XANES and wet-chemical analyses of the charge balance in (Hg,Pb)(Ba,Sr)2Ca2Cu3O8+z

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Received 13 November 2002; accepted 27 January 2003

Abstract

Here we present the results revealed from iodometric, coulometric and cerimetric titrations and Cu L-edge and O K-edge X-ray absorption near-edge structure analyses of the concentration and distribution of holes in a series of polycrystalline (Hg,Pb)(Ba,Sr)2Ca2Cu3O8+z samples. By means of oxygen-content tuning only, the average valence of copper in the pristine Hg-1223 phase can be controlled in the range of 2.03–2.10. Substituting Hg partly with Pb increased considerably the amount of excess oxygen z in the (Hg,Pb)O+z charge-reservoir block. Lead was found to enter the phase with an oxidation state higher in average than III so as to increase the positive charge at the Hg site. However, the increase in the oxygen content counter-balanced the effect of higher-valent (PbIII/IV) for lower-valent (HgII) cation substitution such that the average CuO2-plane hole concentration was found higher for the (Hg,Pb)-1223 sample with Tc = 115 K than for the optimally doped pristine Hg-1223 sample with Tc = 134.5 K.

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PACS: 74.72.Jt
Keywords: Hg-1223 superconductor; Metal valences; Hole-doping level; XANES spectroscopy; Wet-chemical redox analysis

1. Introduction

The record-high-Tc superconductor, HgBa2Ca2Cu3O8+z or Hg-1223, is a challenging target for detailed chemical substitution and hole-doping studies. Here we present the results of such studies for polycrystalline (Hg,Pb)(Ba,Sr)2Ca2Cu3O8+z or (Hg,Pb)-1223 samples based on iodometric or coulometric titrations for the oxygen content, cerimetric titrations for the valence of Pb, and Cu L-edge and O K-edge X-ray absorption near-edge structure (XANES) analyses for the valence of Cu and the relative CuO2-plane hole concentration, respectively.

Partial substitution of Hg by Pb has been found to stabilize the Hg-1223 phase [1,2] and enhance the irreversibility field (Hirr) characteristics [3,4]. Such substitution also increases the solubility limit.
of Sr at the Ba site [5,6]. For both powder and single-crystal samples substituted simultaneously by Pb and Sr, i.e. (Hg,Pb)-1\(_{\text{Ba}}\text{Sr}_{223}\), it has been well documented that the \(H_{\text{irr}}\) values are strongly enhanced with increasing Sr content [7–9]. Similar enhancement due to the Sr-for-Ba substitution was earlier reported for Ba-free Re-for-Hg substituted (Hg,Re)\(_{\text{Sr2Ca2Cu3O8+z}}\) samples [10]. Furthermore, a pronounced peak effect was observed for a single-crystal (Hg,Pb)-1\(_{\text{Ba}}\text{Sr}_{223}\) sample [11]. Nonetheless, experimental data that would explain how the Pb and/or Sr substitution affects the charge balance and hole-doping in the (Hg,Pb)-1\(_{\text{Ba}}\text{Sr}_{223}\) system are still lacking.

2. Experimental

Powder samples of (Hg\(_{1-x}\)Pb\(_x\))(Ba\(_{1-x}\)Sr\(_x\))\(_2\text{Ca2Cu3O8+z}\) \((x = 0.25, 0.75; y = 0, 0.2, 0.3)\) were synthesized in an encapsulated fused-quartz ampoule from HgO and PbO powders and spray-dried and vacuum-decomposed \((\text{Ba}_{1-x}\text{Sr}_{x})_2\text{Ca2Cu3O_d}\) precursors, following the procedure described by Lee et al. [5,6]. Prior to use, the oxygen content of each \((\text{Ba}_{1-x}\text{Sr}_{x})_2\text{Ca2Cu3O_d}\) precursor batch was determined by iodometric titration, and accordingly to decrease or increase the overall oxygen content a small pellet of either CuO or Cu\(_2\text{O}_2\) of carefully adjusted mass was added together with the pellets of compacted starting material mixtures into the ampoule. Before evacuating and sealing the ampoule, a fused-quartz rod of suitable length was inserted into it to reduce the volume of empty space. The ampoule was protected against a possible explosion by placing it in a stainless-steel container and applying an external gas pressure of 50–100 atm to it. The synthesis was carried out at 850 °C for 15 h.

Part of the as-synthesized, pristine Hg-1\(_{\text{Ba}}\text{Ca2Cu3O8+z}\) sample was subjected to a post-annealing to either increase or decrease the oxygen content. The oxygenative annealing was performed in 150-atm \(O_2\) gas atmosphere at 300 °C. For the reductive annealing, the sample was encapsulated together with an accurately weighed amount of Cu\(_2\text{O}\) in a fused-quartz ampoule and annealed at 400 °C. Here the amount of Cu\(_2\text{O}\) was selected such that it corresponded to removal of 0.1 oxygen atoms per formula unit. Since our preliminary experiments for the Pb-substituted samples indicated that wide-range tuning of oxygen content is impossible, no such efforts were made for the present Pb/Sr containing samples.

The phase composition of the samples was determined by X-ray diffraction (XRD; MAC Science: MXP18VAHF\(_{22}\); CuK\(_\alpha\) radiation). The \(T_c\) values assigned for the samples are the onset temperatures of diamagnetic signal measured with a SQUID magnetometer (Quantum Design: MPMS-XL). Oxygen contents were determined for selected samples using either the iodometric titration or the Cu\(^{+}/\text{Cu}^{2+}\) coulometric titration method. The valence of Pb was analyzed by cerimetric titrations. For each titration analysis, several parallel experiments were made. A summary of the principles of the titration methods and details of the experimental parameters used are given in Table 1 [12,13]. The Cu L-edge and O K-edge XANES measurements were performed for pow-

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Principles and experimental parameters of the wet-chemical redox analysis methods used for determining the oxygen content and the valence of Pb in the present (Hg,Pb)(Ba,Sr)(_2\text{Ca2Cu3O8+z}) samples</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Iodometry</strong></td>
<td><strong>Coulometry</strong></td>
</tr>
<tr>
<td>Reductant</td>
<td>I(^-) (KI)</td>
</tr>
<tr>
<td>Detected species</td>
<td>Cu(^{III}), Pb(^{IV}), Pb(^{III})</td>
</tr>
<tr>
<td>Mass of reductant</td>
<td>(~1) g</td>
</tr>
<tr>
<td>Mass of sample</td>
<td>(~50) mg</td>
</tr>
<tr>
<td>Solvent</td>
<td>100 ml of 1 M HCl</td>
</tr>
<tr>
<td>Titrant</td>
<td>(~0.015) M Na(_2\text{S}_2\text{O}_3)</td>
</tr>
<tr>
<td>End-point detection</td>
<td>Visual (starch)</td>
</tr>
<tr>
<td>Reference material</td>
<td>CuO</td>
</tr>
</tbody>
</table>
under samples in the bulk-sensitive X-ray fluorescence-yield mode on the 6-m high-energy spherical grating monochromator beam-line at Synchrotron Radiation Research Center (SRRC) in Hsinchu, Taiwan. The obtained spectra were corrected for the energy-dependent incident photon intensity variation as well as for self-absorption effects and normalized to tabulated standard absorption cross sections in the energy range of 600–620 eV for the O K-edge and 1000–1020 eV for the Cu L-edge. Details of the XANES experiments were as in Ref. [14].

3. Results and discussion

Based on the XRD data the synthesized (Hg,Pb)(Ba, Sr)2Ca2Cu3O8±z samples were of high-quality but not totally free from secondary phases. In Table 2, the impurity phases detected by XRD are summarized for each sample studied. For the pristine Hg-1(Ba)223 samples no clear impurity peaks were distinguished, while for the Pb/Sr-substituted samples the presence of Ca2CuII3O5 and BaCO3 or Sr2CuIII2O3 besides the (Hg,Pb)- 1(Ba,Sr)223 main phase was concluded. No other superconductive phases were present in any of the samples according to the magnetic susceptibility versus temperature curves that showed a sharp single-step transition and a superconducting volume fraction larger than 50% for each sample.

Another important aspect was the selectivity of analytical methods for the determination of Cu and Pb in the present experimental conditions using the oxygenated Hg-1(Ba)223 sample as a reference sample: no reaction between the Fe2+ ions and CuIII from the sample was detected. The obtained values for the valence of Pb, V(Pb)wet-chem, from the cerimetric titration analysis for the two Pb-containing PbIVO3, could seriously invalidate the interpretation of the present wet-chemical and XANES results, whereas oxygen-stoichiometric compounds containing divalent copper and alkaline earth elements only, i.e. such as those observed for the present samples, are nearly benign.

The amount of excess oxygen, z, was analyzed with iodometric titrations for three samples, i.e. synthesized HgBa2Ca2Cu3O8±z, (Hg0.8Pb0.2)(Ba0.25Sr0.75)2Ca2Cu3O8±z and (Hg0.7Pb0.3)(Ba0.75-Sr0.25)2Ca2Cu3O8±z. Coulometric titrations were used for the analysis of the oxygenated HgBa2- Ca2Cu3O8±z sample. Here it should be firstly noted that the values revealed for z should be considered to represent the minimum limit for the real, phase-specific value of z, and thus be called as zmin. This is because the presence of impurity phases (such as the present ones) that contain no high-valent cation species results in underestimation of the z value by “diluting” the amount of high-valent Cu/Pb species present in the (Hg,Pb)-1(Ba,Sr)223 phase. Here, from the zmin values given in Table 2, we may nevertheless conclude that the Pb-for-Hg substitution results in a clear increase in the oxygen content.

The valence of Pb was analyzed by means of cerimetric titrations using divalent Fe as the reductant (see Table 1). This method is selective for the detection of high-valent Pb in the presence of CuIII [12,13]. The selectivity was confirmed under the present experimental conditions using the oxygenated Hg-1(Ba)223 sample as a reference sample: no reaction between the Fe2+ ions and CuIII from the sample was detected. The obtained values for the valence of Pb, V(Pb)wet-chem, from the cerimetric titration analysis for the two Pb-containing

Table 2
Experimental data for the (Hg,Pb)(Ba,Sr)2Ca2Cu3O8±z samples: value of Tc, impurity phases detected by XRD, lower-limit estimation for the amount of excess oxygen (zmin) as calculated from the results of iodometric or coulometric titrations, valence of Pb [V(Pb)wet-chem] as estimated from cerimetric titration data, and valence of Cu [V(Cu)XAS] as estimated from Cu L-edge XANES data

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tc (K)</th>
<th>Identified impurities</th>
<th>zmin</th>
<th>V(Pb)wet-chem</th>
<th>V(Cu)XAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgBa2Ca2Cu3O8±z (reduced)</td>
<td>123</td>
<td>None</td>
<td>–</td>
<td>–</td>
<td>2.03 (±0.01)</td>
</tr>
<tr>
<td>HgBa2Ca2Cu3O8±z (as-synthesized)</td>
<td>125</td>
<td>None</td>
<td>0.08 (±0.01)</td>
<td>–</td>
<td>2.06 (±0.01)</td>
</tr>
<tr>
<td>HgBa2Ca2Cu3O8±z (oxygenated)</td>
<td>134.5</td>
<td>None</td>
<td>0.19 (±0.01)</td>
<td>–</td>
<td>2.10 (±0.01)</td>
</tr>
<tr>
<td>(Hg0.7Pb0.3)(Ba0.75Sr0.25)2Ca2Cu3O8±z</td>
<td>129.5</td>
<td>Ca2CuO3, BaCO3</td>
<td>0.50 (±0.02)</td>
<td>3.4 (±0.2)</td>
<td>–</td>
</tr>
<tr>
<td>(Hg0.5Pb0.5)(Ba0.25Sr0.75)2Ca2Cu3O8±z</td>
<td>114.5</td>
<td>Sr2CuO3</td>
<td>0.39 (±0.02)</td>
<td>3.5 (±0.5)</td>
<td>2.12 (±0.01)</td>
</tr>
</tbody>
</table>

*Performed only once.
samples are given in Table 2. It is concluded that Pb enters the Hg-1223 phase with an oxidation state higher than III in average. The Pb\textsuperscript{III}/IV-for-Hg\textsuperscript{II} substitution thus increases the positive charge at the charge-reservoir cation site. Concomitantly the oxygen content increases, as was revealed from the results of iodometric and coulometric titrations. Now the question is, if the overall charge of the (Hg,Pb)O\textsubscript{z} charge-reservoir increases or decreases as a consequence of Pb/Sr substitution. Here note that the higher the amount of (positive) charge in the charge-reservoir block is, the less doped with holes are the CuO\textsubscript{2} plane(s) \[12,13\]. Unfortunately, the accuracy of values for the amount of excess oxygen, z, and the valence of Pb as obtained from the results of titration analyses is not high enough to allow us to estimate the valence state of Cu or the hole concentration of the CuO\textsubscript{2} planes. Therefore we utilized XANES spectroscopy for more precise discussions on the Cu valence/CuO\textsubscript{2}-plane hole concentration in the present (Hg,Pb)-1\textsuperscript{(Ba,Sr)}223 system.

The Cu L\textsubscript{2,3}-edge absorption spectra for the three Hg-1\textsuperscript{(Ba)}223 samples with different oxygen contents are shown in Fig. 1. Two narrow peaks centered at \(~931.2\) and \(~951.2\) eV dominate the spectra. These peaks are due to Cu\textsuperscript{II} \[15,16\], i.e. transitions from the Cu(2p\textsubscript{3/2,1/2})3d\textsuperscript{9} ground states into the Cu(2p\textsubscript{3/2,1/2})\textsuperscript{1}d\textsuperscript{10} excited states where (2p\textsubscript{3/2,1/2})\textsuperscript{1} denotes a 2p\textsubscript{3/2} or 2p\textsubscript{1/2} hole. For the oxygenated sample, both peaks are clearly asymmetric having a shoulder at the higher-energy side, i.e. at \(~932.6\) eV for the \(~931.2\) eV peak in the L\textsubscript{3} area. Such shoulders, first seen for fully-oxygenated CuBa\textsubscript{2}YCu\textsubscript{2}O\textsubscript{7−δ} \[17\] and later for various other p-type doped high-\textbf{T}_c superconductive copper oxides, have been assigned to Cu\textsuperscript{III} and interpreted as the transitions from the Cu(2p\textsubscript{3/2,1/2})3d\textsuperscript{9} L\textsubscript{2} ground states into the Cu(2p\textsubscript{3/2,1/2})\textsuperscript{1}d\textsuperscript{10} L\textsubscript{2} excited states (L\textsubscript{2} denotes a ligand hole in the O 2p orbital). For the three Hg-1\textsuperscript{(Ba)}223 samples, the relative intensities of the shoulders, as revealed from Fig. 1, clearly decrease as the oxygen content decreases. For quantitative estimation of the valence of Cu the Cu L\textsubscript{3}-edge area (that is more intense than the L\textsubscript{2}-edge area) was used. First the background, fitted with an arctangent curve, was subtracted from the spectra. Fitting of the peak due to Cu\textsuperscript{II} about 931.2 eV was done using a combination of Lorentzian and Gaussian functions while for the shoulder about 932.6 eV (Cu\textsuperscript{III}) a Gaussian function was assumed. The integrated intensity of the shoulder against the total spectral weight of the ~932.6 eV peak and the shoulder gives us the ratio of Cu\textsuperscript{III} to the sum of Cu\textsuperscript{II} and Cu\textsuperscript{III} and thereby the average valence of Cu, \(V(Cu)\textsubscript{XAS}\). Values of \(V(Cu)\textsubscript{XAS}\) thus obtained are given in Table 2. It is concluded that by means of oxygen-content tuning the average valence of copper in the pristine Hg-1\textsuperscript{(Ba)}223 phase can be controlled in the range of 2.03–2.10. Next we focus on the Cu L\textsubscript{2,3}-edge XANES spectrum obtained for the Pb and Sr substituted (Hg\textsubscript{0.8}Pb\textsubscript{0.2})(Ba\textsubscript{0.25}Sr\textsubscript{0.75})\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{8+z} sample shown in Fig. 1(d). Substituting the Hg-1\textsuperscript{(Ba)}223 phase with Pb/Sr
apparently increases the average valence of Cu. Quantitative analysis of the spectrum reveals 2.12 as the valence value of Cu in $(\text{Hg}_{0.8}\text{Pb}_{0.2})_{2}(\text{Ba}_{0.25}\text{Sr}_{0.75})_{2}\text{Ca}_{2}\text{Cu}_{3}\text{O}_{6+z}$, suggesting that this sample with $T_c = 115$ K is in an overdoped state since 2.12 exceeds the value of 2.10 obtained for the Cu valence in the oxygenated Hg-1223 sample with the maximized $T_c$ value of 134.5 K. In Fig. 2, the value of $T_c$ is plotted against $V$(Cu)$_{\text{XAS}}$ for the present (Hg,Pb)-1223 system.

The increase in the CuO$_2$-plane hole concentration due to Pb/Sr substitution is revealed from the O K-edge XANES data as well. Fig. 3 displays the O K-edge XANES spectrum for the $(\text{Hg}_{0.8}\text{Pb}_{0.2})(\text{Ba}_{0.25}\text{Sr}_{0.75})_{2}\text{Ca}_{2}\text{Cu}_{3}\text{O}_{6+z}$ sample together with those for the reduced and oxygenated Hg-1223 samples. The lowest-energy pre-edge peak about 528.3 eV is attributed to the excitation of O 1s electrons to O 2p holes in the CuO$_2$ planes. The integrated intensity of this peak is known to reflect the average hole concentration of CuO$_2$-plane(s) in Hg-1223 and other high-$T_c$ superconducting copper oxides [15]. We fitted the peak to a Gaussian function. Before that the background within 527–529 eV was fitted with a straight line and subtracted from the spectra. The obtained value for the integrated intensity of the 528.3-eV peak (in a.u.) increases as follows: 0.2 for reduced HgBa$_2$Ca$_2$Cu$_3$O$_{6+z}$, 1.0 for oxygenated HgBa$_2$Ca$_2$Cu$_3$O$_{6+z}$, and 1.4 for $(\text{Hg}_{0.8}\text{Pb}_{0.2})(\text{Ba}_{0.25}\text{Sr}_{0.75})_{2}\text{Ca}_{2}\text{Cu}_{3}\text{O}_{6+z}$. Thus, the O K-edge XANES data verify that the Pb-for-Hg and Sr-for-Ba substituted (Hg,Pb)-1223 sample possesses more strongly doped CuO$_2$ planes than the optimally doped, oxygenated Hg-1223 sample. Finally we suggest that the possible hole states at the oxygen atom attached to Pb in the (Hg,Pb)O$_2$ charge-reservoir correspond to the peak seen in the O K-edge spectrum of the $(\text{Hg}_{0.8}\text{Pb}_{0.2})(\text{Ba}_{0.25}\text{Sr}_{0.75})_{2}\text{Ca}_{2}\text{Cu}_{3}\text{O}_{6+z}$ sample about 529 eV. Among the presently analyzed three samples it is seen only for this sample that contains Pb. No such peak is seen in the spectra previously reported for pristine Hg-1223 [15] and Tl-2223 [18] samples. On the other hand, very similar spectral features are seen...
in the spectra for Pb-substituted (Hg,Pb)-1\(^{89}\)Sr\(^{212}\) [19] and (Tl,Pb)-1\(^{89}\)Sr\(^{212}\) [20] samples. The O 2p hole states hybridized with the upper Hubbard band are seen for all these and present samples about 530 eV.

4. Conclusion

The results from wet-chemical and XANES analyses for the (Hg,Pb)-1\(^{89}\)Ba;Sr\(^{223}\) system suggest that Pb enters the Hg-1223 structure with an oxidation state higher than III. It has further been concluded that substituting the phase with Pb increases the amount of excess oxygen, \(z\), in the (Hg,Pb)O\(_z\) charge-reservoir block. This was found to counter-balance the higher-valent for the lower-valent cation substitution effect, i.e. Pb\(^{III}/IV\) for Hg\(^{II}\), and thereby to result in an increase in the CuO\(_2\)-plane hole concentration.

References