Distortion of ReO$_6$ octahedron in the Hg$_{0.82}$Re$_{0.18}$Ba$_2$Ca$_2$Cu$_3$O$_{8+d}$ superconductor

M.T.D. Orlando $^a$, C.A.C. Passos $^a$, J.L. Passamai Jr. $^a$, E.F. Medeiros $^a$, C.G.P. Orlando $^a$, R.V. Sampaio $^a$, H.S.P. Correa $^b$, F.C.L. de Melo $^c$, L.G. Martinez $^d$, J.L. Rossi $^d$

$^a$ Preditlab—High Pressure Laboratory, UFES, Vitoria, ES 29075-910, Brazil
$^b$ Departamento de Física, Universidade Federal do Mato Grosso do Sul, Brazil
$^c$ Centro Técnico Aeroespacial—IAE, São José dos Campos-SP, CEP 12228-904, Brazil
$^d$ Instituto de Pesquisas Energéticas e Nucleares, Campus USP, Brazil

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Abstract

Rhenium (Re) L$_{III}$ edge X-ray absorption spectroscopy was used in order to determine rhenium valence and the local oxygen coordination in Hg$_{0.82}$Re$_{0.18}$Ba$_2$Ca$_2$Cu$_3$O$_{8+d}$ polycrystalline samples prepared with three different oxygen content. Thermoelectric power measurements confirmed small increments of charge carrier number as a function of oxygen content. The X-ray absorption near-edge spectroscopy (XANES) analysis showed a valence variation for Re (+6.8, +6.9 and +7.0) in these samples. The extended X-ray absorption fine structure (EXAFS) analysis indicated that the oxygen local order around Re atoms in these Hg$_{0.82}$Re$_{0.18}$Ba$_2$Ca$_2$Cu$_3$O$_{8+d}$ samples can be described as a distorted ReO$_6$ octahedron with two different Re–O bound lengths. The valence evaluated by the bound length in the distorted ReO$_6$ octahedron is in agreement with the XANES measurements. Moreover, the distorted ReO$_6$ octahedron and the Cu–O$_{pl}$ angle built a scenario which can justify the high intrinsic term value found in the optimal doped sample under external hydrostatic pressure.

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1. Introduction

After the discovery of high-$T_c$ superconductor (La–Ba–Cu–O system) by Bednorz and Müller [1] in 1986, several others ceramic superconductors have been produced. Regarding ceramic superconductor families, the scientific community has shown a growing interest in relating variation of the cell parameters, oxidation state of the atoms, and other physical properties to the oxygen content or carrier doping state [2–13].

Among these several superconductor families, the mercury family HgBa$_2$Ca$_{n-1}$Cu$_n$O$_y$ or Hg-12$(n-1)n$ with $(n = 1, 2, 3, \ldots)$ obtained by Putilin et al. [14] have shown the highest $T_c$ (134 K). Although loss of superconductor properties due to CO$_2$ contamination have been observed on Hg family, this matter has been overcome by partial substitution of mercury (Hg) by rhenium (Re) [15,16]. In addition, Orlando et al. [17] have observed a clear influence of Re content on the oxygen amount present in the HgO$_6$ layer: Re brings additional oxygen to this site. These additional oxygen atoms are very stable and complete the mercury layer. Specifically, samples with 18% nominal atomic Re have presented an improvement of the superconducting properties [17], such as the critical current density [18], when compared with Hg-1223 ($n = 3$ without Re).

Studies concerning the influence of oxygen partial pressure used during precursor preparation and its correlation with bulk properties of Hg$_{1-x}$Re$_x$Ba$_2$Ca$_2$Cu$_3$O$_{6+d}$...
[(Hg,Re)-1223] polycrystalline compounds have been reported since 1999 [19–21]. These different precursor annealing treatments can modify the charge carrier number in the CuO2 layers inside the Hg,Re-1223 superconductor. Evaluation of this charge carrier number is important to determine if the sample is over doped, optimal doped or under doped. A direct correlation between charge carrier number and the Hg-based samples produced with different annealing treatments can be obtained by thermoelectric power measurements [22,23]. Through the analysis of Hg-1223 phase diagram, a study from the under doped to over doped regions revealed a change of the thermoelectric power value at room temperature.

The charge carrier number can be correlated with the average valence of the Cu in the Cu-O layer, which, for the Hg,Re-1223 compound, depends on the Re valence in the reservoir layer. To the best of our knowledge, there are no reports in the literature about Re valence measurements. In this way, X-ray absorption spectroscopy (XAS) was used for investigating Re neighbour. In X-Ray absorption near-edge structure (XANES) the average valence state of the selected type of the atom in the sample can be obtained from the information hidden in the energy shift of the X-ray absorption edge itself [24]. The X-ray absorption near-edge spectroscopy (XANES) provides Re average valence for Re inside the (Hg,Re)-1223 as an oxygen function. Moreover, extended X-ray absorption fine structure (EXAFS) signal allows us to investigate the structural oxygen symmetry surrounding Re atom.

2. Experimental

2.1. Precursor preparation

Firstly, the standard preparation of the ceramic precursor began with a mixture of Ba2Ca2Cu3Ox (99.0% PRAX-AIR) and ReO3 (99.0% Aldrich) in powder form with a molar relationship of 1:0.18 [19]. These powders were homogenized in an agate mortar and compacted in a pill form with an uniaxial pressure of 0.5 GPa. The produced pellet was heated at 850 °C in a flow of oxygen (99.5%) for 15 h. The obtained precursor was crushed, homogenized and compacted again before being heated a second time at 920 °C for 12 h in a flow of oxygen. The later procedure was repeated seven more times. These thermal treatment processes are thought to provide a good homogenization of rhenium and to eliminate the carbonates remaining in the precursor sample [19,25].

2.2. Precursor annealing

The obtained precursor material was then submitted to an annealing at 920 °C for 24 h in a flowing mixture of argon (99.5% purity) and oxygen (99.5% purity) maintained at 1 bar. Three ceramic precursors have been prepared using distinct partial pressure of oxygen: 5% of O2 and 95% of Ar (sample A), 10% of O2 and 90% of Ar (sample B) and 15% of O2 and 85% of Ar (sample C) [26]. One Quanta Chrome Inc. gas mixer, with controlled flow rate, was used in order to control the oxygen and the argon gas mixture proportion [20].

The XRD patterns of these sintered precursors as function of the oxygen partial pressure, PO2, are shown in Fig. 1. The X-ray diffraction measurements were carried out at Laboratório Nacional de Luz Sincrotrons (LNLS-Campinas-Brazil) with $\lambda = 1.54056$ Å. The identified phases were BaCuO2+x (101 phase), Ba2Cu3O5+x (203 phase), Ba4CaCu3O8+x (413 phase), Ca2CuO3, and Ca3-Re2O12. It can be noticed that the peaks associated with the 101 phase, which has oxygen stoichiometry variation, are slightly displaced to low angle. Thus, it indicated that there was an increase in the oxygen content of the precursor ceramics B and C, as compared with ceramic A. This interpretation is in agreement with Fujinami et al. [23]. They have achieved Hg-1223 samples with different doping state using the oxidized precursor (BaCuO2+x). It is important to state that the displacement of the peaks have not come from the zero shift since peaks of Ca3CuO3 have not presented any displacement, as shown in Fig. 1.

2.3. Superconductor synthesis

Finally, the precursors prepared with different O2 partial pressure were blended with HgO at the molar relationship of 1:0.82. They were homogenized in an agate mortar and compacted in a pellet form with an uniaxial pressure of 1 GPa. The pellets with a typical dimensions $5 \times 5 \times 20$ mm3 were wrapped in a gold foil (99.999%) and were introduced in a 8 mm inner diameter quartz tube. A quartz rod (7 mm diameter and 40 mm length) was also introduced together with each pellet. Each wrapped sample (A, B and C) received an extra quantity of Hg (l) which turned immediately into amalgam form with gold. The ratio between the mercury mass and the gold mass was 0.045. Based on the study of the effect of the quartz tube filling factor (ff) [27], we used ff $\approx 1.0$ g cm$^{-3}$ and ff$_{Hg}$ $\approx 0.010$ g cm$^{-3}$ [20]. The quartz tubes were sealed in a high vacuum of $3 \times 10^{-6}$ Torr. The average density of the pellet samples was $\rho = 4.2(2)$ g cm$^{-3}$. All procedures have taken place inside a glove box filled with argon gas. In order to improve the grain size growth, we have also changed the annealing time to 72 h at 865 °C, as compared to Sin et al. [26]. Moreover, three sealed quartz tubes, each one with a sample inside, were put together in the same place inside an isostatic pressure furnace. The furnace was filled with 14 bar of Ar in order to avoid explosion of any quartz tube.

2.4. Sample characterization

2.4.1. X-ray diffraction and Rietveld refinement

XRD measurements were performed using laboratory diffractometers models Rigaku Multiflex and D-MAX with CuKα radiation. The spectra were measured from 2θ up to
122° with step size of 0.01° and counting times varying from 15 to 25 s. The instrumental parameters were obtained from the refinement of standards LaB₆ and Al₂O₃ (NIST) samples. Rietveld refinements [28] were performed using the program GSAS [29] with the interface EXPGUI [30].

A typical refinement is shown in Fig. 2. The main phase found was Hg,Re-1223 (93 wt.%) residues of HgCaO₂, Ba₂CuO₄₋ₓ, Ba₄Ca₂Cu₃O₇₋ₓ, Ca₂Re₂O₁₂ and Ca₂CuO₄.

![XRD patterns](image1)

Fig. 1. XRD patterns of the precursor ceramics with different oxygen partial pressure. The identified phases were: BaCuO₂₋ₓ, Ba₂CuO₄₋ₓ, Ba₄Ca₂Cu₃O₇₋ₓ, Ba₃Re₂O₁₂ and Ca₂CuO₄.

![Reitveld refinement](image2)

Fig. 2. Reitveld refinement of the sample B (optimal doped).
in the crystal structure of the phase Hg-Re-1223. Table 1 shows the refinements results.

### 2.4.2. Magnetic susceptibility under hydrostatic pressure

The ac magnetic susceptibility versus temperature measurements at room pressure have exhibited closer $T_{\text{conset}}$ ($A = 132.6$ K, $B = 133.2$ K, and $C = 132.7$ K) for the three samples, which indicates the similar oxygen content in all samples [21]. The high-$T_c$ cuprates superconductors have been found to show a parabolic variation of $T_c$ as a function of the hole concentration,

$$T_c = T_{c}^{\text{max}} - 8.26T_{c}^{\text{max}}[(n - 0.160)^2],$$

where $n$ is hole number per Cu–O layer [31]. Using this equation $n = 0.152$, 0.160, and 0.167 were found for $A$, $B$, and $C$ samples respectively. Taking into account the small variation for $n$, similar physical properties for the three samples were expected. The ac magnetic susceptibility and ac resistivity have confirmed this assertion. However, the ac magnetic susceptibility versus temperature under external pressure have shown different $T_{\text{conset}}$ pressure dependent for each (Hg,Re)-1223 sample [21].

In order to complete Passos et al. [21] study, ac magnetic susceptibility versus temperature under different pressure range were measured: in the first pressure range, from 0 up to 1.4 GPa, a CuBe cell was used to confirm previous results [21] whereas a B4C anvil cell was required for wider pressure range, from 0.4 up to 7 GPa, in order to extend the optimal doped sample curve. Experimental details of the set up used in the first range were described in Ref. [21]. For the broader pressure range a B4C-anvil cell was built with an anvil made of B4C powder manufactured by “Hermann Starck”, with 7.9 m$^2$/g and pyrolitic carbon. This cell has worked at hydrostatic conditions obtained with a methanol–ethanol mixture (4:1) in a pressure cavity of 0.2 mm diameter of a CuBe gasket pressed to 0.3 mm. The inner pressure was detected by a superconducting manometer (Pb 99.9999%, Koch-Light-Lab) placed in a gasket hole next to the sample. The primary coil (300 turns) and the astatic pair of pickup coils ($2 \times 520$ turns) were produced with copper wire of 45 $\mu$m diameter. The temperature set up was the same used in Ref. [4]. Fig. 3 displays the pressure dependence of $T_c$. The $T_c$ criterion was defined as the point where the $\chi_{\text{ac}}$ signal is twofold the average noise value, which was measured before superconductor transition.

In the insert of Fig. 3 it can also be observed the different $dT_c/dP$ for samples $A$, $B$ and $C$. Sample $B$ presented $dT_c/dP = 1.9 \pm 0.3$ K/GPa, as a fit to a linear dependence. Sample $A$ presented the highest value of $dT_c/dP = 8 \pm 1$ K/GPa, followed by nonlinear behaviour within 0.6–1.4 GPa pressure range. On the order hand, sample $C$ showed negative valued of $dT_c/dP = -1.6 \pm 0.1$ K/GPa. As reported in Ref. [21], the ac magnetic susceptibility $\chi_{\text{ac}}$

![Fig. 3. $T_c$ as a function of applied external hydrostatic pressure for sample B (optimal doped). The inset with $T_c$ dependent of external hydrostatic pressure up to 1.4 GPa for (Hg,Re)-1223 samples prepared with different oxygen partial pressure.](image-url)
versus temperature measurements under external hydrostatic pressure can be used as a tool to confirm the doping state of $\text{Hg}_{0.82}\text{Re}_{0.18}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$ samples. Therefore, samples A, B and C were associated with the under doped, optimal doped and over doped samples, respectively.

The different $T_c$ dependence shown in Fig. 3 may be discussed on the basis of the pressure induced charge transfer model (PICTM) modified by Almasan et al. [32]. The variation on $T_c$ can be given by Neumeier and Zimmermann [33] equation

$$\frac{dT_c}{dP} = \frac{\partial T_c}{\partial P} + \left[ \frac{\partial T_c}{\partial n} \right] \left[ \frac{\partial n}{\partial P} \right],$$

where the first term is an intrinsic variation of $T_c$ with external pressure, while the second term represents changes on $T_c$ due to the hole concentration modified by the external pressure. For optimal doped sample the second term vanishes. Therefore, for the (Hg,Re)-1223 system $dT_c/dP = 1.9 \pm 0.3$ K/GPa correspond to the intrinsic term value found only for optimal doped sample [34].

In order to confirm the oxygen content of each sample, thermoelectric power measurements were done in the samples. The aim was to correlate the oxygen content in the precursor annealing with the charge carrier number, and, as consequence, the average hole number present in each Cu–O plane.

2.4.3. Thermoelectric power measurements

The thermoelectric power was measured on pellets with $1 \times 1 \times 7$ mm$^3$. Each pellet was mounted with a small heating resistance on the top and fixed on a sapphire sample holder in the bottom. The thermoelectric power measurements were carried out at constant temperature controlled by the Lake Shore Temperature 330 controller. Temperature gradients $V T_x$ of the order of 0.5 K/mm were applied using a KEITHLEY 228 A power source to supply a controlled power on the small heating resistance. The $V T_x$ were measured by a calibrated Au/0.07 at.% Fe–Chromel–P thermocouples made by Leico Industries Inc., and using a HP3444 digital multimeter. The voltage between the top and bottom of each sample was measured by a KEITHLEY 182 nanovoltmeter. All instrumentals were controlled and read by an IEEE-488 GPIB communication setup [35].

The results are shown in Fig. 4, and it can be observed that the thermoelectric power signal has presented a typical behaviour as described by MacIntosh and Kaiser [36]. Moreover, the thermoelectric power signal is positive and distinct at room temperature. It was shown by Obertelli et al. [37] the universal dependence of the thermoelectric power signal (at room temperature) on the hole concentration. In general, the thermoelectric power signal changes (from positive to negative) close to $n \approx 0.20$.

For $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$ [22] compounds, the hole concentration was found to be $n \leq 0.20$, which results in a positive thermoelectric power signal up to room temperature. The measurements data of the three Hg,Re-1223 samples are summarized in Table 2. The hole number per Cu–O layer $n$ were determined by Obertelli et al. [37]

<table>
<thead>
<tr>
<th>Sample</th>
<th>$P_{O_2}$ (bar)</th>
<th>$S$ ($\mu$V/K)</th>
<th>$n$ (hole/Cu–O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.05</td>
<td>3.0</td>
<td>0.15</td>
</tr>
<tr>
<td>B</td>
<td>0.10</td>
<td>1.8</td>
<td>0.16</td>
</tr>
<tr>
<td>C</td>
<td>0.15</td>
<td>0.5</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Fig. 4. Thermoelectric power of the (Hg,Re)-1223 samples with different oxygen partial pressure of the precursor annealing.
universal behaviour. The values are in agreement with the hole number \( n \) from Eq. (1).

The (Hg,Re)-1223 compounds have presented a hole concentration \( n < 0.20 \) which is justified by the phase diagram proposed by Sin et al. [19]. When \( P_{O_2} > 0.20 \) oxygen partial pressure is used in the precursor annealing (over doped), the (Hg,Re)-1223 synthesis presents a segregation of (Hg,Re)-1212 and HgCaO\(_2\) phases. In this case, the oxygen increment goes to the atmosphere inside the sealed quartz tube during the synthesis, as demonstrated by the TBA of the diagram \( P \times T \) measurement [19]. The increase of partial pressure of oxygen, inside sealed quartz tube, shifts the equilibrium in order to form (HgRe)-1223, (Hg,Re)-1212 and HgCaO\(_2\) phases. As the (Hg,Re)-1212 and HgCaO\(_2\) phases are rich in oxygen, they cause a reduction of the oxygen content present in the (Hg,Re)-1223. This is the reason why a negative thermoelectric power signal in (Hg,Re)-1223 system is not found when the oxygen partial pressure was increased.

2.4.4. X-ray absorption near-edge structure measurement

Samples A, B and C were analyzed by X-ray absorption (XAS) at the XAFS station of the Laboratório Nacional de Luz Sincrotron (LNLS, Campinas-Brazil), on beam line using a Si(111) double-crystal monochromator [38]. The three (Hg,Re)-1223 prepared samples as well as reference samples (ReO\(_2\) 99.9\%, ReO\(_3\) 99.9\%, CaCO\(_3\) 99.999\%, BaCO\(_3\) 99.999\% and HgO 99.99\%) were ground to fine powder (20 \( \mu \text{m} \)) and then mixed with ethanol. Each mixture was vacuum decanted over a special thick (0.9 mm) paper film. The five films were mounted on the same sample holder. All spectra were taken at room temperature and they were recorded in the transmission mode using a current from 160–80 mA. The measurements of all powder were carried out at the same machine work period. The data were analyzed by the reference method with the parameters obtained from the reference powder.

In order to start the investigation about the average valence of each atom in the Hg\(_{0.82}\)Re\(_{0.18}\)Ba\(_2\)Ca\(_2\)Cu\(_3\)O\(_{8+d}\) (except copper), the samples were studied by X-ray Absorption near-edge (XANES) with step energy of 1 eV, scanning time of 1 min and 100 eV as pre-edge. The three superconductors samples were investigated using the following targets: the Re in the L\(_{III}\) edge (10.535 keV), Ba in the L\(_{III}\) edge (5.247 keV), Ca in the K edge (4.038 keV) and Hg in the L\(_{III}\) edge (12.284 keV). By XANES analysis the average valence of each element inside the (Hg,Re)-1223 compound could be determined. The results for Ba, Ca and Hg confirm the nominal valence +2 for each one (see Table 3). The rhenium (Re) valence was obtained by a fit of the energy edge shift related with each ReO\(_2\) and ReO\(_3\) oxides. Fig. 5 represents the measurements of XANES in the Re L\(_{III}\) edge (10.535 keV) on the five compounds (ReO\(_2\), ReO\(_3\), sample A, sample B and sample C). The valence of Re was assumed to be +4 and +6 in the ReO\(_2\) and ReO\(_3\) oxides, respectively. The energy edge values were taken at the zero of the derivate curve and correspond to abscissa of the energy edge shift versus average valence Re graphic (Fig. 5 inset). Using \( E_0 = 10.535 \text{ keV} \)
and the ReO\textsubscript{2} and ReO\textsubscript{3} valences as reference, it was built the linear dependence of the Re valence as a function of the absorption edge shift $E - E_0$. From the line in Fig. 5 inset it was possible to extra pole the valence of rhenium (Re) for all (Hg,Re)-1223 samples. The three samples A, B and C have presented +6.8, +6.9 and +7.0 valence respectively, which is in agreement with previous valence estimated by Chmaissem et al.\cite{12} using the Brown and Altermatt model\cite{39}.

2.4.5. Extended X-ray absorption fine structure measurement

The local Re–O octahedral oxygen coordination was investigated by extended X-ray absorption fine structure (EXAFS). The measurements were done with step energy of 1 eV, scanning time of 1 min, 100 eV as pre-edge, and 1000 eV after the edge. The three superconductors samples were investigated using the Re edge L\textsubscript{III} at $E = 10.535$ keV in the transmission mode. Fig. 6 presents the EXAFS
signal of A, B, C, ReO₂ and ReO₃ after 50 eV from the edge. Inspections of the A, B, and C data reveals a general signal behaviour analogous to ReO₂. Correa et al. [40] have studied X-ray powder diffraction by Rietveld refinement of the same ReO₂ (99.9%) AlfaAesar no. 62109 used here in EXAFS analysis. They have pointed out that there are two distances between Re and O in the ReO₂ (2.110 Å and 1.941 Å). In ReO₃, there is only one distance (1.875 Å) Ref. [41]. This analogous behaviour among ReO₂ and A, B, and C samples strongly suggest that the ReO₆ octahedron symmetry will present two distances also.

Data analysis of the EXAFS spectra were performed using the ATOMS, FEFF8 [42], and FEFFIT [43]. Fig. 3 shows our fit related with sample B. The fitted parameters indicated two distances in the ReO₆ octahedron introduced in superconductor P4/mmmm symmetry. The first distance is Re–Oₐp = 2.1166 Å (rhenium to apical oxygen) and the second Re–Oₚl = 1.8247 Å (rhenium to planar oxygen). These two distances in the Brown and Altermatt model [39] give +6.93 as a valence value for the Re in Hg₆Re₁₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋₂₋二人教 1223. These effects were confirmed by EXAFS measurements, which revealed the ReO₆ octahedral distortion for all samples.

The EXAFS signal analysis indicated that the ReO₆ octahedron introduced in the superconductor crystal symmetry is distorted with distance for Re–Oₐp different from distance for Re–Oₚl. Moreover, the sample produced with 10% of PO₂ has presented a shorter distance for Re–Oₚl and a longer distance for Re–Oₐp than the corresponding distances on the others samples (A and C). The valence evaluated by the bound length (EXAFS) in the distorted ReO₆ octahedron is in agreement with XANES analysis results (Table 4).

The distortion of the ReO₆ octahedron can be related with the Tc versus external pressure behaviour shown in the Fig. 3. In our opinion the longer Re–Oₐp distance in sample B indicates that apical oxygen is closer to Ba and Cu in this sample than in the others samples (A and C). As consequence there exist a reduction between Cu–Oₐp distance, which is associated to changes in the Cu–Oₚl angle. This reduction in Cu–Oₐp distance improves the symmetry on the CuO₄ tetrahedron. It was revealed from the Rietveld refinement (XRD) that the optimal doped sample (sample B) has presented the highest value (180°) for the Cu–Oₚl angle (Table 1). Considering that this angle can not be changed under hydrostatic pressure, a pressure increases causes only a reduction of the distance between Cu–O₃ and Cu–Oₐp without loss of symmetry in the CuO₄ tetrahedron. This scenario can justify high intrinsic value (Eq. (2)) found in the optimal doped sample under external hydrostatic pressure (Fig. 3 inset).

Acknowledgements

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References


Table 4
EXAFS fit parameters and Re average valence estimation [39]

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<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
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<tbody>
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<td>r-Factor of fit</td>
<td>0.008405</td>
<td>0.009172</td>
<td>0.008689</td>
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<td>Reduced χ²</td>
<td>3.190922</td>
<td>2.715733</td>
<td>2.300376</td>
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<tr>
<td>Dist. Re–O₃l (Å)</td>
<td>1.85 (2)</td>
<td>1.83 (2)</td>
<td>1.87 (2)</td>
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<tr>
<td>Dist. Re–O₃p (Å)</td>
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<td>2.15 (2)</td>
<td>2.00 (5)</td>
</tr>
<tr>
<td>Re estimation valence</td>
<td>6.87</td>
<td>6.93</td>
<td>7.03</td>
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