Synthesis of superconducting ceramics Hg$_{0.82}$Re$_{0.18}$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ with different values of δ

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Abstract. Samples of the superconducting ceramics Hg$_{0.82}$Re$_{0.18}$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ were prepared by solid-vapor reaction technique. The preparation of the ceramic precursor started with a mixture of Ba$_2$Ca$_2$Cu$_3$O$_x$ and ReO$_2$ powders with molar ratio 1:0.18. The precursor material was submitted to annealing under three different partial pressures of oxygen using a mixture of oxygen/argon at ratios: 5/95 (sample A), 10/90 (sample B) and 15/85 (sample C). X-ray powder diffraction analysis of the precursors identified the phases BaCuO$_{2+x}$, Ba$_2$Cu$_3$O$_{5+x}$, Ba$_4$CaCu$_3$O$_{8+x}$, Ca$_2$CuO$_3$ and Ca$_5$Re$_2$O$_{12}$ at different ratios in the samples, indicating an increment in the oxygen content from sample A to sample C. Finally, the precursors with different oxygen contents were blended with HgO at molar ratio 1:0.82 and treated in a sealed high pressure furnace to produce the high Tc superconducting ceramics. Rietveld refinement of XRD data showed differences in the crystal structures of the samples. The measurement of thermopower at room temperature resulted in distinct values, confirming the different oxygen sample doping.

Introduction

In 1993, Putilin et al [1] have discovered a new family of superconducting compounds, represented by the general composition HgBa$_2$Ca$_{n-1}$Cu$_n$O$_y$ (n = 1, 2, 3 ...), which has presented the highest critical temperatures known (Tc ~ 134 K). This Hg-cuprate system loses its superconducting properties due to CO$_2$ contamination, however this matter has been overcome by partial substitution of mercury (Hg) by rhenium (Re) [2,3]. In addition, Orlando *et al*. [4] have observed a clear influence of Re content on the oxygen amount present in the HgO$_\delta$ 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 [4], such as the critical current density [5], when compared with HgBa$_2$Ca$_2$Cu$_3$O$_y$, Hg-1223 (without Re).

Experimental Procedure
Precursor preparation

Firstly the preparation of the ceramic precursor began with a mixture of Ba$_2$Ca$_2$Cu$_3$O$_x$ (99.0% PRAXAIR) and ReO$_2$ (99.0% Aldrich) in powder form with the molar relationship 1:0.18 [6]. These powders were compacted with an uniaxial pressure of 0.5 GPa and were heated at 850° C in an oxygen flow (99.5% purity) for 15 h. The obtained precursor was crushed, homogenized and compacted again before being heated a second time at 920° C for

12 h in a flow of oxygen [7]. The obtained precursor material was fractioned in three parts and each of then was submitted to a new treatment at 920° C for 24 h in a flowing of gas mixture of argon (99.5%) and oxygen (99.5%) maintained at 1 bar. The precursor fraction treated under gas ratio 5% of O_2 : 95% of Ar was nominated precursor A, the fraction treated under gas ratio 10% of O_2 : 90% of Ar was nominated precursor B and the fraction treated under gas ratio 15% of O_2 : 85% of Ar was nominated precursor C [6-10].

X-ray powder diffraction analysis of each precursor was done in order to evaluate the oxygen content, as is shown in Fig. 1. The XRD measurements were carried out with a Rigaku X-ray diffractometer model 4053A3 with CuK_α radiation (λ= 1.5418 Å). The identified phases were $BaCuO_{2+x}$, $Ba_2Cu_3O_{5+x}$, $Ba_4CaCu_3O_{8+x}$, Ca_2CuO_3 and $Ca_5Re_2O_{12}$ [6].
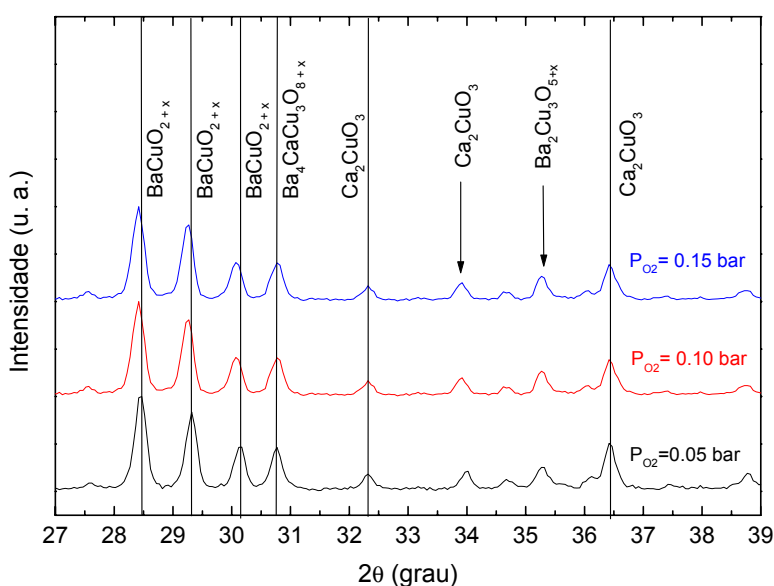

Figure 1: XRD patterns of the precursor ceramics with different oxygen partial pressure. The identified phases were: $BaCuO_{2+x}$, $Ba_2Cu_3O_{5+x}$, $Ba_4CaCu_3O_{8+x}$, $Ca_5Re_2O_{12}$ and Ca_2CuO_3.

Superconductor synthesis

Finally, the precursors prepared with different oxygen partial pressures were blended with HgO at molar the relationship 1:0.82. Each sample was homogenized in an agate mortar and uniaxially compacted with a pressure of 1 GPa. Each sample was wrapped in a gold foil (99.999%) and introduced into a quartz tube with 8 mm inner diameter [8]. The quartz tubes were sealed in a high vacuum of 3×10^{-6} torr and each of then, with a sample inside, were introduced together in an isostatic pressure furnace. The furnace was filled with 14 bar of Ar in order to avoid an explosion of the quartz tubes.

Samples Characterization

For the superconductor samples, X-ray diffraction measurements were carried out in the D10B-XPD beamline of the Brazilian National Synchrotron Light Laboratory (LNLS) – Campinas, Brazil. Two different energies were used to perform the experiments: 8.950 eV and 10.600 eV. In addition, the thermopower measurements were carried out at constant temperature. Temperature gradients ∇Tx of the order of 0.5 K/mm were applied using a small

resistance heater mounted on the top of samples and ∇Tx were measured by a calibrated AuFe-chromel thermocouples.

Results and Discussion

A typical Rietveld plot is shown in Fig. 2. For each XRD pattern, the better spectrum fit was obtained including an extra Hg-1223 phase additionally to the main (Hg,Re)-1223 phase, as compared to our previous work [12]. 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 $BaCuO_2$ [13]. The main (Hg,Re)-1223 and Hg-1223 phases, their fitted parameters, and goodness-of-fit are shown in the Tab. 1 [13]. The existence of two superconducting phases was first detected by anomalous X-ray diffraction carried out at 8.950 eV and 10.600 eV (see inset of Fig.2). Moreover, it was confirmed by anomalous X-ray diffraction that Re distribution on the Hg-O plane did not produce a supercell (2a×2b×1c) in any sample (A, B and C) [14].

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

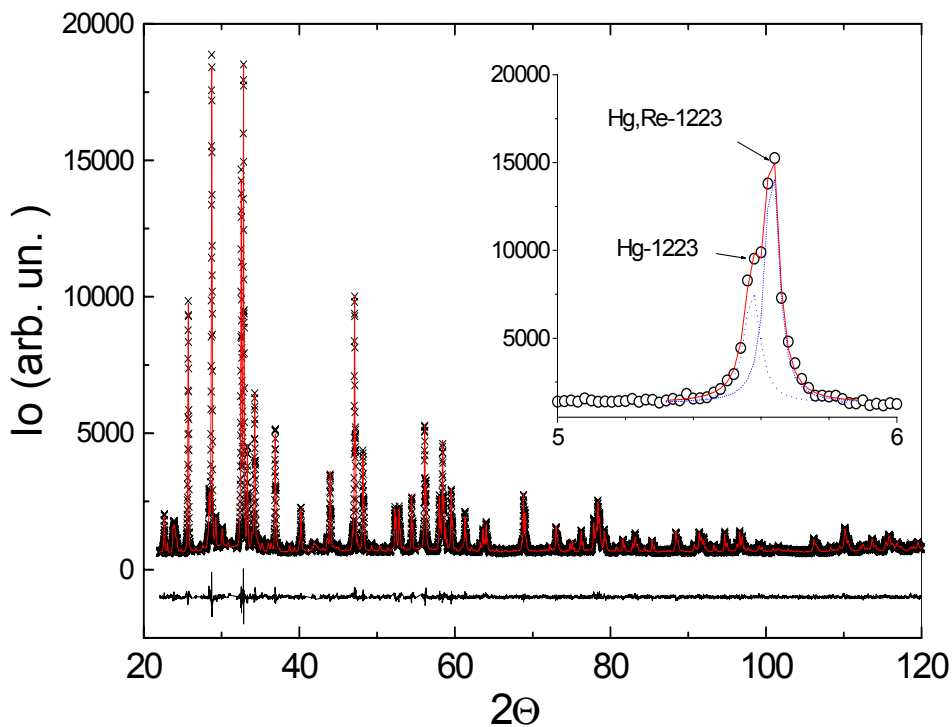|	Parameter	Sample A	Sample B	Sample C
I	% (Hg,Re)-1223	61.4	68.7	50.3
II	% Hg-1223	26.1	24.7	40.8
I	a (Å)	3.85452(1)	3.85412(1)	3.85438(1)
	c(Å)	15.68744(4)	15.68806(5)	15.68909(7)
	l (Å)	> 1000	> 1000	> 1000
II	a (Å)	3.85430(2)	3.85353(2)	3.85432(1)
	c(Å)	15.69878(6)	15.70157(7)	15.69278(7)
	l (Å)	590	380	470
	χ^2	1.465	1.882	1.496
	Rwp (%)	3.83	3.03	3.70

Figure 2: Rietveld plot of the sample B (optimal). The spectrum was plotted in a range from 20° up to 120°. The insert shows 001 peak (5° up to 6°) and the convolution of two phases at 8.950 eV.

The main (Hg,Re)-1223 phase was very crystalline as considering small broadening of their peaks. Besides, the crystallite average sizes were determined from the pseudovoigh profile coefficients of Le Bail fitting [15-19]. For all samples the estimated crystallite sizes of the (Hg,Re)-1223 phase was larger than the range measurable by this method (l ~ 1000 Å). This indicates that during the final step of the synthesis occurs a strong growth of crystallites. On the other hand, the extra Hg-1223 phase has smaller crystallite as shown Table 1. Both phases did not present micro strains.

In Fig. 3 can be observed that the thermopower signals S have the typical behavior described by MacIntosh and Kaiser [20]. The thermopower signal is positive and distinct at room temperature. From the S value at room temperature it is possible determine the parabolic variation of doping carrier p, and as consequence Tc , $Tc = Tc^{max} - 82.6\ Tc^{max}\ (p - 0.16)^2$ [21]. Our results of Tc, S(300 K) and p are summarized in Table 2.
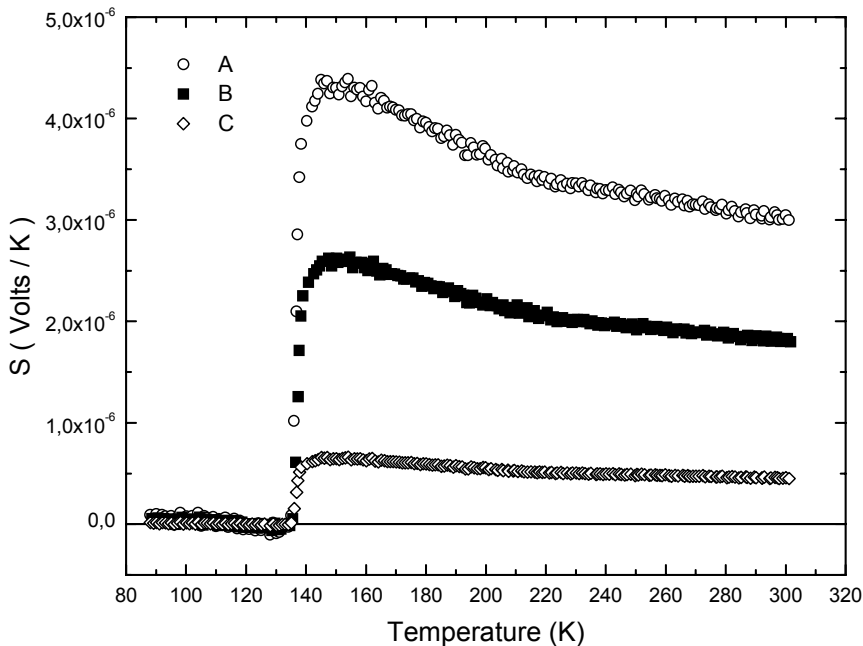
Figure 3: Thermopower of the (Hg,Re)-1223 samples produced with different oxygen partial pressure in the precursor annealing.

Table 2: The Values of Oxygen Partial Pressure, Critical Temperature, Thermoelectric Power Signal at 290 K and Hole Number per Cu-O Layer.

Samples	PO_2 (bar)	Tc (K)	S (μV/K)	p (hole/Cu-O)
A	0.05	132.6	3.0	0.15
B	0.10	133.2	1.8	0.16
C	0.15	132.7	0.5	0.17

Conclusion

Samples of the superconducting ceramics $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8+\delta}$ with distinct oxygen partial pressure were prepared by solid-vapor reaction technique. The Rietveld analysis of synchrotron X-ray diffraction measurements confirmed the presence of two superconductor phases present in the sample produced with optimal oxygen doping content (Hg-1223 and Hg,Re-1223). The thermopower measurements have determined that the optimal oxygen doping content is associated with the sample B. As this sample, produced by precursor with 10% of partial oxygen pressure, presented the best physical properties (Tc, crystal size, Thermopower, etc..) we conclude that this is stable chemical route to produce this superconductor ceramic.

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