O-1s x-ray near-edge absorption spectroscopy studies of La$_{1.5-x}$Ca$_x$Ba$_{1.5}$Cu$_3$O$_y$ and La$_{1.5}$Ca$_x$Ba$_{1.5-x}$Cu$_3$O$_y$

Y. F. Song
Synchrotron Radiation Research Center, Hsinchu, Taiwan, Republic of China

C. N. Chang
Synchrotron Radiation Research Center, Hsinchu, Taiwan, Republic of China
and Department of Physics, National Taiwan Normal University, Taipei, Taiwan, Republic of China

H.-C. I. Kao
Department of Chemistry, Tamkang University, Tamsui, Taiwan, Republic of China

C. H. Hsieh and H. F. Liu
Department of Physics, National Taiwan Normal University, Taipei, Taiwan, Republic of China

H. D. Lin and W. W. Huang
Department of Chemistry, Tamkang University, Tamsui, Taiwan, Republic of China
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The O-1s x-ray near-edge-absorption spectra of La$_{1.5-x}$Ca$_x$Ba$_{1.5}$Cu$_3$O$_y$ and La$_{1.5}$Ca$_x$Ba$_{1.5-x}$Cu$_3$O$_y$ have been measured by using synchrotron radiation. Their spectral features of the pre-edge spectra indicate that there is an electronic structure change similar to the effect of Pr in Y$_{1-x}$Pr$_x$Ba$_2$Cu$_3$O$_{7-\delta}$; the holes on the CuO$_2$ planes increase with the doping concentration of Ca ions; not all the excess oxygen (for $y \gtrsim 7.0$) in the basal plane supply holes; and there is a sign of increasing, rather than decreasing, the holes around the apical oxygen O(4) with the increase of the replacement of Ba by La on the Ba sites, an indication of a redistribution of holes. [S0163-1829(99)03930-2]

I. INTRODUCTION

A series of single-phase La$_{1.5-x}$Ca$_x$Ba$_{1.5}$Cu$_3$O$_y$ ($0 \leqq x \leqq 0.5$) and La$_{1.5}$Ca$_x$Ba$_{1.5-x}$Cu$_3$O$_y$ ($0 \leqq x \leqq 0.5$) compound with tetragonal symmetry (similar to the YBa$_2$Cu$_3$O$_y$ nonsuperconducting phase) had been prepared and studied by x-ray powder diffraction using Rietveld analysis.[1] It was found that the Ca ions were solely on the Y sites and the rest were occupied by La^{3+} for $x \leqq 0.4$. Therefore, La$_{1.5-x}$Ca$_x$Ba$_{1.5}$Cu$_3$O$_y$ can be written as (La$_{1-x}$Ca$_x$)(Ba$_{1.5}$La$_{0.5}$)Cu$_3$O$_y$, and La$_{1.5}$Ca$_x$Ba$_{1.5-x}$Cu$_3$O$_y$ as (La$_{1-x}$Ca$_x$)(Ba$_{1.5-x}$La$_{0.5+x}$)Cu$_3$O$_y$ for $x \leqq 0.4$. Referring to the lattice structure of YBa$_2$Cu$_3$O$_y$, (La$_{1-x}$Ca$_x$) represents the ions on the Y site, while (Ba$_{1.5}$La$_{0.5}$) and (Ba$_{1.5-x}$La$_{0.5+x}$) represent the ions on the Ba sites. It is clear that the only difference between these two series of samples is the elements on the Ba sites; one remains to be (Ba$_{1.5}$La$_{0.5}$), while the other varies with x as (Ba$_{1.5-x}$La$_{0.5+x}$).

La$_{1.5}$Ba$_{1.5}$Cu$_3$O$_y$ ($x = 0$) is a semiconductor and will become a superconductor with Ca^{2+} doping. The superconductivity appears in La$_{1.5-x}$Ca$_x$Ba$_{1.5}$Cu$_3$O$_y$ (abbreviated as LC-123) for $x \geqq 0.15$ and in La$_{1.5}$Ca$_x$Ba$_{1.5-x}$Cu$_3$O$_y$ (abbreviated as BC-123) for $x \geqq 0.25$. The superconductivity was attributed to the increase of holes in the CuO$_2$ planes by Ca^{2+} doping. The method of Tokura *et al.*[2] was used by Kao *et al.*[1] to assign the number of holes in the CuO$_2$ plane and in the chain. No universal correlation between the holes in the

CuO$_2$ planes and the T_c of both series of La$_{1.5-x}$Ca$_x$Ba$_{1.5}$Cu$_3$O$_y$ and La$_{1.5}$Ca$_x$Ba$_{1.5-x}$Cu$_3$O$_y$ was found. They found instead, a universal curve of $\Delta F = OF_{Ca/Y} - OF_{La/Ba}$ versus T_c, where $OF_{Ca/Y}$ and $OF_{La/Ba}$ designate, respectively, the occupation factor of Ca on the Y site and La on the Ba site. This inspired our interest to look into this matter by using O-1s x-ray near-edge-absorption spectroscopy to directly probe the hole around each oxygen site (the site of each oxygen is shown in Fig. 1) since O-1s x-ray near-edge-absorption spectra (XNEAS) of YBa$_2$Cu$_3$O$_y$ and other relevant compounds have been studied and proved to contain the information of the distribution of holes on different oxygen sites, namely the O(2,3) (in the CuO$_2$ planes), O(1) (in the CuO chain) and O(4) (the apical oxygen surrounded by four barium ions).[3,4] We thus conduct an experiment to measure the O-1s XNEAS of the two series of LC-123 and BC-123.

In this paper, we will show that the holes in the CuO$_2$ planes indeed play a major role in the transition of nonsuperconductivity to superconductivity by doping Ca^{2+} ions in La$_{1.5}$Ba$_{1.5}$Cu$_3$O$_y$. In addition, we observe an indication of the increase of holes on the O(4) site with the increase of x in BC-123. It appears that the hole will be redistributed when the La^{3+} substitution of Ba^{2+} increases. No such redistribution is indicated in LC-123 due to the constant percentage of La^{3+} substitution of Ba^{2+}.

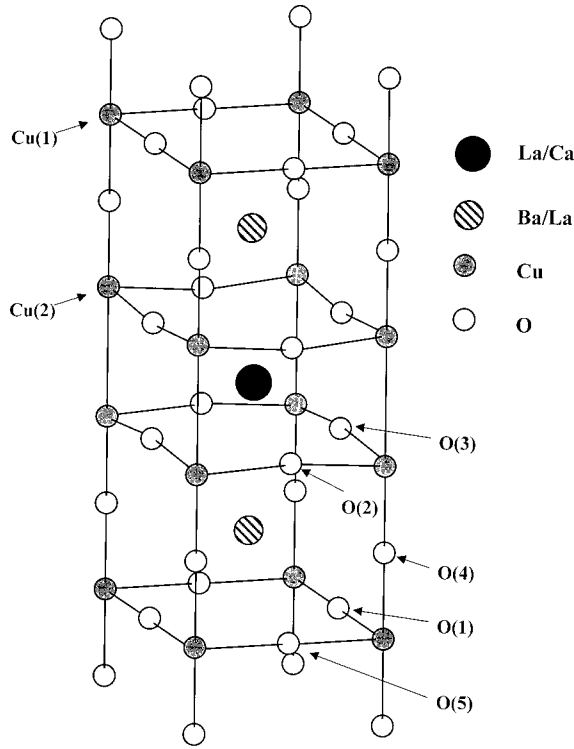Although there is intercalation of oxygen in the basal plane in excess of the O$_7$ stoichiometry to compensate the

FIG. 1. The sketch of the lattice structure of the perovskite cuprate $La_{1.5}Ba_{1.5}Cu_3O_y$.

hole reduction by the La^{3+} substitution of Ba^{2+} in both LC-123 and BC-123, the compensation is found incomplete or partial for a large amount of La^{3+} substitution of Ba^{2+} similar to what found in $YBa_{2-x}La_xCu_3O_{7+\delta}$.[5] This fact was apparently ignored in the use of the method of Tokura *et al.* to assign the total number of holes as well as the holes in the CuO_2 planes (P_{sh}) and in the chain (P_{ch}) for LC-123 and BC-123. We will make a comment based on our O-1s XNEAS data in the last section.

II. EXPERIMENTS

The samples used in this study had been prepared and characterized by x-ray powder diffraction to be a single-phase tetragonal structure.[1] The volume of the unit cell was found to decrease with the increase of the doping concentration in both series of $La_{1.5-x}Ca_xBa_{1.5}Cu_3O_y$ (LC-123) and $La_{1.5}Ca_xBa_{1.5-x}Cu_3O_y$ (BC-123). The Rietveld analysis was used to reveal the occupation site of Ca^{2+}. Up to $x=0.4$, all the doped Ca^{2+} was found on the Y site. When $x>0.4$, some Ca^{2+} would go to the Ba site. The oxygen content and the T_c had been determined, respectively, by the iodometric method[6] and the four-point-probe method. Their values are listed in Table I.

The synchrotron radiation from the high-energy spherical grating monochromator beam line at the Synchrotron Radiation Research Center (SRRC), Taiwan, R.O.C. is used to

TABLE I. P_{sh}, P_{ch}, and P defined in the text are the calculated values by using the method of Tokura *et al.* The values of P_{ex} are the total number of holes per unit cell derived from the pre-edge spectra of the O-1s XNEAS. y and T_c are, respectively, the oxygen content and the onset superconducting transition temperature. The numbers in the parentheses are the errors of the last digit.

x	y	P_{sh}	P_{ch}	P	P_{ex}	T_c(onset)
		$La_{1.5-x}Ca_xBa_{1.5}Cu_3O_y$	(LC-123)			
0	7.200(2)	0.200	0.700	0.900	0.79(1)	
0.05	7.164(2)	0.214	0.664	0.878	0.82(1)	
0.10	7.104(2)	0.204	0.604	0.808	0.83(1)	
0.15	7.095(4)	0.245	0.595	0.840	0.84(1)	48.3
0.20	7.086(3)	0.286	0.586	0.872	0.89(1)	58.6
0.25	7.085(2)	0.335	0.585	0.920	0.91(1)	74.1
0.30	7.061(4)	0.361	0.561	0.922	0.92(1)	80.9
0.35	7.053(2)	0.403	0.553	0.956	0.95(1)	84.3
0.40	7.008(2)	0.408	0.508	0.916	0.91(1)	82.2
0.45[a]	7.000(2)	0.450	0.500	0.950	0.91(1)	83.3
0.50[a]	6.945(2)	0.445	0.445	0.890	0.85(1)	83.7
		$La_{1.5}Ca_xBa_{1.5-x}Cu_3O_y$	(BC-123)			
0	7.200(2)	0.200	0.700	0.900	0.79(1)	
0.05	7.184(2)	0.184	0.684	0.868	0.83(1)	
0.10	7.158(2)	0.158	0.658	0.816	0.80(1)	
0.15	7.165(2)	0.165	0.665	0.830	0.81(1)	
0.20	7.225(2)	0.225	0.725	0.950	0.82(1)	
0.25	7.175(3)	0.175	0.675	0.850	0.83(1)	41.8
0.30	7.196(4)	0.196	0.696	0.892	0.84(1)	51.2
0.35	7.225(2)	0.225	0.725	0.950	0.80(1)	53.6
0.40	7.231(1)	0.231	0.731	0.962	0.85(1)	77.6
0.45[a]	7.251(2)	0.251	0.751	1.000	0.81(1)	64.9
0.50[a]	7.227(3)	0.227	0.727	0.954	0.79(1)	62.2

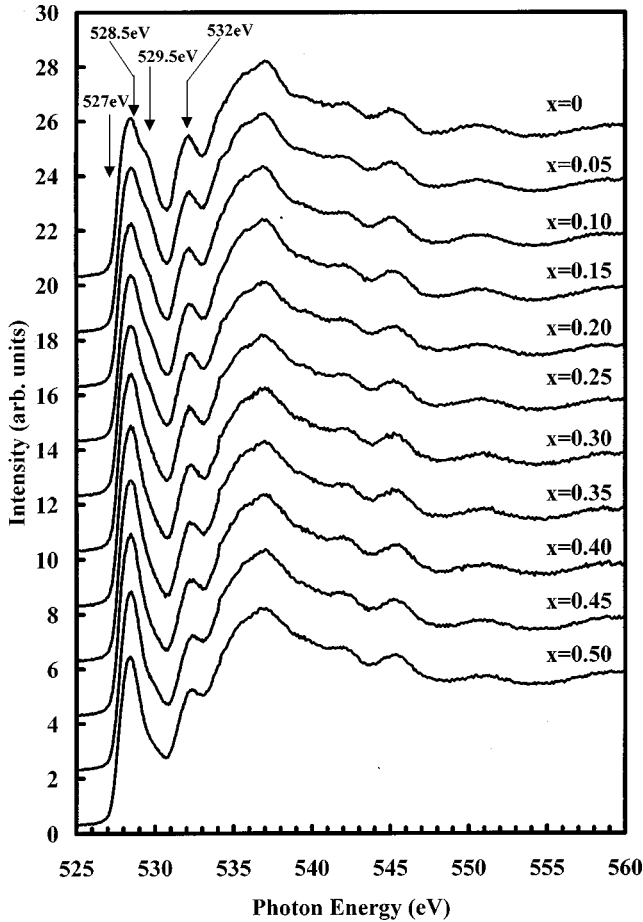[a]P_{sh}, P_{ch}, and P are calculated by assuming the Ca ions are solely on the Y sites.

FIG. 2. The O-1*s* XNEAS of $La_{1.5-x}Ca_xBa_{1.5}Cu_3O_y$ for $x = 0$ to 0.5. The threshold energy 527.0 eV and the main peak energies about 528.5 and 529.5 eV of the pre-edge are indicated by arrows. The peak of 532 eV (see text) is also indicated.

FIG. 3. Same as Fig. 2 but for $La_{1.5}Ca_xBa_{1.5-x}Cu_3O_y$.

measure the O-1*s* XNEAS. The energy resolution of the photon beam is adjusted to be 0.25 eV at about 530 eV. The openings of both the entrance and exit slits are at 30 μm. Although the oxygen K x-ray fluorescence yield (XFY) is measured by a seven-element Ge detector to obtain the x-ray-absorption spectrum, the sample current generated by the photoabsorption is also monitored. Since the latter is surface sensitive, a signal coming from the surface defect of the sample can be readily detected. No substantial surface effect is observed for all the series of samples used in this study. This is in contrast to the fully oxygenated $YBa_2Cu_3O_{7-\delta}$ (YBCO), its surface was always observed to be oxygen deficient.

All the spectra obtained from the XFY detection have been normalized such that the absorption intensity between 550–560 eV is the same. The x-ray self-absorption effect on the intensity of the normalized spectrum has also been corrected by using the same method as we did for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.[7] The final spectra are shown in Fig. 2 and Fig. 3, respectively, for LC-123 and BC-123.

III. RESULTS AND DISCUSSION

A. Spectrum above the energy of 531 eV

The spectral structure above 537 eV looks very much the same for both series of samples. The spectral similarity of
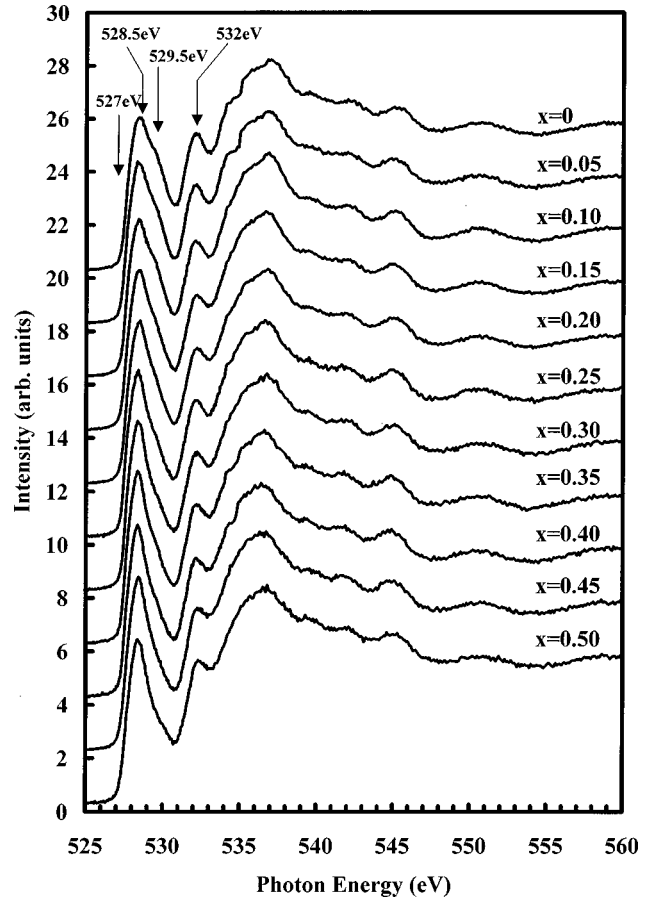
this energy region is extended to other samples we have studied, such as $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ (Ref. 7) and $Y(Ba_{1-x}Sr_x)_2Cu_3O_{7-\delta}$.[8] This observation supports the suggestion made by Nücker *et al.*[9] that they probably related to the presence of unoccupied states of oxygen p character from the covalent mixing of the copper and the oxygen states. No correlation with T_c has ever been found in this portion of the spectral structure.

The rapid rise of the portion of the spectrum starting from 531 to 537 eV can be attributed to the unoccupied states of oxygen p character. They are the covalent mixing states of the oxygen states and the states of metal cations other than copper, such as Ba 5d and 4f, and La 5d and 4f, etc. The relative pronounced peak at 532 eV has also been observed previously in the study of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.[4,7] The shift of the peak energy as well as the variant of the peak intensity is observed to be very similar to that of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. In $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, it was ascribed to coming from the hybridization of the Pr $4f_{z(x^2-y^2)}$ and O $2p_\pi$ states,[10] and therefore, this peak is probably induced by the hybridization of the La $5d4f$ states (on the Y site) and the oxygen $2p$ states. As shown in Fig. 2 and Fig. 3, its energy is observed to shift to higher energy and its intensity becomes smaller with the increase of the concentration of Ca. Both of these phenomena indicate that the La occupation on the Y site is decreased when the Ca concentration is increased, in agreement with the result of the Rietveld analysis of the x-ray powder diffraction data aforementioned in the previous section.
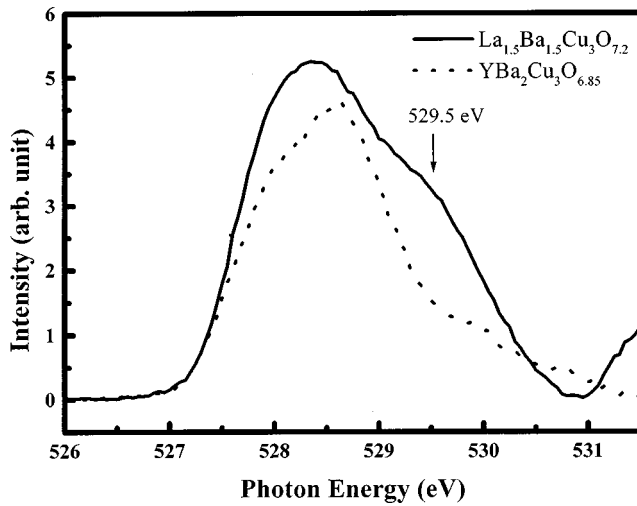
FIG. 4. The comparison of the pre-edge spectra between $La_{1.5}Ba_{1.5}Cu_3O_{7.2}$ and $YBa_2Cu_3O_{6.85}$. The smooth backgrounds of both spectra have been subtracted. The position of the peak corresponding to about 529.5 eV is also indicated.

B. Pre-edge spectrum

The portion of the spectrum in the energy range of 527–530 eV is called the pre-edge of the spectrum. The profile of the pre-edge spectra of the two series of samples are similar to that of $YBa_2Cu_3O_{6.85}$ ($T_c = 91.5$ K) observed in our previous work,[7,8] but the spectral intensity is distributed differently. In Fig. 4, we compare the profile of $La_{1.5}Ba_{1.5}Cu_3O_{7.2}$ and $YBa_2Cu_3O_{6.85}$. One notices immediately that the rise of the edge starting from the threshold at about 527 eV is steeper for $La_{1.5}Ba_{1.5}Cu_3O_{7.2}$. This steep rise of the edge persists for all other samples in the series of LC-123 and BC-123. Next, the shoulder at about 529.5 eV is seen more pronounced in $La_{1.5}Ba_{1.5}Cu_3O_{7.2}$ than in $YBa_2Cu_3O_{6.85}$. Its energy is smaller in $La_{1.5}Ba_{1.5}Cu_3O_{7.2}$ than in $YBa_2Cu_3O_{6.85}$. The energy shift of this shoulder is similar to that of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. In the O-1$s$ XNEAS study of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, this energy shift is attributed to the rise of both the binding energy of the O-1s level and the Fermi level in the valence band but leaves the energy of the upper Hubbard band unchanged due to the presence of the Pr ions on the Y sites.[4,7] A similar change of the energy level of the O-1s state and the Fermi level in the valence band can occur in LC-123 and BC-123 due to the presence of La^{3+} ions on the Y sites for the size of the La^{3+} ion being larger than that of the Pr^{3+} ion and its ionicity being comparable to that of Pr^{3+}. However, the energy shifts of this peak among the samples in both series of LC-123 and BC-123 are not so noticeable within the limit of our spectroscopic resolution.

In order to look into the spectral weight in the pre-edge spectrum more clearly, we compare the differences of the pre-edge spectra of $x = 0$, 0.1, 0.2, 0.3, and 0.4 in Fig. 5 for LC-123 and BC-123. In Fig. 5, the spectral differences relative to $x = 0$ are plotted. For clarification, not all the spectral differences are shown. The spectra of $x > 0.4$ are rejected in the figures for the partial occupation of Ca^{2+} on the Ba site. It appears that the peak height at about 529.5 eV decreases whenever the peak height at about 528.5 eV increases. This feature has been observed in YBCO with different oxygen content.[3,11] In combination with the studies of the experiment
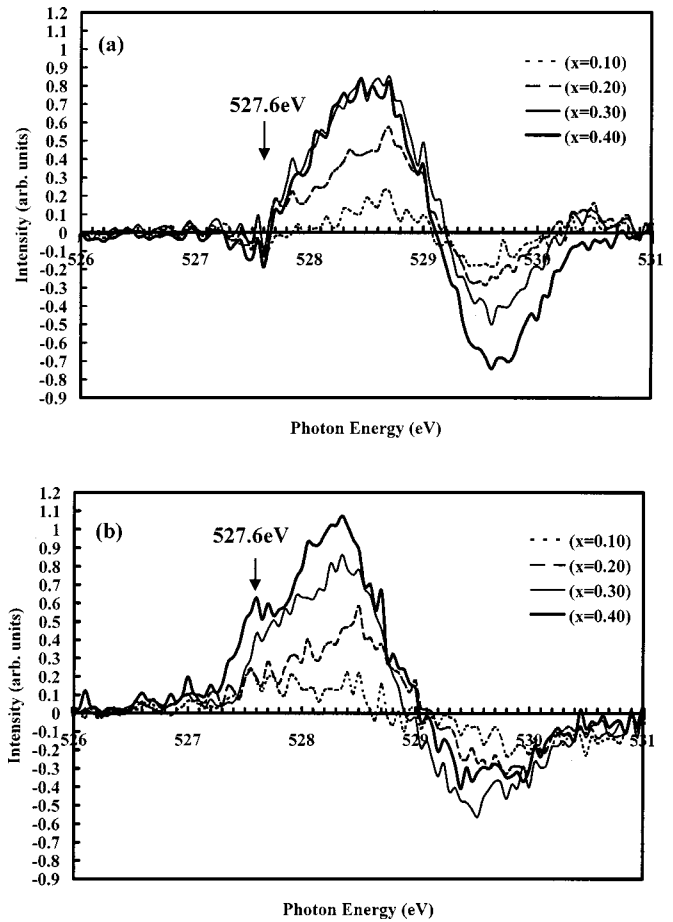

FIG. 5. The spectral difference of the pre-edge spectra relative to the one with $x=0$ for (a) $La_{1.5-x}Ca_xBa_{1.5}Cu_3O_y$ and (b) $La_{1.5}Ca_xBa_{1.5-x}Cu_3O_y$. For the purpose of clarification, only $x = 0.1$, 0.2, 0.3, and 0.4 are plotted. The energy corresponding to the pre-edge of O(4) is indicated.

and the theory,[12] one concludes that it comes from the change of the electronic structure in the CuO_2 planes induced by the change of the number of holes in those planes. Similar change of these two spectral weights was also observed in $La_{2-x}Sr_xCuO_4$ and the same interpretation was given.[13]

Based on the multiband calculation,[12] the peak at 528.5 eV is due to the transitions from the O-1s states to the Fermi level in the valence band. The peak at 529.5 eV is due to the transitions to the conduction band (the upper Hubbard band with mainly Cu 3d character). The counter change of the spectral weight of these two spectral lines correlates with the hole doping in the CuO_2 planes, which will form the hole states (the Zhang-Rice singlet states)[14] in the valence band. When the hole doping increases in the CuO_2 planes, the number of hole states increases and the spectral weight of 528.5 eV increases and that of 529.5 eV decreases accordingly. With this in mind, our data as shown in Fig. 2 and Fig. 3, or more clearly in Fig. 5, indicate that the number of holes in the CuO_2 is increased by the Ca doping, qualitatively in agreement with the results given by using the method of Tokura *et al.* The total number of holes P, the number of holes in the CuO_2 planes P_{sh}, and the number of holes in the chain P_{ch} calculated by using the method of Tokura *et al.* are listed in Table I for reference. In the method of Tokura *et al.*, the total number of holes P is calculated by using the for-

mula $Q+6+P=2y$, where Q is the total charge of the non-copper cations, and y is the oxygen contents. This formula is derived on the basis of an ionic model. P_{ch} is obtained by a formula of $P_{ch}=y-6.5$ as derived by looking at a lot of 123 materials in which La substitution on the Ba site, Ca substitution on the Y site were made, and the substitution concentration as well as the oxygen content is purposely varied. And P_{sh} is obtained by $P_{sh}=P-P_{ch}$. We will not attempt to make a quantitative comparison of P_{sh} and P_{ch} between our data and the values obtained by the method of Tokura *et al.* since the pre-edge spectrum contains components from the oxygen sites other than the O(2,3) in the CuO$_2$ planes. It is hard to separate them even though a curve-fit analysis has been tried.[7,8] The peak at about 529.5 eV is, however, relatively uncontaminated by the others and it can be separated by using the curve-fit analysis method aforementioned. A quantitative comparison of the total number of holes P between our data and the value obtained by the method of Tokura *et al.* (based purely on an ionic model) becomes therefore possible.

For separating the peak relevant to the conduction band (at about 529.5 eV) from the other components relevant to the valence band, we use four Gaussians to fit the profile of the pre-edge spectrum. The width, height, and position of these Gaussians are free parameters of the fitting. However, in the first attempt, the width, height, and position of each component in the spectrum are chosen by looking up the spectra of the different oxygen sites as obtained from a polarization-dependent x-ray absorption spectroscopy study on single crystals of YBCO.[3] The width of each spectrum in Ref. 3 for each oxygen site is different, ~1.4 eV for O(4), and ~0.9 eV for O(2,3), much larger than the width of the core level of oxygen. The broadening of the x-ray-absorption spectrum must stem from the electronic structure of the valence band.

A typical fit is shown in Fig. 6 for La$_{1.5}$Ba$_{1.5}$Cu$_3$O$_{7.2}$, La$_{1.2}$Ca$_{0.3}$Ba$_{1.5}$Cu$_3$O$_{7.061}$, and La$_{1.5}$Ca$_{0.3}$Ba$_{1.2}$Cu$_3$O$_{7.196}$. Here, one notes that the centers of the four Gaussians are respectively, at 527.8, 528.5, 529.4, and 530.1 eV. From previous studies,[3,4,7,8] the first and the second Gaussians can be regarded as coming mainly from the transitions to the Fermi level in the valence band of the apical oxygen O(4), and of O(2,3) in the CuO$_2$ planes, respectively. Some contributions from O(1) in the CuO chain is inevitable. The last two Gaussians can be regarded as the transitions to the conduction band of O(2,3) in the CuO$_2$ planes. The sum of the area of the first two Gaussians thus can be regarded as a measure of the total number of holes of the sample. In order to compare the measured value with the calculated one on the basis of the ionic model, we assume that the corresponding intensity of this portion of spectrum in YBa$_2$Cu$_3$O$_{6.85}$ be 0.7 per unit cell. The spectrum of YBa$_2$Cu$_3$O$_{6.85}$ has been taken in our previous work on the study of Y$_{1-x}$Pr$_x$Ba$_2$Cu$_3$O$_{7-\delta}$ (the experimental setup is identical to the present work) and the spectral intensity of this portion is 120.5 ± 6.0. By using the spectral intensity equivalent of holes/unit cell, 120.5/0.7, we obtain the total number of holes per unit cell for the series of samples of LC-123 and BC-123. These values as well as the values calculated by the ionic model are listed in Table I for comparisons.
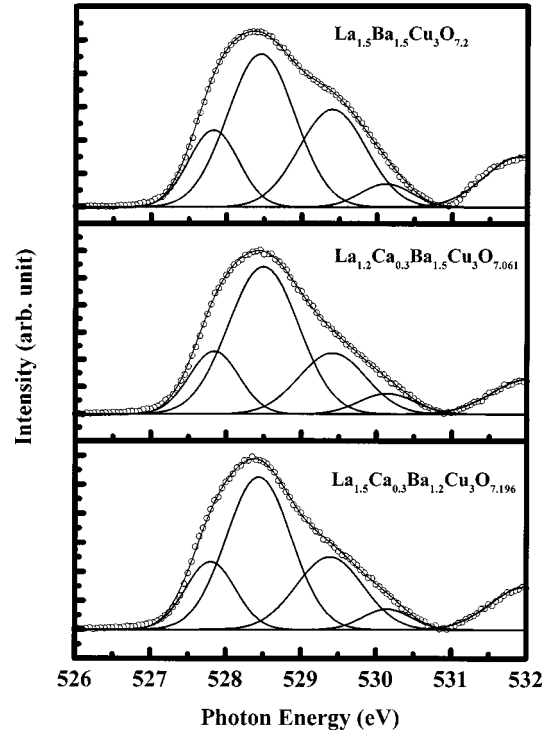

FIG. 6. Some typical curve-fit pre-edge spectra of La$_{1.5-x}$Ca$_x$Ba$_{1.5}$Cu$_3$O$_y$ and La$_{1.5}$Ca$_x$Ba$_{1.5-x}$Cu$_3$O$_y$. The solid curves are the four Gaussians, while the lighter solid curves are the sum of the four Gaussians. The experimental data are shown by open circles.

The overall agreement between the calculated and the measured values is better for LC-123 than for BC-123. The discrepancies are observed mostly to occur in the samples of high content of oxygen. In BC-123, a better agreement occurs for the oxygen content of about 7.17 or less. In LC-123, it is about 7.1 or less, and a large discrepancy is observed for Ca concentration $x<0.1$, where the oxygen contents are greater than 7.15.

Furthermore, we note that in terms of the ionic model, the holes will come solely from the oxygen in the basal plane, and independent of the doping concentration of Ca in BC-123. Because in BC-123 there is a La to be repelled to the Ba site for adding every one Ca in the Y site. The hole increased by Ca on the Y site will be canceled by La on the Ba site. Accordingly, the necessary oxygen contents required to give the measured number of hole per unit cell can be calculated from the ionic model. They are 7.145–7.175 for BC-123, a slight increase with the Ca concentration x. The actual oxygen contents as shown in Table I are mostly higher than these values. This indicates that some of the oxygen in the basal plane does not dope holes. We attribute it to that the oxygen may intercalate as dimeric, O$_2^{2-}$ peroxide ions rather than as a monomeric species assumed in the ionic model calculation. The presence of dimeric O$_2^{2-}$ peroxide ions on the basal planes was first suggested by Manthiram *et al.* in their studies of YBa$_{2-x}$La$_x$Cu$_3$O$_{7-\delta}$.[5]

The apical oxygen O(4) was suggested to play a significant role in the superconductivity of the superconducting cuprates.[15] We are interested in looking into the spectral difference around the threshold where the apical oxygen O(4)

contributes the most, although as aforementioned, it is hard to obtain a quantitative hole distribution from the pre-edge spectrum of a powder sample. Since in BC-123, the La^{3+} occupation on the Ba site is increased by Ca^{2+} doping, while it remains unchanged in LC-123, and thus one would expect that there is no difference between the pre-edge spectra of the sample in the LC-123 series around the threshold. And we indeed find no significant difference as show in Fig. 5(a) around the threshold. However, some differences are found in the BC-123 series as shown in Fig. 5(b). The spectral intensity close to 527.6 eV increases with the doping concentration of Ca, x, in BC-123. This should not be the case in term of the ionic model since more concentration of Ca will let more La^{3+} occupy on the Ba site, and the holes there will become less because of the hole filling by the additional electron given by La^{3+} on the Ba site. The spectral intensity of O(4) should decrease with x, not opposite as we observe in this work. Our observation indicates that a redistribution of holes occurs when La^{3+} is on the Ba site.

IV. SUMMARY AND REMARKS

The O-1s x-ray near-edge-absorption spectra of $La_{1.5-x}Ca_xBa_{1.5}Cu_3O_y$ (LC-123) and $La_{1.5}Ca_xBa_{1.5-x}Cu_3O_y$ (BC-123) have been measured by using synchrotron radiation. Their spectral features of the pre-edge spectra indicate that (1) there is an electronic structure change induced by La on the Y site similar to what happened in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ induced by Pr on the Y site; (2) the hole on the CuO_2 planes increase with the doping concentration of Ca ions; (3) the excess oxygen (for $y \geqq 7.0$) in the basal plane induced by the La substitution of Ba on the Ba site supplies holes, too, but incomplete; and (4) there is a sign of increasing the holes at the apical oxygen O(4) in

BC-123 with the increase of the replacement of Ba by La, indicating a redistribution of holes.

The increase of holes on the CuO_2 planes is in agreement with the x-ray Rietveld analysis, which showed that all the Ca ions occupied the Y sites for $x \leqq 0.4$. The increase of Ca occupation on the Y sites will dope more holes in the CuO_2 planes. The reason that the method of Tokura et al. cannot give a universal correlation between the holes on the CuO_2 planes and the T_c may rest on the fact that not all the excess oxygen in the basal plane provides holes. As to why both of the series of samples show that the change of T_c with $\Delta F = OF_{Ca/Y} - OF_{La/Ba}$ remains open. Nevertheless, by considering the redistribution of holes induced by the replacement of Ba by La, it looks like the ΔF may be a better value to represent the holes in the CuO_2 planes than the value of P_{sh} that was calculated by the method of Tokura et al. by full account of the holes supplied by the excess oxygen in the basal plane. In LC-123, $OF_{La/Ba}$ remains constant for all Ca concentration x, and ΔF simply describes the change of the hole on the CuO_2 planes by $OF_{Ca/Y}$. While in BC-123, both $OF_{La/Y}$ and $OF_{La/Ba}$ are increased with x, and ΔF describes the change of the hole on the CuO_2 plane by $OF_{Ca/Y}$ but reduced by the amount of $OF_{La/Ba}$. And therefore, ΔF in BC-123 might have implicitly taken the holes transferred from the CuO_2 planes to the chain [namely, to O(4)] into account.

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