X-ray absorption near-edge structure study of Bi$_{2-x}$Pb$_x$Sr$_2$(Sm$_{0.85}$Ce$_{0.15}$)$_2$Cu$_2$O$_{10+y}$

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Abstract

Near-edge X-ray absorption spectroscopy results of Ce L$_3$-, Pb L$_3$-, Bi L$_3$-, and Cu K-edge for Bi$_{2-x}$Pb$_x$Sr$_2$(Sm$_{0.85}$Ce$_{0.15}$)$_2$Cu$_2$O$_{10+y}$ ($0 \leq x \leq 1$) series are presented. Ce in this series is found to be in a valence state similar to that in CeO$_2$. The lack of the 2p → 6s transition feature in both the Bi and Pb L$_3$-edge spectra indicates that Bi and Pb have valence values close to +3 and +2, respectively. With the Pb substitution level $x$ increasing from 0.0 to 0.6, the Cu valence $v_K$ increases from 2.20 to 2.34, indicating that the substitution of Bi$^{3+}$ by Pb$^{2+}$ draws electronic charge out of the CuO$_2$ layers, increasing the oxygen hole concentration as well as the superconducting transition temperature $T_c$. We also found that for $0.0 \leq x \leq 0.6$, the Cu valence determined from mean characteristic energy of the Cu K-edge spectra is very close to the formal Cu valence estimated by charge neutrality consideration. The decrease of Cu valence with increase of $x$ for samples with $x > 0.6$ could be due to the formation of a second phase in these samples.

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1. Introduction

In the big family of high-$T_c$ oxide superconductors there exist several superconducting cuprate systems containing the same fluorite-like (R,Ce)$_2$O$_2$ layers where R is the rare earth elements [1–3]. These fluorite-like layers play important roles in stabilizing the crystal structure and in regulating the charge carrier density in the conducting CuO$_2$ layers in these materials. The Bi$_2$Sr$_2$(R,Ce)$_2$Cu$_2$O$_{10+y}$ (the so called Bi-2222) compound, originally discovered by Tokura et al. [2], is a compound with such fluorite-like layers. This compound has a “double sandwich” structure:

$$\text{Bi}_2\text{Sr}_2(\text{R,Ce})_2\text{Cu}_2\text{O}_{10+y}$$
first a (R,Ce)\textsubscript{2}O\textsubscript{2} block of fluorite-type structure is between two pyramidal CuO\textsubscript{2} layers, then the whole unit is between two double BiO layers. This structure is very similar to that of Bi\textsubscript{2}Sr\textsubscript{2}Ca\textsubscript{1−x}Cu\textsubscript{x}O\textsubscript{8+δ} (or Bi-2212) in that Bi-2222 can be obtained with the replacement of the Ca layer in Bi-2212 by a fluorite-type (R,Ce)\textsubscript{2}O\textsubscript{2} block (see Fig. 1). For the Bi\textsubscript{2−x}Pb\textsubscript{x}Sr\textsubscript{2}(Sm\textsubscript{0.85}Ce\textsubscript{0.15})\textsubscript{2−x}Cu\textsubscript{x}O\textsubscript{10+y} series with 0 \leq x \leq 1 (hereafter referred as (Bi,Pb)-2222 series), the effects of this substitution of Bi by Pb on the superconducting properties were previously studied by X-ray diffraction, transport, magnetic susceptibility, and transmission electron microscopy measurements [4]. It was found that with the increase of Pb substitution level \(x\), the cell volume decreases, both \(T_c\) and carrier concentration increase, and Meissner fraction peaks at \(x = 0.6\). In the absence of the valence data about the constituent elements in the (Bi,Pb)-2222 series, these results were explained only by assuming certain valence values for Ce, Bi, and Pb. Thus measuring the valence values of the constituent elements in the (Bi,Pb)-2222 series should provide valuable information about how electronic charges are transferred between the conducting CuO\textsubscript{2} layers and the neighboring (Bi,Pb)-O charge reservoir layers. This was our first motivation for carrying out this X-ray absorption near-edge structure (XANES) study on this series.

Another motivation for studying the (Bi,Pb)-2222 series is to see if the variation of \(T_c\) or Meissner fraction are correlated with the Cu valence. A common feature of high \(T_c\) superconductors (HTS) is that high-temperature superconductivity appears to be produced by doping semiconductor-like divalent Cu compounds with electrons or holes. An important work for understanding high-\(T_c\) superconductivity is the experimental determination of the electronic states of Cu and O in the CuO\textsubscript{2} layers due to such doping. In the past, much effort has been made to establish correlation between \(T_c\) and Cu valence (as well as the hole concentration in the O-2p orbitals) for various Pb-substituted Bi- and Tl-based HTS [5–8]. We would like to determine the Cu valence by Cu K-edge measurement and see whether the Pb doping on the Bi sites draws electrons out of the Cu sites or inject electrons into the Cu sites. Particularly, we would like to determine if the Cu valence variation is correlated to the superconducting properties in the Bi-2222 series. To evaluate the Cu valence, the Ce L\textsubscript{3}-edge measurement and valence determination for the Ce ions in the fluorite-like (Sm,Ce)\textsubscript{2}O\textsubscript{2} layers are also needed.

In this paper, we present the Ce L\textsubscript{3}-, Bi L\textsubscript{3}-, Pb L\textsubscript{3}-, and Cu K-edge spectra for Bi\textsubscript{2−x}Pb\textsubscript{x}Sr\textsubscript{2}(Sm\textsubscript{0.85}Ce\textsubscript{0.15})\textsubscript{2−x}Cu\textsubscript{x}O\textsubscript{10+y} (0 \leq x \leq 1). To our knowledge, this is the first X-ray absorption spectroscopy study on this compound series. In the data presentation and discussion, we always compare the XANES results for (Bi,Pb)-2222 series with that of the Bi-2212 compound due to the previously mentioned similarities in their crystal structures.

2. Experimental

\textit{Bi\textsubscript{2−x}Pb\textsubscript{x}Sr\textsubscript{2}(Sm\textsubscript{0.85}Ce\textsubscript{0.15})\textsubscript{2}Cu\textsubscript{x}O\textsubscript{10+y} (0 \leq x \leq 1) polycrystalline samples used in this study were provided by Tarascon, which were synthesized by}
solid-state reaction as described in Ref. [4]. All samples were confirmed to be single phase by X-ray diffraction measurements. The values of oxygen content of the samples were determined by thermogravimetric analysis (TGA) by Remschnig et al. [4]. These values are listed in Table 1. The X-ray absorption near-edge structure (XANES) spectra were collected from the X-11A beam line at the National Synchrotron Light Source (NSLS) in Brookhaven National Laboratory. During the measurement, NSLS was operated at an energy of 2.5 GeV and electron current from 40 to 100 mA. A double-crystal monochromator with Si (111) crystals was used for energy selection. At the Cu K-edge, the monochromator was detuned by reducing the incident photon flux about 10% in order to suppress contamination from harmonics. The energy resolution ($\Delta E/E$) of the X-11A beam line was $2 \times 10^{-4}$. At the Cu K-edge and Pb L$_3$-edge, the energy resolutions were about 2 eV and 3 eV, respectively. The data were measured in transmission mode with gas-filled ion chamber detectors. The samples were made in the form of four to eight layers of fine powders dusted onto scotch tapes. Energy calibrations of the spectra were made by simultaneously measuring the absorption spectra of the samples with chosen reference compounds. The reference compounds used in this study for Ce L$_{3\gamma}$, Bi L$_{3\gamma}$, Pb L$_{3\gamma}$, and Cu K-edge measurements were CeO$_2$, Bi$_2$O$_3$, PbO, and Cu$_2$O, respectively. The XANES measurements were carried out at room temperature. All of the XANES spectra for samples and reference compounds presented in Fig. 2 through Fig. 8 of this paper were our own data measured at beam line X-11A, and are normalized to unity in the continuum region.

![Fig. 2. Ce L$_{3\gamma}$-edge absorption spectra of Bi$_2$Sr$_2$(Sm$_{0.85}$Ce$_{0.15}$)$_2$Cu$_2$O$_{10+y}$ and reference compound CeO$_2$.](image)

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>$S$ (eV)</th>
<th>$\sigma$ (eV)</th>
<th>$y$</th>
<th>$v_K$</th>
<th>$v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-metal</td>
<td>3.59</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>4.18</td>
<td>0.03</td>
<td>+1</td>
<td>+1</td>
<td></td>
</tr>
<tr>
<td>Nd$_2$CuO$_4$</td>
<td>6.95</td>
<td>0.15</td>
<td>+2</td>
<td>+2</td>
<td></td>
</tr>
<tr>
<td>Bi$_2$Sr$_2$CaCu$<em>2$O$</em>{8+x}$ (Bi-2212)</td>
<td>7.96</td>
<td>0.20</td>
<td>+2.25</td>
<td>(2 + $\delta$)</td>
<td></td>
</tr>
<tr>
<td>Bi$_{2-x}$Pb$<em>x$Sr$<em>2$(Sm$</em>{0.85}$Ce$</em>{0.15}$)$_2$Cu$<em>2$O$</em>{10+y}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x = 0.0$</td>
<td>7.79</td>
<td>0.38</td>
<td>0.320</td>
<td>+2.20</td>
<td>+2.25</td>
</tr>
<tr>
<td>$x = 0.1$</td>
<td>7.93</td>
<td>0.34</td>
<td>0.280</td>
<td>+2.24</td>
<td>+2.26</td>
</tr>
<tr>
<td>$x = 0.4$</td>
<td>8.04</td>
<td>0.38</td>
<td>0.160</td>
<td>+2.28</td>
<td>+2.29</td>
</tr>
<tr>
<td>$x = 0.5$</td>
<td>8.10</td>
<td>0.30</td>
<td>0.125</td>
<td>+2.30</td>
<td>+2.31</td>
</tr>
<tr>
<td>$x = 0.6$</td>
<td>8.23</td>
<td>0.25</td>
<td>0.080</td>
<td>+2.34</td>
<td>+2.32</td>
</tr>
<tr>
<td>$x = 0.8$</td>
<td>8.04</td>
<td>0.22</td>
<td>0.030</td>
<td>+2.28</td>
<td>+2.34</td>
</tr>
<tr>
<td>$x = 0.9$</td>
<td>8.00</td>
<td>0.23</td>
<td>−0.030</td>
<td>+2.27</td>
<td>+2.35</td>
</tr>
<tr>
<td>$x = 1.0$</td>
<td>8.06</td>
<td>0.22</td>
<td>−0.001</td>
<td>+2.28</td>
<td>+2.37</td>
</tr>
</tbody>
</table>

The mean values are based on 10 different upper limits ($L_1$) of integration between 30 and 40 eV at 1 eV steps. The values of $v_K$ for (Bi,Pb)-2222 series are given by $v_K = 2 + (S - 7.20)/3.02$. The last column displays the formal Cu valence, $v$, estimated by charge neutrality consideration and can be expressed as a function of $x$ as $v = 0.122x + 2.245$ for the (Bi,Pb)-2222 series. The values for the oxygen content, $y$, are from Ref. [4].
3. Results and discussion

3.1. Ce L$_3$-edge

Fig. 2 shows the Ce L$_3$-edge spectra for the reference sample CeO$_2$ and the Bi$_{1.5}$Pb$_{0.5}$Sr$_2$(Sm$_{0.85}$Ce$_{0.15}$)$_2$Cu$_2$O$_{10+y}$ sample with $x = 0.5$. The valence of Ce is related to the relative magnitude of the lower energy Ce$^{3+}$ and higher energy Ce$^{4+}$ peaks. By the standard peak fitting and valence determination method [9], the Ce L$_3$ valence for these two compounds is found to be almost the same, i.e., about +3.5. Our Ce L$_3$ edge valence for the entire (Bi,Pb)-2222 series in the entire range $0 \leq x \leq 1$ are almost identical to the $x = 0.5$ spectrum shown in Fig. 2, indicating that the average Ce valence for the entire (Bi,Pb)-2222 series is unchanged with the substitution of Bi by Pb. Even though the measured Ce valence is about +3.5 rather than the formal valence +4, if one considers that this reduced valence of Ce is compensated by holes on neighboring oxygen ligands arising from hybridization, then the net charge doping due to Ce could be similar to what expected for Ce$^{4+}$.

3.2. Bi L$_3$-edge

In Fig. 3, we show the Bi L$_3$-edge spectra for the (Bi,Pb)-2222 compound at $x = 0$, i.e., the Bi$_2$Sr$_2$-(Sm$_{0.85}$Ce$_{0.15}$)$_2$Cu$_2$O$_{10+y}$, together with the spectra of Bi$_2$Sr$_2$CaCu$_2$O$_8$ (Bi-2212), Tl$_{0.7}$Bi$_{0.3}$Sr$_2$CuO$_5$, and reference compound Bi$_2$O$_3$ (with formal valence 3+). In general, there are three main features to note in the Bi L$_3$-edge absorption spectra. Our previous polarized Bi L$_3$-edge spectra for Bi-2222 single crystals [10] clearly showed that features A and B are due to the $2p \rightarrow 6d_{2g}$ and $2p \rightarrow 6d_{eg}$ transitions, respectively. These two features converge in Bi$_2$O$_3$. The pre-edge feature a can be assigned to the $2p \rightarrow 6s$ transitions [6,10,11]. This feature is absent in Bi$_2$O$_3$ because Bi$^{3+}$ has a filled $6s^2$ configuration. Feature a indicates of the presence of the empty Bi-6s orbitals, or Bi$^{5+}$ state. This feature is prominent for the Bi$^{3+}$/Bi$^{5+}$ mixed material Tl$_{0.7}$Bi$_{0.3}$Sr$_2$CuO$_5$ [11], but it is absent for both the Bi-2222 and Bi-2212 samples. Thus, Bi in both Bi-2222 and Bi-2212 has the same filled $6s^2$ configuration as that in Bi$_2$O$_3$.

The valence value of Bi for the Bi-2222 compound can be estimated by the edge-energy shift with respect to the edge energy of the reference sample Bi$_2$O$_3$. This estimate is based on a general rule in the XANES that the chemical shift characterized by the edge energy usually increases with the increase of valence of the cation, unless the shift is either suppressed by the covalent character of the bond or enhanced by the formation of a metal-metal bonding [12]. According to our previous and Retoux et al.’s Bi L$_3$-edge results for other Bi-based high-$T_c$ superconducting compounds, a valence change of Bi from +3 to +5 should correspond to a 2.2–2.5 eV upward edge-energy shift of the Bi L$_3$-edge [6,11]. Fig. 3 shows that the edge energy $E_0$ for the Bi-2222 compound, defined as the midpoint energy (corresponding to absorption coefficient $\mu(E) = 0.5$) of the main step of the edge, is almost identical to that for Bi-2212 and Bi$_2$O$_3$. This suggests that the formal valence of Bi for the Bi-2222 compound should be close to +3, similar to that for Bi$_2$O$_3$. For the Bi L$_3$-edge spectrum of the Bi$^{3+}$/Bi$^{5+}$ mixed material Tl$_{0.7}$Bi$_{0.3}$Sr$_2$CuO$_5$ (see Fig. 3), the edge energy is shifted about 1.6 eV toward the higher energy side, indicating the valence of Bi for this compound is about +4.28 to +4.45.

The Bi L$_3$-edge spectra for several Bi$_{2-x}$Pb$_x$-Sr$_2$(Sm$_{1-x}$Ce$_x$)$_2$Cu$_2$O$_{10+y}$ samples with $x = 0.0$, $x = 0.5$, and $x = 1.0$ are shown in Fig. 3.
0.1, 0.3, 0.5, 0.7, 0.9, and 1.0 were measured, and it was found that the spectra (including edge energy) for these compounds are almost identical. In Fig. 4 we compare the Bi \( L_3 \)-edge for the \( x = 0 \) sample with the \( x = 1.0 \) sample, along with the reference spectrum of Bi\( _2 \)O\( _3 \). Both the lack of the feature \( a \) and the same value for the edge energies indicate that the Bi valence is close to +3 for all of these three compounds. From our Bi \( L_3 \)-edge results, we conclude that the average Bi valence for the entire (Bi,Pb)-2222 series is close to +3, and it is not affected by the Pb for Bi substitution.

### 3.3. Pb \( L_3 \)-edge

In Fig. 5, the Pb \( L_3 \)-edge spectrum for the \( x = 0.5 \) sample is shown in comparison to the spectra of the reference compounds PbO and PbO\( _2 \), which have formal valence +2 and +4, respectively [5,13]. Similar to the feature assignments for Bi \( L_3 \)-edge spectra, the broaden features A and B, observed in all of the three spectra, are assigned to the \( 2p \rightarrow d_{\text{t}_{2g}} \) (\( d_{xy}, d_{yz}, \) and \( d_{xz} \)) and \( 2p \rightarrow 6d_{s_{g}} \) (\( d_{2z^2} \) and \( d_{x^2-y^2} \)) transitions, respectively. The pre-edge feature, labeled by letter \( a \), is assigned to \( 2p \rightarrow 6s \) transition. The intensity of the feature \( a \) is a measure of the 6s hole population, or the Pb\(^{4+} \) concentration. It can be seen that this Pb\(^{4+} \) feature is absent in both the spectra of the Pb\(^{2+} \) compound PbO and the \( x = 0.5 \) (Bi,Pb)-2222 sample, but it is quite prominent in the spectrum of the Pb\(^{4+} \) compound PbO\( _2 \). The absence of this feature in the spectra of PbO and \( x = 0.5 \) sample indicates that the Pb 6s-orbitals in these two compounds are completely filled. Thus the Pb valence for the \( x = 0.5 \) sample should be similar to that for PbO, and a valence close to +2 should be observed. This conclusion is also supported by the fact that the edge energy for the \( x = 0.5 \) sample is almost the same as that for PbO. On the other hand, compared with the \( x = 0.5 \) sample and PbO, the edge energy for the Pb\(^{4+} \) compound PbO\( _2 \) has a big chemical shift (about 2.5 eV) toward the higher energy side.

The Pb \( L_3 \)-edge spectra for the (Bi,Pb)-2222 series were measured for samples with \( x = 0.0, 0.1, 0.4, 0.5, 0.6, 0.8, 0.9 \) and 1.0. Since these spectra for all of these samples are almost identical, we only show in Fig. 6 the spectra for samples with \( x = 0.3 \) and 1.0. The disappearance of the feature \( a \) in all the spectra together with the same values for the edge energies clearly indicates that Pb valence for the entire (Bi,Pb)-2222 series \( (0 < x \leq 1.0) \) is +2.

### 3.4. Cu K-edge

We measured Cu K-edge spectra for eight Bi\( _{2-x} \)Pb\( _x \)Sr\( _2 \)(Sm\(_{0.85} \)Ce\(_{0.15} \))\( _2 \)Cu\( _2 \)O\(_{10+y} \) samples with \( x = 0.0, 0.1, 0.4, 0.5, 0.6, 0.8, 0.9 \) and 1.0. In

![Bi L\(_3\)-edge absorption spectra of Bi\( _2 \)Pb\( _x \)Sr\( _2 \)(Sm\(_{0.85} \)Ce\(_{0.15} \))\( _2 \)Cu\( _2 \)O\(_{10+y} \).](image1)

![Pb L\(_3\)-edge absorption spectra for Bi\( _2 \)Pb\( _x \)Sr\( _2 \)(Sm\(_{0.85} \)Ce\(_{0.15} \))\( _2 \)Cu\( _2 \)O\(_{10+y} \) with \( x = 0.5 \) and reference compounds PbO and PbO\( _2 \).](image2)
Fig. 7, we compare the spectra of the $x = 0.0$ and 0.6 samples with two well-studied reference compounds Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (or Bi-2212) [6,10] and Nd$_2$CuO$_4$ [14]. In Fig. 8 we compare the spectra between the $x = 0.6$ and $x = 1.0$ sample. The spectra for the $x = 0.8$ and $x = 0.9$ are not plotted in Fig. 8 because they are almost identical to that for the $x = 1.0$ sample. The formal Cu valence values in Nd$_2$CuO$_4$ and Bi-2212 are +2 and +(2 + $\delta$), respectively. The noticeably weak feature a (located at about 8977 eV) appearing at the foot of the edges is due to the quadruple 1s $\rightarrow$ 3d transition. The presence of this feature in the Cu-edge spectra is a signature of the existence of 3d holes in the ground states. The double-peak features labeled by the letters A and B are assigned to the 1s $\rightarrow$ 4p$_x$ (3d$^{10}$ L) and 1s $\rightarrow$ 4p$_y$ (3d$^{10}$ L) transitions, respectively; whereas the double-peak features labeled by the letter C and D are assigned to the 1s $\rightarrow$ 4p$_x$ (3d$^{10}$ L) and 1s $\rightarrow$ 4p$_y$ (3d$^{9}$) transitions [14]. Here L denotes a hole in the ligand shell caused by the transfer of an electron from a ligand O-2p state to a Cu-3d state. The Cu K-edge features corresponding to different Cu 3d configurations in Nd$_2$CuO$_4$ have been interpreted successfully with a cluster model description [14].

To qualitatively estimate the Cu valence, one needs to examine the edge energies of the Cu K-edge spectra. One can observe in Fig. 7 that the edge-energy increases in the following order for three samples: the Cu$^{2+}$ compound Nd$_2$CuO$_4$, Bi-2212 (which has almost the same edge energy as that for the Bi-2222 at $x = 0.0$), and then the (Bi,Pb)-2222 with $x = 0.6$ sample. This observation suggests that the Cu valence for the (Bi,Pb)-2222 series is substantially greater than +2, and it increases with the increase of $x$ from 0.0 to 0.6. Fig. 8 shows that the edge energy for the $x = 1.0$ sample is lower than that for the $x = 0.6$ sample indicating that the Cu valence decreases with the increase of $x$ from 0.6 to 1.0.
A more quantitative method for determining Cu valence from Cu K-edge absorption spectra is by calculating the so-called “characteristic Energy” or the “average position” of the absorption edge [15,16]. In this method, the characteristic energy S for an absorption edge is defined in terms of the moments of the energy with respect to the absorption coefficient \( \mu(E) \) in an energy region [15,16]. It has been shown that the value of characteristic energy S is linearly proportional to the effective charge on Cu theoretically calculated using discrete variational method of a molecular cluster in the local density approximation [17].

Thus, the higher the characteristic energy S, so too is, the Cu valence higher. Based on a detailed analysis on the S values for a multitude of Cu compounds, Alp et al. found that there is a shift by about 3.1 eV to higher energies for each electron removed from a Cu atom (or a 1.0 increase in Cu valence) [16]. Following the definition of the characteristic energy S given by Alp et al. [15,16], we calculated S and its standard deviation for the Cu K-edge spectra of this (Bi,Pb)-2222 series and other Cu compounds. These results are listed in Table 1. Note that all of the XAS spectra data (for all samples and reference compounds) used in the calculation were our own originally measured data, no spectra data from any other reference or group were used in this calculation. In the calculation, the photon energy E was expressed in eV relative to the first inflection point (located at \( E_0 = 8977.33 \text{ eV} \)) of the derivative of the Cu-metal absorption spectrum (not shown here), and the lower limit \( L_0 \) of the integration was set to be \(-5 \text{ eV} \) (corresponding to 8972.33 eV in Fig. 7) on this energy scale. The upper limit \( L_1 \) was chosen to be in the lower end of the energy range of the extended X-ray absorption fine structure (EXAFS), i.e., from 30 to 40 eV above \( E_0 \) in step of 1 eV. Table 1 shows that the mean characteristic energy values are 4.18, 6.95, 7.79, 7.96, and 8.23 for Cu\(^{1+}\) compound Cu\(_2\)O, Cu\(^{2+}\) compound Nd\(_3\)CuO\(_4\), Bi-2222 (x = 0), Bi-2212, (Bi,Pb)-2222 (x = 0.6) samples, respectively. In Fig. 9, the mean characteristic energy S is plotted against x for the (Bi,Pb)-2222 series. Fig. 9 shows that the S peaks up at x = 0.6 for this series. Alp et al. studied the characteristic energy S for 10 Cu compounds with formal Cu valence +2 [16]. Their data showed that S values for these Cu\(^{2+}\) compounds range from 6.46 to 7.94, with an average value of 7.20. Using this average value for Cu\(^{2+}\) and \( S = 4.18 \) (from our Cu K-edge spectrum of Cu\(_2\)O) for Cu\(^{1+}\), one can see that a 3.02 eV change in S corresponds to a 1.0 increase in the Cu valence. If one assumes that S increases linearly with Cu valence at rate of 3.02 eV from Cu\(^{2+}\) to Cu\(^{3+}\), then the values of Cu valence, \( v_K \), estimated from the S values of Cu K-edge spectra, will be \( v_K = 2 + (S - 7.2)/3.02 \). Using this relationship and the measured S values, the \( v_K \) values are +2.20, +2.25, and +2.34, respectively, for the Bi-2222 (x = 0), Bi-2212, and (Bi,Pb)-2222 (x = 0.6) samples (see Table 1). The \( v_K \) value (+2.25) for Bi-2212 estimated here is located at the lower end of the Bi valence range estimated by Retoux et al. [6], but it is close to the value obtained from our previous polarized X-ray absorption studies on Bi-2212 single crystals [10].

Interestingly, we found from Table 1 that the values of \( v_K \) for samples with x from 0.0 to 0.6 are very close to those estimated from charge neutrality consideration. Previous TGA measurement made by Remschnig et al. [4] on these Bi\(_{2-x}\)Pb\(_x\)-Sr\(_2\)(Sm\(_{0.85}\)Ce\(_{0.15}\))\(_2\)Cu\(_2\)O\(_{10+y}\) samples showed that the excess of oxygen content, y, in these series (see Table 1) decreases almost linearly with x from about 0.32 at x = 0.0 to about -0.02 at x = 0.9.
Using this result, a linear relationship between \( x \) and \( y \) can be obtained as:

\[
y = -0.378x + 0.32.
\]

With the valence values (i.e., +3.5 for Ce, +3 for Bi, and +2 for Pb) measured in this study and the charge neutrality condition for all compounds, one can obtain the formal Cu valence as:

\[
y = 0.122x + 2.245.
\]

According to this \( v-x \) relationship, the formal copper valence can be estimated to be:

- \( v = +2.25 \) at \( x = 0 \)
- \( v = +2.32 \) at \( x = 0.6 \)

(see Table 1), which are quite close to the values of \( v_K \).

Fig. 9 and the data in Table 1 shows that the mean characteristic energy \( S \) for the \((\text{Bi,Pb})_{2222}\) series, \( \text{Bi} \text{2}_{0.85}\text{Ce}_{0.15}\text{Sr}2\text{Cu}2\text{O}_{10+y} \), decreases from 8.23 at \( x = 0.6 \) to 8.06 at \( x = 1.0 \). This is consistent with the downward shift of the edge-energy observed in Fig. 8. Corresponding to the decrease in both \( S \) and edge-energy, the Cu valence decreases from \( v = 2.34 \) at \( x = 0.6 \) to \( v = 2.28 \) at \( x = 1.0 \). We notice that the decrease of \( v_K \) with increasing \( x \) from 0.6 to 1.0 is actually opposite to the variation trend of \( v \) estimated from the formula \( v = 0.122x + 2.245 \). This decrease of \( v_K \) with increase of \( x \) from \( x = 0.6 \) to \( x = 1.0 \) might be due to the possible formation of second phase (although not detectable by X-ray diffraction) in samples over the range of composition \( 0.7 \leq x \leq 1.0 \). Such second phase also was used by Remschnig et al. [4] as an evidence for explaining the peaking value of Meissner fraction at \( x = 0.6 \) in this compound series.

4. Conclusion

We have measured the near-edge X-ray absorption spectra for the \( \text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2(\text{Sm}_{0.85}\text{Ce}_{0.15})_2\text{Cu}_2\text{O}_{10+y} \) \((0 \leq x \leq 1)\) series at Ce L\(_3\)-, Pb L\(_3\)-, Bi L\(_3\)-, and Cu K-edge. Ce valence state in this series is found to be similar to that in CeO\(_2\). The Bi and Pb L\(_3\)-edge results indicate that Bi and Pb in this series have valence values close to +3 and +2, respectively. The Cu valence in this series is estimated by both the mean characteristic energy \( S \) and the charge neutrality consideration. It is found that with the increase of Pb for Bi substitution level \( x \) from \( x = 0.0 \) to \( x = 0.6 \), Cu valence increases. This suggests that the substitution of \( \text{Bi}^{3+} \) by \( \text{Pb}^{2+} \) draws electronic charge out of the CuO\(_2\) layers and increases oxygen hole (charge carrier) concentration in these layers. This decrease of Cu valence with increasing \( x \) from \( x = 0.6 \) to \( x = 1.0 \) could be attributed to a possible formation of second phase in samples with \( x > 0.6 \).

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References


