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Important Factors for Electron-Doping in T′-Type 214 Compounds

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Various factors were investigated in order to improve superconductivity of T′-type 214 compounds with Ln = Pr, Nd, Sm, or Eu. Lattice constants shrank with the substitution in a series from Pr through Eu. The compounds showed superconductivity after their reduction. Their lattice constants and oxygen content did not change so much with the reduction. The reduced Nd compound had a maximum oxygen content of $y = 3.93$ in spite of its highest $T_c = 24$ K among the T′ compounds. The T_c value was directly related to neither the lattice constants nor the oxygen content. Both Cu $2p_{1/2}$ and $2p_{3/2}$ peaks in XPS were most effectively shifted to lower binding energy in the Nd compound by the reduction process. Their satellite peak intensities were also most typically reduced in the compound. The Cu K-edge XANES spectrum showed a $1s$–$4p^*(\pi)$ transition for the $3d^{10}$ final state most clearly in the reduced Nd compound. These electronic phenomena were most prominently observed in the Nd compound among the T′-type compounds. These results suggest that electrons are effectively doped from the fluorite layer to the conduction plane without oxygen vacancy in order to obtain a good superconductor in the Nd compound. The Ce^{4+} doping may be necessary to introduce enough oxygen vacancy in the fluorite layer. Size matching between the CuO_2 conduction plane and the fluorite layer is important to determine which layer has a tendency to induce oxygen vacancies. © 1994 Academic Press, Inc.

1. INTRODUCTION

Among the oxide high temperature superconductors, $Nd_{1.85}Ce_{0.15}CuO_y$ is characteristic because of its electron-doped nature. Both Ce-doping and reduction processes are required to obtain the superconductivity (1). Their roles for the occurrence of superconductivity have not yet been clearly understood. The presence of extra oxygen was reported in Ce- and Th-doped $Nd_2CuO_{4+\delta}$ and $Gd_2CuO_{4+\delta}$ (2). The reduction step was assumed to remove the extra oxygen. However, their oxygen contents of more than 4 conflict with most of the previous data similarly determined using iodometric titration (1).

Variation in T_c with Ln was discussed for $Ln_{1.85}Ce_{0.15}CuO_y$, relating to the pressure dependence of T_c (3). The highest T_c value was reported in the case of Ln = Nd (1). Both oxygen content and Cu–O distance have been assumed to be important for the superconductivity. The electronic state of copper may be critical to explaining the reason for the maximum T_c at Ln = Nd as well as the oxygen content. Distribution of oxygen vacancy may also be very important for the superconductivity.

In the present investigation, lattice parameters, T_c value, and oxygen content were measured in $Ln_{1.85}Ce_{0.15}CuO_y$, where Ln = Pr, Nd, Sm, Eu. Change in the electronic state of copper was studied by XPS and XANES, comparing before and after the reduction process. Effects of annealing were also investigated to change the oxygen vacancy distribution.

2. EXPERIMENTAL

The starting materials, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Eu_2O_3, CuO, and CeO_2, were dried at 800°C. The desired mixtures of these starting materials were reacted at 950°C for 16 hr and then sintered at 1100°C for 16 hr. The products were reduced in Ar flow for 16 hr at 900, 1000, and 1100°C, respectively, and quenched. These procedures are almost similar to those described in the previous paper (1). X-ray powder diffractions were taken by using RAD-RB with Cu$K\alpha$ radiation. Lattice parameters were refined by a least-squares method. Oxygen content was determined by an oxygen analyzer (Horiba EMGA-650/550). The analyses were performed more than three times for each sample using Y_2O_3 as a standard. Electrical conductivity was measured by the four-point method using indium as electrodes. Ulvac-Phai ESCA MT-5500 was used for the XPS measurements. Cu K-edge XANES spectra were measured at beam line 10B of the Photon Factory at the National Laboratory of High Energy Physics. Powdered samples were pressed into 5-mm-thick pellets with dry BN. The reduced products at 1000°C were sealed in evacuated quartz tubes to keep the oxygen contents almost constant, annealed at 1000°C for 16 hr, and then gradually cooled to change the oxygen vacancy distribution.

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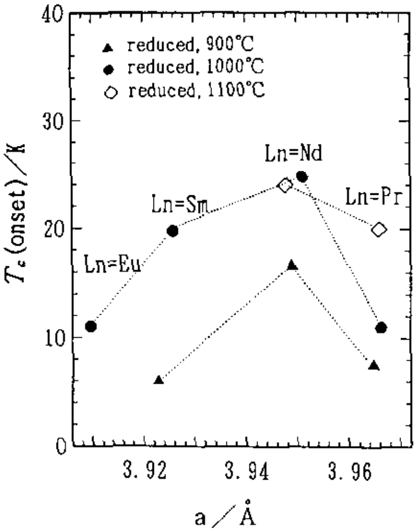

FIG. 1. T_c against lattice constant a of the T'-type $Ln_{1.85}Ce_{0.15}CuO_y$ reduced at various temperatures.

3. RESULTS AND DISCUSSION

Lattice Parameters

T'-type $Ln_{1.85}Ce_{0.15}CuO_y$ compounds were obtained where Ln = Pr, Nd, Sm, Eu and their reduced products showed superconductivity having maximum T_c (onset) value at Ln = Nd as represented in Fig. 1 (3). Lattice parameters a and c shrank with the Ln substitution in a series from Pr to Eu, as shown in Fig. 2. The variation in T_c with Ln cannot be directly related to the lattice size as discussed for the pressure dependence of T_c (3). The lattice parameters are plotted against the value of ionic radius for trivalent lanthanide with an 8-coordination number, as represented in Fig. 2 (4). The c parameter for Pr is a little smaller and the data for Eu are larger than the expected values from the linear extrapolation between Nd and Sm. These deviations suggest relative preferences for tetravalent Pr and divalent Eu. The average valences of Pr and of Eu may be a little higher and lower than trivalent. In these cases, we can expect a slightly smaller ionic size for Pr and a larger value for Eu. On the other hand, the a parameter, whose value is affected by the copper valency, is a little longer for Pr, and the value for Eu is shorter than the value expected from the join between Nd and Sm. The average valence of copper is expected to be a little lower in the Pr compound and higher in the Eu one. Both lattice parameters a and c did not change so much by the reduction procedure. The lower T_c (onset) value in the Eu compound can be correlated to the preference of Cu^{2+} toward trivalent, but that in the Pr compound conflicts with the above-expected lower copper valency.

Oxygen Content

As for the role of the reduction process, it is not clear whether it simply removes oxygen or rearranges oxygen atoms to make the T'-phase superconductive. The oxygen content was precisely determined using Y_2O_3 as a standard. The total oxygen contents were less than 4 for all T'-type compounds, as shown in Fig. 3, even before the reduction process. The oxygen amount only slightly decreased with the reduction, except for the Pr compound, which showed an explicit change. The superconductivity appeared after the reduction process but the change in oxygen content was slight. The Nd compound with the largest oxygen content showed the highest T_c. The reduction process was necessary to make the compounds superconductive (1). This result seems to suggest that less oxygen content corresponds to a higher T_c value. The present results do not support this assumption. The total oxygen content cannot be directly related to the T_c value.

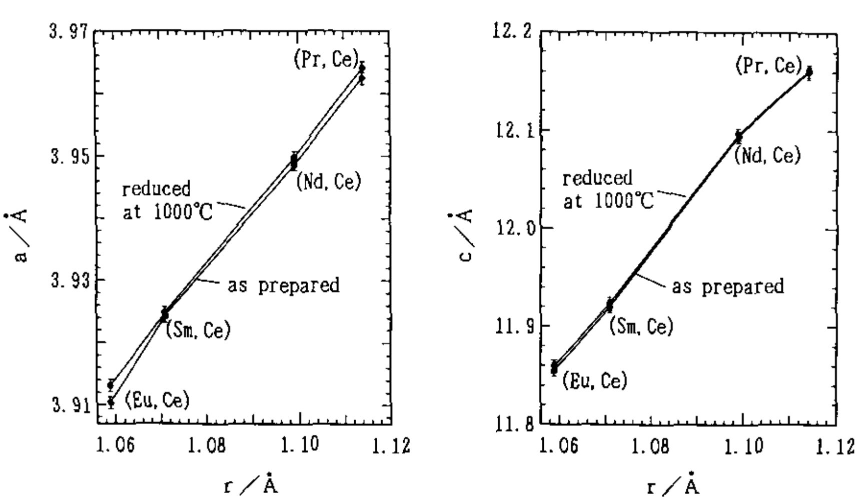

FIG. 2. Lattice parameters a and c against ionic radius of lanthanide before and after reduction.

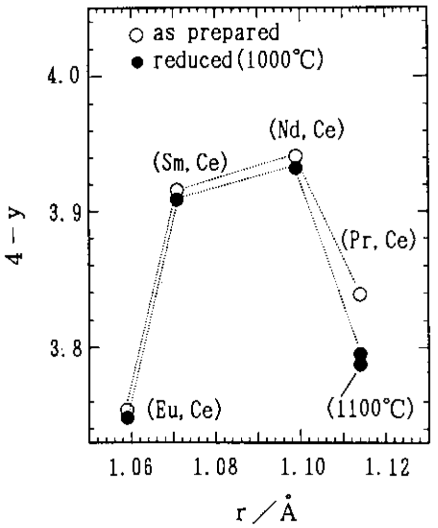

FIG. 3. Oxygen content for T′-type compounds against ionic radius of lanthanide.

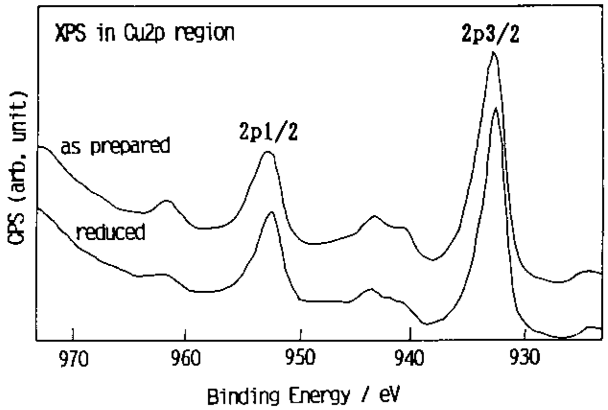

FIG. 4. XPS in the Cu $2p$ region for $Nd_{1.85}Ce_{0.15}CuO_y$ before and after the reduction.

XPS and XANES

X-ray photoemission spectra were measured for the samples before and after the reduction. Cu $2p_{3/2}$ and $2p_{1/2}$ peaks were shifted 0.3 and 0.5 eV, respectively, to the lower energy side by the reduction for the Nd compound, as described in Fig. 4. Their satellite peaks were observed around 942 and 962 eV, respectively. Their intensities decreased with the reduction. These changes in XPS with the reduction were most typically observed in the Nd compound among the T′-type compounds. The chemical shifts were less than 0.1 eV in other T′-type compounds. Both the peak shifts and the decreases in the satellite peak intensity may suggest that copper in the Nd compound is most effectively reduced in the reduction process. Cu K-edge XANES spectra are shown in Fig. 5. All samples before the reduction showed peak B for $1s$–$4p^*(\pi)$ of $3d^{10}$ final state (5). The Eu compound also showed peak A assigned for $1s$–$3d$ transition. Peak B disappeared after the reduction for the compounds with Pr, Nd, and Sm. The Nd compound most clearly showed peak C for $1s$–$4p^*(\pi)$ of $3d^9$ final state among the reduced products. On the other hand, the spectrum for the Eu compound did not change in the reduction. Both XPS and XANES seem to show that the copper in the conduction plane is the most effectively reduced in the Nd compound. The XPS of Eu showed that the trivalent Eu was slightly reduced after the reduction process.

Size Effect

The available size for the lanthanide site in the respective T′-type compounds was calculated using the lattice parameters a and c for each product and the positional parameters in Nd_2CuO_4 (6). The sizes are respectively larger than the ionic radius of lanthanide for Ln = Sm, Eu, as shown in Table 1. Thus, these lanthanides can be easily accommodated without expanding the available site in the crystal structure. The size is smaller than the ionic radius in the case of Ln = Pr. The conduction plane

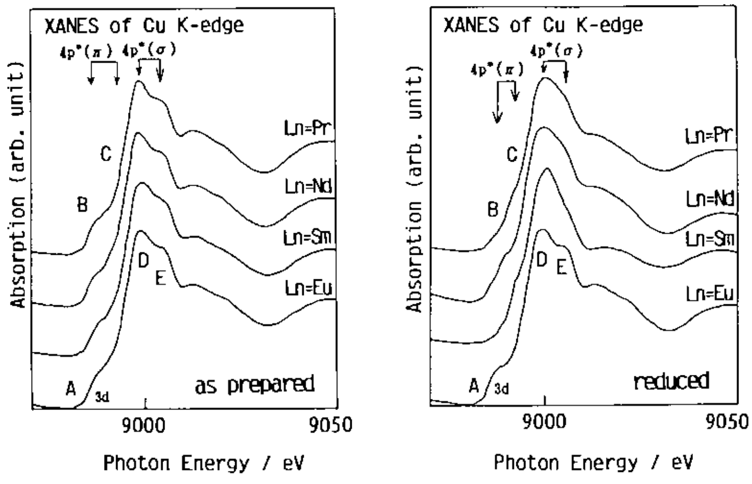

FIG. 5. XANES of Cu K-edge for T′-type compounds before and after the reduction.

TABLE 1
Average Ionic Radius (Å) between Ln^{3+} and Ce^{4+}

Ln	Ionic radius (4)	Calcd. value from lattice constant
Pr	1.114	1.108
Nd	1.099	1.098
Sm	1.071	1.075
Eu	1.059	1.065

has compressive and tensile stresses, respectively, in the former and the latter cases. Generally speaking, cations expand and contract their ionic size with the decrease and increase of valency, respectively. Electron-doping may be difficult in the CuO_2 conduction plane with the compressive stress because the ionic size of copper slightly expands with the doping in the reduction. To decrease the total oxygen content, oxygen vacancy is introduced to the fluorite layer for the lanthanide ion, to be reduced in the *Ln* = Sm and Eu cases. On the other hand, the Pr compound may have a small amount of oxygen vacancy in the CuO_2 conduction plane to reduce the tensile stress. The vacancy in the conduction plane may reduce the T_c value. Neodymium seems to have the most suitable ionic size to fit the lattice site in the fluorite layer. Partial substitution of Nd^{3+} with Ce^{4+} leads to enough oxygen vacancy in the fluorite layer. Excess electrons produced with the oxygen vacancy may be transferred to the CuO_2 conduction plane to make the compound superconductive.

Heat Treatment

Heat treatment may change the oxygen vacancy distribution in T'-type 214 compounds. There are two kinds of oxygen sites in the T'-type structure; one is in the CuO_2 conduction plane and the other is in the fluorite layer. The reduced T'-type compounds were annealed in sealed tubes to change the oxygen vacancy distribution, keeping their oxygen content. Annealing in sealed tubes did not much affect their electrical behavior of superconducting $Nd_{1.85}Ce_{0.15}CuO_y$, as shown in Fig. 6b. Electrical resistivity was reduced in the case of *Ln* = Sm and Eu but was enhanced on *Ln* = Pr, with the annealing as represented in Figs. 6a, 6c, and 6d. These results on the annealing can also be understood from the size matching between the

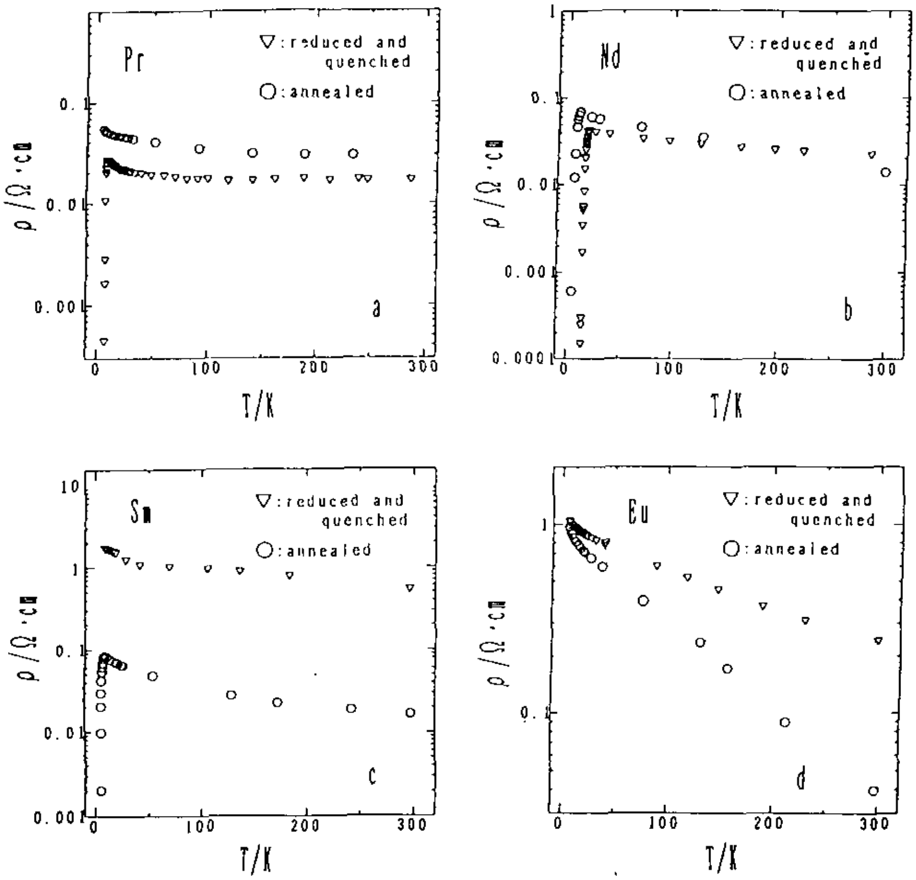

FIG. 6. Temperature dependencies of electrical resistivity for the reduced and its annealed T'-type $Ln_{1.85}Ce_{0.15}CuO_y$ where *Ln* = Pr, Nd, Sm, or Eu.

CuO_2 conduction plane and the fluorite layer. The trivalent neodymium ion has a suitable ionic size in T′-type structure. Electrical resistivity did not change so much because a distribution of oxygen vacancy did not change so much in the Nd compound with the annealing. Samarium and europium ions are too small, so that oxide ion defects are easily introduced into the fluorite layer to expand its size to fit with that of the CuO_2 conduction plane. A small oxygen vacancy, which remained in the CuO_2 conduction plane in the reduction–quenching process, is redistributed to the fluorite layer. The CuO_2 layer becomes oxygen-vacancy-free to reduce its electrical resistivity. Praseodymium is so large compared to the size of the available site that the CuO_2 conduction plane obtains more oxide ion vacancy from the fluorite layer, resulting in an increase of electrical resistivity with the annealing.

In summary, copper in the conduction plane must be effectively reduced in T′-type 214 compounds to obtain a good superconductor. Oxygen vacancy is only in the fluorite layer with a small amount of Ce^{4+} in the Nd superconductor, where the sizes coincide very well between the conduction plane and the fluorite layer. Trivalent europium was slightly reduced in the fluorite layer with tensile stress so that the electron could not be doped to the conduction plane. The conduction plane may have a small oxygen vacancy in the Pr compound, where the conduction plane has tensile stress. The situation in which a charge carrier can be effectively doped to the vacancy-free conduction plane is necessary to obtain a good superconductor.

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