

Study on the crystal structure of the high T_c superconductor (Hg,Re)–1223

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(Received 16 May 2007; accepted 28 February 2008)

Samples of the superconducting compound (Hg,Re)–1223 of nominal composition $\text{Hg}_{0.82}\text{Re}_{0.18}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ and different oxygen contents were studied using X-ray absorption and diffraction techniques. In the synthesis process, treatments under different ratio oxygen/argon gas mixtures of 5%, 10%, and 15% O_2 resulted in samples named as Sample A, Sample B, and Sample C, respectively. It was determined by using the XANES technique that in these compounds the Re cation has valence +7. The study by EXAFS determined that the octahedral coordination is distorted and the distances of Re–O bonds are of the order of 1.85 Å for equatorial oxygen and 2.10 Å for the apical ones. The Rietveld refinement of X-ray powder diffraction data revealed that the studied samples presented segregation of two superconducting phases with space group $P4/mmm$ and distinct lattice parameters, also confirmed by anomalous X-ray scattering. The main phase was associated to the phase (Hg,Re)–1223 with higher oxygen content and the secondary superconducting phase was associated with the undoped Hg–1223 phase. Measurements of ac magnetic susceptibility showed that the sample treated under 10% O_2 atmosphere presented the best superconducting properties. © 2008 International Centre for Diffraction Data.

[DOI: 10.1154/1.2903506]

Key words: XRD, XANES, EXAFS, Rietveld refinement, crystal structure, Hg-based superconductor

I. INTRODUCTION

Since the discovery of the high critical transition temperature (high T_c) superconductors in 1986 by Berndt and Müller (1986), a great effort has been put towards the research of high T_c materials. In a period of a few years some new ceramics were discovered, and it was reported in 1993 a new family of superconducting compounds known as “Hg-based superconductors” presented the highest critical temperatures attained until now (Putilin *et al.*, 1993). These superconductors have a general formula $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ or $\text{Hg}-12(n-1)n$ for $n=1, 2, 3, \dots$, particularly the composition with $n=3$, known as Hg-1223; i.e., $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ presents the highest T_c yet reported, that is, 134 K at ambient pressure, and up to 160 K at high hydrostatic pressure (Martinez, 2005).

This family of superconducting compounds has a very complex synthesis route and most of the process must be carried out in controlled atmospheres because of the highly toxic mercury vapor and high-pressure furnaces (Passos *et al.*, 2002). Moreover, the compounds are very sensitive to humidity and atmospheric contamination by CO_2 , which reacts with Ba forming BaCO_3 and degrading the superconducting properties. This problem was overcome somewhat by partial substitution of Hg by higher valence cations like Au, Pb, and Re. Of these dopants, it was shown that Re is the

most interesting one, since it can stabilize the compound, favoring the synthesis and causing the material to incorporate additional oxygen anions at the octahedral coordination of Re into the Hg(Re) plane (de Mello *et al.*, 2002). This is an important advantage, since the oxygen stoichiometry determines the superconducting properties of these compounds (Altshuler *et al.*, 2002). Hence, most of the investigations on the Hg-based compounds are being made on the Hg+Re system, especially on the phase (Hg,Re)–1223.

Shimoyama *et al.* (1994) shows that the Re cation substitutes on the Hg site in these compounds. The addition of dopants does not alter the critical temperature of these ceramic superconductors, but changes other properties such as critical current (Gonzalez *et al.*, 2001). It was shown (Passos *et al.*, 2002) that 18% nominal atomic Re is the optimal doping content.

The synthesis route for these compounds was strongly improved with the development of a process that controls the pressure inside the sealed quartz tubes that were used for synthesis. This procedure allowed the control of the oxygen content and, consequently, the level of oxygenation of the final product. By this technique it was possible to obtain samples of the ceramic superconductor (Hg,Re)–1223 with nominal Re doping of 18% atomic and differing oxygen contents for the present study (Oliveira *et al.*, 2006).

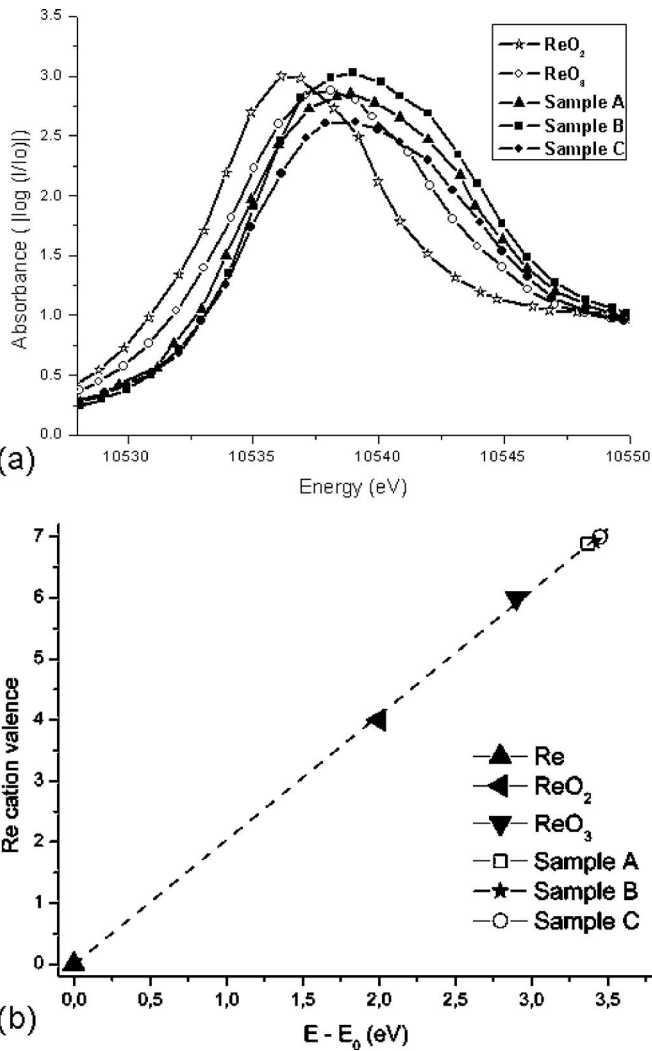


Figure 1. (a) Re L_{III} absorption edges for superconducting Samples A, B, C, ReO_2 , and ReO_3 , and (b) edge shift versus valence.

The samples were studied by X-ray absorption techniques in order to determine the coordination and valence of the cation Re in the crystal structure. The crystal structures of the superconducting phases were studied by X-ray diffraction using conventional laboratory equipment and also synchrotron radiation (both normal and anomalous scattering) with Rietveld fitting to X-ray powder diffraction (XRD) data. The crystal structures of the rhenium-doped (Hg,Re)-1223 main phase of the studied samples are reported herein; the Re-undoped phase Hg-1223 and other residual phases were quantified.

II. EXPERIMENTAL

The samples were produced by the solid state route (Passos *et al.*, 2002). However, during the synthesis of the pre-

TABLE I. Valence of the Re cation in Re oxides and elementary rhenium and valence values in the superconducting samples determined by XANES.

	Re	ReO_2	ReO_3	Sample A	Sample B	Sample C
Valence	0	+4	+6	+6.89	+6.93	+7.00

TABLE II. Results of EXAFS analysis for the atomic displacement factors (σ^2) and distances Re- O_{pl} (where O_{pl} is the oxygen in the basal plane) and Re- O_{ap} (where O_{ap} is the apical oxygen in the [001] direction) for the Re-O coordination. Reduced χ^2 is the parameter that indicates the quality of each adjustment, given by the program FEFFIT (Ravel, 2001).

Parameter	Sample A	Sample B	Sample C
Reduced χ^2	3.19	2.72	2.30
$\sigma^2 O_{pl}$ (\AA^2)	0.0155 (9)	0.0137 (17)	0.0157 (13)
Distance Re- O_{pl} (\AA)	1.85 (5)	1.83 (9)	1.87 (9)
$\sigma^2 O_{al}$ (\AA^2)	0.0201 (20)	0.0165 (17)	0.0204 (34)
Distance Re- O_{ap} (\AA)	2.09 (10)	2.15 (2)	2.00 (14)

cursor compound, the material was divided into three parts. Each of these parts was submitted to an oxygenation heat treatment in a flux of argon/oxygen gas mixture. The ratio 95% Ar/5% O_2 resulted in a sample named Sample A, the ratio 90% Ar/10% O_2 resulted in a sample named Sample B, and the ratio 85% Ar/15% O_2 resulted in a sample named Sample C, as described by Passos *et al.* (2006). By means of gravimetric measurements it was observed that the treatments introduced different quantities of oxygen in the compounds. An analysis by iodometric titulation (Nazzari *et al.*, 1988) was performed in order to measure the oxygen content in the superconductor samples and the results confirmed the different oxygenation.

The samples and also two rhenium oxides standards, namely ReO_2 and ReO_3 (Aldrich, Saint Louis, Missouri), were analyzed by X-ray absorption at the D04B-XAS beamline of the National Synchrotron Light Laboratory (LNLS), Campinas, Brazil, in transmission mode, at the Re L_{III} absorption edge (10535 eV). The XAS spectra were measured from 10.4 to 10.6 keV at 1 eV steps in the near edge region (XANES) and from 10.6 to 11 keV at 2.5 eV per step in the extended region (EXAFS). The rhenium oxides were used to calibrate the edge shift versus valence relationship in order to determine the Re valence in the compounds.

The XRD measurements were performed in two configurations. First, the measurements were made using Rigaku D-MAX2000 and Multiflex conventional laboratory diffractometers operating at 40 kV and 30 mA, Cu-target sealed X-ray tube, scintillation counter, pyrolytic graphite monochromator, and divergence, scatter, and receiving slits of $\frac{1}{2}^\circ$, $\frac{1}{2}^\circ$, and 0.3 mm, respectively. The diffraction patterns were taken from 3° to $122^\circ (2\theta)$ at 0.01 steps and counting time ranging from 7 to 20 s/step. A special glass sample holder was developed to spread the specimen powder in a major area in order to illuminate only the specimen surface when the incidence angle was low as 3° (Martinez, 2005). The second series of measurements was performed at the X-ray Powder Diffraction D-10B-XPD beamline at LNLS (Ferreira *et al.*, 2006), at two different energies, 8950 eV (normal scattering) and 10 600 eV (anomalous scattering), using a Na(Tl)I scintillation counter in low-resolution mode. The measurements were taken from 3 to $100^\circ 2\theta$ at 0.01° steps. NIST standard reference materials LaB_6 and Al_2O_3 were measured in the same experimental conditions in order to obtain the instrumental parameters for both laboratory and synchrotron diffraction measurements.

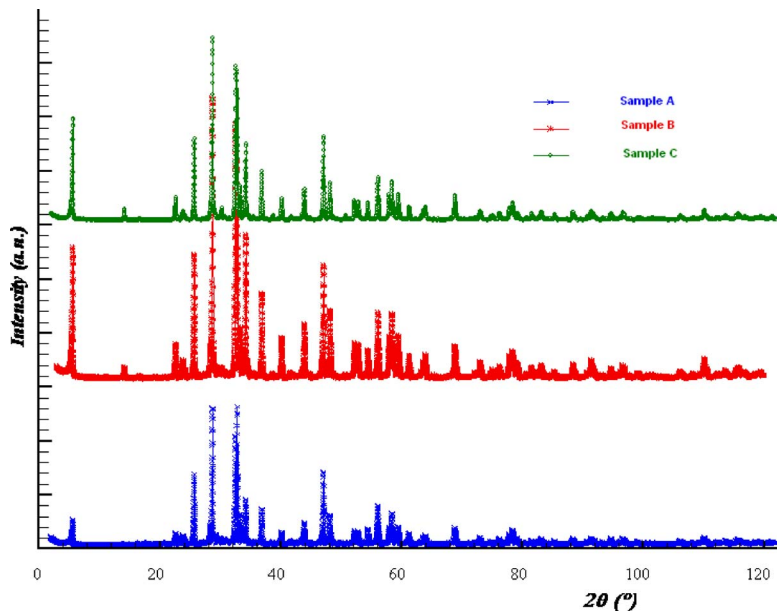


Figure 2. (Color online) Typical diffraction patterns of superconducting Samples A, B, and C obtained with a conventional laboratory diffractometer.

Both laboratory and synchrotron X-ray powder diffraction were used to refine the crystal structure by means of the Rietveld method. Rietveld refinements were performed using the GSAS program (Larson and Von Dreele, 2000) under EXPGUI interface (Toby, 2001), using the Thompson-Cox-Hastings modified pseudo-Voigt profile function (Thompson *et al.*, 1987).

III. RESULTS AND DISCUSSION

The study by XANES consisted in measure the shift of the Re absorption edge in two rhenium oxides and in the superconducting samples, shown in Figure 1(a), and correlate the edge shifts with the Re valences. Plotting the edge shift versus valence for the rhenium oxides and elementary

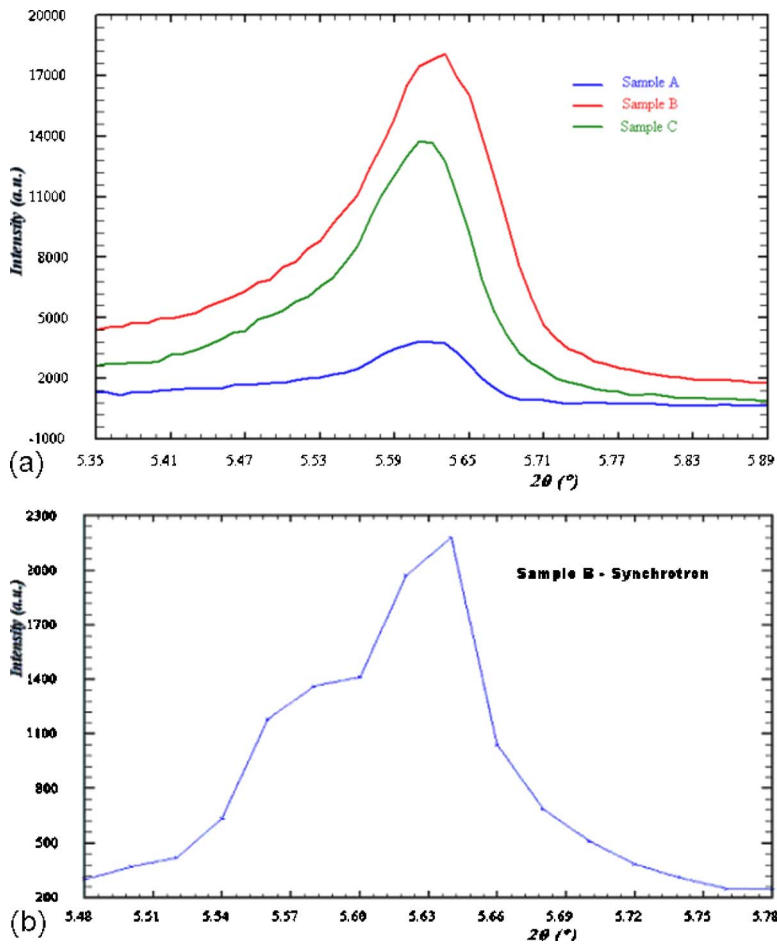


Figure 3. (Color online) Detail of the reflection (001) of (Hg,Re)-1223 measured with (a) laboratory equipment and (b) higher resolution synchrotron diffractometer at the LNLS.

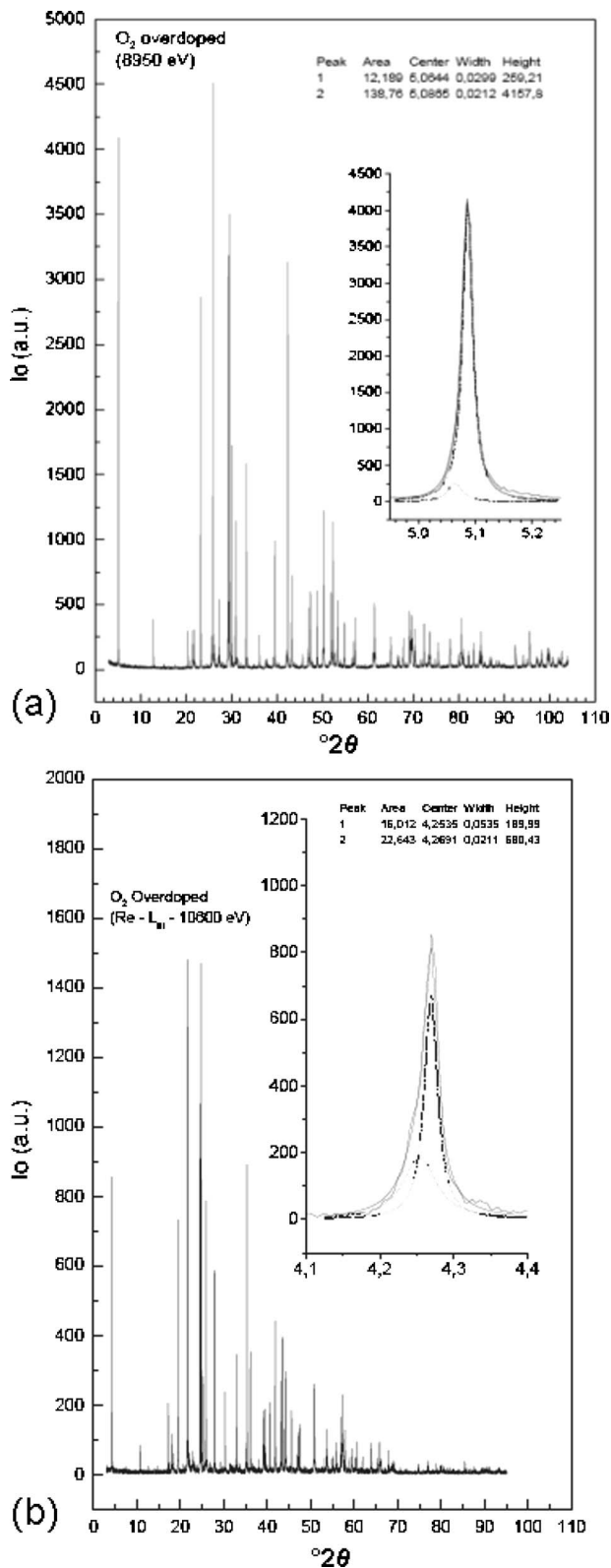


Figure 4. Synchrotron diffraction profiles of one of the superconducting sample taken at (a) 8950 eV and (b) 10600 eV. The inserts of the figures show details of the reflection (001) and the adjustments of curves evidencing the two phases with different Re contents.

renium, whose valence is known, it was possible to observe that this dependence is linear, as shown in Figure 1(b). Therefore, from the edge shift in the superconducting compounds, it was possible to determine the valences of the Re

cation in each of the samples, as shown in Figure 1(b). The obtained Re cation valence values are shown in Table I.

The EXAFS study allowed the determination of the Re–O coordination. As the oxygen in the basal plane of the unit cell is located at a plane occupied by heavy cations (Hg and Re), the scattering of the low Z anions vanishes. Therefore, the determination of this O position and occupation by X-ray powder diffraction is not trustworthy. In order to overcome this limitation, EXAFS was used. This is sensitive to the local coordination around the Re cation, and by means of this analysis of the extended part of the absorption spectra and using the computer programs ATOMS (Ravel, 2001), FEFF, and FEFFIT (Newville, 2001), it was determined that the Re–O coordination is a distorted octahedron similar to the coordination found in ReO_3 submitted to high pressure or high temperature (Martinez, 2005; Orlando *et al.*, 2006). The distances of the Re cation to the equatorial oxygen (in the basal plane of the structure—direction [110]) and to apical oxygen (in the direction [001]) with the atomic displacement factors are shown in Table II. Using the Bond-valence method (Brown and Altermatt, 1985), the valences for the distances given in Table II were estimated and the obtained values are in good agreement with the determined valences presented in Table I.

Typical X-ray diffraction patterns of Samples A, B, and C taken from a conventional laboratory diffractometer are shown in Figure 2. As can be seen in the XRD patterns shown in Figure 2, the main phase in all samples can be identified as (Hg,Re)–1223 among other residual phases. The first reflection in these patterns exhibits a strong asymmetry, as is shown in Figure 3(a). When the same reflection is scanned in a higher resolution synchrotron diffractometer, it can be seen that, in reality, this peak is a doublet, as shown in Figure 3(b). This observation led to the suspicion of the existence of two quite similar superconducting phases, and led to the investigation of the hypothesis of the co-existence of the phases Hg–1223 (not Re doped) and (Hg,Re)–1223 (Re doped). In order to investigate this hypothesis, an anomalous scattering experiment was performed at an energy close to Re L_{III} absorption edge energy. The difference between the diffraction profiles in normal and anomalous scattering conditions is shown in Figures 4(a) and 4(b), respectively, for one of the samples. The insets in Figures 4(a) and 4(b) show details of the reflection (001) at each energy level and the fit of two Lorentzian curves to the XRD reflections. From Figures 4(a) and 4(b), it is evident that the asymmetry is present, confirming the presence of two phases and also that the areas under the fitted Lorentzian curves are different for normal and anomalous scattering conditions, proving the coexistence of two phases with different content of Re (Orlando *et al.*, 2003).

With the introduction of two superconducting phases, the convergence and goodness-of-fit factors of the Rietveld refinements were improved greatly. As starting structural data for the refinements, ICSD entries were used that were most similar to the composition of the superconducting phases of the samples, i.e., ICSD 85285 for phase (Hg,Re)–1223 and ICSD 75736 for phase Hg–1223. Among the two superconducting phases, other residual phases resulting from the synthesis process were identified: CaHgO_2 (PDF 86-0037, ICSD 080717), BaCO_3 (PDF 85-0720, ICSD 026718), $\text{Ca}_{0.85}\text{CuO}_2$

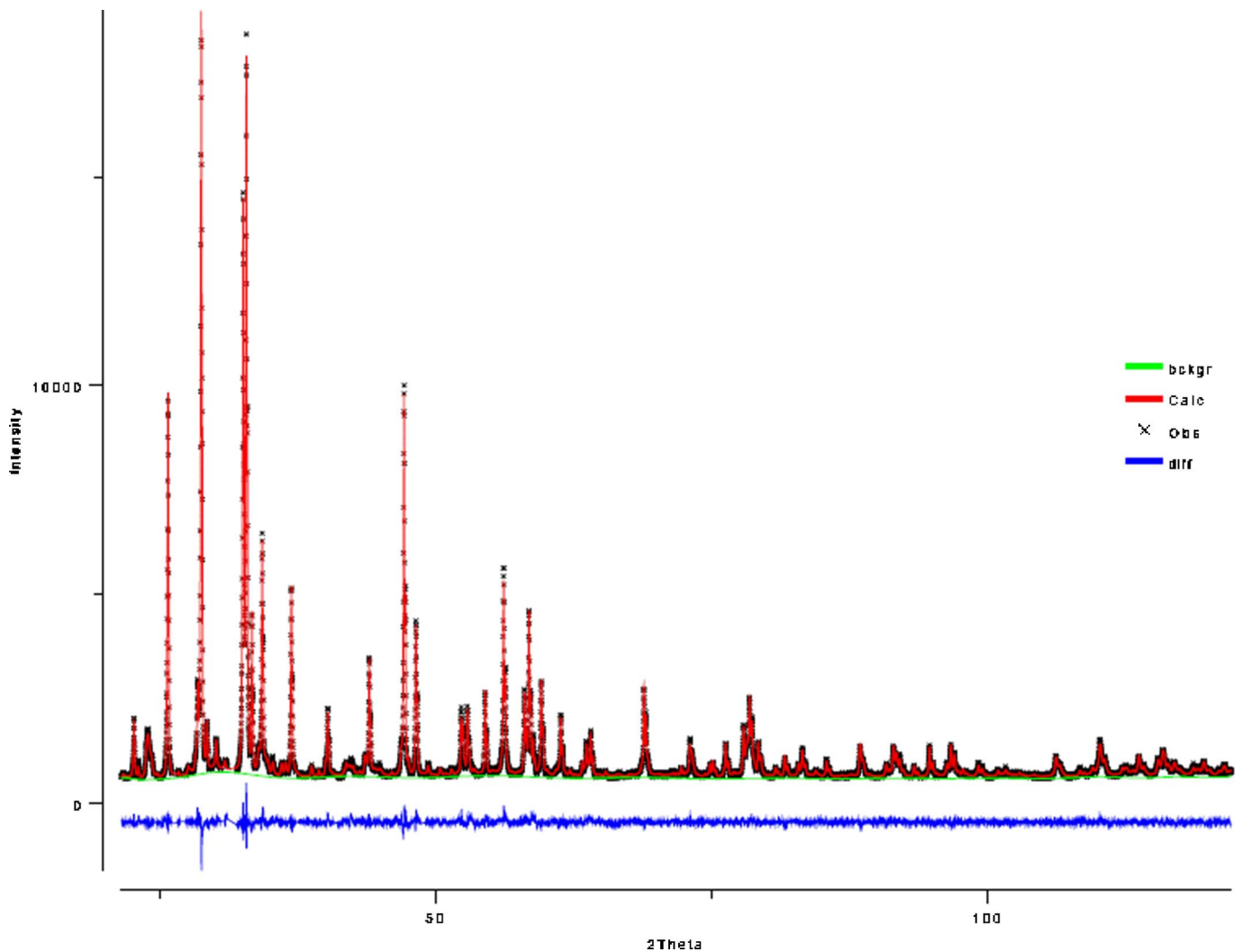


Figure 5. (Color online) Rietveld plot of one refinement of phase (Hg,Re)-1223 for Sample B.

(PDF 88-1879, ICSD 040615), CaCuO_3 (PDF 85-2491, ICSD 080666), BaCuO_2 (PDF 79-0838, ICSD 065801), CuO (PDF 89-5899, ICSD 087126), and HgO (PDF 72-0520, ICSD 015895) (ICDD, 2003; FIZ and NIST 2003).

For phase Hg-1223 and residual phases, it was refined only the profile parameters, cell parameters, atomic positions, and atomic displacement parameters. For the superconducting phase (Hg,Re)-1223, all crystallographic parameters except the positions of the oxygen in the Re coordination, whose values were fixed as the values obtained by EXAFS, as presented in Table II, were refined. Figure 5 shows one of the Rietveld plots for Sample B. The occupation factors of Re and Hg were refined and the occupation of oxygen in the Re equatorial coordination was restrained to the occupation of the Re cation. The atomic displacement factors of Hg and Re were constrained, once they occupy the same crystallographic site. The main results for the refinements of Samples A, B, and C are shown in Table III. The refined crystal structure of the main phase (Hg,Re)-1223 for the three samples are shown in Table IV.

The results of the refinements for phase (Hg,Re)-1223 showed that Sample B (optimally doped) presents the maximum quantity for these phases and also for the sum of superconducting phases. The (Hg,Re)-1223 main phase in

Sample B presents the higher c/a ratio, the minimum cell volume, and the bond-angle O-Cu-O for the outermost Cu plane is closest to 180° . These characteristics can be reputed as the determinant factors for the best superconducting properties presented by Sample B, as discussed by Passos *et al.* (2002, 2006). Figure 6 shows the results of ac magnetic susceptibility for the three samples, which reveals that Sample B (optimally oxygen doped) presents the highest T_c (Passos *et al.*, 2002). In the inset of Figure 6, the critical temperatures of the superconducting samples versus the oxygen percent of the treatment gas flux are shown. This typical behaviour of T_c versus oxygen content leads us to classify Samples A, B, and C as “under-doped,” “optimally doped,” and “over-doped,” respectively (Passos *et al.*, 2006).

IV. CONCLUSION

The synthesis process of (Hg,Re)-1223 by the treatment of the precursors with gas flux of different ratio O_2/Ar produced samples that can be classified as under-doped, optimally doped, and over-doped, with respect to the oxygen content. All three samples demonstrated the segregation of

TABLE III. Results of Rietveld refinements for Samples A, B, and C.

Parameter	Sample A	Sample B	Sample C
wt% phase (Hg,Re)–1223	52.0(1)	70.1(1)	47.8(1)
wt% phase Hg–1223	26.2(1)	11.8(1)	34.4(1)
Unity cell parameter <i>a</i> phase (Hg,Re)–1223 (Å)	3.8544(1)	3.8542(1)	3.8544(1)
Unit cell parameter <i>c</i> phase (Hg,Re)–1223 (Å)	15.6877(1)	15.6883(1)	15.6898(1)
Angle Cu–O–Cu phase (Hg,Re)–1223 (°)	176.9(4)	179.2(1)	177.5(3)
Oxygen stoichiometry (8 + δ) phase (Hg,Re)–1223	8.694	8.793	8.853
Occupancy Hg phase (Hg,Re)–1223	0.720(2)	0.750(1)	0.765(2)
Occupancy Re phase (Hg,Re)–1223	0.160(2)	0.184(1)	0.187(2)
Unit cell parameter <i>a</i> phase Hg–1223 (Å)	3.8555(1)	3.8527(2)	3.8552(1)
Unit cell parameter <i>c</i> phase Hg–1223 (Å)	15.6933(2)	15.7083(9)	15.6935(2)
χ^2	1.94	3.08	2.38
R_{wp}	0.0441	0.0387	0.0465
R_p	0.0349	0.0298	0.0366
R_F^2	0.0451	0.0429	0.0490

two superconducting phases, a minor phase with no Re doping and the majority phase with Re-doping. This result has not been previously seen, but is expected in accordance with theoretical previsions (Passos *et al.*, 2006). The experimental determination of the Re cation valence is in agreement with theoretical predictions made by Chmaissem *et al.* (1996). The phase containing Re is richer in oxygen than the undoped phase. Sample B with precursor treated with 90% Ar/10% O₂ presented the best superconducting properties.

Crystal structures for (Hg,Re)–1223 phases for these three samples were determined by means of the Rietveld fitting to XRD powder data, extended by X-ray absorption results. The structural parameters found in Sample B (the higher *c/a* ratio, the minimum cell volume, the oxygen content, and also that the bond-angle O–Cu–O for the outermost Cu plane being closest to 180°) compared with the other samples can be associated with the best superconducting properties presented by Sample B.

TABLE IV. Results of structure refinement of phase (Hg,Re)–1223 for Samples A, B and C.

	Sample A	Sample B	Sample C
Formula	Hg _{0.720} Re _{0.160} Ca ₂ Ba ₂ Cu ₃ O _{8.694}	Hg _{0.750} Re _{0.184} Ca ₂ Ba ₂ Cu ₃ O _{8.793}	Hg _{0.765} Re _{0.187} Ca ₂ Ba ₂ Cu ₃ O _{8.853}
Space group	<i>P4/mmm</i>	<i>P4/mmm</i>	<i>P4/mmm</i>
Unit cell (Å)	<i>a</i> =3.85442(1) <i>c</i> =15.6877(1)	<i>a</i> =3.8542(1) <i>c</i> =15.6883(1)	<i>a</i> =3.8544(1) <i>c</i> =15.6898(1)
Hg,Re <i>x y z</i>	0 0 0	0 0 0	0 0 0
Hg Occ.	0.720(2)	0.750(1)	0.765(2)
Re Occ.	0.160(2)	0.184(1)	0.187(2)
Hg,Re <i>U</i> (Å ²)	0.0108	0.0077	0.0154
Ca <i>x y z</i>	$\frac{1}{2}$ $\frac{1}{2}$ 0.3942(2)	$\frac{1}{2}$ $\frac{1}{2}$ 0.3955(1)	$\frac{1}{2}$ $\frac{1}{2}$ 0.3974(2)
Ca <i>U</i> (Å ²)	0.0077	0.0064	0.0055
Ba <i>x y z</i>	$\frac{1}{2}$ $\frac{1}{2}$ 0.8313(1)	$\frac{1}{2}$ $\frac{1}{2}$ 0.8285(1)	$\frac{1}{2}$ $\frac{1}{2}$ 0.8299(1)
Ba <i>U</i> (Å ²)	0.0065	0.0094	0.0063
Cu1 <i>x y z</i>	0 0 $\frac{1}{2}$	0 0 $\frac{1}{2}$	0 0 $\frac{1}{2}$
Cu1 <i>U</i> (Å ²)	0.0086	0.0077	0.0064
Cu2 <i>x y z</i>	0 0 0.3019(1)	0 0 0.2985(1)	0 0 0.2983(1)
Cu2 <i>U</i> (Å ²)	0.0083	0.0074	0.0071
O1 <i>x y z</i>	$\frac{1}{2}$ 0 $\frac{1}{2}$	$\frac{1}{2}$ 0 $\frac{1}{2}$	$\frac{1}{2}$ 0 $\frac{1}{2}$
O1 <i>U</i> (Å ²)	0.0158	0.0129	0.0149
O2 <i>x y z</i>	$\frac{1}{2}$ 0 0.2986(4)	$\frac{1}{2}$ 0 0.2993(2)	$\frac{1}{2}$ 0 0.3010(3)
O2 <i>U</i> (Å ²)	0.0128	0.0169	0.0153
O3 <i>x y z</i>	$\frac{1}{2}$ $\frac{1}{2}$ 0	$\frac{1}{2}$ $\frac{1}{2}$ 0	$\frac{1}{2}$ $\frac{1}{2}$ 0
O3 Occ.	0.06(5)	0.06(1)	0.10(5)
O3 <i>U</i> (Å ²)	0.0138	0.0122	0.0162
O4 <i>x y z</i>	0 0 0.133 ^a	0 0 0.137 ^a	0 0 0.128 ^a
O4 <i>U</i> (Å ²)	0.0141	0.0130	0.0167
O5 <i>x y z</i>	0.339 ^a 0.339 ^a 0	0.336 ^a 0.336 ^a 0	0.343 ^a 0.343 ^a 0
O5 Occ.	0.160(2)	0.184(1)	0.187(2)
O5 <i>U</i> (Å ²)	0.0130	0.0136	0.0149

^avalues from Table II.

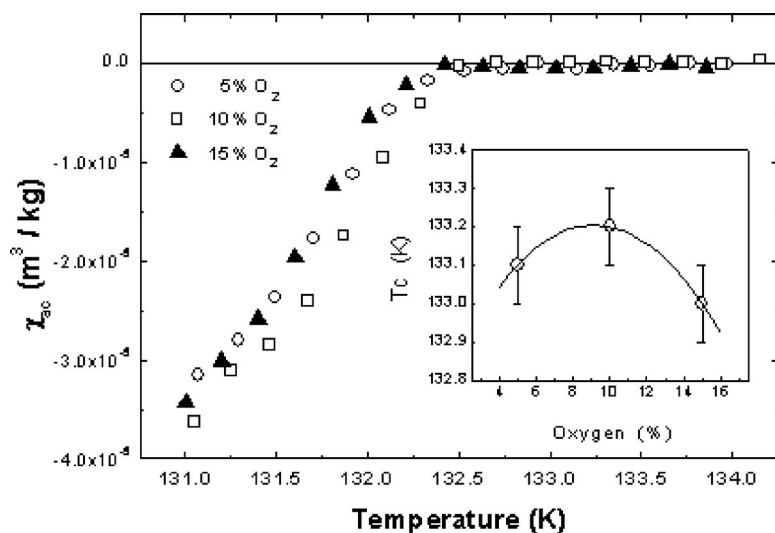


Figure 6. Measurements of ac magnetic susceptibility ($f=43$ Hz, $H_a=6$ A/m) for Samples A, B, and C. The inset shows the plot of T_c versus O percent for the samples.

ACKNOWLEDGMENTS

The authors thank Brazilian agencies CNPq (Proj. 504578/2004-9, 154424/2006-4, and 150824/2007-6) and LNLS.

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