STUDY OF THE CRYSTAL STRUCTURE OF THE HIGH Tc SUPERCONDUCTOR

$Hg_{1-x}Re_xBa_2Ca_2Cu_3O_{8+\delta}$ BY USING EXAFS, XANES AND XRD

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ABSTRACT

The Hg based superconducting ceramics presents the highest critical temperatures reported, particularly the phase 1223 whit highest Tc obtained – 135 K. However, these compounds have a complex synthesis and suffer degradation at ambient atmosphere. Additions of higher valence cations, like Re, can favour the synthesis and improve its stability. Samples of nominal composition $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8+\delta}$ and different oxygen content were studied using X-ray absorption and diffraction techniques. Using the XANES it was determined the Re valence +7 in an octahedral distorted co-ordination. By EXAFS it was determined the distances of Re-O bonds (1.85 Å and 2.10 Å). XRD Rietveld refinement showed segregation of two superconducting phases whit distinct lattice parameters. The main phase is associated to the phase Hg,Re-1223 with higher oxygen content and the second superconducting phase is associated with the undoped Hg-1223 phase.

Keywords: high Tc superconductor, XRD, EXAFS, XANES, Rietveld.

RESUMO

Três diferentes amostras do composto supercondutor Hg,Re-1223 de composição nominal $Hg_{0,82}Re_{0,18}Ba_2Ca_2Cu_3O_{8+\delta}$, com diferentes teores de oxigênio foram estudadas por técnicas de absorção e difração de raios X, visando compreender o comportamento de cada uma delas em função do grau de oxigenação. A diferença na síntese das amostras consistiu em tratamentos sob fluxos de misturas de gases oxigênio / nitrogênio (5%, 10% e 15% de oxigênio). As três diferentes razões O_2/N_2 durante o processo de síntese, produziram amostras classificadas como "subdopada", "otimamente-dopada" e "sobredopada", respectivamente. Por meio da técnica de XANES (*X-Ray Absorption Near Edge Spectroscopy*) determinou-se que o cátion Re nestes compostos tem valência da ordem de +7 e que a coordenação octaédrica deste cátion é distorcida, similarmente à encontrada no óxido ReO_3, quando submetido à alta pressão ou alta temperatura. Os estudos através de EXAFS (*Extended X-Ray Absorption Fine Structure*) determinaram que as distâncias de ligação no octaedro de coordenação Re–O são da ordem de 1,85 Å para os oxigênios equatoriais e 2,10 Å para os oxigênios apicais. Os refinamentos de Rietveld de dados de difração de raios X mostraram a segregação de duas fases

supercondutoras com estruturas cristalinas *P 4/mmm* e parâmetros de rede distintos. A fase principal foi associada à fase Hg,Re-1223 e a fase supercondutora secundária foi associada a uma fase Hg-1223 sem rênio. A amostra "otimamente-dopada" apresentou maior proporção de fases supercondutoras, maior ocupação do sítio cristalográfico do Hg(Re) e maior temperatura crítica de transição - T_c. Foram determinados, para cada amostra, a estequiometria de Hg, Re e O para a fase dopada, os parâmetros de rede das fases supercondutoras, as frações volumétricas das fases supercondutoras e das fases residuais. Contrariamente às indicações da literatura, não foram encontradas evidências de formação de uma super-rede com o ordenamento dos sítios cristalográficos ocupados pelo Re. Pela primeira vez reporta-se a valência do cátion Re nestes compostos e também a segregação em duas fases, com diferentes teores de rênio e de oxigênio.

INTRODUCTION

Since the discovery of the high Tc superconductor by Bednorz and Muller [1] in La-cuprate system, several other families of ceramic superconductors were obtained. In 1993, Putilin et al [2] have obtained a new family $HgBa_2Ca_{n-1}Cu_nO_y$ (n=1, 2, 3...), which has presented the highest Tc (134 K) already reported. When exposed to the ambient atmosphere this Hg-cuprate system loss its superconducting properties due to CO_2 contamination, however this matter has been overcome by partial substitution of mercury by rhenium [3]. It was observed a clear influence of Re content on the oxygen amount present in the HgO layer where the presence of Re cations brings additional oxygen to this plane [3]. These additional oxygen atoms are very stable and complete the mercury layer. Specifically, samples with 18% nominal atomic Re content have presented an improvement of the superconducting properties, such as the critical current density, when compared with $HgBa_2Ca_2Cu_3O_y$, Hg-1223 without Re [3].

The crystal structure of Hg,Re-1223 has being intensively studied by some authors [4] and discrepant results have been reported. For instance the Re coordination in the Hg crystallographic site and the oxygen content, i.e., the term δ in the oxygen stoichiometry - one of the most important parameters in all ceramic high Tc superconductors - is still a matter of discussion [4].

In the present work it was studied three different samples of $Hg_{1-x}Re_xBa_2Ca_2Cu_3O_{8+\delta}$ with 18% nominal content of Re and different oxygen content, obtained by means of different oxidation treatment during the synthesis process. In order to study the crystal structure of the samples we employed different techniques such as X-rays Absorption Near Edge Structure (XANES), Extended X-Rays Absorptions Fine Structure (EXAFS) and X-Ray Diffraction (XRD) with application of

the Rietveld method in order to fully characterize the crystallography of the compounds. The techniques revealed to be useful and complementary allowing the determination of the valence of Re cations in the samples, the Re-O coordination and bond lengths by absorption techniques and these results were used as input in the Rietveld refinement of XRD data.

The Rietveld refinement shows the segregation in two superconducting phases with slight different cell parameters and different contents of rhenium and oxygen beyond other minor residual phases due the incomplete synthesis. The superconducting phases were classified as one main phase oxygen and rhenium rich and a second one absent in rhenium and oxygen poor.

EXPERIMENTAL

Three samples of $Hg_{0.8}Re_{0.2}Ba_2Ca_2Cu_3O_{8.7+\delta}$, whit δ values of 0, 0.10 and 0.15, labelled as A, B and C respectively, were prepared as described elsewhere [4]. Rietveld refinement of X-ray diffraction (XRD) data was performed in these samples with the purpose of completing previous study [3, 5]. The X-ray diffraction measurements were carried out in conventional laboratory diffractometers and in the X-ray Powder Diffraction beam line, D10B-XPD of the Brazilian Synchrotron Light Laboratory (LNLS), located at Campinas, Brazil. The laboratory XRD measurements employed Cu K_α radiation and the synchrotron measurements where performed also whit energy near the rhenium L_{III} absorption edge, where the rhenium scattering factor is higher (anomalous scattering). The spectra were measured from 2° to 122° in 2θ with 0.01° step scan. The instrumental parameters were obtained from the refinement of standards LaB_6 and Al_2O_3 samples (NIST-Standard Reference Materials) for each energy. Rietveld refinements were performed using the program GSAS [6] with the interface EXPGUI [7].

The absorption measurements were also made at the Brazilian Synchrotron Light Laboratory (LNLS) using the X-ray absorption spectroscopy beam line D04B-XAS. The Re L_{III} absorption edge spectra at 10.535 keV were measured from 10.400 keV up to 11.400 keV, in 1 eV steps in the XANES region and 2.5 eV steps in the EXAFS region. The absorption data was analyzed using of the programs FEFF and FEFFIT [8, 9].

3. Results and discussion

The XANES study consisted in correlating the known valences of Re cations in elementary Re and two different rhenium oxides to the energy of its L_{III} absorption edges, in order to establish the relationship to be applied to the Re edge energy of the superconducting samples. This was done with the purpose of estimating their valences in the compound. FIG.1a shows details of the top of Re absorption edges in the oxides ReO_2, ReO_3 and in the samples A, B and C of the compound. The FIG.1b shows the values of valence versus edge displacement in elementary Re and in Re oxides, which determine the calibration line.
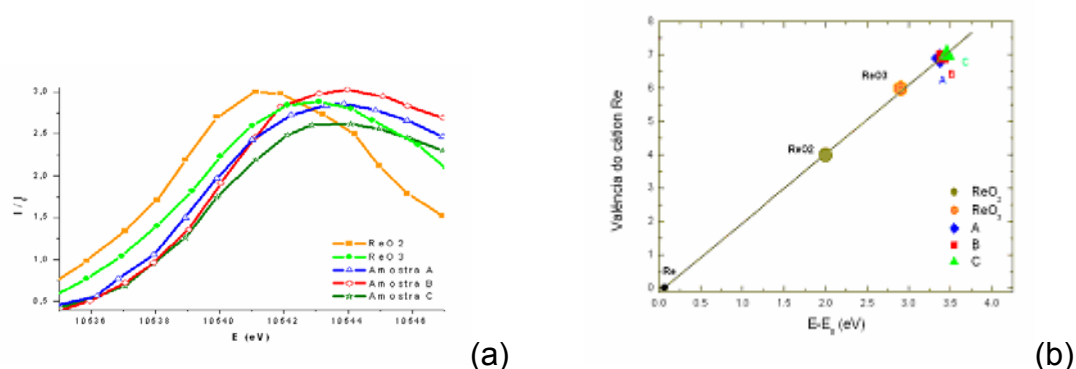

(a)   (b)

FIGURE1 – (a) details of the Re L_{III} absorption edges in ReO_2, ReO_3 oxides and in the samples A, B and C and (b) valences of Re in the samples of the Hg,Re-1223, B and C, determined from the L_{III} e absorption edge displacements.

Thus the valence of Re in the superconducting samples was estimated and is presented in TAB.1.

TABLE 1 – Re valence in elementary and Re oxides and in the superconducting samples.

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

The valence values for the samples are in agreement with value 6.85 estimated by Chmaissem [10] for a similar sample, using the Bond Valence Method [11].

As the intensity of X-rays scattering by an atom is proportional to the square of its atomic number, the X-ray scattering by basal planes of Hg,Re superconductors is mainly determined by the heavy cations. Thus, the contribution of anions O^{2-} in the basal planes to XRD reflections is very small avoiding information gathering about its atomic position, vibrations and occupation. To overcome the difficulty it has been employed EXAFS, a short-range technique suitable to supply information about the

local coordination around the absorbing atom. The theoretical model of EXAFS, calculated by the programs ATOMS and FEFF [8, 9], started with the values of the cell parameters, the space group and a model for the atomic positions reported in literature [4, 5, 10]. The analyses were carried out in the same spectra used for XANES, however using the far region above the absorption edge, (from 30 eV to 1000 eV above of the edge). For the EXAFS analysis it has been employed the program ATOMS [9] for calculating the scattering paths, the program AUTOBK for background corrections and the program FEFF to calculate the scattering amplitude, angles and phases for each scattering path. The program FEFFIT performs the adjustment between the calculated and measured data. The results for the two first coordination shells are shown in Tab.2.

TABLE 2 - Results of the EXAFS analysis for the first and second coordination shells: O_{eq} are the equatorial oxygens (in the basal plane) and O_{ap} are the apical (in the *00l* direction).

	Sample A	Sample B	Sample C
$\sigma^2 O_{eq}$ (Å2)	0.0155 (9)	0.0137 (17)	0.0157 (13)
dist. Re - O_{eq} (Å)	1.85 (5)	1.83 (9)	1.87 (9)
$\sigma^2 O_{ap}$ (Å2)	0.0201 (20)	0.0165 (17)	0.0204 (34)
dist. Re – O_{ap} (Å)	2.09 (10)	2.15 (2)	2.00 (14)

The Re-O bond lengths indicate a distorted octahedral coordination with C_{4V} symmetry, similar to that found in ReO_3 under isostatic pressure [4]. In order to confirm the reliability of the EXAFS results it has been applied the Bond-Valence Method [11] to calculate the valences for the bond distances obtained and the results were very similar to these presented in TAB.1, showing the coherence of the methodology.

In the beginning of the Rietveld refinements it was found difficulties in adjusting the profile function using only one superconducting phase, due to a strong asymmetry in the 001 reflection, as shown in FIG. 2a, b and c. However, when using high resolution Synchrotron diffraction it was observed that this asymmetry is a split of two very close peaks, as can be seen in FIG.2d.

This split leads us to propose the co-existence of two superconducting phases with small difference in parameter c. In order to take it into account it was introduced a second superconducting phase together other residual phases, as shown in TAB. 3.
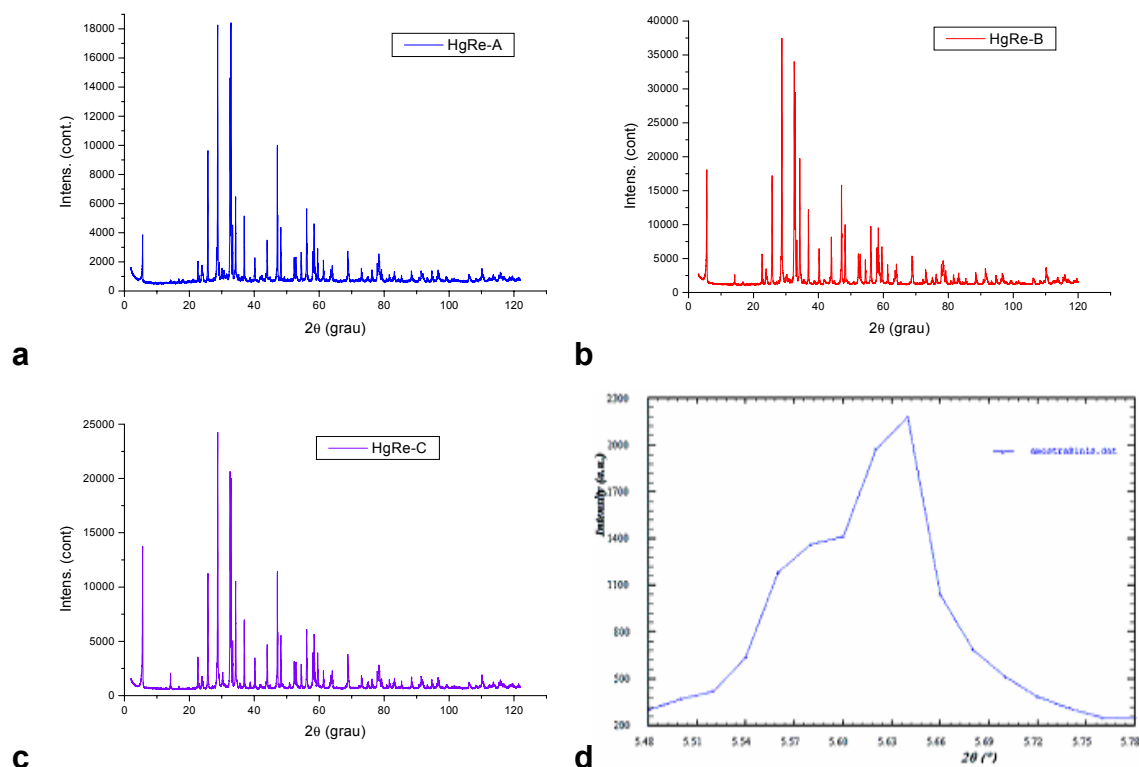
FIGURE 2 – XRD for the samples A (a), B (b) and C (c) with $Cu_{k\alpha}$ radiation and detail of the 001 reflection using high resolution Synchrotron diffraction (d).

TABLE 3 – Identified phases according Powder Diffraction File - PDF- ICDD.

Phase	PDF Nº	Space Group	Cell Parameters(Å)
$Hg_{0.80}Re_{0.20}Ba_2Ca_2Cu_3O_{8+\delta}$	51-0490	P4/mmm	a = 3.853 c = 15.683
$HgBa_2Ca_2Cu_3O_{8+\delta}$	87-1338	P4/mmm	a = 3.852 c = 15.851
$CaHgO_2$	86-0037	$\overline{R3m}$	a = 3.586 c = 18.653
$BaCO_3$	85-0720	Pmcn	a = 5.280 b = 8.830 c = 6.390
$Ca_{0.82}CuO_2$	89-6533	Fmmm	a = 2.805 b = 6.320 c = 10.576
Ca_2CuO_3	34-0282	Immm	a = 12.23 b = 3.776 c = 3.257
$BaCuO_2$	70-0441	Im-3m	a = 18.27
CuO	89-5899	Cc	a = 4.689 b = 3.420 c = 5.130

Using high-resolution anomalous synchrotron diffraction at the Re L_{III} edge

energy, it was confirmed the presence of two phases with different content of Re, as can be seen in FIG. 3.
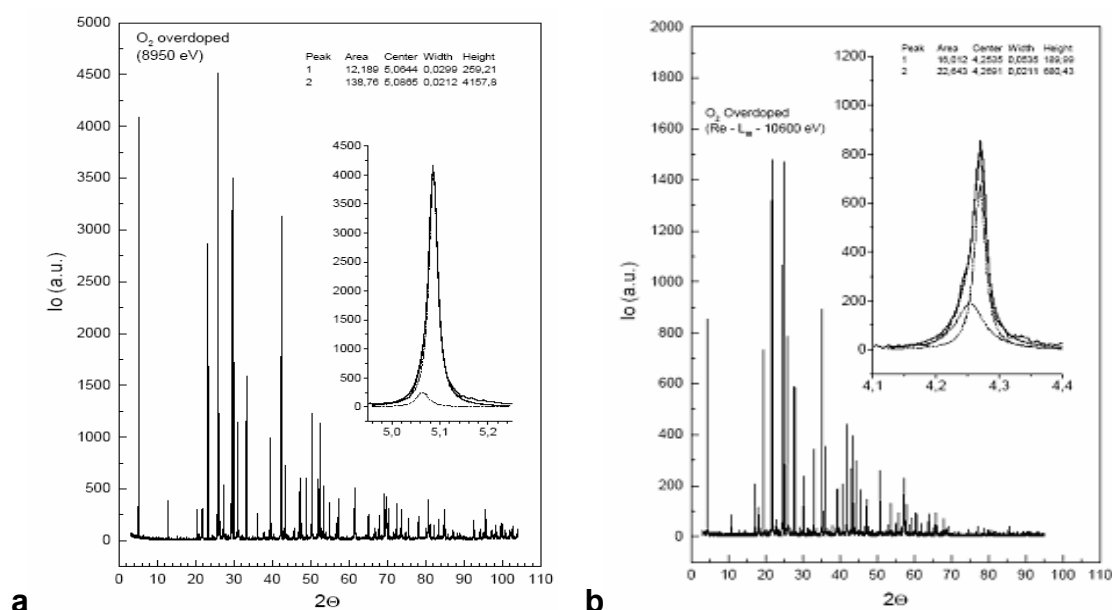

a   **b**

FIGURE 3 – Synchrotron anomalous diffraction at energies 8.950 keV (a) and 10.600 keV (b) for the same sample. The inserts show the asymmetry and different proportions of the splitted 001 reflection caused by anomalous scattering [12].

The Rietveld refinements of XRD data were performed fixing the oxygen co-ordination around Re (values obtained by EXAFS) and refining all other parameters. The details of the refinement are described in Ref. [4]. The main results of Rietveld refinement are shown in TAB. 4. The Rietveld plot and the crystal structure of one of the samples are shown in FIG. 4.
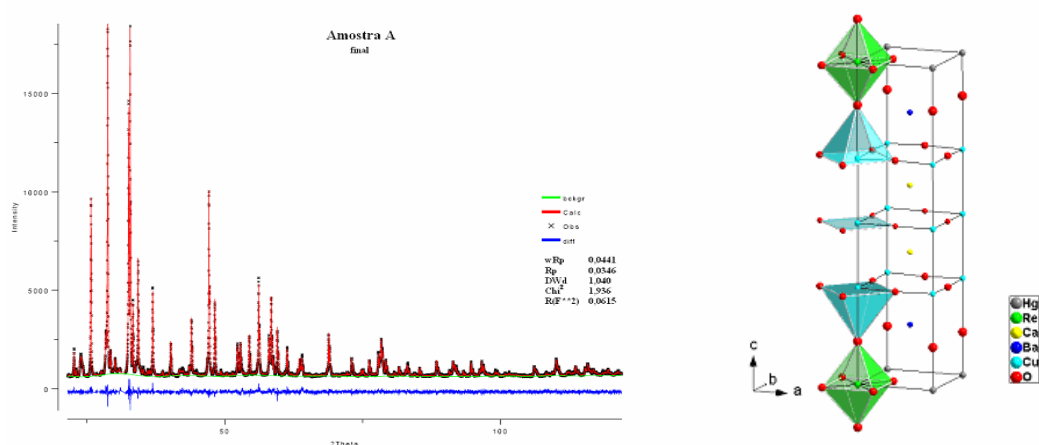

FIGURE 4 – Rietveld plot and corresponding calculated unit cell for sample A.

TABLE 4 – Main results of Rietveld refinement for the samples A, B and C.

Parameters	Sample A	Sample B	Sample C
%$_{mass}$ phase Hg,Re-1223	61.4	68.7	50.3
%$_{mass}$ phase Hg-1223	16.1	14.7	30.8
%$_{mass}$ superconducting phases	77.5	83.4	81.1
%$_{mass}$ residual phases	22.5	16.6	19.0
Parameter a phase Hg,Re-1223 (Å)	3.854512	3.854124	3.854388
Parameter c phase Hg,Re-1223 (Å)	15.687437	15.688051	15.689096
c/a phase Hg,Re-1223	4.070	4.070	4.070
Unit cell vol. phase Hg,Re-1223 (Å^3)	233.072	233.035	233.082
Angle Cu-O-Cu phase Hg,Re-1223 (º)	176.92	179.93	178.33
O Stoichiometry σ phase Hg,Re-1223	8.707	8.747	8.752
Occupation Hg phase Hg,Re-1223	0.738	0.749	0.749
Occupation Re phase Hg,Re-1223	0.177	0.187	0.188
Occupation site 000 phase Hg,Re-1223	0.915	0.936	0.937
Parameter a phase Hg-1223 (Å)	3.854295	3.853526	3.854320
Parameter c phase Hg-1223 (Å)	15.698784	15.701567	15.692780
c/a phase Hg-1223	4.073	4.075	4.071
Unit cell vol. phase Hg-1223 (Å^3)	233.215	233.163	233.129
Chi^2	1.936	3.268	2.330
Rwp	0.0441	0.0399	0.0461
Rp	0.0346	0.0307	0.0359
DWd	1.040	1.247	0.0888
RF^2	0.0615	0.0503	0.0514

These results allowed the explanation of intrinsic superconducting properties of these Hg,Re-1223 compounds in terms of their crystal structures [13].

CONCLUSION

For the present case, the use of combined techniques allowed the resolution of the crystal structure of a complex compound. The application of different techniques, in a complementary way, was necessary in order to fully characterize a complex crystal structure. The application of different techniques of X-rays diffraction (normal and anomalous scattering) and absorption (XANES and EXAFS), allowed the characterization of the crystal structures of Hg,Re-1223 superconducting compounds whit different oxygen contents and this procedure can be empathized as a possible way to solve other complex crystallographic structures.

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