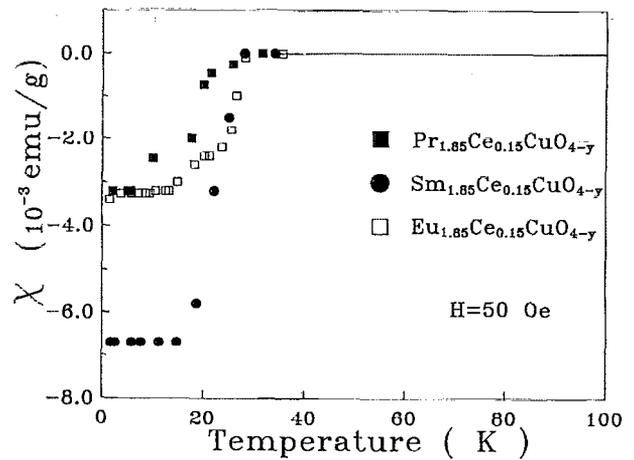


FIG. 2. The Meissner effects of the three high-pressure sintered samples (field cooled at $H=50$ Oe).

ties of the three samples decrease from the usual tens of $\text{m}\Omega\text{ cm}$ to a few $\text{m}\Omega\text{ cm}$. Resistance versus temperature behaviors for $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ and $\text{Eu}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ change from semiconductorlike in conventional samples to metallic in the high-pressure sintered samples. Such is the case for single crystals^{14,15} and epitaxial films.^{16,17}

Because of the highly anisotropic resistivity in n -type systems,¹⁸ the low resistivities in the high-pressure sintered samples indicate that the a - b plane contributions dominate the electrical transport in the three samples. Normal-state resistivity changes shown in Fig. 1 can be roughly divided into two parts: a linear part at high temperatures from 300 K to T_k , and a nonlinear part at low temperatures from T_k to T_c , where T_k is the crossover temperature from linear to nonlinear behaviors. T_k has different values for the three samples (ranging from 100 to 150 K). For example, $\text{Sm}(\text{Eu})_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ remain metallic in the whole temperature range measured, but their R - T curve deviates from linear below T_k . A shallow resistance minimum has been observed in $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$, which means a localized tendency of the charge carriers below T_k .¹⁹ Both the resistance minimum measured in the $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ and the deviation from linear in $\text{Sm}(\text{Eu})_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ have been observed in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ single crystals.²⁰ So it is believed that the behavior shown in Fig. 1 may be intrinsic to the materials, rather than the contribution from grain boundaries. Possible reasons for these electrical transport behaviors include the composition inhomogeneity¹⁹ (here, the cation-ion inhomogeneity, i.e., the sophisticated difference on the oxygen content and its distribution, may play an important role) and the processing-sensitive microstructure, on which high-pressure sintering is considered to be effective.²¹

Figure 2 shows the Meissner effect for the three samples. All the superconducting phase fractions are larger than 10%. The superconducting phase fraction in $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ is as high as 50%, which is much higher than those of samples prepared by conventional methods.⁴⁻⁷ Apparently, pressure strongly enhances the formation of an n -type superconducting phase.

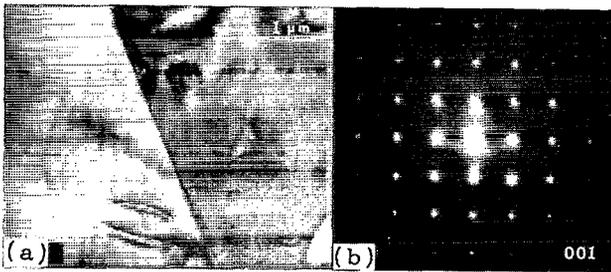


FIG. 3. The electron diffraction contrast image (a) and (b) selected-area diffraction pattern along [001] of high-pressure sintered $\text{Eu}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$.

Figure 3 is the electron diffraction contrast image (a) and selected-area diffraction (SAD) pattern (b) along the [001] direction of one of the high-pressure sintered samples, $\text{Eu}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$. It is indicated in Fig. 3(a) that the neighboring grains form a close contact. The SAD patterns show that there exist c -axis preferential orientations among the neighboring grains in the high-pressure sintered samples.²² High-pressure sintering produces well-matched polycrystals in which the intergranular contributions to the electrical transport are effectively weakened. This leads to the similar resistivity values and R - T curves in the normal state among the high-pressure sintered samples (Fig. 1) to those of single crystals.^{13,14} The SAD spots in Fig. 3(b) is diffusive, implying that there are some displacements in the intragranular caused by pressure. The improved weak links at the grain boundaries and the mechanical faults in the intragranular, which may act as pinning centers, are also beneficial to the improvement of critical current density (J_c) of polycrystals. Calculations from the M - H curves show that high-pressure sintered samples have higher J_c than those of conventional samples. (Details will be published elsewhere.) Because of the improved weak links, high-pressure sintered n -type polycrystalline superconductors may be used to investigate some intrinsic properties supplementing small-sized single-crystal samples which are difficult to grow because of the high melt temperature of the parent materials.

In summary, $\text{Ln}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ ($\text{Ln}=\text{Pr}$, Sm , and Eu) superconductors have been successfully processed by directly reducing the as-prepared pellets under 6.0 GPa and at about 600 °C for a short time. The samples show a higher critical temperature, higher superconducting phase fractions, lower resistivities in normal states, and improved

weak links compared with the conventionally prepared samples. The effect of high-pressure sintering on $\text{Eu}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ is most obvious. The high-pressure treated samples show metallic resistivities in normal states similar to those found for single crystals. In addition, high temperature and high-pressure treatment enhances the stability of the T' phase, which effectively accelerates the formation of the superconducting phase, and therefore greatly shortens the reduction time needed. The results demonstrate that high temperature and high-pressure processing is a good way to synthesize high-quality n -type superconductors.

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