Research Article

Chemical Reduction of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ Powders in Supercritical Sodium Ammonia Solutions

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$\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ powders are chemically reduced in supercritical sodium ammonia solutions from room temperature to 350°C. The crystallographic structure of the reduced powders is investigated from Rietveld refinement of X-ray powder diffraction. The atomic positions are maintained constant within experimental errors while temperature factors of all atoms increase significantly after the chemical treatments, especially of Nd/Ce atoms. The ammonothermally reduced $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ powders show diamagnetic below 24 K which is contributed to the lower oxygen content and higher temperature factors of atoms in the treated compound. The ammonothermal method paves a new way to reduce oxides in supercritical solutions near room temperature.

1. Introduction

The electron-doped $(\text{Nd,Ce})_2\text{CuO}_{4-\delta}$ T' -phase is the best candidate to investigate superconductivity mechanisms [1–4] because of its simple crystallographic structure as well as the hole-doped $\text{La}_2\text{CuO}_{4+y}$ T-phase. The T' -phase superconductor has been synthesized through rare-earth substitution on the Nd site by Ce [5, 6], through fluorine substitution for oxygen [6, 7], or through reduction process [1, 8–10] at high temperatures of 800–1100°C. These traditional high temperature procedures have successfully reduced copper on CuO_2 sheets, inducing superconductivity of the T' -phase with transition temperature $T_c = 22$ –27 K [1, 5–10]. However it is still challenging to adjust the chemical state of the CuO_2 sheets through low temperature treatments. Up to date there is no report on chemical reductions of the T' -phase at low temperatures to induce superconductivity.

On the contrary, the hole-doped $\text{La}_2\text{CuO}_{4+y}$ T-phase, the counterpart of the electron-doped T' -phase, can be chemically oxidized by both traditional high temperature treatments [11, 12] and low temperature treatments [13–15] to achieve superconductivity. It is well known that

the superconducting T-phase can be prepared through alkaline earth substitution [11] and high-oxygen pressure treatment [12] at high temperature over 800°C. La_2CuO_4 has also been oxidized in aqueous solutions below 150°C to achieve superconductivity when strong oxidizing agents (such as potassium permanganate [13, 14] and sodium hypochlorite [15]) are dissolved in water as solvents. Superconductivity transition temperatures T_c of the low-temperature oxidized T-phase are ~40 K [13–15], higher than that of the T-phase ($T_c \sim 30$ K [11, 12]) prepared by high temperature treatments, indicating the effectiveness of low-temperature aqueous chemical treatments.

The reduction of the electron-doped $(\text{Nd,Ce})_2\text{CuO}_{4-\delta}$ T' -phase is the counterpart of the oxidization of the hole-doped $\text{La}_2\text{CuO}_{4+y}$ T-phase. It has been reported that supercritical hydrothermal technique is a unique method to successfully dope oxygen into the hole-doped $\text{La}_2\text{CuO}_{4+y}$ T-phase in aqueous solutions at 100–180°C. The achieved transition temperature T_c (42 K [14, 16]) of the T-phase superconductors is slightly higher than that achieved by traditional low-temperature chemical treatments ($T_c \sim 40$ K [13]), showing the best capability to oxidize superconductors among various

low-temperature aqueous oxidization treatments. Then two questions raise: (1) is there a supercritical reduction method (counterpart of supercritical hydrothermal technique) to reduce oxides? (2) Is it possible to reduce the electron-doped T' -phase (counterpart of the T -phase) at low temperatures?

In this research, $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ T' -phase powders are chemically reduced in a supercritical sodium metal ammonia solution, counterpart of the oxidation hydrothermal solutions, below 350°C . The low-temperature reduction treatments greatly affect crystallographic structures and magnetic properties of the powders.

2. Materials and Methods

The polycrystalline $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ samples used for the experiments are prepared from oxides by a solid state reaction. Appropriate quantities of Nd_2O_3 , CeO_2 , and CuO powders are mechanically mixed, ground in an agate mortar, sintered in air at $950\text{--}1100 \pm 5^\circ\text{C}$ for four days, with intermittent regrindings, removed from furnaces, and quenched in air to room temperature. X-ray powder diffraction patterns indicate that the samples are single phase. The single phase samples are then ground into powders and further annealed in a floating Ar atmosphere at $930 \pm 5^\circ\text{C}$ for 24 h as starting samples.

An autoclave is pre-cooled by liquid nitrogen. Then liquid ammonia is poured from a high pressure (130 PSI) tank into the autoclave. An alkali metal bar is cut to a desired weight under a protected atmosphere and dropped into the liquid ammonia contained in a clean quartz cuvette to form an alkali metal ammonia solution. $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ starting powders are then dropped into the ammonia solution once the alkali solution turns blue completely. The autoclave is cooled down to -33°C , the boiling point of ammonia at one atmosphere. The autoclave is then sealed quickly at one atmosphere before the autoclave is warmed up. The sealed autoclave is heated up to $10\text{--}350^\circ\text{C}$ for 72 h in a furnace. According to ammonia phase diagram, the ammonia pressure in the autoclave is $20\text{--}1000\text{ kPa}$ depending on the treatment temperature and the liquid ammonia filling rate. Then the ammonothermally treated powders are collected, filtered, thoroughly washed with distilled water and ethanol in sequence, and dried at room temperature in vacuum. The details of the ammonothermal procedure have been described in other literatures [17–19].

The X-ray powder diffraction (XRD) patterns are measured on a Rigaku D/max-2400 diffractometer with $\text{Cu-K}\alpha$ radiation at room temperature. All data are collected in a step scanning mode with a step of 0.02° (2θ) and a measuring time of 0.5 s per step. An angular range from 10° to 80° is applied and NBS SRM 640 Si is added as an internal standard for lattice parameter determinations. The lattice parameters are calculated using the DICVOL91 program [20] after the experimental peak positions are calibrated. The X-ray diffraction data are also collected over an angular range of $10\text{--}130^\circ$ for Rietveld refinements. The divergence, scattering, and receiving slits are set at 1° , 1° , and 0.10 mm , respectively. A total of 6001 points with a maximum count of about 15,000

and 123 independent reflections are measured for Rietveld refinements. The Rietveld refinement is then carried out using the computer program DBWS-9411 [21].

Magnetic susceptibility of the powders is measured with a SQUID magnetometer under a DC magnetic field down to 4.2 K.

The oxygen content of the samples is chemically determined by an iodometric titration [22]. Sodium thiosulfate titrant is standardized against 99.999%-pure CuO powders. The $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ powders are put into 50% potassium iodide solutions at room temperature and dissolved with 10% hydrochloric acid. Starch with a concentration of 2% is used as an endpoint indicator.

3. Results and Discussion

The powders are black before and after the ammonothermal treatments when the treatment temperature is lower than 150°C . Scanning electron microscopic observation shows that the grain size of the powders is slightly decreased by 5% to 10% after the treatments. XRD studies indicate that the T' -phase is thermally stable up to 150°C in the sodium ammonia solution. All the powders are single phase with a space group of $I4/mmm$ (T' -phase) before and after the reduction treatments. Figure 1 shows XRD patterns of the T' -phase powders before and after the ammonothermal treatments at 54°C . Lattice parameters are nearly identical within experimental errors. $a = b = 3.9430(4)\text{ \AA}$ and $c = 12.070(2)\text{ \AA}$ before the powders are ammonothermally treated while $a = b = 3.9433(3)\text{ \AA}$ and $c = 12.072(1)\text{ \AA}$ after the powders are ammonothermally treated at 54°C .

The ammonothermal reduction treatments affect magnetization properties of the T' -phase. SQUID magnetic measurements indicate that the untreated T' -phase $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ powders did not show any magnetization transition above 4.2 K to 50 K, similar to the reported earlier [23]. After the powder is ammonothermally treated at 54°C , a magnetic transition is observed near 24 K. Figure 2 is the susceptibility χ versus temperature T in a temperature range of $4.2\text{--}50\text{ K}$ for the $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ powders that are ammonothermally treated at 54°C . The powders are paramagnetic above 24 K while they are diamagnetic below 22 K. The transition temperature of 24 K is comparable to that ($T_c = 22\text{--}24\text{ K}$) achieved by the traditional high temperature reduction treatments at $850\text{--}1050^\circ\text{C}$ [1, 3, 8–10], slightly lower than that ($T_c = 27\text{ K}$) achieved by the fluorine substitution for oxygen [7]. Therefore the supercritical ammonothermal reduction treatments are a simple but effective method to achieve superconductivity in the T' -phase.

The oxygen content ($4-\delta$) of the T' -phase powders is determined by the iodometric titration. The oxygen content of the as-prepared powders is $3.975(5)$ while it is $3.961(5)$ of the chemically treated powders at 54°C . Therefore the supercritical ammonothermal treatments lower the oxygen content of the T' -phase and reduce the chemical state of the CuO_2 sheets, resulting in the diamagnetic properties of the T' -phase powders.

FIGURE 1: X-ray diffraction patterns of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ powders (a) before and (b) after ammonothermal treatments at 54°C in sodium ammonia solutions.

FIGURE 2: Magnetic susceptibility χ of treated $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{3.961}$ as a function of temperature T . The zero-field-cooled measurement is carried out under 10 Oe. The insert shows enlarged susceptibility as a function of temperature near the transition. The powders are ammonothermally reduced at 54°C in sodium ammonia solutions.

It is well known that alkali metal, such as sodium, is very soluble in liquid ammonia [24]. Sodium produces solvated cations and solvated electrons in liquid ammonia:

where e^- is the solvated electron in the ammonia solution. The $[e^-(\text{NH}_3)_x]$ ions can reduce oxides effectively. Thus the alkali ammonia solution is one of the strongest reductive solutions [24], providing a homogeneous environment to reduce $(\text{Nd,Ce})_2\text{CuO}_{4-\delta}$ T' -phase compounds here under supercritical conditions. The abundant solvated electrons in the ammonia solution can directly dope into the CuO_2 sheets of the T' -phase, changing the carrier concentration of CuO_2 sheets to induce diamagnetic properties of the T' -phase below 24 K.

However, the sodium ammonia solution is not thermally stable at high temperatures, $2\text{Na} + 2\text{NH}_3 \rightarrow 2\text{NaNH}_2 + \text{H}_2 \uparrow$, and loses reduction activity over 100°C . In order to examine

temperature effects, the $(\text{Nd,Ce})_2\text{CuO}_{4-\delta}$ T' -phase powders are also chemically treated in the sodium ammonia solution over 100°C . No diamagnetic behavior of the treated powders is detected. The reduction activity of the sodium solution is also lower at lower temperatures (room temperature to 30°C), resulting in no significant magnetic change of the T' -phase powders. The optimum treatment temperature is 54°C .

Besides sodium ammonia solution, other alkali metal (such as potassium and lithium) ammonia solutions have similar chemical activities and should also work as reduction solutions to induce diamagnetic characterization of T' -phase powders. We test potassium ammonia solutions and $(\text{Nd,Ce})_2\text{CuO}_{4-\delta}$ T' -phase powders can be reduced in potassium ammonia solutions at 50°C .

In order to explore how the ammonothermal treatments affect the crystallographic structures of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ powders besides the lattice parameters and oxygen content, X-ray Rietveld structural refinements of the powders are carried out to determine more detailed crystallographic structures of the powders.

The Rietveld refinements are performed with initial positional parameters according to those of Nd_2CuO_4 [25]. Nd and Ce atoms are located statistically on the site $4e(0, 0, z)$ with the initial atomic ratio Nd:Ce = 1.85:0.15. The oxygen atoms are set on the sites $4c(0, 0.5, 0)$ and $4d(0, 0.5, 0.25)$. The total oxygen content $4-\delta$ is 3.961 for the reduced samples (Figure 3(b)) and 3.975 for the untreated samples (Figure 3(a)), according to the iodometric titration. The Cu atoms are put on the site $2a(0, 0, 0)$. The space group of the powders is $I4/mmm$. X-ray diffraction peaks are fitted as a pseudo-Voigt function in shape. Background values are obtained by linear interpolation between average values in regions between diffraction peaks. The Debye-Waller factor for the compounds is corrected for absorption.

Figure 3 shows the final Rietveld refinement patterns of the untreated and treated powders. Table 1 lists the final Rietveld refined positional and thermal parameters of atoms in the samples.

TABLE 1: Final Rietveld refined parameters of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ powders from X-ray powder diffraction data.

Atom	Site	x/a	y/b	z/c	B ($\text{\AA}^2$)
Cu	2a	0	0	$0^\dagger, 0^\S$	$0.44(7)^\dagger, 0.19(6)^\S$
Nd	4e	0	0	$0.3523(5)^\dagger, 0.3524(5)^\S$	$0.44(6)^\dagger, 0.04(2)^\S$
Ce	4e	0	0	$0.3523(5)^\dagger, 0.3524(5)^\S$	$0.44(6)^\dagger, 0.04(2)^\S$
O(1)	4c	0	1/2	$0^\dagger/0^\S$	$0.90(1)^\dagger, 0.20(1)^\S$
O(2)	4d	0	1/2	$1/4^\dagger, 1/4^\S$	$0.80(1)^\dagger, 0.70(1)^\S$

† Treated $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{3.961}$. § Untreated $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{3.975}$.

FIGURE 3: Final Rietveld refinement patterns of (a) $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{3.975}$ powders without treatments and (b) $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{3.961}$ powders ammonothermally treated at 54°C in sodium ammonia solutions. Black crosses represent the experimental values and the red solid line the calculated pattern. The green solid line at the bottom is the difference between the experimental and calculated data. The blue bars represent the position of Bragg reflections.

The ammonothermal treatments do not affect the atomic positions within experimental errors. The fact is in good agreement with previous neutron Rietveld refinements [26] of superconducting and nonsuperconducting $(\text{Nd,Ce})\text{CuO}_{4-y}\text{T}'$ -phases.

The thermal parameters of the T' -phase compounds are increased significantly by the ammonothermal treatments. The B in Table 1 is the isotropic temperature factor, $B = 8\pi^2\overline{u^2}$, where u is the vibrational amplitude of atoms. The ammonothermal treatments have enhanced the isotropic temperature factor B of O(1) atoms 4.5 times while they have not affected that of O(2) atoms within experimental errors. The result is in agreement with the Raman and infrared transmission studies [2] and the microscopic oxygen-reduction mechanism of T' -phase [4, 5]. It is suggested that the reduction processes only remove oxygen in the CuO_2 sheets to destroy the long-range antiferromagnetism and increase the mobility of charge carriers for superconductivity, while they do not affect apical oxygen, resulting in the great change of thermal vibration of O(1) atoms but not O(2) atoms.

Simultaneously, the thermal parameter B of Nd atoms and Ce atoms is increased 11 times after the ammonothermal treatments while that of Cu is increased 2.3 times. The significant changes of the thermal parameters should also be

important factors to cause the diamagnetic behavior shown in Figure 2.

4. Conclusions

The T' -phase $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ compounds were chemically reduced at 54°C in supercritical sodium ammonia solutions, resulting in a diamagnetic transition near 24 K. X-ray Rietveld refinements indicated that the ammonothermal treatments enhanced the isotropic temperature factors of atoms, especially Nd/Ce atoms and O(1) atoms, of the oxide powders while their lattice parameters were unchanged. The strong reduction environment of sodium ammonia solutions induced the diamagnetic properties of the T' -phase.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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