

Phase segregation of (Hg,Re)-1223 superconductor

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Abstract

Synchrotron Anomalous X-Ray Scattering near Re (rhenium) edge reveals that the short range structure of $Hg_{0.8}Re_{0.2}Ba_2Ca_2Cu_3O_{8+d}$ compound is not form part of $(2a \times 2b \times 1c)$ super cell. Moreover, even for a high quality sample (highest T_c and single phase diamagnetic transition), the Synchrotron X-Ray diffraction pattern analyzed by Reitveld refinement confirms there exist two superconductor phases present in the sample produced with optimal oxygen doping content (Hg-1223 and Hg,Re-1223). Extended X-Ray Absorption Fine Structure measurements of the rhenium oxide (VI) sample under external hydrostatic pressure (up to 1.9 GPa) reveal that the ReO_6 octahedron spectrum obtained at 1.76 GPa is similar to the ReO_6 octahedron inside the (Hg,Re)-1223 structure at ambient pressure. The ReO_6 distorted octahedron inside Hg,Re-1223, and the non-existence of $(2a \times 2b \times 1c)$ super cell can justify the scenario where charge inhomogeneities distribution are present in the outer CuO_2 layers.

Key words: (Hg,Re)-1223 samples, diffraction, lattice

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1. Introduction

Since the discovery of the high T_c superconductor by Bednorz and Muller [1] in La-cuprate system, several other families were produced. In 1993, Putilin et al [2] have obtained a new family $HgBa_2Ca_{n-1}Cu_nO_y$ ($n=1,2,3 \dots$), which has presented the highest T_c (134K). This Hg-cuprate system loss its superconducting properties due to CO_2 , however this matter has been overcome by partial substitution of mercury (Hg) by rhenium (Re) [3,4]. In addition, Orlando *et al.* [7] have observed a clear influence of Re content on the oxygen amount present in the HgO_δ layer: Re brings additional oxygen to this site. These additional oxygen atoms are very stable and complete the mercury layer. Specifically, samples with 20%

nominal atomic Re have presented an improvement of the superconducting properties [7], such as the critical current density [5], when compared with $HgBa_2Ca_2Cu_3O_y$, Hg-1223 (without Re).

2. Experimental

Three samples of $Hg_{0.8}Re_{0.2}Ba_2Ca_2Cu_3O_{8.7+d}$, $d=0, 0.10$ and 0.15 labeled as A, B and C were prepared as described elsewhere [6,7]. X-ray diffraction (XRD) analysis with Rietveld refinement were performed in these samples with the purpose of completing Orlando *et al.* [7] study.

The X-ray diffraction measurements (Fig.1) were carried out in the X-ray Powder Diffraction beamline, D10B-XPD, of the Brazilian Synchrotron Light Laboratory (LNLS), located in Campinas, SP,

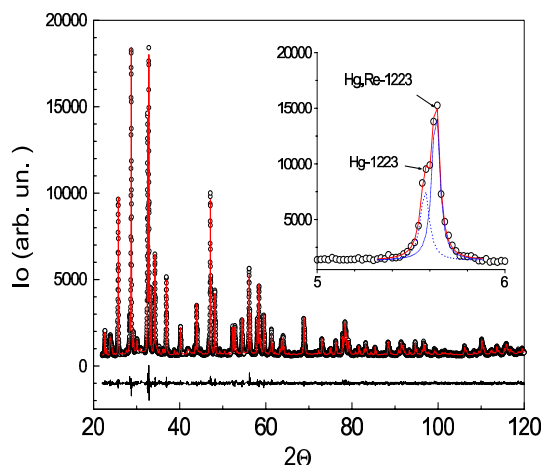


Fig. 1. The Rietveld plot using Synchrotron X-Ray diffraction pattern measured at 8950eV. No trace of super cell ($2a \times 2b \times 1c$) was detected.

Brazil. Two different energies were used to perform the experiments: 8950eV and 10600eV. The first energy is similar to $CuK\alpha$ and the second one was chosen 65eV after the rhenium edge L_{III} , where the rhenium scattering factor is higher than in 8950eV. The measurements were performed with 0.01° step scan and variable counting time statistics that took into account the decrease of the beam current in the LNLS storage ring. Moreover, the spectra were measured from 2° up to 122° in 2θ . The instrumental parameters were obtained from the refinement of standards LaB_6 and Al_2O_3 (NIST-Standard Reference Materials) samples at each energy. Rietveld refinements [8] were performed using the program GSAS [9] with the interface EXPGUI [10].

3. Result and discussion

The Rietveld plot for the sample B is shown in figure 1. For each XRD pattern, the better spectrum fit was obtained including an extra Hg-1223 phase to the main (Hg,Re)-1223 phase, as compared to our previous work [7]. All refinements have considered the following phases: (Hg,Re)-1223 (rich at oxygen) and Hg-1223 (poor at oxygen), $HgCaO_2$, $BaCO_3$, $CaCuO_2$ and $BaCuO_2$ [11–13]. The oxygen position were determined by EXAFS measurements of the rhenium oxide (VI) under external hydrostatic pressure (up to 1.9 GPa), which reveals that the ReO_6 octahedron spectrum at 1.76 GPa is similar to the Re_6 octahedron inside the (Hg,Re)-1223 structure at ambient pressure [14].

The main (Hg,Re)-1223 and Hg-1223 phases, their fitted parameters, and goodness-of-fit are shown in the Table 1 [11]. The existence of two superconducting phases was confirmed by anomalous X-ray diffraction (synchrotron at 10600eV) took into account that Re distribution on the Hg-O plane did not produce a super cell ($2a \times 2b \times 1c$) in any sample (A, B and C) [11,13]. The crystallite average sizes were determined by Le Bail fitting, using the formalism of Stephens [9,15], Thompson approach [16], and the Finger asymmetry correction [17].

Table 1

The Hg,Re-1223 and Hg-1223 phases are labeled by I and II, respectively. Crystallite size was labeled as l

Parameter	Sample A	Sample B	Sample C
% (Hg,Re)-1223	61.4	68.7	50.3
% Hg-1223	26.1	24.7	40.8
I a (Å)	3.854516(14)	3.854120(12)	3.854382(16)
c (Å)	15.687440(40)	15.688061(56)	15.689091(70)
l (Å)	> 1000	> 1000	> 1000
II a (Å)	3.854295(18)	3.853526(15)	3.854320(10)
c (Å)	15.698784(60)	15.701567(65)	15.692780(76)
l (Å)	590	380	470
χ^2	1.465	1.882	1.496
Rwp (%)	3.83	3.03	3.70

The ReO_6 distorted octahedron inside Hg,Re-1223 [7,14], and the non-existence of ($2a \times 2b \times 1c$) super cell [13] can justify the scenario where charge inhomogeneities distribution are present in the outer CuO_2 layers.

References

- [1] J G Bednorz and K A Muller, Z. Phys. B **64** (1986) 189.
- [2] S N Putilin, *et al.*, Nature **362** (1993) 226.
- [3] J Shimoyama *et al.*, Physica C **235-241** (1994) 2795
- [4] K Kishio *et al.*, J. Low Temp. Phys. **105** (1995)1359
- [5] Y Matsumoto *et al.*, Physica C **421-414** (2004) 435
- [6] F D C Oliveira, *et al.* IEEE Trans. on Appl. Supercond. **16** (2005) 15.
- [7] M T D Orlando, *et al.*, Physica C **434**, 53 (2006).
- [8] H M Rietveld, Acta Crystallogr. **22**, 151 (1967).
- [9] A C Larson and R B Von Dreele, GSAS, Los Alamos National Laboratory Report LAUR, 86 (2004).
- [10] B H Toby, J. Appl. Cryst. **34**, 210 (2001).

- [11] L G Martinez, PhD. Thesis, IPEN-USP, São Paulo, 2005.
- [12] F F Ferreira *et al.*, J. Synchrotron Rad. **13**, 46 (2006).
- [13] M T D Orlando *et al.*, Activity Report - LNLS, 311, (2003).
- [14] M T D Orlando *et al.*, Activity Report - LNLS, 179, (2005).
- [15] P W Stephens, J. Appl. Cryst. **32**, 281 (1999).
- [16] I P Thompson, D E Cox, J B Hastings, J. Appl. Cryst. **20**, 79 (1987).
- [17] L W Finger, D E Cox, A P Jephcoat J. Appl. Cryst. **27**, 890 (1994).