Electronic structure in \((\text{Hg}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7\) compounds studied by soft X-ray absorption spectroscopy

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Abstract

We report O K-edge and Cu L\(_{2,3}\)-edge X-ray-absorption near-edge-structure (XANES) spectra for the series of \((\text{Hg}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7\) compounds \((x = 0.3-0.7)\) obtained using a bulk-sensitive total-X-ray-fluorescence-yield technique. Near the O 1s edge, the pre-edge peak with maxima at \(\sim 528.3\) eV is ascribed to the transitions to O 2p holes located in the CuO\(_2\) planes. The intensity of this pre-edge peak monotonically increases with increasing doping level of Ca\(^{2+}\) into the \(\text{Y}^{3+}\) sites. The effect of chemical substitution of Ca\(^{2+}\) for \(\text{Y}^{3+}\) in \((\text{Hg}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7\) is to induce O 2p hole states in the CuO\(_2\) planes near the Fermi level which cause an increase of \(T_c\) from 15 K for \(x = 0.6\) to 90 K for \(x = 0.3\). Moreover, the generation of O 2p holes within the CuO\(_2\) planes is probably responsible for inducing a transition from a semiconductor to a superconductor. In the Cu L-edge absorption spectra, high-energy shoulders at 933.2 and 953.0 eV are attributed to the transitions to \(\text{Cu}(2\text{P}_{3/2,1/2})\text{L}\) states in the CuO\(_2\) layers, where L denotes the O \(2p\) ligand hole. The behavior of these shoulders correlates with that of the pre-edge peak at \(\sim 528.3\) eV in the O K-edge absorption spectra.

1. Introduction

The discovery of high superconducting transition temperature \((T_c)\) in the mercury-based Hg-Ba-Ca-Cu-O compounds has generated intense research aimed both at increasing the \(T_c\) value and understanding mechanisms of high-\(T_c\) superconductivity. The new Hg-containing Ba-based HgBa\(_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}\) compounds have been found for \(n = 1, 2,\) and 3 with \(T_c\) around 97, 128 K and 135 K, respectively \([1-3]\). Recently, \(T_c\)'s can be increased to over 150 K when the HgBa\(_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}\) (HgBa-1223) phase is subjected to quasihydrostatic pressure above 10 Gpa \([4,5]\). Several local-density approximation band-structure calculations on the HgBa\(_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}\) series for \(n \leq 4\) have been performed which reveal an insight into the electronic structure of these compounds \([6-8]\). However, the experimental studies on the electronic structure in Hg-based cuprates are still in infancy.

In addition, to date, the isotropic Sr-based cuprates, corresponding to the formula HgSr\(_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}\), have been not synthesized. Recently, Hu et al. have demonstrated, for the first time, that the stabilization of the strontium-based cuprates can be performed by the combined substitution of Pb and Y ions into the Hg and Ca sites, respectively, resulting in a new series of Hg-containing Sr-based super-
conducting \((\text{Hg}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7\) compounds with \(T_c\) around 90 K for \(x = 0.3\) [9]. This new high-\(T_c\) superconducting system has a space group of \(P4/nmm\) with a tetragonal unit cell of \(a = 3.8159\) Å and \(c = 11.950\) Å. The crystal structure of \((\text{Hg}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7\), as illuminated in Fig. 1, is similar to that of \(\text{HgBa}_2\text{CaCu}_2\text{O}_6+\delta\) but with some Hg replaced by Pb in the rock-salt layers and Ba totally replaced by Sr [10]. The superconducting transition temperatures \((T_{c,\text{midpoint}})\) plotted against the compositional parameter \(x\) in \((\text{Hg}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7\) are shown in Fig. 2 [9,10]. The substitution of \(\text{Ca}^{2+}\) for \(\text{Y}^{3+}\) increases the superconducting temperature from \(T_c = 15\) K for \(x = 0.6\) to \(T_c = 90\) K for \(x = 0.3\). For \(x < 0.3\), the hole concentration could not be further increased, which may arise from the solubility limit of Ca incorporated in the Y sites being about 70%. Consequently, the superconducting transition temperature decreases and also becomes broader for the \(x = 0.2\) sample, perhaps due to the contribution from the impurity phases [9].

In \((\text{Hg}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7\) system, a change in the electronic structure arisen from chemical substitution can lead to a transition from a semiconductor to a superconductor. To date, the precise mechanism of high-temperature superconductivity has been not delineated. A precise knowledge of the electronic structure of cuprate superconductors is an important step toward the comprehensive understanding of the origin of high-\(T_c\) superconductivity. Therefore, direct experimental information on the electronic structure of these compounds is of great importance. In this study, \(\text{O}\) 1s and \(\text{Cu}\) 2p X-ray absorption measurements were applied to probe the changes in the electronic structure of Hg-containing Sr-based \((\text{Hg}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7\) compounds.

2. Experimental

The detailed procedures for making the \((\text{Hg}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7\) compounds have been reported elsewhere [9]. In brief, the \((\text{Hg}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7\) samples were prepared by mixing high-purity powders of PbO, HgO, SrO, CaO, \(\text{Y}_2\text{O}_3\), and \(\text{CuO}\). This mixtures were then pressed into pellets. These were wrapped in gold foil to prevent the loss of lead as well as mercury and then encapsulated in an evacuated (~\(10^{-4}\) Torr) quartz tube. Subsequently, the pellets were heated at a rate of 10°C/min up to 970°C for 24 h and then cooled to room temperature at 2°C/min. After heat treatment, all samples showed a black coloration.

In the X-ray absorption measurements, each sintered sample was crushed into powder form. The
resulting powder was glued onto a carbon-based conducting tape. The X-ray absorption measurements were carried out on the 6-m high-energy spherical grating monochromator (HSGM) beamline of the Synchrotron Radiation Research Center (SRRC) in Taiwan. The X-ray-fluorescence yield spectra were recorded using a microchannel plate (MCP) detector [11]. This detector consists of a dual set of MCP’s with an electrically isolated grid mounted in front of them. For X-ray fluorescence detection the grid was set to a voltage of 100 V, while the front of the MCPs was set to $-2000$ V, and the rear to $-200$ V. The grid bias insured that positive ions would not be detected while the MCP bias insured that no electrons were detected. The MCP detector was located $\sim 2$ cm from the sample and oriented parallel to the sample surface. Photons were incident at an angle of 45 with respect to the sample normal. The incident photon flux ($I_0$) was monitored simultaneously by a Ni mesh located after the exit slit of the monochromator. All the absorption measurements were normalized to $I_0$. The photon energies were calibrated within accuracy of 0.1 eV using the O K-edge absorption peak at 530.1 eV and Cu L$_3$ white line at 931.2 eV of CuO compound. The energy resolution of the monochromator was set to ~ 0.25 eV and ~ 0.5 eV at O 1s and Cu 2p absorption edges, respectively. All the measurements were carried out at room temperature.

3. Results and discussion

In Fig. 3 we show O K-edge X-ray-absorption near-edge structure (XANES) spectra for the series of (Hg$_{0.5}$Pb$_{0.5}$)Sr$_2$(Ca$_{1-x}$Y$_x$)$_2$O$_7$ compounds with $x = 0.3, 0.5, 0.6, and 0.7$ obtained using the total-X-ray-fluorescence-yield detection method. These spectra have been normalized to have the same height at the main peak of $\sim 537$ eV.

![Fig. 3. O K-edge X-ray-absorption near-edge-structure spectra for the series of (Hg$_{0.5}$Pb$_{0.5}$)Sr$_2$(Ca$_{1-x}$Y$_x$)$_2$O$_7$ compounds with $x = 0.3, 0.5, 0.6, and 0.7$ obtained using the total-X-ray-fluorescence-yield detection method. These spectra have been normalized to have the same height at the main peak of $\sim 537$ eV.](image)

absorption spectra for various compounds with different $x$ values in Fig. 3 were normalized to have the same height at the main peak of $\sim 537$ eV.

At high level of Ca doping for $x \leq 0.6$, this gives rise to a new pre-edge feature at $\sim 528.3$ eV. Based on the recent studies of electronic structures in the HgBa$_2$Ca$_{n-1}$Cu$_{n+2}$O_{10+8} compounds for $n \leq 3$ by Pellegrin et al. [13], they have assigned the low-energy pre-edge peak at $\sim 528.2$ eV to O 2p hole states within the CuO$_2$ planes. This assignment was supported by the polarized X-ray absorption measurements on single-crystalline HgBa$_2$Ca$_2$Cu$_4$O$_8$ compounds [13]. Furthermore, based on the X-ray photoemission spectroscopy studies on the O 1s core levels of epitaxial HgBa$_2$CaCu$_2$O$_{6+\delta}$ (HgBa-1212) films, the O 1s binding energy in the CuO$_2$ planes is smaller than that in the BaO layers [14]. The structural arrangement of (Hg$_{0.5}$Pb$_{0.5}$)Sr$_2$(Ca$_{1-x}$Y$_x$)$_2$O$_7$ (HgSr-1212) is similar to that of HgBa$_2$CaCu$_2$O$_{6+\delta}$ (HgBa-1212). We therefore adopt the same scheme in the discussion of the present data. In analogy to results from other p-type cuprate superconductors
[13,15,16], the pre-edge peak at ~ 528.3 eV in Fig. 3 for the series of \( (\text{Hg}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7 \) samples can be ascribed to the excitations of O 1s electrons to O 2p holes located in the CuO\(_2\) planes. As seen from Fig. 3, the intensity of this pre-edge peak increases with increasing doping level of Ca\(^{2+}\) into the Y\(^{3+}\) sites. This indicates that chemical substitution of the low valent Ca\(^{2+}\) ions for the high valent Y\(^{3+}\) ions gives rise to O 2p hole states within the CuO\(_2\) planes near the Fermi level. This was partly supported by the observed contraction of the lattice constant \( a \) with increasing the Ca doping [9].

In addition, as shown by arrows in the top of peaks in Fig. 3, this pre-edge peak for \( x = 0.3 \) shifts by 0.1–0.2 eV to higher energies as the increase of the yttrium content. The same behavior for the low-energy pre-edge peak has been observed in the La\(_{2-x}\)Sr\(_x\)CuO\(_4\) compounds which can be considered as a characteristic for the hole-doped cuprate superconductors [17,18]. In this respect, the titled series compounds are a typical p-type cuprate superconductor [19,20].

The broad peak at ~ 530 eV is difficult to characterize. One possible contribution to this peak is due to the transitions to the O 2p hole states originated from the SrO and HgO planes [13]. However, another possible final state associated with the transition at ~ 530 eV is the upper Hubbard band of the Cu 3d states highly hybridized with the O 2p states. Due to strong on-site correlation on the copper sites in the cuprate compounds, such a band has always been assumed to exist [21]. Therefore, the broad peak at ~ 530 eV may be due to a superposition of unoccupied O 2p states originated from the SrO and HgO layers and the upper Hubbard band related to the CuO\(_2\) planes. Moreover, we propose that the peaks at ~ 529.3 eV and ~ 530.2 eV, particularly in the \( x = 0.3 \) and \( x = 0.5 \) samples, may be due to the excitations of O 1s to the unoccupied O 2p states derived from the SrO and HgO planes, respectively. An increase in \( x \) leads to a decrease in intensity of the peak at ~ 529.3 eV. This may demonstrate that the O 2p holes are localized at the HgO layers in the \( (\text{Hg}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7 \) samples with higher Y\(^{3+}\) content (e.g., \( x = 0.7 \)). More detailed studies are needed to confirm such a suggestion.

The absorption features shown in Fig. 3 were analyzed by fitting Gaussian functions to each spectrum. In Fig. 4 the integrated intensity of the pre-edge peak at ~ 528.3 eV, normalized against the intensity of main peak at ~ 537 eV, is plotted as a function of compositional parameter \( x \) in \( (\text{Hg}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7 \). It can be seen from Fig. 4 that the intensity of this pre-edge peak monotonically increases with increasing the doping concentration of Ca\(^{2+}\) ions (i.e., the smaller \( x \) values). It should be also pointed out that the system goes through a transition from a semiconductor to a metal-superconductor at \( x = 0.6 \). We proposed that, at low levels of Ca doping, the hole states are localized close to the substitution site and there is a negligible overlap between the bound-state wavefunction. At high levels of Ca doping, corresponding to the introduction of more hole states, the overlap of the wave functions of the acceptor states will result in charge delocalization as the system moves through an insulator (or semiconductor) to superconductor transition. A related proposal has been made by Jarrell et al.
who have outlined a phenomenological model of the magnetic properties of La$_{2-x}$Sr$_x$CuO$_4$ [22]. Therefore, the generation of O 2p holes within the CuO$_2$ planes is probably responsible for inducing a transition from a semiconductor to a superconductor. Furthermore, the intensity of the pre-edge peak at \( \sim 528.3 \) eV closely correlates with the compositional variation of superconducting transition temperature, indicating that holes generated in the O 2p orbitals within the CuO$_2$ planes play an important role to control the \( T_c \) of the titled system.

The absorption peaks at \( \sim 532.3 \) and \( \sim 533.7 \) eV, as shown in Fig. 3, may be due to surface contamination since these peaks show a greater intensity in surface-sensitive total-electron yield spectra. Existence of surface contamination has been reported by many researchers. Based on the results of photoemission measurements, Iqbal et al. concluded that these peaks are due to absorption of hydrides, water, and CO$_2$ on surface [23].

The Cu L$_{2,3}$-edge X-ray-absorption near-edge-structure total-X-ray-fluorescence-yield spectra of (Hg$_{0.5}$Pb$_{0.5}$)Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_7$ with \( x = 0.3, 0.5, 0.6, \) and 0.7 in the energy range of 926 to 956 eV are shown in Fig. 5. For \( x = 0.6 \), the Cu L$_{2,3}$-edge absorption spectrum shows two narrow peaks centered at 931.6 eV and 951.4 eV, respectively. These strong excitonic peaks are very close to the L$_{2,3}$ peaks observed in the Cu L$_{2,3}$-edge absorption spectrum of CuO and attributed to transitions from the Cu(2p$_{3/2,1/2}$)-3d$^9$O$^2$p$^6$ ground states to the Cu(2p$_{3/2,1/2}$)$^{-1}$3d$^{10}$O$^2$p$^6$ excited states, where \( (2p_{3/2,1/2})^{-1} \) denotes a 2p$_{3/2}$ hole [24].

For samples with the higher Ca doping for \( x \leq 0.6 \), the absorption peaks become asymmetric and two new shoulders appear to exhibit at the high-energy side of the main peak. According to the curve-fitting analysis, the new features are found to center at \( \sim 933.2 \) and 953.0 eV, respectively. These spectral features, first reported by Bianconi et al. for YBa$_2$Cu$_3$O$_{7-\delta}$, are assigned as transitions from the Cu(2p$_{3/2,1/2}$)$^{-1}$3d$^{9}$L ground states to the Cu-(2p$_{3/2,1/2}$)$^{-1}$3d$^{10}$L excited states, where L denotes the O 2p ligand hole [25]. In Fig. 6 the area of the high-energy shoulder at \( \sim 933.2 \) eV, normalized against the area of the L$_3$ peak at 931.6 eV, is
plotted as a function of the compositional parameter \( x \) in \((\text{Hg}_{0.5}\text{Pb}_{0.5})\text{Sr}_{2}(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7\). The areas were analyzed by fitting the main peak and the shoulder by Gaussian functions. As seen from Fig. 6, the normalized intensity of this high-energy shoulder shows a monotonic increase for samples from \( x = 0.6 \) to \( x = 0.3 \). Because there is only one type of Cu site in the unit cell for the series of \((\text{Hg}_{0.5}\text{Pb}_{0.5})\text{Sr}_{2}(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7\) compounds, these high-energy features in the Cu L-edge absorption spectra can be apparently identified as a result of the hole doping in the CuO\(_2\) layers due to the chemical substitution of Ca\(^{2+}\) for Y\(^{3+}\). It is noted that the curve in Fig. 6 resembles the behavior for the pre-edge peak at \( \sim 528.3 \) eV in the O K-edge absorption spectra shown in Fig. 4. This gives an evidence in support of the suggestion that the pre-edge peak at \( \sim 528.3 \) eV originates from the CuO\(_2\) planes. Increasing the Ca doping in the \((\text{Hg}_{0.5}\text{Pb}_{0.5})\text{Sr}_{2}(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7\) system is to induce more O 2p holes in the CuO\(_2\) planes corresponding to produce more Cu3d\(^{9}\)L defect states, and consequently increase in intensity at high-energy shoulder in Cu L-edge absorption spectra.

4. Conclusion

In this study, we perform O K-edge and Cu L\(_{2,3}\)-edge X-ray-absorption near-edge-structure measurements for the series of \((\text{Hg}_{0.5}\text{Pb}_{0.5})\text{Sr}_{2}(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7\) compounds (\( x = 0.3-0.7 \)) using a bulk-sensitive total-fluorescence-yield technique. Near the O 1s edge, the pre-edge peak at \( \sim 528.3 \) eV is ascribed to the excitations of O 1s electrons to O 2p holes located in the CuO\(_2\) planes. The intensity of this pre-edge peak monotonically increases with increasing doping level of Ca\(^{2+}\). This indicates that the effect of chemical substitution of Ca\(^{2+}\) for Y\(^{3+}\) is to induce hole states in the CuO\(_2\) planes near the Fermi level. The intensity of this pre-edge peak closely correlates with the compositional variation of superconducting transition temperature, showing that holes generated in the O 2p orbitals within the CuO\(_2\) planes play an important role to control the \( T_c \). In the Cu L-edge absorption spectra, high-energy shoulders at 933.2 and 953.0 eV are assigned to the transitions from the Cu(2p\(_3/2\),1/2)\(^{3}d^0\)L ground states to the Cu(2p\(_{3/2}\),1/2)\(^{3}d^0\)L excited states, where L denotes the O 2p ligand hole. The behavior of these shoulders correlates with that of the pre-edge peak at \( \sim 528.3 \) eV in the O K-edge absorption spectra. Based on the present X-ray absorption studies, the generation of O 2p holes within the CuO\(_2\) planes is probably responsible for inducing a transition from a semiconductor to a superconductor.

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References


