

Influence of conditions of synthesis on superconductivity in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$

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Samples of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ were prepared using two different methods of synthesis (series A and B). The superconductivity was characterized by electrical resistivity and dc magnetic susceptibility measurements. X-ray diffraction (XRD) and energy dispersion X-ray analysis (EDAX) were used to characterize the structure composition and the sample quality. The resistivity measurements show a double transition to the superconducting state. It is proposed that the grains consist of a core with the optimum cerium content (~ 0.15) and a shell where the cerium content is different. The homogeneity of the samples was estimated through the determination of the slope of resistivity in the superconducting transition region ($d\rho/dT$). Ce content is higher and it is more homogeneously distributed in the samples treated at higher temperatures. EDAX analysis shows that the quantity of Cu on the surface of the samples increases with the temperature of the reduction process.

Key words: *superconductivity; doping; $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$*

1. Introduction

Superconducting materials with a general formula $\text{Ln}_{2-x}\text{Me}_x\text{CuO}_{4-y}$ ($\text{Ln} = \text{Nd}, \text{Pr}, \text{Sm}, \text{Eu}; \text{Me} = \text{Ce}, \text{Th}$) are an example of layered copper oxide high-temperature superconductors (HTSC) in which the charge carriers appear to be electrons rather than holes [1, 2]. For the $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ system, the crystal structure is tetragonal at all temperatures; it is the so-called T' phase with two-dimensional CuO_2 square planes. There is a nominal absence of apical oxygen atoms O(3). Doping with four-valence cerium ($0.13 < x < 0.18$) and additional heat treatment (reduction process) results in the appearance of superconductivity. It is accepted that a small number of oxygen atoms is removed from the T' structure ($y \approx 0.01-0.04$) to achieve superconductivity

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[3, 4]. However, the role of heat treatment and of accompanying effects on superconductivity are not fully understood.

The system is characterized by a relatively low critical temperature $T_c \approx 19\text{--}25$ K at the concentration of Ce around $x \approx 0.15$. Different methods and conditions of the synthesis as well as heat treatment could produce samples with different T_c . One of the methods to obtain $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ is preparing samples by solid state reactions using oxides as starting materials [1, 5–9]. It is difficult to prepare a homogeneous sample, mainly due to the highly refractory nature of Ce oxide. Some authors [10, 11] used $\text{NdCeO}_{3.5}$ as starting material or CeO_2 freshly made from $\text{Ce}(\text{CO}_3)_2$. They obtained samples with better Ce distribution. Chemical routes such as nitrate decomposition and liquid mix methods make it possible to get homogeneous samples of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ [9].

The aim of this work was to show how the conditions of the synthesis and reduction process influence the quality of samples, transport and superconductivity characteristics.

2. Experimental

Samples of $\text{Nd}_{(2-x)}\text{Ce}_x\text{CuO}_{4-y}$ were prepared by a solid state reaction from a stoichiometric mixture of respective oxides. The starting materials were Nd_2O_3 , CeO_2 (Fluka Chemie, 99.95%) and CuO (Fluka Chemie, >99%). The starting powder Nd_2O_3 was calcinated at 900°C for 2 hours in air before use in order to eliminate impurities.

After a thorough mixing, two samples with $x = 0.15$ (optimal doping) were pressed into pellets. The pellets were placed in a furnace chamber with an Al_2O_3 boat and treated as is shown in Table 1. Samples A and B were cut into plates ($1.2 \times 1.4 \times 8.6$ mm³) and finally heated in reducing atmosphere (Ar, 99.999%), in the temperature range from 800°C to 1100°C (with the step of 50°C) for 19 hours.

Table 1. The conditions of the synthesis of the samples A and B

Sample A		Sample B	
Temperature of reduction [$^\circ\text{C}$]	Time [h]	Temperature of reduction [$^\circ\text{C}$]	Time [hrs]
950	48	950	17
1000	48	1000	12
1050	24	1050	12
		1100	15
		1140	2

All samples were examined by the resistivity measurements in the temperature range $4.8\text{--}300$ K, using the standard four-point method [12]. Four Cu wires ($50\ \mu\text{m}$) were glued onto the surface with the silver paste. The contact resistance was smaller

than 0.3Ω at room temperature. Zero field cooling dc ($H_{dc} = 1$ and 10 Oe) magnetizations were measured in the range of 1.8 – 30 K (MPMS Quantum Design).

X-ray diffraction (XRD) and energy dispersion X-ray analysis (EDAX) of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ were used to characterize the structure composition and the quality of sample (porosity, surface density).

3. Results and discussion

3.1. X-ray diffraction analysis

X-ray diffraction analysis showed that the starting material synthesized at higher temperature (series B) is a pure $Nd_{1.85}Ce_{0.15}CuO_4$ phase, whereas samples of series A contained impurities, characterized by low-intensity reflection at $2\theta = 28.29^\circ$ corresponding to the (222) reflection of $NdCeO_{3.5}$, and a reflection at $2\theta = 35.59^\circ$ – (002) reflection of CuO (Fig. 1).

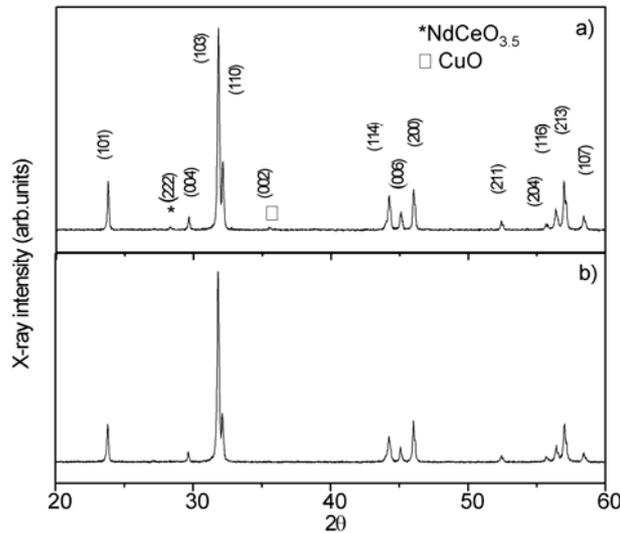


Fig. 1. X-ray diffraction patterns of $Nd_{(2-x)}Ce_xCuO_{4-y}$ after two different processes of synthesis

From the result of the Rietveld refinement, the lattice constants were found: $a = 3.9469(1) \text{ \AA}$, $c = 12.0782(6) \text{ \AA}$ for series A, and $a = 3.9473(1) \text{ \AA}$, $c = 12.0772(6) \text{ \AA}$ for series B. It is well known that increasing Ce content in $Nd_{2-x}Ce_xCuO_{4-y}$ unit cell results in a significant decrease of the c/a ratio of the lattice parameters. The displacement between the (110) and (103) reflections is directly proportional to this ratio with smaller displacement indicating a smaller c/a ratio

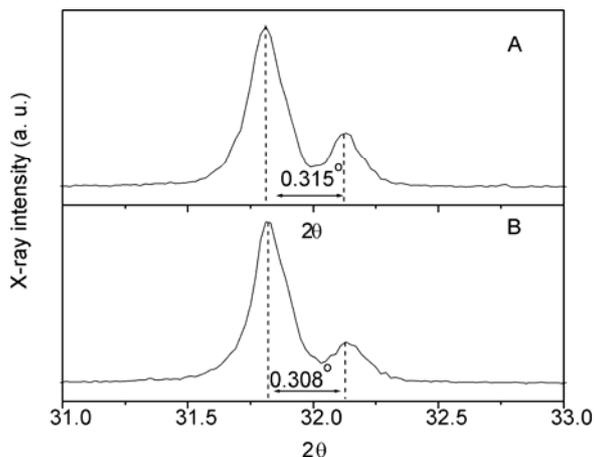


Fig. 2. Displacement between the (110) and (103) peak reflections of $\text{Nd}_{(2-y)}\text{Ce}_x\text{CuO}_{4-y}$ for samples A and B

[7, 10, 11]. The estimated $\Delta(2\theta)$ values are $0.315(1)^\circ$ and $0.308(4)^\circ$ for the sample from series A and B, respectively (Fig. 2). This suggests that the Ce content is higher and possibly more homogenous in the series B.

3.2. Resistivity measurements

Figure 3 shows the temperature dependence of the resistivity $\rho(T)$ for representative samples treated at various temperatures (T_{red}). Semiconducting behaviour ($d\rho/dT < 0$) is observed for samples treated at temperatures below $T_{\text{red}} = 900^\circ\text{C}$ for the series

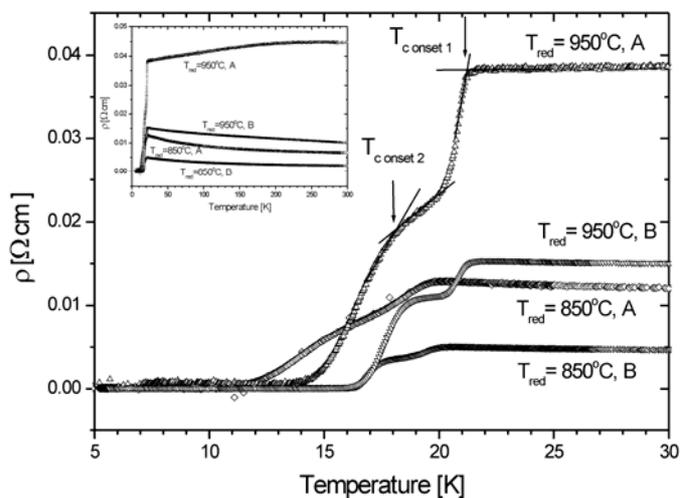


Fig. 3. Resistivity measurements. The curves $\rho(T_{\text{red}})$ for sample A and sample B reduced at 850 and 950°C. In the inset, the whole temperature range (4.2–300 K) is presented

A and below 950 °C for the series B. The resistivity increases with increasing T_{red} and the slope ($d\rho/dT$) becomes positive, which means that metallic behaviour prevails.

The resistivity measurements show a double transition to the superconducting state, as was previously observed by Klamut and Gerber [13, 14]. Mang et al. examined reduced $Nd_{2-x}Ce_xCuO_{4-y}$ crystals and showed that the interior of the sample was less damaged than its exterior [3]. The core piece protected by the shell is less exposed to the reducing atmosphere. Similar topics were also discussed in [15].

It is proposed that grains contain a core with cerium content close to the optimal value (~ 0.15) and the shell, where the quantity of cerium is different. Consequently $T_{c\text{onset}1}$ corresponds to the temperature at which the grain core becomes a superconductor, and $T_{c\text{onset}2}$ is the critical temperature of the grain shell. Below $T_{c\text{onset}2}$, percolating chains of the Josephson intergrain couplings are created, and zero resistance is achieved.

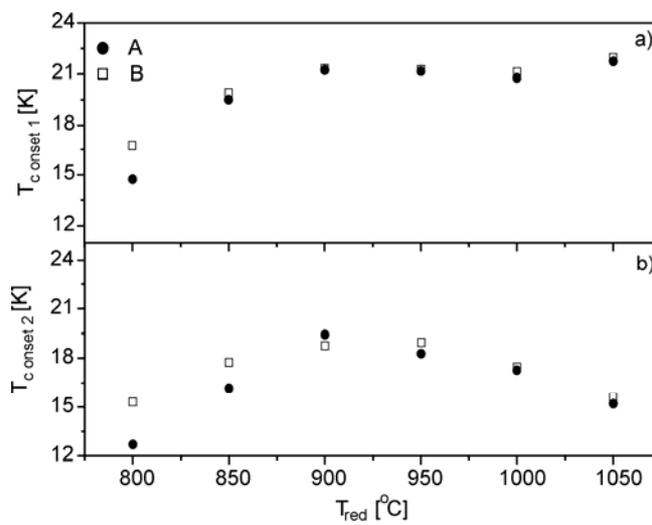


Fig. 4. Dependence of $T_{c\text{onset}1}$ and $T_{c\text{onset}2}$ versus temp. of reduction

Increase of the reduction temperature (T_{red}) causes the increase of $T_{c\text{onset}1}$ (Fig. 4a). Similarly, $T_{c\text{onset}2}$ increases but only for samples treated below 900 °C (series A) and 950 °C (series B). This feature confirms that $T_{c\text{onset}2}$ corresponds to the grain shell because every change in the material, namely decomposition process, starts from the shell.

Both critical temperatures for the series A and B (Fig. 4a and 4b) show the same behaviour, T_c 's being slightly higher for the series B. It is caused by higher purity of the samples synthesized at higher temperature. The homogeneity of samples was estimated through calculation of $d\rho/dT|_1$ and $d\rho/dT|_2$ (Fig. 5). The best superconducting properties (the highest T_c and homogeneity) is exhibited by the samples reduced at 950 °C (series A) and at 1000 °C (series B).

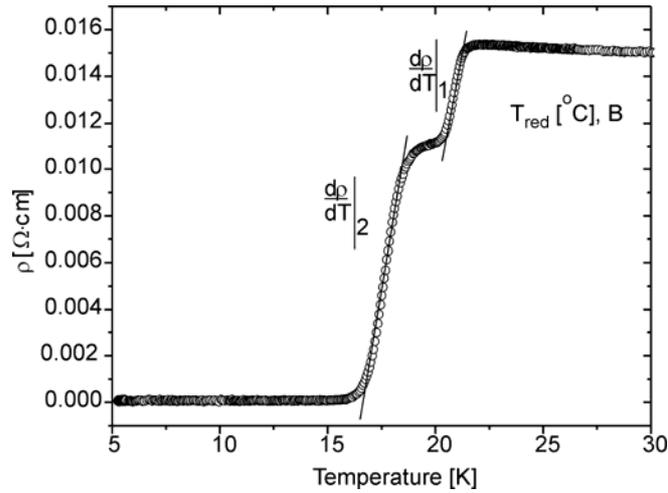


Fig. 5. Example of the determination of homogeneity of a sample

3.3. Magnetic measurements

Figure 6 shows zero-field cooling dc ($H_{dc} = 10$ Oe) susceptibility $\chi_{dc}(T)$ data for $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}_{4-y}$ samples: series A (upper figure) and series B (lower figure). It can

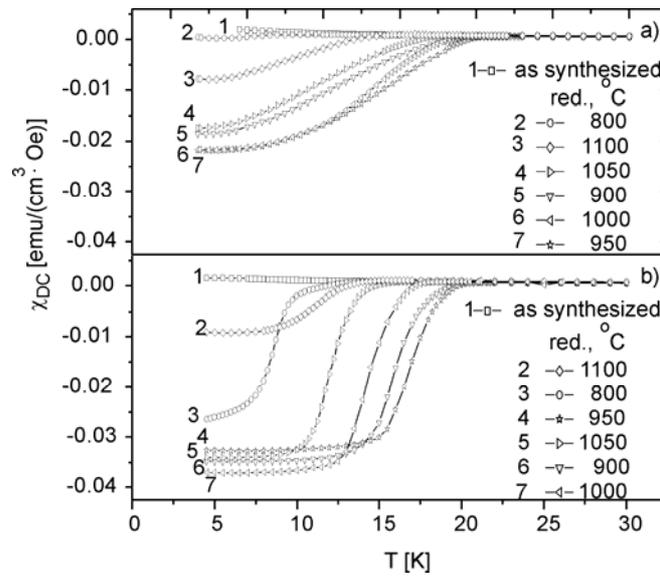


Fig. 6. The dc magnetic measurements, ZFC. The magnetic susceptibility χ_{dc} vs. temperature in the samples: a) A, b) B for various temperatures of annealing in the magnetic field of 10 Oe

be observed that only as-synthesized samples are bulk superconductors. The additional reducing process is necessary to obtain superconductivity. Contrary to the resistivity measurement, the transition is one step-like in character and the highest critical temperature (about 20 K) for both series is observed for samples treated at $T_{\text{red}} = 950^\circ\text{C}$.

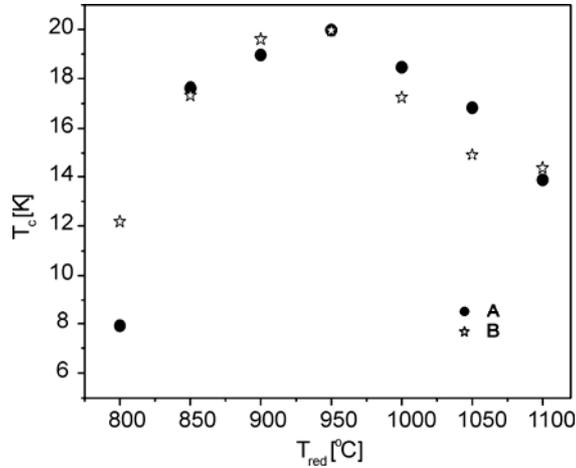


Fig. 7. $T_{c\text{onset}}$ versus temperature of reduction in the field of 10 Oe

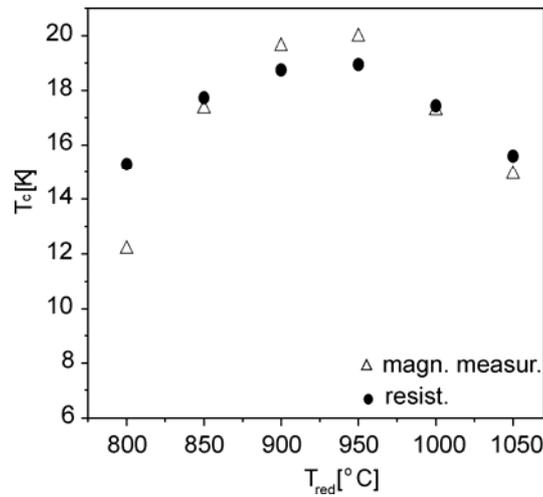


Fig. 8. $T_{c\text{onset}}$ from magnetic measurement and $T_{c\text{onset}2}$ from resistivity measurement for samples B

Figure 7 presents the dependence of T_c (determined from magnetic measurements) as a function of T_{red} . The dependence is very similar to that observed for $T_{c\text{onset}2}$ taken from resistivity measurements (compare with Fig. 4b). Figure 8 proves that the magnetic T_c corresponds to $T_{c\text{onset}2}$ which confirms our proposed model with an optimal doped core and a shell.

Figure 9 presents field dependence of the magnetization at 5 K for six representative samples.

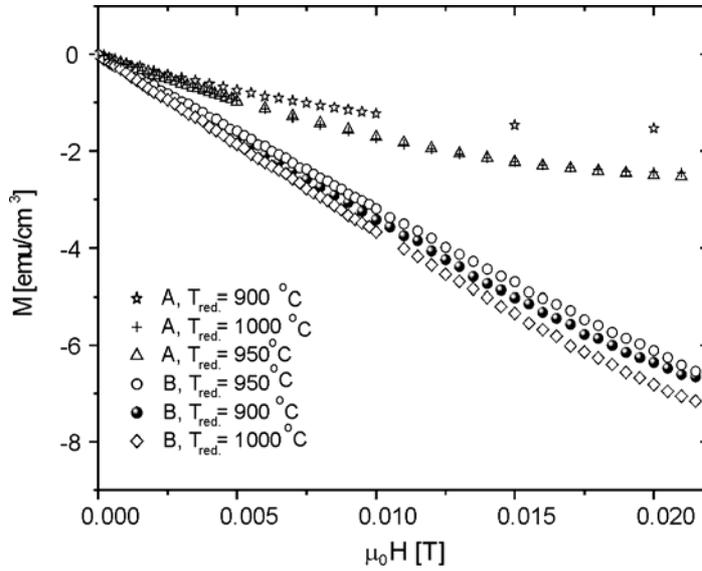


Fig. 9. Magnetic field dependences of the magnetization of the samples A and B treated at various temperatures. The measurements were taken at 5 K

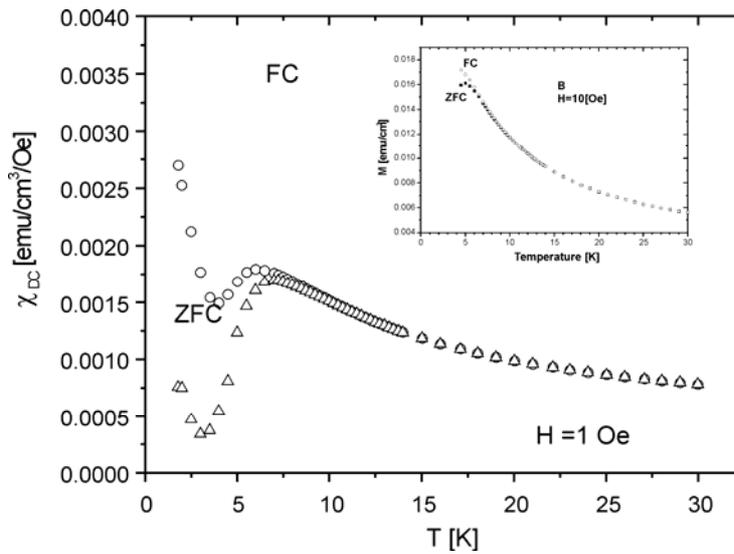


Fig. 10. The magnetic susceptibility χ_M versus temperature T for the sample B in the magnetic fields of 1 Oe and 10 Oe (in the inset). The samples were measured immediately after the synthesis

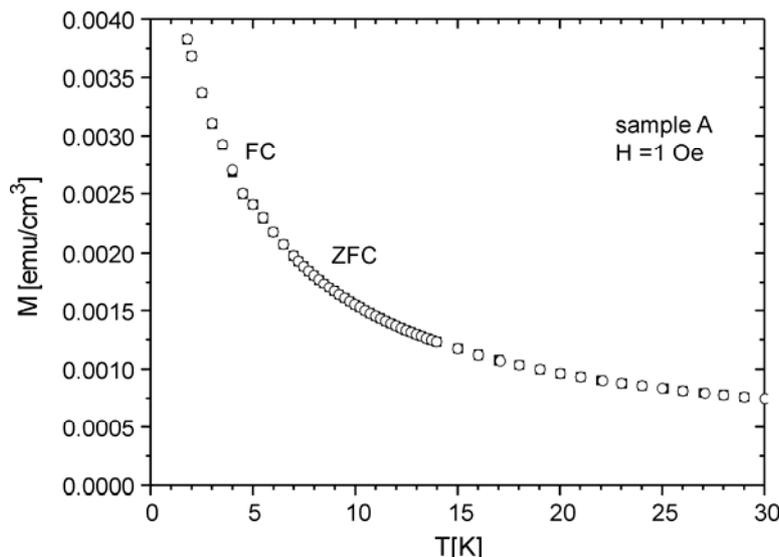


Fig. 11. The magnetization M versus temperature T for the as-synthesized sample A in the magnetic field of 1 Oe

Both $M(\mu_0H)$ and $\chi_{dc}(T)$ measurements indicate that samples from the series B contain more superconducting fraction and an optimal sample was obtained after the treatment at $T_{red} = 1000$ °C.

It is interesting to note that as synthesized samples from the series B show a slight sign of superconductivity (Fig. 10), in contrast to samples from series A (Fig. 11). This suggests that the synthesis conducted in air at a suitably high temperature may yield superconducting samples. However, the observed superconductivity is not bulk in its character and T_c is very low (7 K).

3.4. EDAX and SEM analyses

For each sample ten EDAX measurements were taken in different places and the mean value was calculated. Before measurements, the samples were mechanically polished. The percentage contribution of holes to the total area (Fig. 12) was estimated, which indicates the influence of the synthesis and the reduction conditions on the porosity. Lower number of holes means lower porosity and higher density of samples. Therefore, we can conclude that samples from the series B are of better quality.

Figure 13 presents the SEM image of the surface after treatment at $T_{red} = 950$ °C. White spots visible in the figure are sites where CuO (the product of decomposition reaction) appears.

Figure 14 presents the ratio of Cu/(Nd + Ce) for samples from series B as a function of T_{red} . With increasing T_{red} , the ratio Cu/(Nd + Ce) increases. Assuming that Nd and Ce content does not change on the surface (Nd + Ce = const.), this means that Cu

diffuses from the bulk to the surface. A rapid drop observed for the sample treated at $T_{\text{red}} = 1100\text{ }^{\circ}\text{C}$, which is higher than Cu melting point ($1083\text{ }^{\circ}\text{C}$), might be explained by the Cu evaporation process.

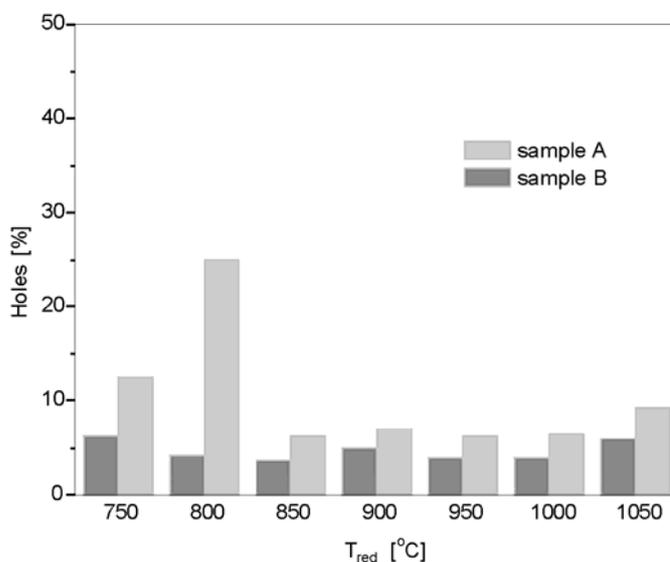


Fig. 12. EDAX analysis of holes on the surface of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ samples in function of temperature of reduction

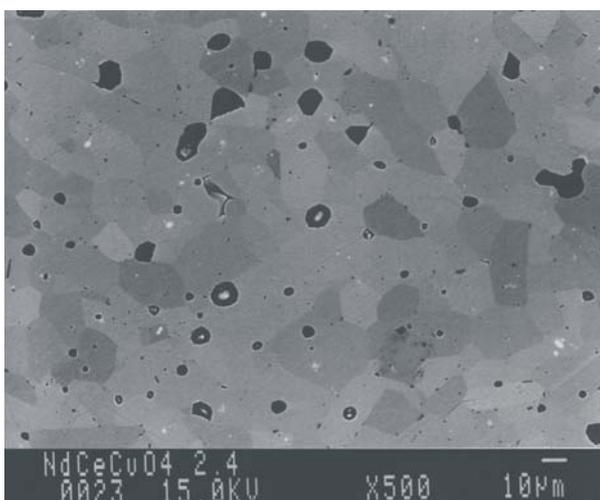


Fig. 13. SEM picture of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ annealed at $950\text{ }^{\circ}\text{C}$

Mang et al. [3] showed that one of the decomposition products, $(\text{Nd,Ce})_2\text{O}_3$, causes the secondary phase to form an oriented quasi-two-dimensional epitaxial structure on $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ crystals.

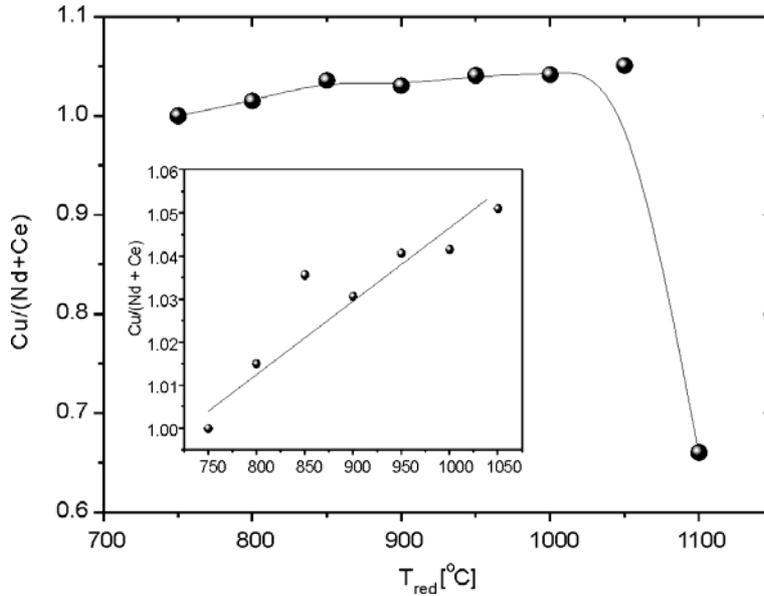


Fig. 14. Analysis of the amount of copper on the surface of sample B versus temperature of reduction. Inset: The temperature range 750–1050 K. Note the expanded vertical scale

For typical reduction conditions the volume fraction of $(\text{Nd,Ce})_2\text{O}_3$ is about 1%. The presence of the secondary phase can be the reason of the difference between the interior and exterior of grains.

4. Conclusions

An appropriate choice of conditions of the synthesis allows us to obtain single -phased $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$. We have shown that the conditions of the process (temperature, number of steps) have a considerable influence on the quality of samples and their superconducting characteristics. Optimal temperatures of reduction of our samples are between 950 °C and 1000 °C.

Increasing temperature of reduction causes the increase in the amount of copper on the surface of the samples but at about 1100 °C we have noticed a rapid drop caused by the evaporation of copper from the surface of the sample.

It is proposed that grains contain the core characterized by the optimum content of cerium (~ 0.15) and the shell where its content is different than that in the core. Consequently, two superconducting transition temperatures are observed in resistivity measurements, where $T_{c\text{onset}1}$ is the temperature in which the core of grain becomes a superconductor. Decreasing of temperature causes that the shell of grain starts to be superconducting ($T_{c\text{onset}2}$), the percolating chains of Josephson intergrain couplings are created, and zero resistance is achieved.

Diffusion of copper and degradation of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ result in a deterioration of superconducting properties. This explains a decrease of $T_{\text{c onset2}}$ above a certain temperature, because every change in the materials, including the decomposition process, is initiated on the surface.

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