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Effects of oxygen content on the properties of the $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8+d}$ superconductor

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Abstract
Mercury superconductor samples doped with rhenium, $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8+d}$, were produced in a very narrow range of oxygen content ($d = 0.05$, 0.10 and 0.15). The lattice parameters indicated a slight change of the unitary cell as a function of the oxygen content. Furthermore, the reduction of the volume cell was associated with the slight increment of T_C. The measurements of χ_{ac} versus temperature, under external hydrostatic pressure, have shown sensitive results as a function of distinct oxygen content. In our opinion, this kind of measurement may be used as a tool to determine the oxygen content (underdoped, optimal or overdoped) of samples. For $dT_C/dP > 1.9$ K GPa^{-1} the sample presents an underdoped oxygen content. One can understand that $dT_C/dP = (1.9 \pm 0.2)$ K GPa^{-1} is associated with an intrinsic term value for the optimal oxygen doped sample, $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8.10}$.

1. Introduction

The mercury family $HgBa_2Ca_{n-1}Cu_nO_y$ (Hg-12($n-1$)n) with $n = 1$, 2, 3 has been investigated since it was discovered by Putilin *et al* [1]. It is well known that the compound with $n = 3$ has a transition critical temperature of 134 K at ambient pressure. Shimoyama *et al* [2] introduced rhenium (Re) doping into the mercury superconducting phases. The Re substitution avoids CO_2 atmospheric contamination. Yamura *et al* [3] were the first to indicate a clear trend for Re to substitute Hg instead of the Cu site. When Hg-1223 ($n = 3$) was submitted to an external hydrostatic pressure, it reached an increment of the order of 30 K compared to T_C at ambient pressure [4]. In the opinion of Gao *et al* [5], the underdoped sample presents an increment of dT_C/dP in the pressure range 0.0–2.0 GPa with a rate of 1.7 K GPa^{-1}. In Hg-1223 doped with Re, Orlando *et al* [6] have found that the critical temperature increases in the pressure range 0.0–1.0 GPa with $dT_C/dP =$ 1.5 up to 6.8 K GPa^{-1}, depending on the rhenium doping content. Since 1994, investigations of $Hg_{1-x}Re_xBa_2Ca_2Cu_3O_{8+d}$ (Hg,Re-1223) have been carried out [7–14]. Moreover, a new technique called thermobaric analysis (TBA) has improved the control of the oxygen content present in the precursor. In particular, $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8+d}$ superconductor samples ($x =$ 0.18), with the oxygen content controlled, have been used since 1999 [15].

In this work we have studied polycrystalline ceramics of Hg,Re-1223 with $x = 0.18$ (nominal) Re content, similar to those reported on by Sin *et al* [15]. This differs from the latter by an investigation into how the oxygenation treatment has influenced the grain growth, $T_{C\,onset}$ and dT_C/dP. Keeping this aim in mind, we have chosen to study an oxygen content interval between 5–15%. We have investigated the cell parameter dependence and grain size distribution as a function of oxygen content. The magnetic

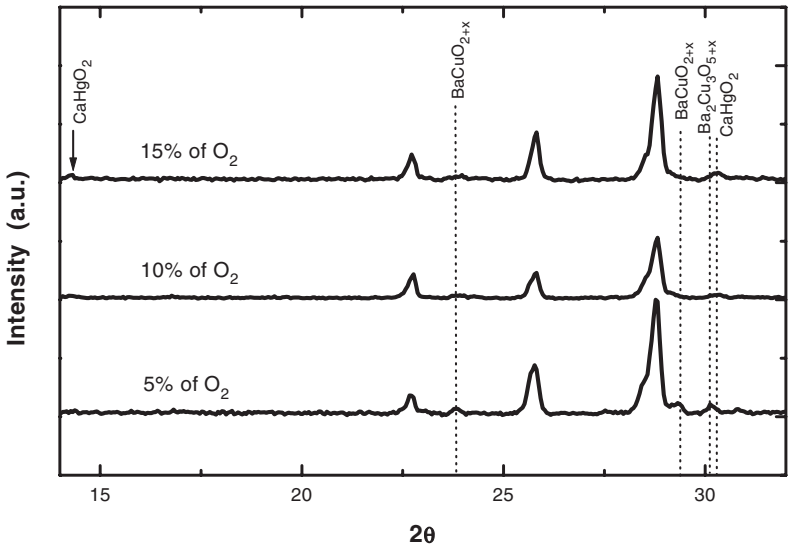

Figure 1. X-ray spectrum for samples of $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8+d}$, where d varies from 5% of O_2 up to 15% of O_2.

ac susceptibility measurements were studied as a function of external hydrostatic pressure, also considering the different oxygen contents. In particular, we have evaluated the intrinsic term dT_C^i/dP [16] associated with the optimal oxygen doped sample.

2. Experimental details

2.1. Synthesis procedure

The procedure to synthesize the superconductor samples starts first with the preparation of the ceramic precursor. This process is very important in the high-pressure synthesis of Hg-based superconductors [17]. The preparation of the ceramic precursor is similar to that reported by Sin *et al* [15], however the thermal treatment was 72 h of the total anneal. Using x-ray diffraction (XRD) analysis and ac susceptibility measurements at ambient pressure, it was possible to qualify the precursors in underdoped (5% of O_2 and 95% of Ar), optimal doped (10% of O_2 and 90% of Ar) and overdoped (15% of O_2 and 85% of Ar) [15] samples.

The synthesis of the superconductor sample $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8+d}$ was carried out using the sealed quartz tube technique [15]. The ff and ff_{Hg} factors used were 0.70 and 0.010 g cm^{-3}, respectively [10, 15]. Here, we have also changed the annealing time to 72 h, as compared to Sin *et al* [15]. In addition, three sealed quartz tubes, each with a sample inside, were installed together in the same region in an isostatic pressure furnace. This latter procedure was done in order to ensure that the three superconductor samples had exactly the same thermal treatment condition.

2.2. Sample characterization methods

Scanning electron microscopy (SEM) images of the pellets were carried out using a Cambridge LEICA S440I. Energy dispersion x-ray spectra (EDS) measurements were performed with the same Cambridge LEICA S440I, which were connected to the energy analyser link Oxford to do the microanalysis.

In order to verify the bulk properties of the samples, all the pellets were crushed in an agate mortar into a glove box under N_2 atmosphere. This procedure was done to guarantee that all samples were crushed without CO_2 or humidity contamination. Besides, the powder was mechanically sifted in order to get particles lower in size than 38 μm.

X-ray powder diffraction patterns (Cu Kα1 and λ = 1.541 78 Å) were recorded by a Rigaku 4053A3 diffractometer with a sample holder filled with dry N_2 gas [14]. The magnetic bulk characterization at ambient pressure was also done in samples with powder form (without intergrain currents) [11]. Also, the ac susceptibility measurements were performed with a driving field $H_{ac} = 5$ A m^{-1} and a frequency $\nu = 423$ kHz [15].

2.3. Susceptibility measurements under hydrostatic pressure

The hydrostatic pressure environment was generated inside a Teflon cell filled with a methanol–ethanol mixture (1:1). This Teflon cell was housed in a BeCu high-pressure clamp with outer and internal diameters of 36 mm and 6 mm, respectively. The primary coil (100 turns) and the astatic pair of pick-up coils (2 × 470 turns) were produced with copper wire of 45 μm diameter. The induced voltage in the pick-up coil was measured with a driving field $H_{ac} = 5$ A m^{-1} and frequency $\nu = 423$ Hz by a lock-in amplifier Stanford Research Systems, model SR830 DSP. The procedure to measure the inner cell pressure was the same as that used in [6].

3. Results and discussion

3.1. Diffraction pattern analysis

Figure 1 displays the XRD patterns of the superconductors prepared with a precursor annealed under different oxygen partial pressures. An analysis of the diffraction patterns was done and the results are shown in table 1. For all samples, the Hg,Re-1233 phase was the main phase present, and some slight impurities were detected. It can also be observed that

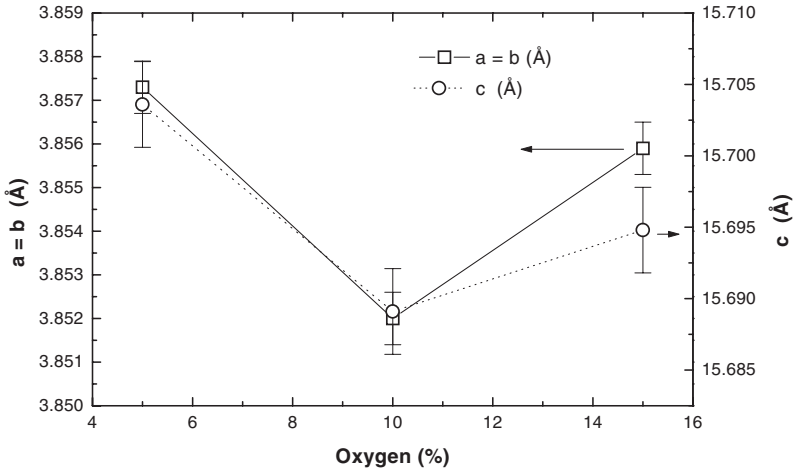

Figure 2. Evolution of the cell parameters of Hg,Re-1223 samples, with different oxygen contents, considering the tetragonal $P4/mmm$ space-group symmetry.

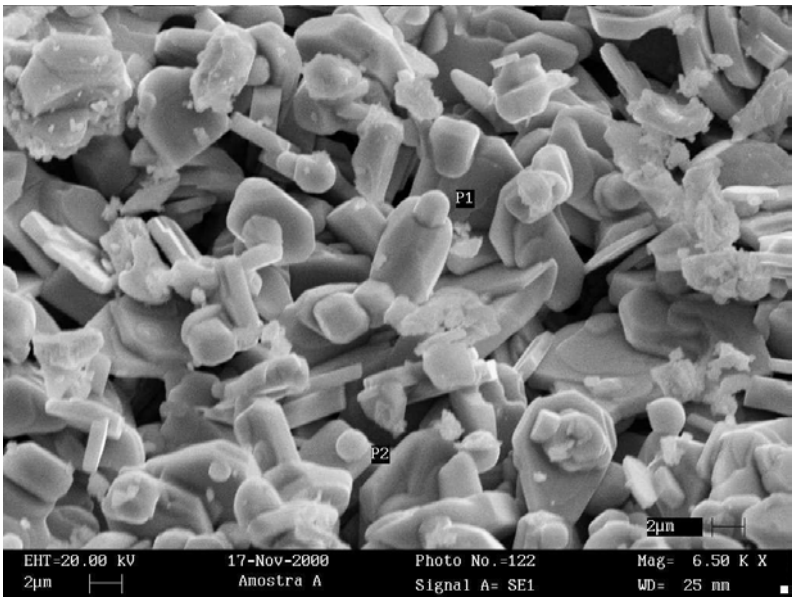

Figure 3. SEM image of Hg,Re-1223 with 5% of O_2.

Table 1. Global analysis of XRD of each superconductor sample with different oxygen contents. These quantities are presented in the form of percentages.

Phases	5% of O_2	10% of O_2	15% of O_2
Hg,Re-1223	93	96	95
$BaCuO_{2+x}$	5	2	1
$Ba_2Cu_3O_{5+x}$	3	2	2
$CaHgO_2$	0	0	2

only the sample with 15% of O_2 presented a trace of $HgCaO_2$ composition. Moreover, the superconductor sample with 10% of O_2 presented a higher phase content of Hg,Re-1223 (96%). As Sin *et al* [15] have shown, below $P_{O_2} \leqslant 0.2$ bar no trace of the $n = 2$ phase was detected.

Figure 2 displays the evolution of cell parameters as a function of oxygen content. These lattice parameters of the superconductor samples were calculated from XRD [18]. We have taken into account the $P4/mmm$ space-group symmetry [19]. The goodness-of-fit, represented by $S(R_{wp}/R_{exp})$, was 1.92, 1.83 and 1.98 for 5%, 10% and 15% of O_2, respectively. For 10% of O_2 there is no substantial difference in the lattice parameters ($\mathbf{a} = 3.852(1)$ and $\mathbf{c} = 15.867(3)$) as compared to what was indicated in [6]. Besides, figure 2 suggests that there is a reduction in the unitary cell volume for the 10% sample.

3.2. SEM and EDS results

Details of the grain morphology can be observed in the SEM images in figures 3–5. In order to obtain more information about phase distribution, EDS measurements were done. The grain centre and grain boundary of each sample were analysed and the results are shown in table 2. In summary, the results indicate that there is a trend of detecting the same Re content, in the grain centre and grain boundary for 10% of O_2. Additionally, the sample with 15% of O_2 has presented a trace of $HgCaO_2$, which can be associated with the oxygen content increment [8, 9].

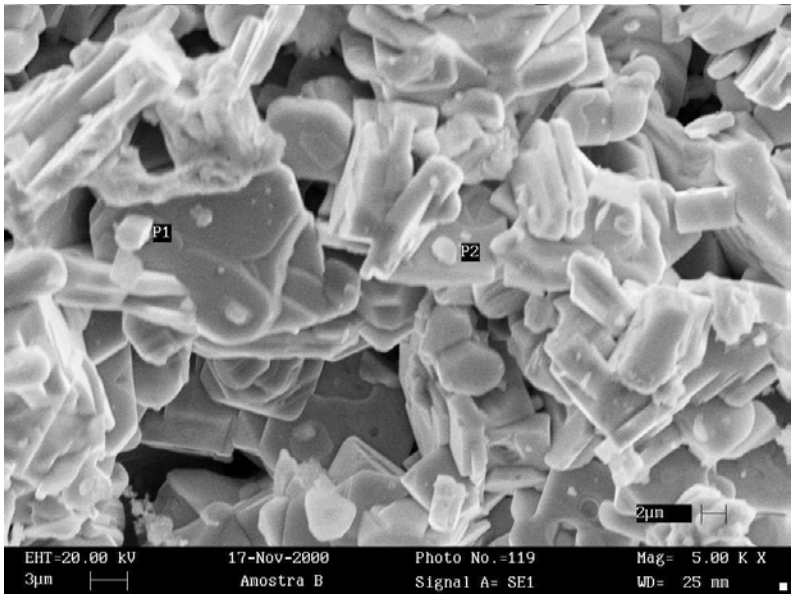

Figure 4. SEM image of Hg,Re-1223 with 10% of O_2.

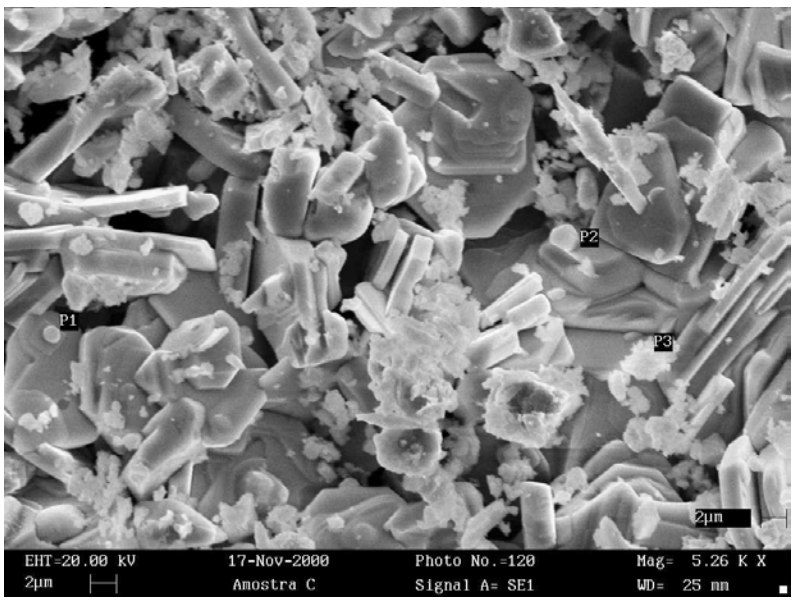

Figure 5. SEM image of Hg,Re-1223 with 15% of O_2.

Table 2. Grain centre and board analysis of the samples measured by EDS analysis.

Samples	Grain centre concentration	Grain board concentration
5% of O_2	$Hg_{0.83}Re_{0.17}Ba_{1.98}Ca_{2.01}Cu_{2.98}O_{8.01}$	$Hg_{0.78}Re_{0.22}Ba_{1.98}Ca_{2.02}Cu_{3.01}O_{8.05}$
10% of O_2	$Hg_{0.80}Re_{0.20}Ba_{1.99}Ca_{2.00}Cu_{2.98}O_{8.09}$	$Hg_{0.82}Re_{0.18}Ba_{2.02}Ca_{2.03}Cu_{2.99}O_{8.01}$
15% of O_2	$Hg_{0.79}Re_{0.21}Ba_{2.03}Ca_{1.98}Cu_{2.99}O_{8.16}$	$Hg_{0.83}Re_{0.17}Ba_{2.01}Ca_{1.97}Cu_{3.01}O_{7.99}$

In the SEM images there are some points of singularities that are identified as P1, P2 and P3 (see figures 3–5). The EDS measurements were done at these points, and the results are summarized in table 3. Some impurities are revealed, which change the initial stoichiometry and do not allow us to obtain 100% of Hg,Re-1223 [13]. This result is in agreement with the XRD analysis (see table 1).

Using the SEM images, we have found the grain junction size distribution [20] by visual inspection. The data were fitted by a gamma distribution function [21] as considered by González *et al* [20]. This function is often used in models which describe physical quantities that only take positive values. Therefore, the gamma distribution function is suitable for determining the mean junction size between grains $\langle d \rangle$. The results are displayed in table 3. We observed that the superconductor sample with 10% of O_2 has a greater average junction size, which corresponds to a sample with larger average grain size.

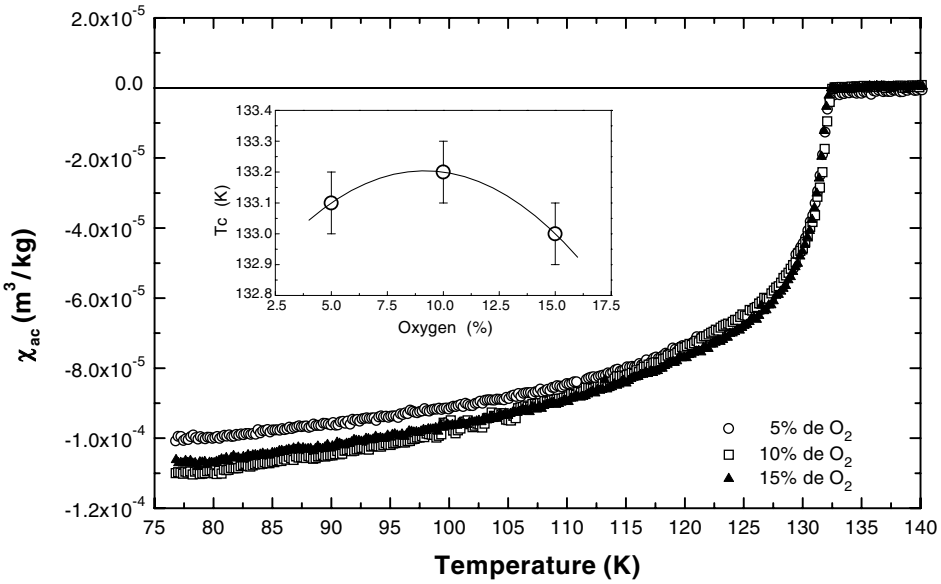

Figure 6. Magnetic ac susceptibility measurement for $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8+d}$ superconductors with different oxygen contents. The inset with T_C versus oxygen shows a parabolic statistical fit.

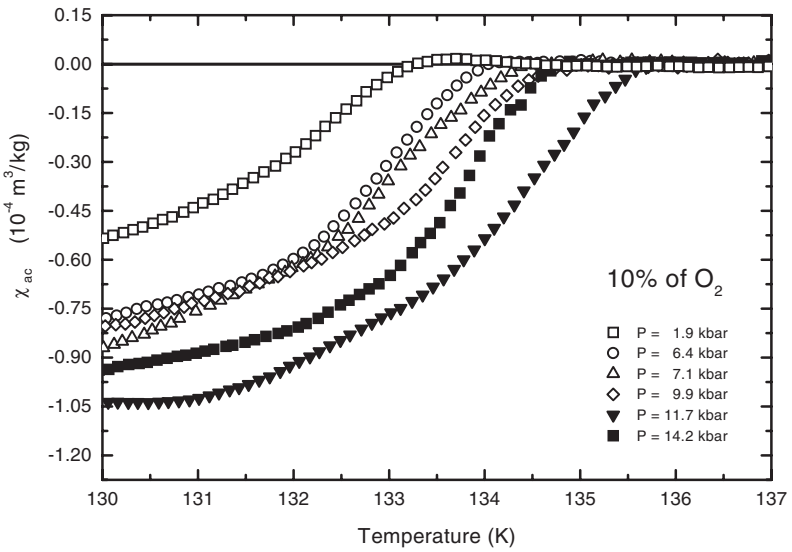

Figure 7. Magnetic ac susceptibility measurement under external hydrostatic pressure for Hg,Re-1223 superconductors with 10% of O_2.

Table 3. EDS analysis of singularities and average junction size of each sample.

Singularity	5% of O_2	10% of O_2	15% of O_2
Particle 1	$BaCuO_2$	$BaCuO_2$	$BaCuO_2$
Particle 2	$Ba_2Cu_3O_5$	$Ba_2Cu_3O_5$	$Ba_2Cu_3O_5$
Particle 3	–	–	$HgCaO_2$
$\langle d\ (\mu\mathrm{m})\rangle$	2.1	2.7	2.4

4. T_C as function of oxygenation

Figure 6 displays ac susceptibility measurements (χ_{ac}) of the powdered samples. The influence of intergrain current on magnetic shielding was reduced, for all samples, since the particle size was lower than 38 μm [15]. As one can see in the inset of figure 6, the sample with 10% of O_2 (optimal) has presented the best magnetic shielding of all the samples, which is in agreement with the larger average grain size detected by SEM. Also, taking into consideration the error bar in the framework of a statistical fit, the sample with 10% of O_2 has presented the higher critical temperature.

As Sin *et al* [15] have indicated, this points out that the transition temperature depends on the oxygen content used in the superconductor samples. Moreover, the statistical fit indicates an inverted parabola, as shown in figure 6. We can understand this behaviour according to the phenomenological model of Almasan *et al* [16], which has been called the pressure-induced charge-transfer model (PICTM) by Lin [22]. This model [23] has introduced $\mathrm{d}T_C^i/\mathrm{d}P$ as one term of $\mathrm{d}T_C/\mathrm{d}P$ not influenced by $\partial n/\partial P$. Figure 6 suggests that the optimal doped superconductor sample is associated with 10% of O_2. The maximum of the parabola fit is related to (9 ± 1)% of oxygen partial pressure. According to this model, the carrier

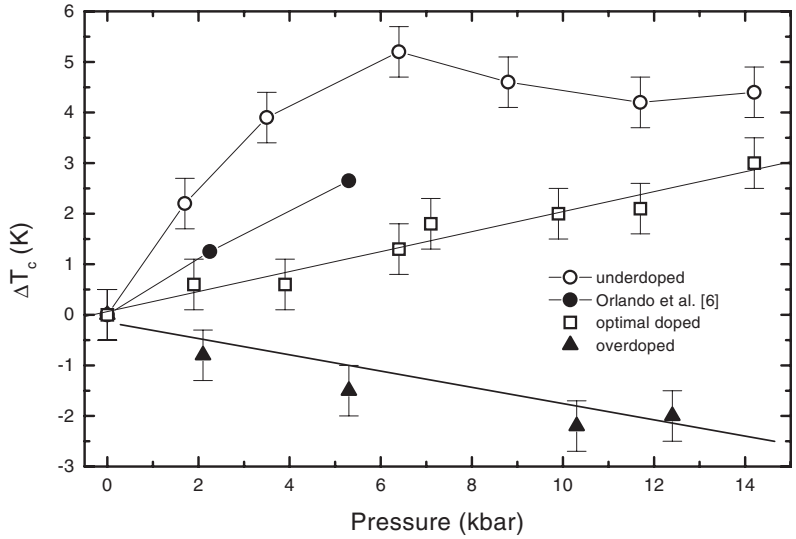

Figure 8. $T_{C\,onset}$ as a function of applied external hydrostatic pressure for the different doped samples.

number present in the CuO_2 sheet is also optimized in the same sample.

5. Effect of pressure on T_C

In resistance measurements, some authors contend that there are different pressure dependences if different T_C criteria are used. For instance, Shen *et al* [24] have shown that there are two different values of dT_C/dP (1.6 and 2.4 K GPa^{-1}) for the same sample. In addition, Jover *et al* [25] have indicated the same matter in the T_C criteria.

Considering the paragraph above, we have used magnetic ac susceptibility measurements to investigate $T_{C\,onset}$ pressure dependence. The $T_{C\,onset}$ criterion was defined as the point where the χ_{ac} signal is two times higher than the average noise value, which was measured before the superconductor transition. Figure 7 shows the magnetic ac susceptibility versus temperature under different external hydrostatic pressure for the optimal doped sample. One can note the signal shift to high temperature in proportion to the pressure increase.

Figure 8 plots the pressure dependence of T_C. We have drawn this figure using $T_{C\,onset}$ as a criterion to define the critical temperature of the superconductor transition phase. It can be seen that there are different values of dT_C/dP for different oxygen contents. The optimal doped sample presented $dT_C/dP = (1.9 \pm 0.3)$ K GPa^{-1}, as a fit to a linear dependence. The underdoped sample has shown a higher value close to $dT_C/dP = (8 \pm 1)$ K GPa^{-1}, followed by nonlinear behaviour in the pressure range (0.6–1.4 GPa). This plateau can be associated with the maximum of the inverted parabola [26]. The overdoped sample has presented a negative value $dT_C/dP = -(1.6 \pm 0.1)$ K GPa^{-1}. These observations confirm the second hypothesis of [6], which concerns the value of $dT_C/dP = (6.8 \pm 0.2)$ K GPa^{-1} being related to an underdoped sample.

6. Discussion and conclusion

The three samples of $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8+d}$ were produced by taking into account a very narrow range of oxygen content. However, the samples have revealed different physical properties. The lattice parameters (figure 2) indicated a slight change of unit cell as a function of the oxygen content. Furthermore, the reduction of the volume cell is associated with the slight increment of T_C (see the inset of figure 6). Orlando *et al* [6] have shown that the reduction of the **c** parameter does not change the value of T_C. According to this observation, we can point out the suggestion made by Wijngaarden *et al* [27], that an intrinsic effect related to in-plane (**a** and **b** parameters) compression enhances T_C. This relation has also been observed in figure 2 and in other works [6, 10, 11].

The measurements of χ_{ac} versus temperature, under external hydrostatic pressure, have shown sensitive results as a function of distinct oxygen content. In our opinion, this kind of measurement may be used as a tool to determine the sample oxygen content (underdoped, optimal or overdoped). Therefore, in the Hg,Re-1223 system the value of $dT_C/dP > 1.9 \pm 0.2$ K GPa^{-1} represents an underdoped oxygen content, which is in agreement with the hypothesis (case 2) of Orlando *et al* [6]. From this point of view, one can understand that $dT_C/dP = (1.9 \pm 0.2)$ K GPa^{-1} is associated with an intrinsic term value for the $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8.10}$ optimal oxygen doped sample.

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