Reduction and oxidation annealing effects on Cu K-edge XAFS for electron-doped cuprate superconductors

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Abstract. Reduction and oxidation annealing effects on the electronic states around the copper sites for Pr2-xCexCuO4 and Nd2-xCexCuO4 with x = 0 and x = 0.15 were investigated by Cu K-edge x-ray absorption measurements. Cu K near-edge spectra were changed by the reduction annealing in a manner similar to the case of Ce substitution for both x = 0 and x = 0.15. This means an increase of electron density at the copper sites, indicating the aspect of electron doping in the reduction annealing. This reduction annealing effect on the near-edge spectra are reverted by the additional oxidation annealing. The amount of electron density around the copper sites is varied by the reduction and oxidation annealing, reversibly, corresponding to the reversible variation of the physical property from insulating to superconductivity.

1. Introduction

High temperature cuprate superconductivity emerges when electron or hole carriers are introduced into an antiferromagnetic Mott insulator. For the emergence of superconductivity in the electron-doped cuprate RE2-xCexCuO4 (RE = Pr, Nd, Sm, Eu), adequate reduction annealing is necessary [1, 2]. As-sintered materials show antiferromagnetic orders and insulating behaviours despite the doping of sufficient number of electron carrier by Ce substitution. It is widely recognized that the reduction annealing induces structural modifications: removal of a small amount of oxygen [3, 4] and repair of Cu deficiency [5]. The superconductivity again disappears by oxidation annealing and turns into an insulator like as-sintered materials. Therefore, the physical property varies reversibly by the reduction and oxidation annealing [6]. However, the relationship between the structural change and the variation of the electric state has not been fully understood. Furthermore, the study of annealing effects was limited to the superconducting sample [3, 5, 7 – 9], and no systematic measurement of physical properties as well as the structure modified by the reduction and oxidation annealing was reported for parent and underdoped compounds. In the present work, we studied the reduction and oxidation annealing effects on the electronic states around the copper sites for Pr2-xCexCuO4 and Nd2-xCexCuO4 with x = 0 and 0.15 by Cu K-edge x-ray absorption measurements with transmission mode.
2. Experimental Details

Polycrystalline samples of Pr$_2$Ce$_x$CuO$_{4+\alpha - \delta}$, Nd$_2$Ce$_x$CuO$_{4+\alpha - \delta}$ with $x = 0$ and 0.15 were synthesized by a solid-state reaction method. The dried powder of Pr$_2$O$_3$, Nd$_2$O$_3$, CeO$_2$ and CuO were mixture with the proper molar ratio. The mixture was pressed into pellets and sintered at 1030 °C with a couple of intermediate grindings. The oxygen reduced samples were prepared by annealing in flowing Ar gas at temperatures between 750°C and 940°C for 12 hours. The amount of oxygen loss and the reduction annealing condition are summarized in Table 1. The $\alpha$ and $\delta$ are the amount of excess oxygen in the as-sintered samples and that of oxygen loss by the reduction annealing, respectively. The oxygenized samples were prepared by subsequent annealing for the oxygen reduced samples in flowing O$_2$ gas at 900 °C for 12 hours.

The x-ray absorption measurements were carried out at the BL01B1 in SPring-8. Cu K-edge absorption spectra were measured in a transmission mode using Si(1 1 1) double-crystal monochromator. All x-ray absorption measurements were performed at 300 K on pressurized pellets of a mixture of the powder samples and boron nitride.

Table 1. The amount of oxygen loss and the reduction annealing condition

| Sample                  | Oxygen loss $\delta$ | Reduction annealing condition |
|-------------------------|-----------------------|-------------------------------|
| Pr$_2$CuO$_{4+\alpha - \delta}$ | 0.035                 | 920°C, 12 hours               |
| Pr$_{1.85}$Ce$_{0.15}$CuO$_{4+\alpha - \delta}$ | 0.016                 | 940°C, 12 hours               |
| Nd$_2$CuO$_{4+\alpha - \delta}$ | 0.035                 | 750°C, 18 hours               |
| Nd$_{1.85}$Ce$_{0.15}$CuO$_{4+\alpha - \delta}$ | 0.011                 | 940°C, 12 hours               |

3. Results and Discussion

Fig. 1 (a) shows Cu K near-edge spectra for as-sintered (AS) Pr$_2$Ce$_x$CuO$_{4+\alpha - \delta}$ (PCCO) with $x = 0$ and 0.15. The intensity of spectra was normalized by the value at high-energy region, which is insensitive to the variation of electric state. In the figure, the near-edge spectrum for Cu$_2$O is plotted as a reference of Cu$^+$. Following previous studies for Pr$_2$CuO$_4$ [8], La$_2$Sr$_x$CuO$_4$ and Nd$_2$Ce$_x$CuO$_4$ [10], the characteristic shoulder and peaks in the spectra were assigned; the shoulder at 8983 eV (labelled a) and 8991 eV (labelled b) corresponds to the dipole transition from 1s to $4p\pi$, and the peaks at 8994 eV (labelled c) and 9000 eV (labelled d) comes from the dipole transition from 1s to $4p\sigma$. The final state for a and c is a well-screened state, and that for b and d is a poorly-screened state. As reported previously for Nd$_2$Ce$_x$CuO$_4$ [8, 10, 11], the effect of Ce doping is observed around near-edge region; intensity of peak corresponding to $1s$-$4p\pi$ transition increases, while that corresponding to $1s$-$4p\sigma$ transition decreases upon Ce doping. In Fig. 1 (d), the difference between the near-edge spectrum of AS PCCO $x = 0$ and $x = 0.15$, denoted as [AS PCCO with $x = 0.15$] − [AS PCCO with $x = 0$], is shown. This remnant spectra correspond to the signal induced by Ce-doping, namely, electron-doping. In the figure, the difference between the near-edge spectrum of Cu$_2$O and that of AS PCCO with $x = 0$, denoted as [Cu$^+O^-$] − [AS PCCO with $x = 0$], is overdrawn. Assuming that the reduced (RE) parent sample is stoichiometry ($\alpha = \delta$), [Cu$^+O^-$] − [AS PCCO with $x = 0$] gives difference between the spectra for Cu$^+$ and Cu$^{2+}$. In the near-edge spectrum of Cu$_2$O, the peak at ~8981 eV corresponds to $1s$-$4p\pi$ transition for Cu$^+$, and the peak structure at this energy becomes clear in the subtracted spectra shown in Fig. (d). This indicates that Cu$^+$ site is formed by the electron-doping and the intensity of peak A corresponds to the relative electron number (Cu$^+$ content) of the samples, as discussed previously [11].

Figs. 1 (b) and (c) show the Cu K near-edge spectra for AS, RE and oxygenized (OX) PCCO with $x = 0$ and $x = 0.15$. Comparing to the Ce substitution effect on the spectra, the degree of change in the spectra by the reduction annealing is smaller. However, as seen in the inset of Figs. 1 (a), (b) and (c), the near-edge spectra were certainly modified by the reduction and oxidation annealing. The spectral intensity around 8980 eV (labelled A) is increased by the reduction annealing in a similar manner to the Ce substitution and decreased by the oxidation annealing. In Figs. 1 (e) and (f), led
(blue) lines represent the remnant spectra obtained by subtracting the data for RE PCCO from that for AS PCCO, denoted as [RE PCCO] − [AS PCCO] (by subtracting the data for OX PCCO from that for the AS PCCO, denoted as [OX PCCO] − [AS PCCO]). The resultant spectra are quantitatively similar to [AS PCCO with \( x = 0.15 \)] − [AS PCCO with \( x = 0 \)] in Fig. 1 (d), indicating that the reduction annealing effect on the near-edge spectra is similar to the Ce-substitution effect, that is, the electron-doping at the copper sites.

The difference between the spectrum for AS and OX PCCO is shown in Figs. 1 (e) and (f) as the subtracted spectrum (blue line). The overall spectral shape is rather flat compared with the difference between the data for RE and AS PCCO (red line), meaning that the near-edge spectra for RE PCCO are reverted to that for AS PCCO by additional oxidation annealing. Therefore, the

![Figure 1](image_url)

Figure 1. (a)−(c) Cu \( K \) near-edge spectra for as-sintered (AS), reduced (RE) and oxygenized (OX)\( \text{Pr}_2_x\text{Ce}_x\text{CuO}_{4+\delta} \) (PCCO) with \( x = 0 \) and \( x = 0.15 \). (a) The spectra for AS PCCO with \( x = 0 \) and 0.15, comparing with the spectrum for CuO. (b) The spectra for AS, RD and OX PCCO with \( x = 0 \). (c) The spectra for AS, RD and OX PCCO with \( x = 0.15 \). Inset is the spectra for the energy between 8978 eV and 8982.5 eV. (d) The subtracted spectrum for AS PCCO with \( x = 0 \) and 0.15, comparing with the subtracted near-edge spectrum for CuO and AS PCCO with \( x = 0 \). The subtracted spectrum for AS PCCO and RE PCCO, comparing with the subtracted spectra for AS PCCO and OX PCCO, with (e) \( x = 0 \) and (f) \( x = 0.15 \).
oxidation annealing reduces the electron density, and the density is reversibly controlled through the reduction and oxidation annealing.

For the quantitative comparison of spectral change induced by Ce-substitution and annealing, we calculated the integrated spectral weight between 8976 and 8983 eV, which corresponds to the energy for peak A, and converted into the electron number \( n \). Fig. 2 (a) shows the evaluated \( n \) as a function of Ce concentration \( x \) for all samples. Note that the carrier number in the as-sintered parent sample is assumed to be zero. In the AS PCCO and NCCO with \( x = 0.15 \), \( n \) is almost comparable to \( x \), supporting that the one Ce ion effectively dopes one electron. For the sample with fixed \( x \), the \( n \) is larger in the annealed sample. Therefore, the reduction annealing also works as the electron doping to CuO\(_2\) plane even for the parent compounds. Fig. 2 (b) shows the \( \delta \)-dependence of increased electron number by Ar annealing \( (\Delta e) \). The \( \delta \) was calculated from the weight loss of the sample after the annealing. The \( \Delta e \) is larger in the parent systems, in which \( \delta \) is relatively large. The solid line in the figure represents a relation of \( \Delta e = 2\delta \), which is expected from the charge neutrality with an assumption that all carrier is doped onto CuO\(_2\) plane. Except for NCCO with \( x = 0.15 \), \( \Delta e \) is slightly smaller than \( 2\delta \), meaning that the removed one oxygen (O\(^{2-}\)) introduce less than two electrons to CuO\(_2\) plane. The possible reason for \( \Delta e < 2\delta \) is that some oxygen removes from the rare-earth layer with remaining electron density within the rare-earth layer.

4. Summary

The Reduction and oxidation annealing effects on the electronic states around the copper sites for the Pr\(_{2-x}\)Ce\(_x\)CuO\(_4\) and Nd\(_{2-x}\)Ce\(_x\)CuO\(_4\) with \( x = 0 \) and \( x = 0.15 \) were investigated by Cu K-edge x-ray absorption measurements. Cu K near-edge spectra were changed by the reduction annealing in a manner similar to the case of Ce substitution for both \( x = 0 \) and \( x = 0.15 \) samples, that is, the increase of electron density at the copper sites. Therefore, the reduction annealing works as the electron doping. We furthermore found the decrease of the electron density by oxidation annealing. Qualitative analysis of the near-edge spectra clarified that one electron is effectively doped by one substituted Ce ion and a little less than two electrons by removed one oxygen ion.

![Figure 2](image_url)

**Figure 2.** (a) Electron number \( n \) as a function of Ce concentration \( x \) for as-sintered (AS), reduced (RE) Pr\(_{2-x}\)Ce\(_x\)CuO\(_4\)\(_{\alpha \rightarrow \delta}\) (PCCO) and Nd\(_{2-x}\)Ce\(_x\)CuO\(_4\)\(_{\alpha \rightarrow \delta}\) (NCCO) with \( x = 0 \) and \( x = 0.15 \). The electron number was evaluated from the intensity of the near-edge spectra in the energy between 8976 eV and 8983 eV in Fig. 1 after normalizing by the near-edge spectrum for CuO standard. (b) The amount of increased electron number by the reduction annealing \( \Delta e \) as a function of the \( \delta \). The \( \delta \) is the amount of the oxygen loss by the reduction annealing.
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References
[1] Tokura Y, Takagi H, Uchida S 1989 Nature 337, 345
[2] Takagi H, Uchida S, Tokura Y 1989 Phys. Rev. Lett. 62, 1197
[3] Radaelli P G, Jorgensen J D, Schultz A J, Peng J L, and Greene R L 1994 Phys. Rev. B 49, 15322
[4] Moran E, Nazzal A I, Huang T C, and Torrance J B 1989 Physica C 160, 30
[5] Kang H J, Dai P, Campbell B J, Chupas P J, Rosenkranz S, Lee P L, Huang Q, Li S, Komiya S, and Ando Y 2007 Nat. Mater. 6, 224
[6] Wang Y L, Huang Y, Shan L, Li S L, Dai P, Ren C and Wen H-H 2009 Phys. Rev. B 80, 094513
[7] Song D, Park S R, Kim C, Kim Y, Leem C, Choi S, Jung W, Koh Y, Han G, Yoshida Y, Eisaki H, Lu D H, Shen Z-X and Kim C 2012 Phys. Rev. B 86, 144520
[8] Oyanagi H, Yokoyama Y, Yamaguchi H, Kuwahara Y, Katayama T and Nishihara Y 1990 Phys. Rev. B 42, 10136
[9] Wilson S D, Li S, Dai P, Bao W, Chung J-H, Kang H J, Lee S-H, Komiya S, Ando Y and Si Q 2006 Phys. Rev. B 74, 144514
[10] Kosugi N, Tokura Y, Takagi H and Uchida S 1990 Phys. Rev. B 41, 131
[11] Liang G, Guo Y, Badresingh D, Xu W, Tang Y, Croft M, Chen J, Sahiner A, Beom-hoan O and Markert J T 1995 Phys. Rev. B 51, 1258