

## XANES STUDY OF THE VALENCE OF Pb IN $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{7-\delta}$

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Near edge x-ray-absorption spectra at Pb  $L_3$ -edges have been measured for  $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{7-\delta}$  compound series. It is found that the intensity of the  $2p \rightarrow 6s$  transition feature decreases with the substitution of  $\text{Ca}^{+2}$  by  $\text{Y}^{+3}$ . This result indicates that some electronic charges have been transferred into the Pb(Tl)-O layers by this substitution. Detailed analysis suggests that the valence value of Pb in this compound series is close to +4 and it decreases with the increase of the Y-doping level  $x$ .

### 1. Introduction

The  $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{7-\delta}$  compound series is interesting because it has the metal-superconductor-insulator transition behavior among the thallium cuprate systems<sup>1–3</sup>. The study of the charge transfer process associated with the Y for Ca substitution is important for understanding the superconducting properties of this system. In a recent Cu K-edge study by Liang *et al.*<sup>4</sup> and O K-edge study by Chen *et al.*<sup>3</sup> and Yuan *et al.*<sup>2</sup>, it was found that the substitution of  $\text{Ca}^{2+}$  by  $\text{Y}^{3+}$  introduces electronic charges into the entire  $\text{CuO}_2$  layers. However, whether or not the electronic charges doped by Y atoms are also transferred into the Pb(Tl)-O layers is not investigated by XANES studies and thus still unclear. Aimed at addressing this issue, we carried out Pb  $L_3$ -edge measurements for the  $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{7-\delta}$  compound series and the results are presented in this paper.

### 2. Experimental

Single phase  $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$  samples used in this study were prepared as has been described earlier<sup>2</sup>. The XANES measurements at Pb  $L_3$ -edge

were performed at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory on beam line X-11A using a Si(111) monochromator and 0.75 entrance slit. Samples for XANES measurements were prepared by rubbing fine powders onto scotch tapes and stacking several layers to obtain desired thickness. The spectra were measured using transmission mode detection. Energy calibrations were made by simultaneously measuring the Pb  $L_3$ -edge spectrum of a reference compound  $\text{PbO}_2$ . All of the spectra presented in this paper have been linear-background subtracted and normalized to unity in the continuum region.

### 3. Results and Discussion

In order to better understand the Y-substitution induced feature changes in the Pb  $L_3$ -edge spectra for the  $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$  series, we first discuss the origin of the main features commonly observed in the Pb  $L_3$ -edge spectra of lead compounds. Fig. 1 shows the measured spectra of three reference materials Pb-metal, PbO and  $\text{PbO}_2$  which have formal Pb valence 0, +2, and +4, respectively. The  $\text{PbO}_2$  was chosen as reference compounds because the chemical environment (O-ligands) for these compounds is similar to that of the  $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$  samples. The broad double features *B* and *C*, seen in all of the three reference spectra, are assigned to the  $2p \rightarrow 6d_{t_{2g}}$  ( $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$ ) and  $2p \rightarrow 6d_{e_g}$  ( $d_{z^2}$  and  $d_{x^2-y^2}$ ) transitions, respectively<sup>5-7</sup>. The pre-edge feature labeled by letter *A* is assigned to  $2p \rightarrow 6s$  transition<sup>5-7</sup>. The intensity of this feature should be a measure of the  $6s$  hole population or the  $\text{Pb}^{+4}$  concentration. It can be seen that the  $\text{Pb}^{+4}$  feature *A* is absent in both the reference spectra of Pb-metal and  $\text{Pb}^{+2}$  compound PbO, but it is very prominent in the spectrum of  $\text{Pb}^{+4}$  compound  $\text{PbO}_2$ . This difference is due to the fact that the Pb- $6s$  orbitals in the Pb-metal and PbO are completely filled.

In Fig. 2, the Pb  $L_3$ -edge spectra of three  $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$  with  $x = 0, 0.3$ , and  $0.7$  are shown in comparison with the spectrum of reference compound  $\text{PbO}_2$ . All of the spectral features *A*, *B*, and *C* are observed in the spectra of  $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$  samples. Particularly, the  $\text{Pb}^{+4}$  feature *A* for the  $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$  series is more prominent than that for the  $\text{PbO}_2$ . This result means that the Pb  $6s$  orbitals for this compound series are essentially empty ( $\text{Pb}^{+4}$ ,  $6s^0$ ) and thus the valence of the Pb in this series should be similar to or even higher than that in  $\text{PbO}_2$ , i.e., close to  $\text{Pb}^{+4}$ .

Fig. 2 also exhibits the following variations in the intensities of spectral features induced by the substitution of Ca by Y. With the increase of the Y concentration  $x$ , (1) the intensity of the  $\text{Pb}^{+4}$  feature *A* decreases, (2) the intensity of the feature *C* (due to the  $2p \rightarrow 6d_{e_g}$  transition) increases, and (3) the intensity of the feature *B* (due to the  $2p \rightarrow 6d_{t_{2g}}$  transition) is almost unchanged. The observation (1) indicates that Y donates electronic charges into the Pb  $6s$  orbitals and reduces the  $6s$  holes. Thus, the substitution of Ca by Y (increasing  $x$ ) decreases the valence of

Pb in the  $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$  series.

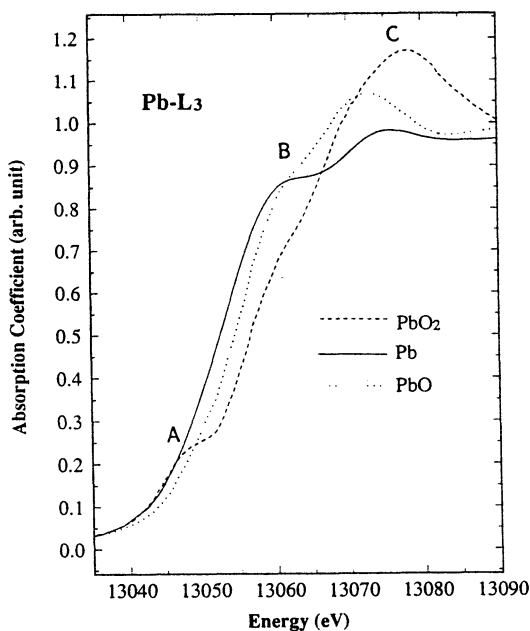


Fig. 1. The Pb  $L_3$ -edge spectra of three reference materials Pb-metal, PbO, and PbO<sub>2</sub>.

The observation (2) and (3) can be accounted for qualitatively by ligand field theory. Since for this compound series the Pb-O2(apical) bonding distance (about 2.049 Å) is much short than the Pb-O3(in-plane) bonding distance (about 2.705 Å) in the PbO<sub>6</sub> cluster<sup>7</sup>, the PbO<sub>6</sub> can be treated as a compressed octahedra. Thus, the  $6d_{t_{2g}}$  and  $6d_{e_g}$  orbitals mentioned above are split such that in the higher-energy  $6d_{e_g}$  orbital set, the energy of the  $6d_{z^2}$  orbital is much higher than that of the  $6d_{x^2-y^2}$  orbital, but the energy of the the  $6d_{xy}$ ,  $6d_{yz}$ , and  $6d_{xz}$  orbitals in the lower-energy  $6d_{t_{2g}}$  orbital set are almost degenerate. In a previous study on  $(\text{Tl}_{0.75}\text{Pb}_{0.25})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$  series, it was found that with the increase of  $x$  from 0 to 0.75, the Pb-O2(apical) distance increases from 2.049 Å to 2.129 Å, whereas the Pb-O3(in-plane) distance is almost unchanged. One can expect that a similar variation of these two Pb-O bonding distances should also occur in our  $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$  series with the increase of  $x$  from 0 to 0.7. The increase of the Pb-O2(apical) distance can decrease the energy of the  $6d_{z^2}$  orbital, whereas the energy of the  $6d_{x^2-y^2}$  orbital is almost unaffected because the Pb-O3(in-plane) distance is almost a constant. The decrease of the energy of the  $6d_{z^2}$  orbital will thus reduce the energy separation between the  $6d_{z^2}$  and  $6d_{x^2-y^2}$  in the  $6d_{e_g}$  orbital set. This will in turn increase the density of states of the  $6d_{e_g}$  band as well as the intensity of the  $2p \rightarrow 6d_{e_g}$  transition feature C( the observation (2)). Since the energies of the three orbitals in the  $6d_{t_{2g}}$  orbital set are almost degenerate,

the decrease of the Pb-O2(apical) bonding distance has little effect on the energy separation between the  $6d_{xy}$  and  $6d_{yz}/6d_{xz}$  orbitals. Thus, the density of states of the  $6d_{t_{2g}}$  band as well as the intensity of the  $2p \rightarrow 6d_{t_{2g}}$  transition feature *B* are almost unaffected by the variation of *x* from 0 to 0.7 (the observation (3)).

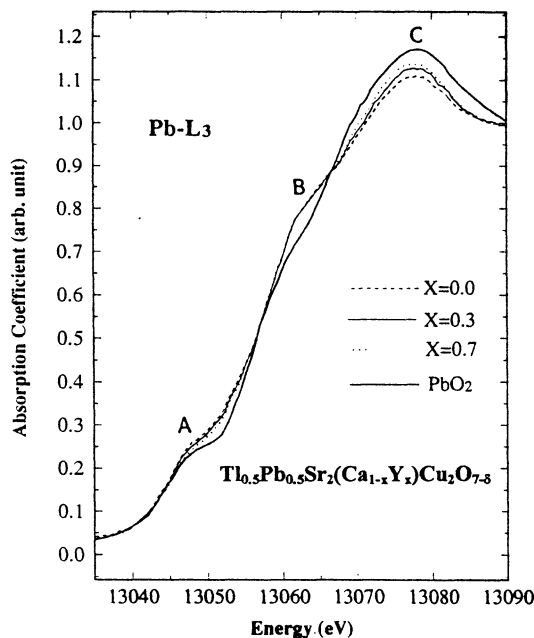


Fig. 2. The Pb  $L_3$ -edge spectra of three  $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{CaCu}_2\text{O}_{7-\delta}$  sample with  $x = 0.0, 0.3,$  and  $0.7$  and reference compounds  $\text{PbO}_2$ .

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