Quantitative XANES Spectroscopy Study on the Prototype Hole- and Electron-Doped High-$T_c$ Superconductor Systems, (La,Sr)$_2$CuO$_4$ and (Nd,Ce)$_2$CuO$_4$

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Here we demonstrate that the Cu L-edge XANES (X-ray absorption near-edge structure) spectroscopy can be employed for quantitative analysis of the level of carrier-doping in the prototype hole- and electron-doped high-$T_c$ superconductor systems, (La$_{1-x}$Sr$_x$)$_2$CuO$_{4+x}$ and (Nd$_{1-x}$Ce$_x$)$_2$CuO$_{4+x}$. The progress in hole-doping in the (La$_{1-x}$Sr$_x$)$_2$CuO$_{4+x}$ system is seen as development of the shoulder peak (due to nominally trivalent copper) on the high-energy side of the main peak (due to nominally divalent copper) in the Cu L$_3$-edge region, whereas the progress in electron-doping in the (Nd$_{1-x}$Ce$_x$)$_2$CuO$_{4+x}$ system results in an additional absorption peak at about 934 eV (due to nominally monovalent copper), together with a decrease in the intensity of the main peak (due to nominally divalent copper). On the basis of these features, Cu-valence values are quantitatively obtained in excellent agreement with those calculated for the same samples from the precise oxygen contents. 4

Introduction

In layered copper oxides, high-$T_c$ superconductivity occurs upon doping the constituent CuO$_2$ planes with either holes ($p$-type doping) or electrons ($n$-type doping). The simplest $p$-type copper-oxide superconductor, (La$_{1-x}$Sr$_x$)$_2$CuO$_{4+x}$, is composed of a one-by-one stacking of a rock-salt-structured (La,Sr)O$_2$-(La,Sr)O block and a single CuO$_2$ plane (so-called $T$-structure), whereas the analogous $n$-type copper-oxide superconductor, (Nd$_{1-x}$Ce$_x$)$_2$CuO$_{4+x}$, possesses a so-called $T$'-structure in which a fluorite-structured (Nd,Ce)$_2$O$_2$-O$_2$-(Nd,Ce) block alternates with an apical-oxygen-free CuO$_2$ plane. The (La$_{1-x}$Sr$_x$)$_2$CuO$_{4+x}$ phase shows superconductivity once the CuO$_2$ plane is doped with a proper amount of holes through either excess oxygen doping or aliovalent Sr$^{II}$-for-La$^{III}$ cation substitution. On the other hand, occurrence of superconductivity in (Nd$_{1-x}$Ce$_x$)$_2$CuO$_{4+x}$ requires not only that the proper amount of electrons is doped through Ce$^{IV}$-for-Nd$^{III}$ substitution but also that the properly doped sample is postannealed under a low oxygen partial pressure; the main role of the low-oxygen-pressure-annealing is most likely to repair the Cu vacancies apparently present in small concentrations in as-air-synthesized (Nd$_{1-x}$Ce$_x$)$_2$CuO$_{4+x}$ samples. 2,3

Another difference between the two systems is that for (Nd$_{1-x}$Ce$_x$)$_2$CuO$_{4+x}$ superconductivity seems to appear in a much narrower doping range ($0.07 \leq x \leq 0.09$) than for (La$_{1-x}$Sr$_x$)$_2$CuO$_{4+x}$ ($0.03 \leq x \leq 0.125$).

Various spectroscopic techniques have been employed to get insights into the electronic structures of both the $p$- and $n$-type copper oxides. X-ray absorption near-edge structure (XANES) spectroscopy at O K, Cu K, and Cu L$_{2,3}$ absorption edges in particular provides us with tools to probe in a site-selective manner the local densities of unoccupied O 2p and Cu 3d states near the Fermi level. The parent La$_2$CuO$_4$ and Nd$_2$CuO$_4$ compounds are believed to be charge-transfer insulators in which the $p$-type doping introduces holes in the valence band of predominantly O 2p character and the $n$-type doping introduces electrons in the conduction band (upper Hubbard band, UHB) of predominantly Cu 3d character. Formation of O 2p holes in the valence band is readily observed as a development of additional absorption peaks in both O K-edge and Cu L$_{2,3}$-edge (due to strong Cu

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3d–O 2p hybridization) XANES spectra. These features have been successfully utilized for quantitative analyses of the doping level in various hole-doped copper-oxide systems such as CuBa$_2$O$_2$–CuO$_{2+y}$, Cu$_{2n+2}$(Bi$_{2n-1}$–Cu$_n$O$_{2+y}$, and Bi$_2$Sr$_2$Ca$_{2–x}$Cu$_{3+y}$O$_{10}$–CuO$_{2+y}$, by using in both cases series of samples with systematically varied carrier-doping levels. The XANES results for the prototype p- and n-type high-$T_c$ superconductor systems, (La$_{1–x}$Sr$_x$)$_2$CuO$_{4+y}$ and (Nd$_{1–y}$Ce$_y$)$_2$CuO$_{4+y}$, and CuO$_{4+y}$, as well as those for the prototype p- and n-type high-$T_c$ superconductor systems, (La$_{1–x}$Sr$_x$)$_2$CuO$_{4+y}$ and (Nd$_{1–y}$Ce$_y$)$_2$CuO$_{4+y}$, have been reported for (Nd$_{1–x}$Ce$_x$)$_2$CuO$_{4+y}$ and (Nd$_{1–y}$Ce$_y$)$_2$CuO$_{4+y}$ were successfully synthesized for $x$ ranging from 0.00 to 0.15 for the former and from 0.00 to 0.10 for the latter. The (La$_{1–x}$Sr$_x$)$_2$CuO$_{4+y}$ samples were prepared through a conventional solid-state synthesis route starting from La$_2$O$_3$, SrCO$_3$, and CuO powders thoroughly mixed into appropriate ratios. Each powder mixture was calcined at 950 °C for 12 h, which yielded a pelletized form at 1100 °C for 20 h in an O$_2$ gas flow and finally annealed in the same atmosphere at 500 °C for 48 h. The (La$_{1–x}$Sr$_x$)$_2$CuO$_{4+y}$ samples were prepared employing a wet-chemical method in which the solution-mixed metal ions (from Nd$_2$O$_3$, Ce(NO$_3$)$_3$, H$_2$O, and CuO) are uniformly chelated using EDTA (ethylenediaminetetraacetic acid) as a chelating agent, as described elsewhere in detail. The thus-obtained gel was burned, and the resultant raw ash was then pressed into pellets and fired in air at 1050 °C for 12 h. This yielded single-phase but not superconductive samples. To superconductize the (Nd$_{1–y}$Ce$_y$)$_2$CuO$_{4+y}$ samples, a portion of each sample was postannealed at 1000 °C for 24 h under an oxygen partial pressure ($P_{O_2}$) of $\sim$3.2×10$^{-4}$ atm for samples with $x \leq 0.06$ and of ~1.0×10$^{-4}$ atm for samples with $x > 0.06$. The level of $P_{O_2}$ used was carefully selected for each cation composition so as to achieve the highest possible $T_c$ value. It should be noted that (as described in previous studies$^{[19]}$) such a reductive annealing is believed to eliminate the Cu vacancies existing in the as-air-synthesized (Nd$_{1–y}$Ce$_y$)$_2$CuO$_{4+y}$ samples in small concentrations ($y = 0.01–0.02$) through the phase-segregation reaction: (Nd$_{2n-1}$xCe$_x$)$_2$CuO$_{4+y}$ → (1–y)(Nd$_{2n-1}$xCe$_x$)$_2$CuO$_{4+y}$ + y(Nd$_{2n-1}$xCe$_x$)$_2$O$_{3+y}$ + 0.5$\delta$O$_2$ + e + e + e). After such annealing, the samples naturally contained minute amounts (1–2%) of the (Nd$_{2n-1}$xCe$_x$)$_2$O$_{4+y}$ phase. Here we however use the nominal sample composition, $y = 0$, for all the (Nd$_{1–y}$Ce$_y$)$_2$CuO$_{4+y}$ samples, i.e., both the as-air-synthesized (AS) and the reductively annealed (RA) samples. All the samples were characterized with X-ray powder diffraction (XRD) Rigaku RINT2000 equipped with a rotating anode; Cu Kα radiation) to confirm the expected phase composition and to determine the lattice parameters. Refinement of the lattice parameters was performed in the orthorhombic space group, Fmmm, for (La$_{1–x}$Sr$_x$)$_2$CuO$_{4+y}$ with $x < 0.075$ and in the tetragonal space group, I4/mmm, for (La$_{1–x}$Sr$_x$)$_2$CuO$_{4+y}$ with $x \geq 0.075$ and (Nd$_{1–y}$Ce$_y$)$_2$CuO$_{4+y}$ using the software JANA2000.$^{[26]}$ Superconductivity properties were measured for powdered samples under an applied magnetic field of 10 Oe using a superconducting-quantum-interference-device magnetometer (SQUID; Quantum Design: MPMS-XL). The $T_c$
value was defined at the onset temperature of the diamagnetic signal. Superconducting volume fraction was estimated from field-cooled (FC) magnetization at 5 K.

The oxygen-content parameter $\delta$ was precisely determined for each sample by means of several parallel iodometric titrations employing an analysis route carefully optimized for the present ($\text{La}_{1-x}\text{Sr}_x\text{CuO}_{4+\delta}$ and ($\text{Nd}_{1-x}\text{Ce}_x\text{CuO}_{4+\delta}$) samples, as described in detail elsewhere.\(^{27}\) From the oxygen-content value, a value was also calculated for the valence of copper, $V(\text{Cu})_{\text{XRD}}$, assuming the valence values of +3, +2, +2, and −2 for La, Nd, Sr, and O, respectively. The valence value of Ce was estimated at +3.82 on the basis of Ce $M_{4,5}$-edge XANES data, as to be described later in detail.

The O K-edge, Cu L$_{2,3}$-edge and Ce $M_{4,5}$-edge XANES measurements were performed on the BL20A high-energy spherical grating monochromator (HSGM) beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan.\(^{\text{15}}\) The spectra were recorded in X-ray fluorescence-yield ($I_f$) mode for the O K-edge and Cu L$_{2,3}$-edge absorption, and in electron-yield ($I_e$) mode for the Ce $M_{4,5}$-edge absorption. The $I_f$ data were collected utilizing a microchannel-plate (MCP) detector system with an electrically isolated grid mounted in front. The grid was set to a voltage of 50 V, the front of the MCPs to −3200 V and the rear to −200 V. The grid bias ensured that positive ions did not enter the detector, while the MCP bias ensured that no electrons were detected. The detector was located at the sample normal and photons were incident at an angle of 45° with respect to the sample normal. In the $I_e$ mode, the sample drain current is measured. Simultaneously to $I_f$ and $I_e$, the incident photon flux was monitored by a Ni mesh located after the monochromator. All measurements were performed on powder samples at room temperature. The photon energies were calibrated with an accuracy of 0.1 eV using the O K-edge absorption peak of a CeO$_2$ reference. The monochromator resolution was set to ~0.22, ~0.45, and ~0.4 eV for the O K-edge, Cu L-edge, and Ce M-edge energy regions, respectively. The recorded spectra were corrected for the energy-dependent incident photon intensity as well as for self-absorption effects\(^{20,27}\) and normalized to the tabulated standard absorption cross-sections\(^{28}\) in the energy range of 600–620 eV for the O K-edge and 1000–1020 eV for the Cu L-edge.

**Results and Discussion**

All the ($\text{La}_{1-x}\text{Sr}_x\text{CuO}_{4+\delta}$ ($0.00 \leq x \leq 0.15$) and ($\text{Nd}_{1-x}\text{Ce}_x\text{CuO}_{4+\delta}$ ($0.00 \leq x \leq 0.10$) samples employed in the present study were found to be XRD-pure (except for the minute amounts of the (Nd, Ce)$_2$O$_3$ phase in the reductively annealed samples of the latter series). Moreover, linear variations in the lattice parameters, $a$, $b$, and $c$, with respect to the substitution level, $x$, were confirmed for both the systems: as $x$ increases in ($\text{La}_{1-x}\text{Sr}_x\text{CuO}_{4+\delta}$, the $a$ parameter (and also the $b$ parameter for the orthorhombic $x \leq 0.05$ samples) decreases but the $c$ parameter increases, while for ($\text{Nd}_{1-x}\text{Ce}_x\text{CuO}_{4+\delta}$ just the opposite behavior is observed (see Tables 1 and 2). The lattice expansion (shrinkage) along the $c$ axis is related to the larger (smaller) size of the substituent Sr$^{II}$ (Ce$^{IV}$) than that of the host cation, La$^{III}$ (Nd$^{III}$). On the other hand, the decreasing $a$ and $b$ parameters in ($\text{La}_{1-x}\text{Sr}_x\text{CuO}_{4+\delta}$ and the increasing $a$ parameter in ($\text{Nd}_{1-x}\text{Ce}_x\text{CuO}_{4+\delta}$ directly reflect the effects of hole-doping and electron-doping, respectively, into the antibonding Cu–O orbitals in the CuO$_2$ plane. Moreover, for the ($\text{Nd}_{1-x}\text{Ce}_x\text{CuO}_{4+\delta}$ system, the $a$ parameter was confirmed to slightly increase upon the reducing annealing (Table 2), as expected.

**Cu L$_{2,3}$-Edge for (La$_{1-x}$Sr$_x$)$_2$CuO$_{4+\delta}$**

The Cu L$_{2,3}$-edge absorption spectra recorded for the ($\text{La}_{1-x}\text{Sr}_x\text{CuO}_{4+\delta}$ samples are shown in Figure 1. Here, the spectral features were normalized on the basis of the main peak in the $L_3$ area centered about 931.2 eV in order to clarify the appearance of spectrum for trivalent copper species. Assignment of the spectral features was straightforward on the bases of previous studies on various superconducting copper-oxide phases. For the quantitative analysis, the $L_3$ area (that is more intense than the $L_2$ area) is commonly used. The main peak in the $L_3$ area centered about 931.2 eV is due to formally divalent copper states, Cu$^{II}$, i.e., transitions from the Cu(2p$^{3/2}$)3d$^9$ ground state to the Cu(2p$^{3/2}$)3d$^9$ excited state [(2p$^{3/2}$)$^{-1}$ denotes a 2p$_{3/2}$ hole], whereas the shoulder peak on the high-energy side of this peak about 932.6 eV is due to formally trivalent copper, Cu$^{III}$, i.e., transitions from the Cu(2p$^{3/2}$)3d$^8$L excited state into the antibonding Cu–O orbitals in the CuO$_2$ plane. Moreover, for the ($\text{Nd}_{1-x}\text{Ce}_x\text{CuO}_{4+\delta}$ system, the $a$ parameter was confirmed to slightly increase upon the reducing annealing (Table 2), as expected.

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the holes induced at the O site through Cu 3d–O 2p hybridization.\textsuperscript{31}

Figure 2 shows the $V(Cu)_{XAS}$ values plotted for the $(La_{1-x}Sr_x)_{2}CuO_{4+\delta}$ system against $x$, together with the $V(Cu)_{TIT}$ values calculated for the same samples from the precise $\delta$ values determined by means of chemical analysis. For the entire sample series, an excellent agreement between the $V(Cu)_{XAS}$ and $V(Cu)_{TIT}$ values is revealed. Moreover, as can be seen from Figure 2, the two independent estimates for $V(Cu)$ both systematically increase with increasing $x$, as expected, but they also show the same trend toward saturation for the larger $Sr^{II}$-for-$La^{III}$ substitution levels. This is apparently due to an increase in the oxygen-vacancy concentration with increasing $x$ (see Table 1).

Ce M$_{4,5}$-Edge for $(Nd_{1-x}Ce_x)_{2}CuO_{4+\delta}$. In Figure 3, the Ce M$_{4,5}$-edge absorption spectra measured for representative $(Nd_{1-x}Ce_x)_{2}CuO_{4+\delta}$ samples are shown, together with the spectrum recorded for CeO$_2$ as a reference compound of tetravalent cerium. For each $(Nd_{1-x}Ce_x)_{2}CuO_{4+\delta}$ sample, shoulder peaks are observed on the low-energy sides of the main peaks centered around 882.5 eV (M$_5$-edge) and 900.1 eV (M$_4$-edge), in contrast to the spectrum of the CeO$_2$ reference, which shows only the main peaks. [Note that for unknown reasons, the low-energy shoulder peaks were not visible in the Ce M$_{4,5}$-edge XANES spectrum reported for a thin-film sample of $(Nd_{0.925}Ce_{0.075})_{2}CuO_{4+\delta}$.\textsuperscript{21}]

![Figure 1. Cu L$_{2,3}$-edge XANES spectra for the $(La_{1-x}Sr_x)_{2}CuO_{4+\delta}$ samples. The inset illustrates the fitting of the spectral features about the L$_3$-edge into Cu$^{II}$ and Cu$^{III}$ components for the $x = 0.075$ sample.](image1)

![Figure 2. Valence of copper, $V(Cu)$, as estimated from the Cu L$_3$-edge XANES data [$V(Cu)_{XAS}$] and the iodometric titration data [$V(Cu)_{TIT}$] with respect to the Sr content $x$ for the $(La_{1-x}Sr_x)_{2}CuO_{4+\delta}$ samples.](image2)

![Figure 3. Ce M$_{4,5}$-edge XANES spectra for representative as-air-synthesized (AS) and reductively annealed samples of $(Nd_{1-x}Ce_x)_{2}CuO_{4+\delta}$. The inset illustrates the fitting of the spectral features about the M$_5$-edge into Ce$^{III}$ and Ce$^{IV}$ components for the $x = 0.090$ sample.](image3)
et al., the low-energy shoulder peaks were interpreted as a signature of trivalent cerium. Because the shoulder peaks are clearly visible for all the present (Nd1−xCe)xCuO4+x samples, we conclude that the valence of cerium, V(Ce), in (Nd1−xCe)xCuO4+x is lower than +4. To gain a quantitative estimate for the V(Ce) value in (Nd1−xCe)xCuO4+x, we analyzed the spectral features about the M5-edge for the four samples displayed in Figure 3 by fitting the intensities of the main peak [I(CeIII)] and its low-energy shoulder [I(CeIV)] and calculated the V(Ce) value as: V(Ce) ≡ 4 − I(CeIII)/[I(CeIII) + I(CeIV)]. For all the four (Nd1−xCe)xCuO4+x samples, the V(Ce) value was determined to be +3.82 ± 0.05, in good agreement with the values of +3.84 and +3.79 previously estimated on the basis of c-axis variation for polycrystalline (Nd1−xCe)xCuO4+x samples33 and thin-film samples of (La1−xNd)xCuO4+x,34 respectively.

**Cu L2,3-Edge for (Nd1−xCe)xCuO4+x.** The Cu L2,3-edge absorption spectra obtained for the as-air-synthesized (AS) samples of (Nd1−xCe)xCuO4+x are displayed in Figure 4. For the corresponding reductively annealed (RA) samples nearly identical spectra were obtained (not shown here). From Figure 4, the main peaks due to CuII (around 931.2 eV at the L3-edge and 950.8 eV at the L2-edge) are symmetric for all the samples, indicating nonexistent of CuII species. On the other hand, the peaks are found to systematically decrease in intensity and to gradually shift to higher energies with increasing x. These observations are consistent with those of several previous studies on the (Nd1−xCe)xCuO4+x system19–21,35 and are taken as an indication that the generated electrons are directed into the Cu site in (Nd1−xCe)xCuO4+x upon the n-type doping. For the systematic shift of the peak positions with increasing x, Alexander et al.19 have proposed three possible reasons: (i) screening effect by electrons generated upon Ce substitution, (ii) potential of Ce ions, and (iii) a change in the Madelung potential of Cu ions by the charge of Ce. From Figure 4, an additional systematic indication of the progress in electron doping appears to be the tiny but systematic enhancement of absorption intensity about 934 eV (in the L3-edge area) with increasing x. From a single spectrum it is somewhat difficult to distinguish this peak from the weak CuII peak at ~937 eV (due to transition to the Cu(2p3/2)−1s3d4s excited state), but it becomes evident once we look at the development of it with increasing x (see the left-hand side inset of Figure 4). We assign the absorption feature at ~934 eV to monovalent Cu species [i.e., transitions from the Cu(2p3/2)3d10 ground state to the Cu(2p3/2)−1s3d4s excited state], because the same feature is clearly observed not only for the monovalent copper-oxide compound Cu2O and oxygen-deficient samples of the CuBa2RCuO6 phase (both containing linearly coordinated CuI) but also for the n-type doped samples of the so-called infinite-layer superconductor, (Sr1−xLa)xCuO2,37 containing four-coordinated CuI. Interestingly, with increasing x, the ~934 eV peak is found to shift to higher energies with the same rate as the main peak (Table 2), such that the energy difference between the two peaks due to CuI and CuII remains essentially constant (~2.8 eV).

Here we use the ~934 eV peak for quantitative determination of the valence of copper in both the AS and RA samples of (Nd1−xCe)xCuO4+x by analyzing the intensities of the two peaks at ~931.2 eV (due to CuII) and ~934 eV (due to CuI) in a way parallel to that used for the (La1−xNd)xCuO4+x spectra (see the right-hand side inset of Figure 4) and calculate the valence of copper as: V(Cu)XAS ≡ 2 − I(CuII)/[I(CuII) + I(CuI)]. The individual intensity values are listed in Table 2, and the V(Cu)XAS values are plotted against x in Figure 5, together with the V(Cu)TIT values calculated for the same samples from the iodometric titration data for δ assuming V(Ce) = +3.82 (as revealed from the Ce M5,5-edge XANES data). From Figure 5, it is seen that the V(Cu)XAS values are highly consistent with the corresponding V(Cu)TIT values, decreasing linearly with increasing x. Also revealed is that the decrease in V(Cu)XAS [and V(Cu)TIT] upon the reductive annealing is very tiny (~0.01), particularly for the heavily Ce-substituted samples.

**Superconductivity Phase Diagram for (La1−xSr)xCuO4+x and (Nd1−xCe)xCuO4+x.** The two independent experimental approaches employed here for the quantitative analysis of the valence state of copper, i.e., Cu L3-edge XANES and iodometric titration (plus Ce M5-edge XANES), have revealed that the influence of the reductive annealing on the V(Cu) value and accordingly on the level of carrier doping is insignificant for (Nd1−xCe)xCuO4+x. At the same time, such an annealing is indispensable for the appearance of the...
of superconductivity in the \((Nd_{1-x}Ce_x)_{2}CuO_4\) system. In fact, the appearance of superconductivity in \((Nd_{1-x}Ce_x)_{2}CuO_4\) cannot be explained in terms of the \(V(Cu)\) value only: for the superconductive RA samples of \(x = 0.065\) and 0.085, \(V(Cu)_{XAS}\) values of +1.90 and +1.88 [\(V(Cu)_{XAS} = +1.877\) and +1.867], respectively, were obtained, whereas for the nonsuperconductive AS sample of \(x = 0.085\), \(V(Cu)_{XAS} = +1.89\) [\(V(Cu)_{XAS} = +1.875\)]. Actually, the recent works on the \((Nd_{1-x}Ce_x)_{2}CuO_4\) system have quite convincingly demonstrated that rather than controlling the doping level, the low-oxygen-partial-pressure annealing repairs the Cu vacancies (which are always present in small concentrations in as-air-synthesized \((Nd_{1-x}Ce_x)_{2}CuO_4\) samples).\textsuperscript{2,3} The present XANES results support this view.

In Figure 6, we plot the \(T_c\) values against the \(CuO_2\)-plane carrier concentration, \(p(CuO_2)\) or \(n(CuO_2)\), for the two prototype high-\(T_c\) superconductor systems, \((La_{1-x}Sr_x)_{2}CuO_4\) and \((Nd_{1-x}Ce_x)_{2}CuO_4\) (RA samples). The carrier concentrations were calculated as: \(p(CuO_2) \equiv V(Cu) - 2\) and \(n(CuO_2) \equiv 2 - V(Cu)\), with both \(V(Cu)_{XAS}\) and \(V(Cu)_{ITT}\). From Figure 6, it is found that the highest \(T_c\) value corresponds to \(p(CuO_2) \approx 0.14-0.15\) for the \((La_{1-x}Sr_x)_{2}CuO_4\) system and to \(n(CuO_2) \approx 0.11-0.12\) for the \((Nd_{1-x}Ce_x)_{2}CuO_4\) system. Moreover, it is seen that the carrier-concentration range within which superconductivity appears in \((Nd_{1-x}Ce_x)_{2}CuO_4\) is much narrower than that in \((La_{1-x}Sr_x)_{2}CuO_4\). Apparently in the case of the \((Nd_{1-x}Ce_x)_{2}CuO_4\) system the concepts of “under-doping”, “optimum doping”, and “over-doping” do not have similar meanings as they are believed to have in the case of the \(p\)-type doped superconductive copper oxides.

\textbf{O K-edge for} \((La_{1-x}Sr_x)_{2}CuO_4\) and \((Nd_{1-x}Ce_x)_{2}CuO_4\). In panels a and b in Figure 7, the very pre-edge energy area (526–532 eV) of the O K-edge absorption spectra is shown for the two systems, \((La_{1-x}Sr_x)_{2}CuO_4\) and \((Nd_{1-x}Ce_x)_{2}CuO_4\) (AS samples), respectively. The spectral weight above \(\sim 531.5\) eV is mainly due to the LaO/ NdO planes,\textsuperscript{19,20,29,40} and is not shown here. Also not shown are the spectra for the RA samples of \((Nd_{1-x}Ce_x)_{2}CuO_4\) that are nearly identical to those of the AS samples. For both the systems, the broad peak about 530 eV is due to transitions into O 2p states hybridized with the UHB.\textsuperscript{4,5,12,15,35,40–43} In \((Nd_{1-x}Ce_x)_{2}CuO_4\), this feature is seen at a somewhat lower energy (\(\sim 529.1\) eV) than in \((La_{1-x}Sr_x)_{2}CuO_4\) (\(\sim 530.2\) eV).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Valence of copper, \(V(Cu)\), as estimated from the Cu L\(_3\)-edge XANES data [\(V(Cu)_{XAS}\)] and the iodometric titration data [\(V(Cu)_{ITT}\)] with respect to the Ce content \(x\), for the as-air-synthesized (AS) and reductively annealed (RA) samples of \((Nd_{1-x}Ce_x)_{2}CuO_4\).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Relationships between the \(T_c\) value and the hole concentration \(p(CuO_2)\) (right) and the electron concentration \(n(CuO_2)\) (left) as estimated on the bases of the iodometric titration data (*) and the Cu L\(_3\)-edge XANES data (○) for the \((La_{1-x}Sr_x)_{2}CuO_4\) samples and the reductively annealed \((Nd_{1-x}Ce_x)_{2}CuO_4\) samples, respectively.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{O K-edge XANES spectra for the (a) \((La_{1-x}Sr_x)_{2}CuO_4\) and (b) \((Nd_{1-x}Ce_x)_{2}CuO_4\) (AS) samples. The insets in the former case show the integrated intensities (left) and the exact positions (right) of the pre-edge peak about 528.9 eV with respect to the Sr content, \(x\).}
\end{figure}
Moreover, it is revealed for the (Nd$_{1-x}$Ce$_x$)$_2$CuO$_{4+x}$ system that the $\sim$530 eV peak systematically gains intensity and gets broader with increasing Ce content, $x$. This is ascribed to the fact that the peak overlaps with the band due to the Ce 5d and/or Ce 4f states hybridized with O 2p states.$^{20,42}$ Here, it is important to note that for the Th-substituted analogue, (Nd$_{1-x}$Th$_x$)$_2$CuO$_{4+x}$, no change in the intensity of the peak due to UHB was observed upon increasing the doping level, $x$.$^{19}$ Therefore, it seems reasonable to assume that the UHB is essentially independent of the level of electron doping also in (Nd$_{1-x}$Ce$_x$)$_2$CuO$_{4+x}$. This means that the Fermi level should be located at the bottom of the UHB$^{24,41}$ and the doped electrons do not go to the O site.

On the other hand, doping the (La$_{1-x}$Sr$_x$)$_2$CuO$_{4+x}$ phase with holes results in a development of an additional pre-edge peak about 528.9 eV. Such a feature is seen in all the $p$-type doped copper-oxide superconductors and ascribed to the excitation of O 1s electrons to O 2p hole states in the CuO$_2$ plane.$^{4,5,12,14-17,35,40,43}$ For the present (La$_{1-x}$Sr$_x$)$_2$CuO$_{4+x}$ samples, we analyzed the spectral features by fitting the two pre-edge peaks at $\sim$528.9 eV (due to CuO$_2$-plane hole states) and at $\sim$530.2 eV (due to UHB) with a combination of Lorentzian and Gaussian functions after approximating the background with a quadratic line. The integrated intensity of the pre-edge peak at $\sim$528.9 eV [$I$(CuO$_2$)] is displayed in the left-hand side inset of Figure 7a. With increasing $x$, $I$(CuO$_2$) gradually increases and simultaneously the peak due to UHB decreases. The increasing $I$(CuO$_2$) is in good agreement with the behavior of $V$(Cu)$_{\text{XAS}}$ as estimated on the bases of the Cu L$_3$-edge absorption spectra (Figure 2). Moreover, hole doping in (La$_{1-x}$Sr$_x$)$_2$CuO$_{4+x}$ also results in a gradual decrease in the exact position of the $\sim$528.9 eV pre-edge peak (see the right-hand side inset of Figure 7a), reflecting the fact that the Fermi level shifts to lower energies.$^{44}$

Conclusions

Utilizing series of high-quality samples with widely varied doping levels and independent analytical probes, i.e., O K-edge, Cu L$_{2,3}$-edge, and Ce M$_{4,5}$-edge XANES spectroscopy and wet-chemical redox analysis, we systematically studied cation valences, carrier concentrations, and electronic structures of the two prototype high-$T_c$ superconductor systems, (La$_{1-x}$Sr$_x$)$_2$CuO$_{4+x}$ and (Nd$_{1-x}$Ce$_x$)$_2$CuO$_{4+x}$. In the hole-doped (La$_{1-x}$Sr$_x$)$_2$CuO$_{4+x}$ system, the increase in hole-doping level achieved through aliovalent Sr$^{II}$ for La$^{III}$ substitution was seen in the L$_3$-edge XANES spectra as the enhanced intensity of the high-energy shoulder peak at $\sim$932.6 eV due to formally trivalent copper, whereas in the electron-doped (Nd$_{1-x}$Ce$_x$)$_2$CuO$_{4+x}$ system, the increase in electron-doping level through aliovalent Ce$^{IV}$-for-Nd$^{III}$ substitution resulted in the increased intensity of the peak at $\sim$934 eV and in the decreased intensity of the main peak at $\sim$931.2 eV. These features of the L$_3$-edge spectra were utilized for quantitative analysis of the valence state of copper and accordingly the level of carrier doping. For both the systems, the resultant values for the copper valence were highly consistent with those calculated on the basis of wet-chemical analysis. Moreover shown was that the low-oxygen-partial-pressure annealing required to superconductorize the as-as-synthesized (Nd$_{1-x}$Ce$_x$)$_2$CuO$_{4+x}$ samples does not significantly affect the Cu-valence value. From the Ce M$_5$-edge XANES spectra, the valence of cerium was revealed to be around +3.8 both in the as-synthesized and postannealed (Nd$_{1-x}$Ce$_x$)$_2$CuO$_{4+x}$ samples.

The present study also clearly revealed the difference between the two systems in regards to the electronic structure and superconductivity phase diagrams. The $p$-type doping in (La$_{1-x}$Sr$_x$)$_2$CuO$_{4+x}$ introduces holes in the valence band of predominantly O 2p character, whereas the $n$-type doping introduces electrons in the conduction band of predominantly Cu 3d character. In the O K-edge spectra, the increase in CuO$_2$-plane hole concentration with increasing $x$ in (La$_{1-x}$Sr$_x$)$_2$CuO$_{4+x}$ was seen as the enhanced intensity of the pre-edge at $\sim$528.9 eV, whereas for (Nd$_{1-x}$Ce$_x$)$_2$CuO$_{4+x}$ no signs were noticed that could be directly assigned to the changes in electron-doping level. Moreover, it was shown that the carrier-concentration range where superconductivity appears is much narrower in the (Nd$_{1-x}$Ce$_x$)$_2$CuO$_{4+x}$ system than the (La$_{1-x}$Sr$_x$)$_2$CuO$_{4+x}$ system. The highest $T_c$ values were found to correspond to $n$(CuO$_2$) $\approx$ 0.11–0.12 for the former and $\rho$(CuO$_2$) $\approx$ 0.14–0.15 for the latter system.

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