You may also like

Influence of precursor oxygen stoichiometry on the formation of Hg, Re-1223 superconductors

To cite this article: A Sin et al 1999 Supercond. Sci. Technol. 12 120

View the article online for updates and enhancements.

- <u>Plc-Based Aerospace Thin-Wall Part</u> <u>Processing Fixture</u> Haoyu Zhao, Bo Tang, Wenchao Li et al.

- <u>Further consideration of the shape-factor</u> relationship for turbulent boundary layers Ghassem Zarbi, A J Reynolds and M M M El Telbany

- <u>Summary of Papers</u> Serge Gauthier, Snezhana I Abarzhi and Katepalli R Sreenivasan

Influence of precursor oxygen stoichiometry on the formation of Hg, Re-1223 superconductors

A Sin[†], A G Cunha[‡]_{\$}, A Calleja[†], M T D Orlando[‡]_{\$}, F G Emmerich[‡], E Baggio-Saitovitch[§], M Segarra^{||}, S Piñol[†] and X Obradors[†]

† Institut de Ciència de Materials de Barcelona (CSIC), Campus de la UAB, Bellaterra E-08193, Barcelona, Spain
‡ Departamento de Física, Universidade Federal do Espírito Santo, 29060-900 Vitória-ES, Brazil
§ Centro Brasileiro de Pesquisas Físicas, Rua Dr Xavier Siguad 150-Urca, 22290-180 Rio de Janeiro-RJ, Brazil

|| Departament d'Enginyeria Química i Metallúrgia, Facultat de Química, Universitat de Barcelona, Diagonal 647, E-08028, Barcelona, Spain

Received 31 July 1998

Abstract. Thanks to a novel technique (thermobaric analyser or TBA) for measuring the *in situ* pressure in quartz tubes, we have investigated the precursor quality for the synthesis of the superconductor Hg-1223 which is an essential parameter to control. We have made this study on the Hg_{0.82}Re_{0.18}Ba₂Ca₂Cu₃O_x samples and we can conclude that this superconductor phase requires a ceramic precursor sintered in a low P_{O_2} mixture gas flux. An excessively oxygenated precursor leads to overdoped superconducting phases, presence of other members with lower *n*, HgCaO₂ and some unreacted precursor. The precursor oxygenation degree also modifies the kinetics of formation of HgCaO₂ and the partial melting of the superconductor material may be affected.

1. Introduction

The superconductors $HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$ (Hg12(*n* – (1)n) have been intensely studied. The member of the series n = 3 is the superconductor that has the highest critical temperature ($T_c \sim 133$ K) at ambient pressure [1] and under high pressures can reach a T_c of 160 K [2]. The synthesis of the n = 3 phase is difficult to obtain in a pure state at low pressures, and has only been possible at high pressures [3,4]. However, it is possible to obtain pure phases with the use of the technique of the sealed quartz tube if atoms of high valency are used (Re, Pb, Tl, Bi, V, ...) to substitute partially the mercury [5–9]. Another advantage of working with this series of dopants, as the cation rhenium, is that the manipulations become easier in all the steps of the synthesis, since it is possible to work without a strictly controlled atmosphere [10], which would be very difficult if one works without any dopant because the sample would be much more reactive to CO₂ and humidity.

An important step in the synthesis of the superconductor ceramic is the sintering of the precursor. This is a fundamental topic for the synthesis of the pure n = 3 phase synthesized at high pressures [11].

An important characteristic on this synthesis type is the homogenization degree of the present cations in the precursor. Lin *et al* [11] showed that the degree of homogenization of

Ca and Cu in the later thermal treatment plays an important role during the synthesis of the superconductor. A precursor in which Ca ions are well reacted with other ions facilitates the formation of Hg-1223. These authors suggested that this well reacted precursor might be insensitive to moist air.

Another very important characteristic is the degree of oxygenation of the precursor. The precursor consists of a mixture of both stoichiometric and non-stoichiometric phases, such as $BaCuO_{2+\delta}$, $Ba_2CuO_{3+\delta}$, $Ba_2Cu_3O_{5+\delta}$, $Ba_4CaCu_3O_{8+\delta}$, Ca_2CuO_3 , CuO, \dots [12]. The non-stoichiometric phases allow modification in the oxygen content, which causes different values in the valency of the Cu. In addition, the distribution of the mixture of precursor phases can be varied [13]. There is a strong evidence that there is a relationship between the valency of the copper in the precursor and the quality of the superconductor phase synthesized at high pressures [11, 14].

In this work, we found that the changes in the copper valency are correlated with the proportion of $Ba_4CaCu_3O_y$ (phase 413) which is identified by XRD in the precursor samples. Kubat-Martin *et al* [15] identified the phase $Ba_4CaCu_3O_x$ (413) like a new phase of the system Ba-Ca-Cu-O which is found in the n = 3 precursor material. Abattista *et al* [16] reported the formation of oxycarbonates in these phases if they are sintered in air; for



Figure 1. XRD patterns showing the principal precursor phases: Ca₂CuO₃, 413, CaO, CaCu₂O₃ and BaCuO_{2+x}.

this reason is very important to handle the precursor phase in a controlled atmosphere. Loureiro *et al* [14] observed that the oxygen stoichiometry which may be modified is reversible and controlled through the thermal treatment. Moreover, it was observed that a higher value for the copper valency in the precursor favours the lower members of the series Hg-12(n - 1)n; on the other hand, a smaller valency favours the superior members of the family [14].

In this work the optimization of the oxygen content in the superconductor phase through a controlled partial pressure of oxygen atmosphere during the precursor synthesis is studied. The partial pressure was controlled by a mixture of gases (Ar, O_2). The basic idea is that the superconductor synthesis occurs in a closed system and the stoichiometry of the oxygen in the superconductor sample, which is a very important parameter for the stabilization of the n = 3 phase is governed by the degree of the precursor oxidation. With this control the obtained superconductor samples do not need any further oxygenation post-treatment, as usually performed, since the degree of oxygenation of the final sample is pre-defined by the precursor polyphasic ceramic.

Consequently, the synthesis of the precursor is very sensitive for the superconductor phase. We prepared the precursor following the next sequence: firstly, several thermal treatments in oxygen flow are carried out on the precursor to assure a good homogenization of the cations and their complete decarbonization. Then, a final treatment is carried out with a controlled flux of a mixture of gases. This step defines the oxygenation degree of the precursor and with it the copper valency which will be mixed with a stoichiometric amount of HgO before proceeding to the last synthesis step leading to the superconductor phase.

The superconductor system which has been investigated is Hg_{0.82}Re_{0.18}Ba₂Ca₂Cu₃O_{8+ δ}. Rhenium substitution leads to enhanced occupancy of the oxygen sites available in the plane HgO_{δ}, because the rhenium cation occupancy is octahedrally coordinated with oxygen [17]. The enhancement of the oxygen content in the precursor associated with the rhenium ions suggests that the precursor has to be annealed in an appropriate reducing atmosphere to avoid any oxygen excess, which could lead to an overdoped state or even to the persistence of a certain amount of impurities. This fact makes extremely difficult the synthesis of a pure n = 3 single phase.

Another important aspect is the formation of the phase HgCaO₂, which was studied recently using the controlled pressure and temperature conditions using a thermobaric analyser (TBA) [18]. This compound is a competitive phase for the formation of the n = 3 phase as has been demonstrated by Sin *et al* [19] and Xue *et al* [20]. In this work we will show that its formation is very sensitive to the oxygen content of the precursor phase. The intermediate formation of the HgCaO₂ phase is minimized with low oxygen content in the precursor phase and we will show that the TBA device allows us to detect a decrease of the pressure–temperature point where it is formed.

2. Experiment

The formation of the multiphasic ceramic precursor begins with the mixture of $Ba_2Ca_2Cu_3O_x$ (99.9%, PRAXAIR) and



Figure 2. XRD patterns of the $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8+\delta}$ synthesis for precursors annealed at $P_{O_2} = 0.0, 0.2, 0.5, 1.0$ bar. The maximum intensity reflections of HgCaO₂, Hg,Re-1212 (n = 2 phase) and Hg, Re-1223 (n = 3 phase) are indicated in the figure.

of ReO₂ (99.9%, Aldrich) in powder form with the molar relationship 1:0.18. They were homogenized in an agate mortar and subsequently pelletized with a uniaxial pressure of 0.5 GPa. The pellet obtained is annealed at $850 \,^{\circ}$ C in a flow of oxygen for 15 h. Subsequently, it is homogenized and compacted again before being annealed a second time at a higher temperature (930 $^{\circ}$ C) for 12 h in a flow of oxygen. These two thermal annealing processes are sought to assure a good homogenization of the rhenium and the elimination of the carbonates remaining in the polyphasic precursor sample.

The obtained precursor material was then submitted to a new heat treatment at 930 °C for 12 h in a flow of a gas mixture of argon (99.95%) and oxygen (99.5%) maintained at 1 bar. Different compositions of oxygen in the mixture were used in order to study their influence in the synthesis of the superconductor ceramic. The different precursor samples were referred as: 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.8 and 1.0 bar, according to the oxygen gas pressure employed. These values should not be taken as the real oxygen partial pressure because the argon and oxygen gases are impure. Therefore the oxygen partial pressure varies from 5×10^{-4} bar to nearly 1 bar between the end gas proportions used. The superconducting samples which were prepared with the respective precursors are named in the text according to the value of the corresponding oxygen partial pressure.

The synthesis of the ceramic superconductor $Hg_{0.82}$ $Re_{0.18}Ba_2Ca_2Cu_3O_{8+{\it x}}$ was carried out by means of the

technique of the sealed quartz tube. The polyphasic precursor material previously described was blended with HgO (99%, Aldrich) with a stoichiometric relationship. The mixture was homogenized in an agate mortar and pelletized as described previously. The sample was then introduced and closed in the quartz tube where the pressure sensor was connected [18]. The applied thermal cycle was a ramp of $300 \,^{\circ}$ C h⁻¹ up to $700 \,^{\circ}$ C (to minimize the formation of HgCaO₂ [19], followed by one of $120 \,^{\circ}$ C h⁻¹ until the temperature of synthesis ($850 \,^{\circ}$ C) where it stayed for 10 h. Subsequently, the sample was cooled at a rate of $120 \,^{\circ}$ C h⁻¹ until ambient temperature. Based on the study of Sin *et al* [21], the filling factor of the quartz tube used in this synthesis was of 0.60 g cm⁻³, which was the minimum to obtain a pure phase.

All the characterizations of the obtained ceramic superconductors were carried out with the samples in powder form. The samples were ground in an agate mortar and dried later in a stove at 105 °C in a N₂ atmosphere during one hour. Then the powder was cooled in a desiccator for one hour and later on sifted to assure that the present material has a particle size smaller than 65 micrometres.

Powder x-ray diffraction patterns (Cu K α) were recorded with a Rigaku Rotaflex Ru-200BV. AC susceptibility measurements were carried out with a home made system [22] which was calibrated with a paramagnetic salt of Gd₂(SO₄)_{3.8}H₂O (99.9%). The measurements were performed at $h_{ac} = 5$ A m⁻¹ and f = 423 Hz.



Figure 3. χ_{ac} as a function of absolute temperature for Hg, Re-1223 samples prepared with precursors annealed at $P_{O_2} = 0.0$, 0.1, 0.2 bar.

3. Results and discussion

3.1. The effect of P_{O_2} on the precursor synthesis

The XRD patterns corresponding to the sintered precursors as a function of the oxygen partial pressure P_{O_2} are displayed in figure 1. The identified phases were BaCuO_{2+ δ}, Ba₄CaCu₃O_x (413 phase), Ca₂CuO₃, CaO, CaCu₂O₃ and BaCu₂O₂. A change in the relative reflection intensity of the marked phases may be observed. This variation is attributed to the difference in oxygenation, which causes the calcium-rich phases (CaO and Ca₂CuO₃) to reduce at the expense of the growth of the 413 compound. This redistribution in the precursor phases was also observed by Loureiro *et al* [14] in precursor samples without rhenium where different thermal treatments were applied, leading to different degrees of oxygenation in the final samples.

After characterizing the precursor composition, we studied the influence of the precursor oxygenation on the Hg, Re-1223 synthesis. The XRD patterns of the superconductors prepared with precursors annealed under different oxygen partial pressures are shown in figure 2. In all cases, the Hg, Re-1223 phase was the main phase with small amounts of BaCuO₂₊₈, HgCaO₂, Hg,Re-1212. All residual phases are observed to decrease as the P_{O_2} is reduced. The disappearance of the n = 2 phase occurs below $P_{O_2} = 0.5$ bar while HgCaO₂ seems to be effectively eliminated below $P_{O_2} = 0.2$ bar.

The cell parameters of the Hg, Re-1223 phase of the highest purity ($P_{O_2} = 0.0$ bar) are a = b = 3.852(18) Å, c = 15.285(73) Å, this last value being significantly lower than previously reported data [17, 23].

The AC susceptibility curves of the corresponding Hg, Re-1223 samples have been divided into two groups according to the critical temperature and number of superconducting transitions: the samples of group I ($P_{O_2} = 0.0, 0.1, 0.2$ bar), which display a single superconductor transition with $T_c \sim 133$ K (figure 3); and those of group II ($P_{O_2} = 0.3, 0.4, 0.5, 0.8, 1.0$ bar), which have a $T_c \leq 130$ K and two superconducting transitions (figure 4).

The single transition of group I can be attributed to the n = 3 phase. This set of samples corresponds to the precursors prepared with a $P_{O_2} \leq 0.2$ bar and the maximum



Figure 4. χ_{ac} as a function of absolute temperature for Hg, Re-1223 samples prepared with precursors annealed at $P_{O_2} = 0.5$, 0.8, 1.0 bar.



Figure 5. Diagram of T_c against P_{O_2} used in the annealed precursor.

superconductor fraction measured is about 70%. However, in group II a clear decrease in the T_c of the Hg, Re-1223 is found up to a maximum difference around 3 K. The second transition around 110 K is assigned to the presence of Hg, Re-1212. Interestingly, the maximum shielding passes through a maximum at $P_{O_2} = 0.1$ bar.

If $T_{c,onset}$ for n = 3 is plotted against the P_{O_2} of the precursor, figure 5 is obtained. Two plateaus are clearly identified with a sharp transition in between at $P_{O_2} \approx$ 0.40 bar. The first plateau lies at $T_c \sim 133$ K; the second one, at $T_c \sim 130$ K. The optimally doped sample of Hg, Re-1223 displays a $T_c = 133.3(2)$ K. As the second plateau is associated with the samples excessively oxygenated at higher P_{O_2} , it can be concluded that the corresponding superconductors are overdoped, while Hg, Re-1223 samples with the plateau at a higher T_c probably are optimally doped. The small difference of 3 K in T_c might be explained taking into consideration the fact that rhenium is the main doping mechanism in these materials, providing the extra oxygen atoms in the HgO_{δ} layers. Chmaissem *et al* [17] found that ReO_6 octahedra arranged in the HgO δ layer in such a way that the four equatorial oxygens locate in the position (0.33,(0.33, 0) while apical oxygen atoms are in (0, 0, z) sites where $z \approx 0.13$. In addition, some extra oxygens are found in (1/2, 1/2, 0) accounting for an occupancy of about 0.07(1)



Figure 6. χ_{ac} as a function of absolute temperature for the superconducting samples annealed for 10 and 72 h.

for a rhenium content of x = 0.17, which is very close to our case. Within this structural model, we could explain the changes in T_c assuming that these (1/2, 1/2, 0) oxygens are responsible for the doping variation since they are loosely bound to the Hg atoms, which leads to easy intercalation or removal during the precursor thermal treatment. However, the covalent Re–O bonding must be stronger so that it would be unlikely that these oxygens could be removed in a reducing atmosphere.

To check whether the observed reduction of T_c varied with the annealing time, we performed an additional experiment with a precursor prepared at a $P_{O_2} = 1.0$ bar for longer annealing times (72 h). Ac susceptibility measurement (figure 6) shows two superconducting transitions but with a further displacement of the transition temperatures (127 and 97 K). These superconducting transitions could be consistently attributed to those of optimally doped n = 1 and n = 2 phases [24, 25]. However, XRD analysis of these two samples shows that actually a mixture of n = 2 and n = 3 phases exists with an increase of the n = 2 phase concentration with the annealing time.

As a result, the observed superconducting transitions have been assigned to overdoped n = 2 and 3 compounds. In fact, such a decrease in T_c has been reported for Hg-1212 and Hg-1223, where the samples deviated from the optimum oxygen content [26, 27]. The present investigated samples needed a longer time to accommodate in the structures of the n = 2 and n = 3 phases. In other words, it seems that there is some atomic diffusion by solid state, because the time to transform a small amount of the n = 3 to n = 2 phase is very large. Also, we note that the presence of HgCaO₂ in the XRD pattern decreases as the annealing time goes up. This suggests that the HgCaO₂ disappears to form other superconducting phases via the solid state mechanism.

Now the P-T curves from the TBA device were studied to ascertain any change in the P-T data of the superconducting samples that had been made with different precursors. As has been previously shown, these curves are a useful tool to monitor the formation of phases in gas–solid systems [19, 21]. Figure 7 shows the thermobaric plots for the samples with $P_{O_2} = 0.0, 0.2, 0.5$ and 1.0 bar in the heating ramps. The HgCaO₂ formation was ascribed to the peak around 500 °C when $P_{O_2} = 1.0$ bar [19]. As observed when





Figure 7. Pressure versus temperature curve of the $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8+\delta}$ synthesis for samples annealed at $P_{O_2} = 0.0, 0.2, 0.5, 1.0$ bar in the region of HgCaO₂ formation. An increment of 2 bar was added to each curve to facilitate the reader's visualization.

 P_{O_2} decreases, the peak becomes flatter and moves to lower temperatures. Eventually, the peak is hardly observable at $P_{O_2} = 0.0$ bar with a monotonic increase of the measured total pressure. A possible explanation for the reduction of HgCaO₂ might be given at this point, if we consider the different oxygen content in the precursor phase. If Ca atoms form primarily the 413 phase, little CaO is left unreacted. Initial HgO would thus find difficult to react with free CaO to form the HgCaO₂. This may also explain the progressive increase in the total pressure that should be associated then with a higher concentration of Hg in the gas phase.

The full TBA curves corresponding to the Hg, Re-1223 formation also exhibit a different behaviour in the two groups of samples defined above. In figure 8, the complete TBA cycles for a typical sample of group I and a typical sample of the group II have been drawn together. Apart from the heating region around 500 °C, the total pressure in the heating ramp above $T \approx 750 \,^{\circ}\text{C}$ is slightly higher in the case of the lower oxygenated precursor while, as regards the cooling ramp, the situation is inverted. We should note also that the condensation of Hg (l) at about 440 °C [21] in the cooling ramp is not observed in the excessively oxygenated precursor. To explain these results, the stability regions have to be considered. The n = 2 and n = 3 phases are stable above 765 and 800 °C, respectively [21]. In the heating ramp up to 750 °C, the increase of the total pressure of group I as compared to group II can be explained on the basis of the higher stability of the n = 2 phase. When the precursor is oxygenated the n = 2 phase becomes more stable and consequently shows a decreased tendency to decompose. A sequential mechanism of the Hg, Re-1223 formation is discussed elsewhere [21].

However, during the cooling ramp, the gas phase is reabsorbed more easily above $\sim 800 \,^{\circ}\text{C}$ by the reduced precursor than by the oxygenated one. This may be due to the higher stability of the n = 3 phase in this region with a reduced precursor. As the temperature decreases the total pressure diminishes more for group II, changing the trend between both groups at higher temperatures. This may be due again to the higher stability of the n = 2 below $\sim 800 \,^{\circ}\text{C}$.



Figure 8. (a) Pressure versus temperature curve of the Hg_{0.82}Re_{0.18}Ba₂Ca₂Cu₃O_{8+ δ} synthesis for samples of group I ($P_{O_2} = 0.1, 0.2$ bar) and group II ($P_{O_2} = 0.3, 0.4, 0.5, 0.8, 1.0$ bar). (b) The inset shows the P-T curve corresponding to an Hg, Re-1223 sample prepared with a precursor sintered at $P_{O_2} = 0.0$ bar.

In addition, the inset of figure 8 displays a TBA cycle of the precursor annealed at $P_{O_2} = 0.0$ bar. This sample showed spots of reaction with the quartz tube, which was not observed in the other samples. This could be an evidence of possible partial melting of the pellet and as a consequence the reactivity with quartz is strongly favoured. In this case, a strong inflexion is seen around 700 °C, in which the rate of decomposition is slowed down. The origin of this effect is still uncertain but it might be due to an onset of partial melting of the superconductor pellet. Further verification is in progress to check this hypothesis. If this consideration is demonstrated the possibility of using melting processing technologies could be accessible because the pressure does not rise dangerously (<30 bar).

In conclusion, the reported results suggest that oxygenated precursors stabilize a mixture of Hg,Re-1212 and 1223 while poorly oxygenated precursors lead to single phase Hg, Re-1223 superconductors.

3.2. Effect of temperature and the total pressure

After the study of the oxygenation of the precursors in conditions of fixed temperature and variable total pressure (up to 1 bar), we investigated the effect of the oxygenation degree on the precursor when both the temperature and total pressure are modified. The selected oxygen partial pressure ranged between $P_{O_2} = 0.0$ and 0.1 bar, which proved to be beneficial for the Hg, Re-1223 phase formation, as has been described in the previous paragraph.

Firstly, the effect of the annealing temperature of the precursors was examined. Two maximum temperatures below that used in the investigation reported above (930 °C) were chosen: 915 °C and 850 °C, maintaining the same ramps and holding time previously detailed. For each maximum temperature, the oxygen partial pressure was varied between $P_{O_2} = 0.0$ and 0.1 bar.

One may observe in the AC susceptibility measurements (figure 9) that, for $P_{O_2} = 0.1$ bar, the ceramic samples present two superconducting transitions while the sample annealed at a higher temperature exhibits an enhanced magnetic shielding and smaller proportion of the n = 2 phase. This result differs from that observed on the sample sintered at 930 °C where a single transition was obtained when $P_{O_2} = 0.1$ bar. Finally, if a more reducing atmosphere is used at the same temperatures with $P_{O_2} = 0.0$ bar a single transition is finally obtained.

The XRD patterns of these samples show that at $P_{O_2} = 0.1$ bar, the n = 2 reflections are more prominent in the case of annealing at 850 °C than at 915 °C. In the case $P_{O_2} = 0.0$ bar, the n = 2 phase is hardly observable at both temperatures. Anyway, the disappearance of the HgCaO₂ reflections at 915 °C is remarkable. This XRD analysis is coherent with the results from the ac susceptibility measurements.

Therefore, we can conclude that if the precursors are annealed under the same P_{O_2} (0.1 bar), using higher temperatures leads to more reduced precursors, and this, in turn, stabilizes the n = 3 phase. On the other hand, when $P_{O_2} = 0.0$ bar there is a strong reducing character of the atmosphere and the reduction of the binary HgCaO₂ at high temperature is outstanding. This is reasonable if we assume that the decomposition reactions are thermodynamically favoured with the increase of temperature so that the sample becomes less oxygenated.

Finally, the effect of the total pressure (P_T) in the precursor synthesis was studied, fixing the annealing temperature (850 °C), the ramps and holding time. The precursor pellet was placed inside a pressure furnace at a $P_T = 5$ bar of Ar (99.95%). The ac susceptibility curve of the corresponding superconductor is shown in figure 10. For comparison purposes we also display the curve corresponding to precursor annealed at $P_T = 1$ bar and in the same conditions of temperature and atmosphere



Figure 9. χ_{ac} as a function of absolute temperature for the Hg_{0.82}Re_{0.18}Ba₂Ca₂Cu₃O_{8+ δ} samples whose precursors are annealed at: 850 °C with $P_{O_2} = 0.0, 0.1$ bar and 915 °C with $P_{O_2} = 0.0, 0.1$ bar.



Figure 10. χ_{ac} as a function of absolute temperature for the Hg_{0.82}Re_{0.18}Ba₂Ca₂Cu₃O_{8+ δ} whose precursors are annealed at: 850 °C with $P_T = 1$ bar and 5 bar of Ar.

composition. The precursor sintered at $P_T = 5$ bar presents a slight decrease of the magnetic shielding and an onset transition temperature 0.5 K lower than the sample prepared under 1 bar.

The XRD patterns of these samples showed an increase of reflexions corresponding to the n = 2 phase in the precursor annealed at $P_T = 5$ bar is clearly observable. This fact demonstrates that the deoxygenation with $P_T > 1$ bar is ineffective. This result may be due to two reasons. First, the P_{O_2} is multiplied by a factor of five when the pressure furnace is used ($P_{O_2} = 25 \times 10^{-4}$ bar). At 850 °C, the equilibrium

$$\frac{\operatorname{Re}_{0.18}\operatorname{Ba}_2\operatorname{Ca}_2\operatorname{Cu}_3\operatorname{O}_x(s)}{+y/2\operatorname{O}_2(g)} \Leftrightarrow \frac{\operatorname{Re}_{0.18}\operatorname{Ba}_2\operatorname{Ca}_2\operatorname{Cu}_3\operatorname{O}_{x-y}(s)}{(1)}$$

may be displaced towards the left by Le Chatelier's principle in the case of $P_T = 5$ bar. The nominal precursor composition is used in reference to the polyphasic mixture and it is meant to show the oxygenation equilibrium. Second, if we assume that the increase of pressure is due to the reduction of the volume of the reactor where the reaction takes place, the volume reduction in the reactor can account also for an increase of P_T . The K_p of this system can be written as $K_p = (P_{O_2})^{y/2}$, where K_p is only temperature dependent, but does not depend on P_T . According to the Le Chatelier principle, an increase in P_T causes a displacement of the equilibrium to the reaction member that has the smaller number of moles of gas [28, 29]. Thus, a higher P_T in this system due to a reduced volume does not make the precursor deoxygenation more effective.

4. Conclusions

As in other previous studies on Hg-1223, the precursor quality for the synthesis of the superconductor Hg, Re-1223 is found to be essential. In our rhenium-doped samples we can conclude that the superconductor n = 3 phase requires a ceramic precursor sintered at low P_{O_2} . To obtain high-quality Hg, Re-1223 superconducting phases, reducing atmospheres (below $P_{O_2} = 0.1$ bar) are needed when the precursors are being prepared. A precursor oxygenated in excess leads to overdoped superconducting phases, as regards T_c , and the presence of other members with lower n, HgCaO₂ and some unreacted precursor. The content of oxygen in the precursor also modifies the kinetics of the formation of HgCaO₂. Precursors annealed with low P_{O_2} values display a decreased proportion of this binary oxide. The oxygenation degree also affects the partial melting of the superconductor material. When poorly oxygenated precursors are used, partial melting can occur at lower temperatures. A guide was therefore given to control the formation of the superconductor phases by choosing appropriately the precursor synthesis.

Acknowledgments

The authors would like to thank CAPES, CICYT(MAT96-1051), CNPq, CST-Cia Siderurgica de Tubarao, DIOPMA, Finep and Generalitat de Catalunya (GRQ95-8029).

References

- Schilling A, Jeandupeux O, Guo J D and Ott H R 1993 *Physica* C 216 6
- [2] Chu C W, Gao L, Chen F, Huang Z H, Meng R L and Xue Y Y 1993 Nature 356 323
- [3] Antipov E V, Loureiro S M, Chaillout C, Capponi J J, Bordet P, Tholence J L, Putilin S N and Marezio M 1993 *Physica* C 215 1
- [4] He Z H, Lin Q M, Gao L, Sun Y Y, Xue Y Y and Chu C W 1995 *Physica* C **241** 211
- [5] Raveau B, Michel C, Hervieu M and Maignan A 1995 J. Mater. Chem. 5 803
- [6] Pelloquin D, Maignan A, Malo S, Hervieu M, Michel C and Raveau B 1995 J. Mater. Chem. 5 701
- [7] Shimoyama J, Hahakura S, Kobayashi R, Kitazawa K, Yamafuji K and Kishio K 1994 *Physica C* 235–240 2795
- [8] Chow J C L, Fung P C W, Shao H M and Lam C C 1996 J. Mater. Res. 11 1367
- [9] Xue Y Y, Huang Z J, Qiu X D, Beauvais L, Zhang X N, Sun Y Y, Memg R L and Chu C W 1994 *Mod. Phys. Lett.* B 7 1833
- [10] Piñol S, Sin A, Calleja A, Fontcuberta J, Obradors X and Espiell F 1998 J. Supercond. 11 125
- [11] Lin Q M, He Z H, Sun Y Y, Gao L, Xue Y Y and Chu C W 1995 Physica C 254 207
- [12] Withler J D and Roth R S 1991 Phase Diagrams for High-Tc Superconductors (Westerville: American Ceramics Society)
- [13] Lindemer T B, Washburn F and MacDougall C S 1992 Physica C 196 390
- [14] Loureiro S M, Stott C, Philip L, Gorius M F, Perroux M, Le Floch S, Capponi J J, Xenikos D, Toulemonde P and Tholence J L 1996 Physica C 272 94

- [15] Kubat-Martin K A, Garcia E and Peterson D E 1990 Physica C 172 629
- [16] Abbattista F, Mazza D and Valino M 1991 J. Mater. Chem. 28 33
- [17] Chmaissem O, Guptasarma P, Welp U, Hinks D G and Jorgensem J D 1997 Physica C 292 305
- [18] Sin A 1998 PhD Thesis Universitat de Barcelona
- [19] Sin A, Cunha A G, Calleja A, Orlando M T D, Emmerich F G, Baggio-Saitovich E, Piñol S, Chimenos J M and Obradors X 1998 *Physica* C 306 34
- [20] Xue Y Y, Meng R L, Lin Q M, Hickey B, Sun Y Y and Chu C W 1997 *Physica* C 281 11
- [21] Sin A, Cunha A G, Calleja A, Orlando M T D, Emmerich F G, Baggio-Saitovich E, Piñol S, Segarra M and Obradors X 1998 Adv. Mater. 10 1126
- [22] Gomes L, Vieira M M F, Baldochi S L, Lima N B, Novak M A, Vieira N D Jr, Morato S P, Braga A J P, Cesar C L, Penna A F S and Mendes Filho J Mendes 1988 J. Appl. Phys. 63 5044
- [23] Kishio K, Shymoyama J, Yoshikawa A, Kitazawa K, Chmaisen O and Jorgensen J D 1996 J. Low Temp. Phys. 105 1359
- [24] Putilin S N, Antipov E V, Chmaissen O and Marezio M 1993 Nature 362 226
- [25] Meng R L, Beauvais L, Zhang X N, Huang Z J, Sun Y Y, Xue Y Y and Chu C W 1993 Physica C 216 21
- [26] Paranthaman M 1994 Physica C 222 7
- [27] Hirabayashi M, Tokiwa K, Ozawa H, Noguchi Y, Tokumoto M and Ihara H 1994 *Physica* C **219** 6
- [28] Bromberg J P 1980 *Physical Chemistry* 2nd edn (Boston: Allynn and Bacon) p 191
- [29] Atkins P W 1990 Physical Chemistry 4th edn (Oxford: Oxford University Press) p 216