Phase segregation of (Hg,Re)-1223 superconductor

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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 ...), 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).

EXPERIMENT

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, Brazil. Two different energies were used to perform the experiments: 8950eV and 10600eV. The first energy is similar to CuK_α 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^o 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].

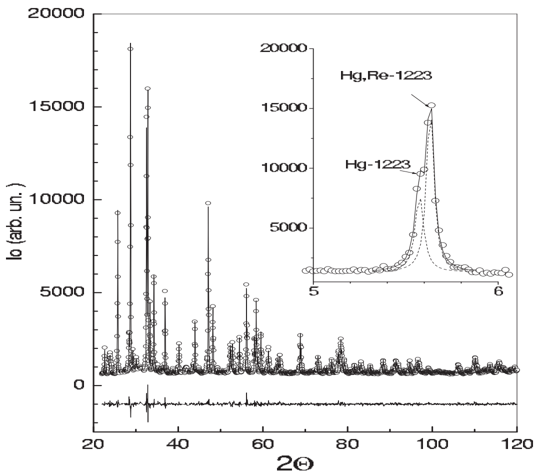

FIG. 1: The Rietveld plot using Synchrotron X-Ray diffraction pattern measured at 8950eV. No trace of super cell $(2a \times 2b \times 1c)$ was detected.

RESULTS 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 I [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 I: 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

CONCLUSION

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.

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