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Phase segregation of (Hg,Re)-1223 superconductor

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Abstract

Synchrotron anomalous X-ray scattering confirmed that Re distribution on the Hg–O plane did not produce a super cell ($2a \times 2b \times 1c$) in our $Hg_{0.8}Re_{0.2}Ba_2Ca_2Cu_3O_{8.7+d}$ samples. Moreover, even for a high quality sample (highest T_c and single phase diamagnetic transition), the synchrotron X-ray diffraction pattern analyzed by Rietveld refinement confirms there exist two superconducting phases present in the sample produced with optimal oxygen doping content (Hg-1223 and Hg,Re-1223). 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.

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Keywords: (Hg,Re)-1223 samples; Diffraction; Lattice parameters

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 $HgBa_2Ca_{n-1}Cu_nO_y$ ($n = 1, 2, 3, \ldots$), which has presented the highest T_c (134 K). Although this Hg–cuprate system loses its superconducting properties due to CO_2, this matter has been overcome by partial substitution of mercury (Hg) by rhenium (Re) [3,4]. In addition, Orlando et al. [5] 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 [5], such as the critical current density [6], 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 [5]. X-ray diffraction (XRD) analysis with Rietveld refinement were performed in these samples with the purpose of completing Orlando et al. [5] 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 energies were used to perform the experiments: 8950 eV and 10600 eV. The first energy is similar to CuKα and the second one was chosen 65 eV after the rhenium edge L_{III}, where the rhenium scattering factor is higher than in 8950 eV. The measurements were performed with 0.01° step scan and variable counting time statistics that took

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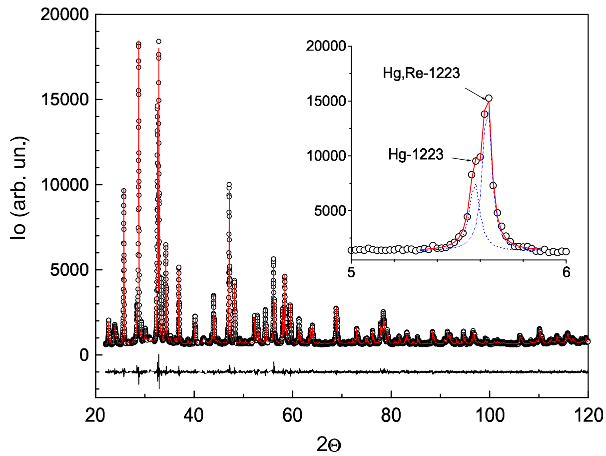

Fig. 1. The Rietveld plot using Synchrotron X-ray diffraction pattern measured at 8950 eV (insert 10600 eV).

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 [7] were performed using the program GSAS [8] with the interface EXPGUI [9].

3. Results

The Rietveld plot for the sample B is shown in Fig. 1. For each XRD pattern, the best spectrum fit was obtained including an extra Hg-1223 phase to the main (Hg,Re)-1223 phase, as compared to Orlando et al. [5]. All refinements have considered the following phases: (Hg,Re)-1223 (rich in oxygen) and Hg-1223 (poor in oxygen), $HgCaO_2$, $BaCO_3$, $CaCuO_2$ and $BaCuO_2$ [10,11]. Since the octahedral oxygen coordination of Re brings additional oxygen atoms to the structure (compared to Hg coordination) [5], we considered the secondary phase as being poor in Re (or with no Re), *i.e.*, poor in oxygen.

The Rietveld refinement with two different energies have shown that there is none supercell ($2a \times 2b \times 1c$) in any sample (A, B and C) [11]. If the superstructure exists the Hg,Re-1223 could be assumed single phase, and, as consequence, the rhenium (Re) will present a regular distribution. However, there was no evidence of superstructure found, which implicate in the existence of Hg,Re-1223 irregular cluster. This hypothesis was confirmed by the detailed analysis of the first peak at 8950 eV. There are two Lorentzian (Hg-1223 and Hg,Re-1223), and the area of each phase depends on the selected energy (see insert in Fig. 1). It was verified by analysis of anomalous X-ray scattering of the (0 0 1) reflection that there are two phases with different content in Re as can be seen by different areas under the adjusted curves [11]. The main (Hg,Re)-1223 and Hg-1223 phases, their fitted parameters, and goodness-of-fit are in Table 1.

Table 1
The Hg,Re-1223 and Hg-1223 phases are labeled by I and II

	Parameter	Sample A	Sample B	Sample C
I	% (Hg,Re)-1223	61.4	68.7	50.3
II	% 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)
II	a (Å)	3.854295(18)	3.853526(15)	3.854320(10)
	c (Å)	15.698784(60)	15.701567(65)	15.692780(76)
	χ^2	1.465	1.882	1.496
	Rwp (%)	3.83	3.03	3.70

4. Conclusion

The presence of two phases (Hg,Re-1223 – oxygen rich and Hg-1223 – oxygen poor), and the non-existence of ($2a \times 2b \times 1c$) super cell [11] can justify the scenario where charge inhomogeneities distribution are present in the outer CuO_2 layers.

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