Hole states in (Cd$_{x}$Pb$_{0.5}$)Sr$_2$(Ca$_x$Y$_{1-x}$)$_2$Cu$_2$O$_7$ studied by X-ray absorption spectroscopy

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The hole distribution of underdoped and optimum doped states in (Cd$_{x}$Pb$_{0.5}$)Sr$_2$(Ca$_x$Y$_{1-x}$)$_2$Cu$_2$O$_7$ compounds has been investigated by high-resolution oxygen K-edge and copper L-edge X-ray absorption near-edge structure spectra. Near the oxygen 1s edge, a pre-edge peak with a maximum at ~528.3 eV was found, which is ascribed to the excitations of oxygen 1s electrons to 2p hole states located in the CuO$_2$ planes. The intensity of this pre-edge peak increased with calcium doping for $0 < x < 0.5$. This demonstrates that the chemical substitution of Ca$^{2+}$ for Y$^{3+}$ in (Cd$_{x}$Pb$_{0.5}$)Sr$_2$(Ca$_x$Y$_{1-x}$)$_2$Cu$_2$O$_7$ gives rise to an increase in hole concentration within the CuO$_2$ planes and a change from a semiconductor to a superconductor with $T_c$ up to 30 K. The results of the copper L-edge absorption are consistent with those observed for oxygen 1s X-ray absorption.

After the discovery of the Cd-containing 1212-type superconductors having the formula (Cd$_{x}$Pb$_{y}$)Sr$_2$(Ca,Y)$_2$Cu$_2$O$_7$, a number of studies of chemical substitution effects and the crystal structure $^{1-8}$ were reported. The Cd$^{2+}$ ion is particularly interesting since its ionic radius and number of valence electrons are similar to those of Hg$^{2+}$ [0.95 Å for Cd$^{2+}$ and 1.02 Å for Hg$^{2+}$ (co-ordination number = 6)] and 4d$^{10}$ for Cd$^{2+}$ and 5d$^{10}$ for Hg$^{2+}$] which has been shown to have the highest $T_c$ up to 135 K among the high-$T_c$ cuprates. $^{9}$ The crystal structure of (Cd,Pb)Sr$_2$(Ca,Y)Cu$_2$O$_7$ resembles that of YBa$_2$Cu$_3$O$_y$ with the rock salt-type (Cd,Pb)O layers replacing the perovskite-type CuO$_2$ chains, Sr replacing Ba, and Ca replacing a part of Y, as shown in Fig. 1. It is also recognized that the calcium content in the (Y,Ca) sites is a key factor in controlling the superconducting properties of the (Cd$_{x}$Pb$_{0.5}$)Sr$_2$(Ca$_x$Y$_{1-x}$)$_2$Cu$_2$O$_7$ phase. $^{5}$

It has been experimentally demonstrated that hole states play a pivotal role for superconductivity in the p-type cuprate superconductors. Therefore, a knowledge of the unoccupied electronic structure near the Fermi level of these compounds is an important step toward comprehensive understanding of the mechanism of superconductivity. The X-ray absorption spectra are determined by electronic transitions from a selected atomic core level to the unoccupied electronic states near the Fermi level. X-ray absorption near edge structure (XANES) is therefore a direct probe of the character and local density of hole states responsible for high-$T_c$ superconductivity. The availability of third-generation synchrotron radiation X-ray sources makes it feasible to measure high-signal-to-noise-ratio and high-resolution X-ray absorption spectra.

It is generally agreed that hole states in the p-type cuprates are localized on the oxygen sites. Moreover, there are generally several inequivalent oxygen sites in the superconducting cuprates. Therefore, it is important to understand the hole distribution among different sites and their role for superconductivity. However, such studies are still in infancy. We have therefore systematically investigated a series of (Cd$_{x}$Pb$_{0.5}$)Sr$_2$(Ca$_x$Y$_{1-x}$)$_2$Cu$_2$O$_7$ for $x = 0–0.5$ with various hole concentrations in order to extract information concerning how the hole states affect superconducting properties in high-$T_c$ cuprates.

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![Fig. 1 Schematic crystal structure of (Cd$_{x}$Pb$_{0.5}$)Sr$_2$(Ca$_x$Y$_{1-x}$)$_2$Cu$_2$O$_7$.](image)

**Experimental**

High-purity powders of CdO, PbO, SrCO$_3$, CaCO$_3$, Y$_2$O$_3$ and CuO were weighted in the appropriate proportions to form nominal compositions of (Cd$_{x}$Pb$_{0.5}$)Sr$_2$(Ca$_x$Y$_{1-x}$)$_2$Cu$_2$O$_7$. The mixed powders were calcined at 850 °C for 15 h in air then pulverized and pressed into pellets (10 mm in diameter and 3 mm in thickness) under a pressure of 5 × 10$^7$ kg cm$^{-2}$. The pellets were sintered at 950 °C for 10 h in air and then cooled to room temperature. Powder X-ray diffraction (XRD) analyses were performed with a SCINTAG (XI) X-ray diffractometer (Ni-filtered Cu-K$_\alpha$ radiation). All the samples with $x = 0–0.5$ are single phase. When $x > 0.5$ an impurity phase appeared in the samples. Low field magnetization data were taken from a superconducting quantum interference device (SQUID) magnetometer (Quantum Design). The induced superconductivity up to 30 K was observed for the $x = 0.5$ sample. However, the $x = 0–0.4$ samples did not show any superconductivity in the temperature range 5–300 K.
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. Spectra recorded by total X-ray fluorescence yield mode were measured using a microchannel plate (MCP) detector. This detector consists of a dual set of MCPs with an electrically isolated grid mounted in front of them. The X-ray fluorescence yield measurement is strictly bulk sensitive with a probing depth of thousands of ångströms. During these measurements the grid was set to 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 negative MCP bias insured that no electrons were detected. The MCP detector was located ∼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 intensity (I₀) was measured simultaneously by a nickel mesh located after the exit slit of the monochromator. All the absorption spectra were normalized to I₀. The photon energies were calibrated with an accuracy of 0.1 eV (eV = 1.6 × 10⁻¹⁹ J) using the known oxygen K-edge and copper L₂-edge absorption peaks of CuO. The energy resolution of the monochromator was set to ±0.22 and ±0.45 eV for the oxygen K-edge and copper L-edge X-ray absorption measurements, respectively. All the measurements were carried out at room temperature.

Results and Discussion

Oxygen K-edge XANES

Based on the strong similarity of oxygen 1s absorption spectra and resonant high-energy inverse photoemission spectra of Ba₅Sr₄CaCu₄O₈₋ₓ, it is suggested that the core-hole effect in the oxygen K-edge X-ray absorption near-edge structure spectrum of the cuprate superconductors can be ignored. Furthermore, according to the dipole selection rules, only the local unoccupied states with oxygen 2p character are probed in the oxygen K-edge X-ray absorption spectra. Therefore, if the hole states near the Fermi level in the p-type cuprates are of primarily oxygen 2p character, a pre-edge peak should be observable in the oxygen 1s XANES spectrum with an intensity proportional to the 2p hole concentration.

In Fig. 2 we show the oxygen K-edge X-ray absorption near-edge structure spectra for the series of (CdₓPb₀.₅₋ₓ)Sr₂(Ca₀.₅₋ₓYₓ)O₃₋ₓ samples with x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 in the energy range 525–555 eV obtained by the bulk-sensitive total X-ray fluorescence yield technique. The X-ray absorption measurements were carried out on the X-ray absorption near-edge structure (XANES) beamline of the Synchrotron Radiation Research Center (SRRC) in Taiwan. Spectra recorded by total X-ray fluorescence measurement is strictly bulk sensitive with a probing depth of thousands of ångströms. During these measurements the grid was set to 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 negative MCP bias insured that no electrons were detected. The MCP detector was located ∼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 intensity (I₀) was measured simultaneously by a nickel mesh located after the exit slit of the monochromator. All the absorption spectra were normalized to I₀. The photon energies were calibrated with an accuracy of 0.1 eV (eV = 1.6 × 10⁻¹⁹ J) using the known oxygen K-edge and copper L₂-edge absorption peaks of CuO. The energy resolution of the monochromator was set to ±0.22 and ±0.45 eV for the oxygen K-edge and copper L-edge X-ray absorption measurements, respectively. All the measurements were carried out at room temperature.

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In order to investigate the variation of hole contents among different oxygen sites as a function of calcium doping, the absorption features shown in Fig. 2 were analysed by fitting Gaussian functions to each spectrum. The integrated intensity of the pre-edge peak at $\approx 528.3$ eV, normalized against the intensity of main peak at $\approx 537$ eV, as a function of calcium content $x$ in (Cd$_{1-x}$Pb$_x$)$_2$Sr(Ca$_{1-x}$Y$_{1-x}$)$_2$Cu$_3$O$_{7}$ is shown in Fig. 3 as a function of calcium content $x$ in (Cd$_{1-x}$Pb$_x$)$_2$Sr(Ca$_{1-x}$Y$_{1-x}$)$_2$Cu$_3$O$_{7}$. The intensity of this pre-edge peak increases with increasing doping level of Ca$^{2+}$ substituted at the Y$^{3+}$ sites. This indicates that chemical substitution of low-valent Ca$^{2+}$ for high-valent Y$^{3+}$ gives rise to oxygen 2p hole states within the CuO$_2$ planes near the Fermi level. However, the curve could not be fitted as a simple straight line and a discrepancy at $x = 0.2$ was found which may imply that defect compensation is occurring in the samples. It should be pointed out that the system goes through a transition from a semiconductor to a superconductor at $x = 0.5$. It is therefore proposed that, at low levels of calcium 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 doping, corresponding to the introduction of more hole states, the overlap of the wavefunctions of the acceptor states will result in charge delocalization as the system moves through an insulator (or semiconductor) to a superconductor transition.

A related model has been proposed by Jarrell et al. who have described a phenomenological model of the magnetic properties of La$_{1.5}$Sr$_x$Cu$_4$O$_8$. Therefore, the generation of oxygen 2p holes within the CuO$_2$ planes is probably responsible for inducing a transition from a semiconductor to a superconductor. In addition, this pre-edge for $x = 0.1$ in Fig. 2 shifts by 0.1–0.2 eV to lower energies as the calcium content increases. The same behaviour of the low-energy pre-edge peak has been observed for La$_{1.5}$Sr$_x$Cu$_4$O$_8$ compounds which can be considered as characteristic for the p-type cuprate superconductors. In this respect, the present compounds are typical of a hole-doped cuprate superconductor. A similar behaviour in the oxygen L$\alpha$ X-ray absorption spectra with the doping concentration of Ca$^{2+}$ in the Y$^{3+}$ sites was reported for (Tl$_{1-x}$Pb$_x$)$_2$Sr(Ca$_{1-x}$Y$_x$)$_2$Cu$_3$O$_7$ compounds.

**Copper L$\alpha$-edge XANES**

The copper L$\alpha$-edge X-ray absorption near-edge-structure total-X-ray-fluorescence-yield spectra of (Cd$_{1-x}$Pb$_x$)$_2$Sr(Ca$_{1-x}$Y$_x$)$_2$Cu$_3$O$_7$ with $x = 0$–0.5 in the energy range 922–958 eV are shown in Fig. 4. For $x = 0$ the spectrum shows two narrow peaks centered at 931.2 and 951.0 eV. These strong excitonic peaks are very close to the L$_2$ peaks observed in the copper L$\alpha$-edge X-ray absorption spectrum of CuO and are attributed to transitions from the Cu(2p$_{3/2}$) 3d$^{-2}$–O 2p$^0$ ground states to the Cu(2p$_{3/2}$) 3d$^{-3}$–O 2p$^1$ excited states, where $2p^0$ and $2p^1$ denote a 2p hole and 2p hole, respectively.

For samples with increasing calcium content (i.e. increasing hole concentration), the absorption peaks become asymmetric and two new features appear at the high-energy side of the L$_2$ peaks (marked by arrows in Fig. 4). From the curve-fitting analysis, the new features are centered at about 933.1 and 952.9 eV, respectively. In Fig. 5 the area of this high-energy shoulder, normalized against the area of the L$_2$ peak at 931.3 eV, is plotted as a function of the compositional parameter $x$ in (Cd$_{1-x}$Pb$_x$)$_2$Sr(Ca$_{1-x}$Y$_x$)$_2$Cu$_3$O$_7$. The areas were estimated by fitting the main peak and the shoulder by Gaussian functions. The normalized intensity of this high-energy shoulder increases with increasing calcium concentration. However, the curve could not be fitted as a simple straight line and a discrepancy at $x = 0.2$ was found which again may imply that defect compensation is occurring in the samples.

It is noted that the curve in Fig. 5 resembles the behavior of the pre-edge peak at $\approx 528.3$ eV in the oxygen K-edge absorption spectra shown in Fig. 3. Therefore, it is suggested that these high-energy shoulders may originate from the oxygen 2p hole states and are assigned as transitions from the Cu(2p$_{3/2}$) 3d$^{10}$ L ground state (formal Cu$^{2+}$ state) to the Cu(2p$_{3/2}$) 3d$^{11}$ L excited state, where L denotes the oxygen 2p ligand hole.

Since there is only one type of copper site in the unit cell for the series (Cd$_{1-x}$Pb$_x$)$_2$Sr(Ca$_{1-x}$Y$_x$)$_2$Cu$_3$O$_7$, these high-energy excitations are considered as characteristic for the p-type cuprate superconductors.
features in the copper L-edge absorption spectra can be apparently identified as a result of the hole doping within the CuO$_2$ layers due to the chemical substitution of Ca$^{2+}$ for Y$^{3+}$. The close resemblance between the high-energy features in the copper L-edge absorption spectra and the pre-edge peak at $\sim$528.3 eV in the oxygen 1s absorption spectra is evidence in support of the suggestion that the pre-edge peak at $\sim$528.3 eV originates from the CuO$_2$ planes.

**Conclusion**

High-resolution oxygen K-edge and copper L$_{3,2}$-edge X-ray absorption near-edge-structure spectra for the series of (Cd$_{1-x}$Pb$_x$)$_2$(Ca$_{1-x}$Y$_x$)$_2$CuO$_4$ compounds ($x = 0 \sim 0.5$) have been obtained using a bulk-sensitive total-fluorescence-yield technique. Near the oxygen K-edge, the pre-edge peak at $\sim$528.3 eV is ascribed to the core-level excitations of oxygen 1s electrons to 2p holes located in the CuO$_2$ planes. The intensity of this pre-edge peak monotonically increases with calcium doping for $0 \leq x \leq 0.5$. 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. In the copper L-edge absorption spectra, high-energy shoulders at 933.1 and 952.9 eV are assigned to the transitions from the Cu(2p$_{3/2}$) 3d$^9$ L ground state to the Cu(2p$_{3/2}$)$^{-1}$ 3d$^{10}$ L excited state, where L denotes the oxygen ligand hole. The normalized intensity of these defect states shows a linear increase with increasing calcium concentration. Based on the present XANES study, it is concluded that the transition from a semiconductor to a superconductor in (Cd$_{1-x}$Pb$_x$)$_2$(Ca$_{1-x}$Y$_x$)$_2$CuO$_4$ with increase in calcium content results mainly from the increase in the hole concentration in the CuO$_2$ planes.

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**References**


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