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Control of hole distribution through isovalent R-cation substitution in Cu$_2$Ba$_2$RCu$_2$O$_8$ superconductors

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Superconductive Cu$_2$Ba$_2$RCu$_2$O$_8$ samples with $R$ ranging from Gd to Tm have been synthesized through a sol-gel route. Both iodometric titration and Cu L-edge x-ray absorption near-edge structure (XANES) spectroscopy data indicate that the average Cu valence remains constant, whereas $T_c$ increases with decreasing size of the $R$ constituent. An explanation for this trend is revealed from O K-edge XANES spectra, which show that the smaller-for-larger $R$-cation substitution results in a shift of holes from the CuO$_2$ charge reservoir to the superconductive CuO$_2$ planes. Since Cu$_2$Ba$_2$RCu$_2$O$_8$ samples are underdoped, such a shift of holes raises the value of $T_c$.

A common feature for isostructural compounds constituting of rare earth ($R$) elements is that the $R$ element can be replaced by most of the other $R$’s without drastically affecting the material properties. However, a certain “size” or “chemical-pressure” effect is often seen which smoothly controls the properties when going from the largest to the smallest $R$ species, or vice versa. For instance, for the prototype “R-123” high-$T_c$ superconductors (more systematically named as CuBa$_2$RCu$_2$O$_8$ or Cu-1212 phases) a decrease in the ionic radius of the trivalent $R$ constituent, $r(\text{III})$, decreases the superconductivity transition temperature $T_c$. Rather interestingly, the opposite is true for the other well-known $R$-based superconductive copper oxide system, “R-124” (i.e., Cu$_2$Ba$_2$RCu$_2$O$_8$ or Cu-2212). Hence changes in $T_c$ cannot simply be explained by the change in the distance between the superconductive CuO$_2$ planes over the $R^{\text{III}}$-cation layer. Instead, we suggest that chemical pressure controls the charge distribution over the different layers in superconductive copper oxide phases. The aim of the present work is to gain deeper understanding on the chemical-pressure effects on multilayered copper oxides. The Cu$_2$Ba$_2$RCu$_2$O$_8$ (Cu-2212) superconductor family was selected for the target system. The advantage of the Cu-2212 system in comparison with, e.g., the Cu-1212 system is that the Cu-2212 copper oxides are believed to be essentially oxygen stoichiometric. (Here it should be emphasized that in order to probe pure chemical-pressure effects, oxygen content of the target system should remain constant throughout the substitution range investigated.) For sample characterization, x-ray absorption near-edge structure (XANES) spectroscopy at both Cu L$_{2,3}$ and O K edges is employed. The former spectral area allows relatively accurate determination of the total amount of excess positive charge, whereas the latter turned out to be selective enough to distinctively probe the CuO$_2$-charge-reservoir and CuO$_2$-plane hole densities.

Polycrystalline samples of Cu$_2$Ba$_2$RCu$_2$O$_8$ with $R$=Gd, Dy, Y, Ho, Er, and Tm were synthesized under ambient pressure from a homogeneous Cu-Ba-R-O precursor prepared by means of a simple acetate tartrate sol-gel route. Stoichiometric amounts of $R_2$O$_3$, Ba(CH$_3$COO)$_2$, and Cu(CH$_3$COO)$_2$-H$_2$O were used as starting chemicals for the three metal constituents. The rare earth oxide $R_2$O$_3$ was dissolved as a powder in a 0.2M aqueous acetic acid solution at 55–60 °C after which Ba and Cu acetates were added to the solution as 0.5M water solutions. Finally, 160 mol % of tartaric acid was added to the acid solution for the gel formation. The excess solvent was evaporated from the solution in approximately 6 h at 65 °C in an open beaker with continuous stirring to obtain a clear blue gel. The gel was dried in air at 120 °C for 12 h and then slowly (2 °C/min) heated in O$_2$ gas flow up to 750 °C and kept at that temperature for 24 h for calcination. After regrinding, the thus obtained homogeneous Cu-Ba-R-O powder was used as a precursor for the Cu-2212-phase synthesis carried out in 1 atm O$_2$ gas flow at 750–785 °C for 24 h. The synthesis temperature was optimized for each $R$ constituent separately, i.e., 750 °C for Gd and Dy, 770 °C for Ho, 780 °C for Y, and 785 °C for Er and Tm. Another important factor was to spread the sample powder as thin as possible on an Al$_2$O$_3$ plate to ensure uniform temperature and atmosphere conditions throughout the sample during the synthesis. For each $R$ constituent, the synthesis yielded phase-pure Cu-2212 samples within the detection limit of powder x-ray diffraction measurements (Rigaku RINT2550VK/U equipped with a rotating Cu anode). Moreover, accurate chemical analysis by means of iodometric titration confirmed that the samples were essentially stoichiometric in terms of oxygen: for each sample an oxygen-content value (per f.u.) of 7.99±0.01 was obtained.

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All the samples were superconductive. The $T_c$ values (defined at the onset of diamagnetic signal) were determined from the field-cooling curves recorded at 10 Oe with a superconducting quantum interference device magnetometer (Quantum Design: MPMS-XL). In Fig. 1, the value of $T_c$ is plotted against $r(R^{III})$ (Ref. 8) for the six Cu-2212 samples. With decreasing $r(R^{III})$, $T_c$ increases almost linearly (from 74 K for $R$=Gd to 82 K for $R$=Tm), in accordance with results from previous reports.3,4

The Cu $L_{2,3}$-edge and O K-edge XANES spectra were collected for the samples at room temperature in x-ray fluorescence-yield mode at the 6 m high-energy spherical grating monochromator (HSGM) beamline of the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. Experimental details are as previously given elsewhere.9 The obtained spectra were corrected for the energy-dependent incident photon intensity variation as well as for self-absorption effects10,11 and normalized to tabulated standard absorption cross sections12 in the energy range of 600–620 eV for the O K edge and 1000–1020 eV for the Cu $L_{2,3}$ edge.

The Cu $L_{2,3}$-edge absorption spectra of the Cu$_2$Ba$_2$RCu$_2$O$_8$ samples look all nearly identical. A representative spectrum is displayed in Fig. 2 (shown here for the smallest $R$ constituent, Tm). The spectra exhibit two narrow peaks centered at $\sim$931.2 and $\sim$951.2 eV. Both peaks are due to divalent copper states.13 Oxidation of copper beyond the divalent state is seen as shoulders on the high-energy side of these peaks.9,14 For each sample, the spectrum was separately analyzed for both the $L_3$ and $L_2$ spectral ranges. The analysis procedure is illustrated for the former case in Fig. 2. In brief, the background, fitted with a straight line, was first subtracted from the spectrum after which the fittings of the main peak (due to Cu$^{II}$) and its shoulder (due to Cu$^{III}$) were done using combined Lorentzian and Gaussian functions to account for the intrinsic and experimental broadenings, respectively. From the integrated intensities of the main peak $[I(Cu^{II})]$ and the shoulder $[I(Cu^{III})]$ an estimate for the average valence of copper was then calculated with $V(Cu) = 2 + I(Cu^{III})/[I(Cu^{II})+I(Cu^{III})]$. For the sake of verification, the $V(Cu)$ value was estimated on the basis of both the $L_3$ and $L_2$ data: for each sample the two $V(Cu)$ estimates agreed with each other within $\pm$0.01. In Fig. 3, the resultant $V(Cu)$ values (each value taken as an average of the two estimates) are given for the samples against $r(R^{III})$. For all the six Cu$_2$Ba$_2$RCu$_2$O$_8$ samples, $V(Cu)=2.255\pm0.005$, in excellent agreement with the value of 2.25 expected on the basis of stoichiometric oxygen content.

In the O K-edge spectra of the Cu-2212 samples shown in Fig. 4 three pre-edge peaks are distinguished below $\sim$530 eV. According to local-density approximation band-structure calculations15 and previous XANES data16 for Cu$_2$Ba$_2$YCu$_2$O$_8$, the peaks are assigned as follows: the most prominent peak at $\sim$528.3 eV is due to superposition of the hole states of the CuO$_2$ planes and the Cu$_2$O$_2$ double chain, the low-energy shoulder at $\sim$527.5 eV accounts for the hole states at the apical oxygen site, and the broad peak about 529–530 eV has its origin in the hole states of the upper Hubbard band (UHB). It is well known that for the $p$-type high-$T_c$ superconductive copper oxides the intensity of the peak due to UHB inversely correlates with the CuO$_2$-plane hole density, and at the same time it is believed not to have

FIG. 1. $T_c$ values for the Cu$_2$Ba$_2$RCu$_2$O$_8$ samples plotted against the ionic radius $r(R^{III})$, of the $R$ constituent.

FIG. 2. Representative example of the Cu $L_{2,3}$-edge XANES spectra obtained for the Cu$_2$Ba$_2$RCu$_2$O$_8$ samples (here $R$=Tm) and illustration of the fitting of the spectral features (in the $L_3$ area) into Cu$^{II}$ and Cu$^{III}$ components.

FIG. 3. Average valence of copper, $V(Cu)$, in the Cu$_2$Ba$_2$RCu$_2$O$_8$ samples as estimated from the Cu $L_{2,3}$-edge XANES spectra and plotted against $r(R^{III})$.

FIG. 4. O K-edge XANES spectra obtained for the Cu$_2$Ba$_2$RCu$_2$O$_8$ samples ($R$=Tm, Er, Ho, Y, Dy, and Gd).
FIG. 5. Variation of the relative intensities of the three pre-edge peaks in the O K-edge XANES spectra of the Cu$_3$Ba$_2$RuCu$_2$O$_8$ samples plotted against $r(R^{III})$: the 527.5 eV peak (due to hole states at the apical oxygen site), the 528.2 eV peak (due to hole states at the Cu$_2$O$_2$-double-chain and CuO$_2$-plane oxygen sites), and the UHB peak (inversely proportional to the CuO$_2$-plane hole states).

any correlation with the CuO-chain hole states.\textsuperscript{15–17} From Fig. 4, we can clearly see that for the present Cu-2212 samples the intensity of the UHB peak decreases with decreasing size of the $R$ constituent, i.e., going from Gd to Tm, indicating that the CuO$_2$-plane hole density increases with decreasing $r(R^{III})$. Since the total amount of holes remains constant, we may conclude that when the size of the $R$ constituent decreases, holes are gradually shifted from the Cu$_2$O$_2$ charge reservoir to the CuO$_2$ planes. To determine the different oxygen sites, we analyzed the spectral features by fitting the three pre-edge peaks with Gaussian functions. In Fig. 5, the relative peak intensities are plotted against $r(R^{III})$. In this figure, it is seen that with decreasing $r(R^{III})$ not only the intensity of the UHB peak but also that of the 527.5 eV peak decreases, whereas the 528.3 eV peak increases. The hole states residing at the apical oxygen site (527.5 eV peak) are commonly counted as part of the charge-reservoir holes.\textsuperscript{17} Hence the observed variations in the pre-edge peak intensities are all consistent with our conclusion that application of chemical pressure forces a portion of the Cu$_2$O$_2$-charge-reservoir holes to shift to the CuO$_2$ planes.

Now we are ready to propose an explanation for the different $T_c$ vs $r(R^{III})$ behaviors of the Cu-1212 and Cu-2212 systems. It is well known that the Cu-2212 superconductors are underdoped (unless $R$ is partly substituted by divalent calcium). This is why $T_c$ increases with decreasing $r(R^{III})$ and increasing CuO$_2$-plane hole density in Cu-2212. Fully oxygenated Cu-1212 superconductors, on the other hand, are in a slightly overdoped state. We suggest that also in this system holes are gradually shifted from the CuO$_{1-\delta}$ charge reservoir to the CuO$_2$ planes with decreasing $r(R^{III})$. (Earlier Seebeck\textsuperscript{18} and bond-valence-sum calculation\textsuperscript{19} data for CuBa$_2$RuCu$_2$O$_{2-\delta}$ are consistent with this view.) Therefore a decrease in $r(R^{III})$ decreases the value of $T_c$ as it makes the Cu-1212 phase more heavily overdoped.

In conclusion, we have synthesized high-quality samples of the Cu$_3$Ba$_2$RuCu$_2$O$_8$ superconductor system with $R$ constituents ranging from Gd to Tm and characterized them by means of iodometric titration and Cu L-edge and O K-edge XANES measurements for the overall and layer-specific hole contents, respectively. The results provided us with a clear explanation for the trend of increasing $T_c$ with decreasing size of the $R$ constituent among samples that possessed the same average Cu valence value. It was concluded that the smaller-for-larger $R$-cation substitution results in a shift of holes from the CuO$_2$ charge reservoir to the superconductive CuO$_2$ planes such that the hole-doping level of the CuO$_2$ planes increases. Since the Cu$_3$Ba$_2$RuCu$_2$O$_8$ samples are underdoped, such a shift of holes increases the value of $T_c$.

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