



Effects of re-doping on superconducting properties and formation of Hg-1223 superconductors

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Abstract

The influence of the rhenium content on the formation of the $\text{Hg}_{1-x}\text{Re}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ superconductors is reported. For the same synthesis conditions, different samples are obtained, as shown by XRD and magnetic measurements. This proves that the synthesis conditions have to be adapted precisely to the rhenium content. Nevertheless, the Re concentration in the superconductor sample has the tendency to form a stable ratio with respect to Hg; i.e., 1/4 Re and 3/4 Hg, as was found by EDX analysis. Moreover, a clear influence of the Re content on the oxygen δ of the HgO_δ plane was observed by micro-Raman analysis. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The superconductor family $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ($n = 1, 2, 3, \dots$) has been intensively studied since its discovery in 1993 [1]. Their members exhibit excel-

lent superconducting properties since they have the highest T_c with respect to the rest of the high- T_c cuprate superconductors [1–3]. The $n = 3$ member of this Hg-superconductor series has the record T_c of 135 K at ambient pressure [3] and under high pressures it can reach 160 K [4]. The synthesis of a pure phase needs to use elevated pressures, in the order of GPa [5,6]. If partial substitution of the mercury by higher-valence cations [7–10], such as Re, is performed, then normal pressure syntheses are sufficient. From the time Shimoyama et al. [9] introduced

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Re doping into the mercury superconducting phases, many different studies about such substitution have been reported.

Yamaura et al. [11] were the first authors to indicate a clear trend for Re to substitute to Hg instead of Cu site, as it was tried initially [9]. The Re is located in the HgO_8 layer in the form of ReO_6 , being octahedrally coordinated with oxygen atoms. According to this structural model, the ideal stoichiometry of Re in the mercury plane is $1/4$ Re and $3/4$ Hg [12–14]. On the other hand, Kishio et al. [15] have studied samples with different Re concentrations and they have shown that the c parameter is practically constant for Re content in the range of 10%–25%. These authors have also shown that the irreversibility line of the Re substituted samples is higher than without Re. In order to ascertain the Re solubility from a solid state reaction synthesis, several authors have found out that the best superconducting volume fraction appeared for a nominal Re composition around $x = 0.15$ [13,16]. These results differ apparently from the ideal Re content expected in the HgO_8 plane as previously discussed. Recently, Reder et al. [17] showed that a difference exists between the nominal Re concentration and the final composition of the superconductor phase.

In this work we report a study of Re doping ($x \leq 0.25$) on polycrystalline ceramics of $(\text{Hg,Re})\text{-}1223$, which is the most promising member of the series with an optimized T_c of 134 K. The material is prepared by means of the recently developed vacuum-sealed quartz tube technique, which has demonstrated its capacity to improve the sample preparation.

However, little is known so far about the thermodynamic stability of such superconductors and more generally about the pressure generated inside the quartz ampoule during the synthesis process. The knowledge of the thermal dependence of the pressure is also an important matter to understand the effect of cation doping on the synthesis conditions. The pressure measurements were obtained by means of the TBA technique which we have already described [18,19]. The influence of Re concentration on the microstructure and on the superconducting properties is discussed. In addition, micro-Raman spectroscopy has also been used to study the changes in the HgO_8 vibration modes due to the presence of Re in this

plane. It was observed a clear influence of the Re concentration on the oxygen content δ .

2. Experimental

The preparation of the multiphase ceramic precursor begins with the mixture of $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (99.0% PRAXAIR) and of ReO_2 (99.9% Aldrich) in powder form with the molar relationship 1: (0.05, 0.10, 0.15, 0.18, 0.20 and 0.25). The mixture was homogenised in an agate mortar and subsequently pelletised with a uniaxial pressure of 0.5 GPa. The pellet, before obtained, was annealed at 850°C in an oxygen flow for 15 h. Subsequently, it was homogenised and compacted again before being annealed the second time at a higher temperature (930°C) for 12 h in an oxygen flow. These two thermal annealing processes are thought to provide a good homogenisation of the Re and to eliminate the carbonates remaining in the multiphase precursor sample.

The precursor material was then submitted to a new heat treatment at 930°C for 12 h in a flow of argon (99.95%) and oxygen (99.5%) gas mixture maintained at 1 bar. The oxygen partial pressure was 0.1 bar. We used this concentration of oxygen because we found out that it provides the best superconducting properties for the $\text{Hg}_{0.82}\text{Re}_{0.18}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ phase [20].

The synthesis of the ceramic superconductor $\text{Hg}_{0.82}\text{Re}_{0.18}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$ was carried out using the sealed quartz tube technique. The multiphase precursor material previously described was blended with HgO (99%, Aldrich) with a stoichiometric ratio. The mixture was homogenised in an agate mortar and pelletised as described previously, then wrapped in a gold foil. The sample then was introduced in the quartz tube. The quartz tube was connected to the pressure sensor previously calibrated [18,19]. The applied thermal cycle consisted of a ramp of 300°C/h up to 700°C (to minimise the formation of HgCaO_2) [21], followed by one of 120°C/h, up to the temperature of synthesis (850°C) where it stayed for 10 h. Subsequently, the sample was cooled at a rate of 120°C/h down to ambient temperature. Based on previous filling factor study [22], $\text{ff} = 0.65 \text{ g/cm}^3$ was used to be sure that a single phase of $(\text{Hg,Re})\text{-}1223$ is obtained.

All the subsequent characterisations (of the obtained ceramic superconductors) were carried out on powdered samples, except for the Raman spectroscopy, EDX analysis and AC susceptibility measurements, to obtain the irreversibility line. The samples were ground in an agate mortar and dried later in a stove at 105°C in a N₂ atmosphere for 1 h. Then the powder was cooled in a dessicator for 1 h and later sifted to assure that the present material had a particle size smaller than 65 μm.

Powder X-ray diffraction patterns (Cu-K_{α1}) was recorded with a Rigaku D-Max 2000 diffractometer. AC susceptibility measurements were carried out in a home-made system and also in a commercial equipment, Physical Properties Measurement System (PPMS) from Quantum Design, with AC field amplitude h_{ac} of 6 A/m and frequency kept at $f = 423$ Hz. A DC field was eventually applied parallel to h_{ac} . The EDX analysis were carried out by a Jeol JSM-6300 with a software Link ISIS 3.00 (Oxford). The ceramic samples analysed were cleaved and polished without any lubricant. Micro-Raman measurements were performed at room temperature using a Jobin Yvon T64000 triple spectrometer equipped with a charge coupled device (CCD) detec-

tor and an Olympus metallurgical microscope. The excitation was provided by the 514.5 nm line generated by an Ar⁺ laser. All Raman spectra were recorded in a back scattering geometry using the microprobe optics, which can focus the laser beam down to 1 μm size (objective ×100) on a single crystallite. Rectangular crystallites (typically 3 × 15 μm²) with the shortest edge corresponding to the c axis, and with an optically clean specular surface, were chosen under the microscope on the surface of the polycrystalline sample. All spectra were collected in the $x(z,z)x$ polarisation configuration (z along the c direction), in which only Raman modes of A_{1g} symmetry are allowed.

3. Results and discussion

3.1. X-ray diffraction

The X-ray diffraction patterns corresponding to the Hg_{1-x}Re_xBa₂Ca₂Cu₃O_y samples with different nominal Re concentrations are shown in Fig. 1. The quality of the sample although prepared under the same conditions seems to depend on the Re concen-

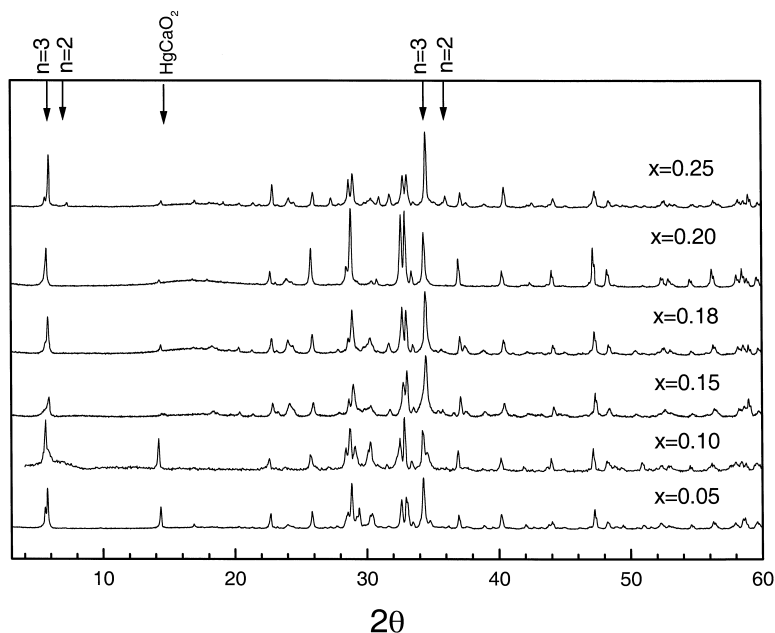


Fig. 1. XRD pattern of (Hg,Re)-1223, with different nominal Re content $x = 0.05, 0.10, 0.15, 0.18, 0.20$ and 0.25 .

tration. The main impurities are HgCaO_2 , BaCuO_{2+x} and their formation is reduced when a nominal concentration of Re $0.10 < x < 0.25$ is used. Therefore, one may observe that the $n = 3$ phase is dominant close to $x \approx 0.15$.

Nevertheless, we can observe some minor amounts of $n = 2$ in the sample with a nominal concentration of $x = 0.25$, while this impurity phase is not observable in samples having a lower concentration of Re ($x = 0.05, 0.10, 0.15, 0.18, 0.20$).

This fact may be explained according to the thermal treatment applied during the precursor phase preparation. The oxygen content of the precursor phase is fixed during its synthesis. Then the barium perhenates [23] content will be higher if the Re content is increased. This perhenates phases are also susceptible to absorb oxygen [24]. Moreover, a similar barium phase has the same property [25]. For this reason, the oxygen content might be higher in the sample with a nominal Re concentration of $x = 0.25$. This situation modifies dramatically the amount of minor n phases [26] favoured for higher oxygen content. These results may be indicative that a specific treatment must be selected for each Re content in order to obtain optimised compositions.

The cell parameters in the superconductor phases have been calculated from the X-ray diffraction patterns and are displayed in Fig. 2. We can observe a slight decrease of the c parameter with increasing nominal Re content while a and b parameters remain constant. However, for a nominal concentration of Re of $x = 0.25$, the c -axis has a slight increase with respect to the other smaller concentrations ($x = 0.15, 0.18$ and 0.20).

3.2. Superconducting properties

In Fig. 3, AC susceptibility measurements of the powdered samples are displayed. In order to compare the sample quality, all samples were crushed up to a particle size of $65 \mu\text{m}$. The magnetic shielding increases as a function of the nominal Re content up to $x \geq 0.15$ above which it decreases. This behaviour is in agreement with X-ray diffraction analysis, showing a maximal content of $n = 3$ phase for $x = 0.15$ – 0.18 . The superconductor volume fraction in this range is around 70% for these samples and for a nominal concentration of Re $x \geq 0.20$ a clear decrease of the magnetic shielding appears.

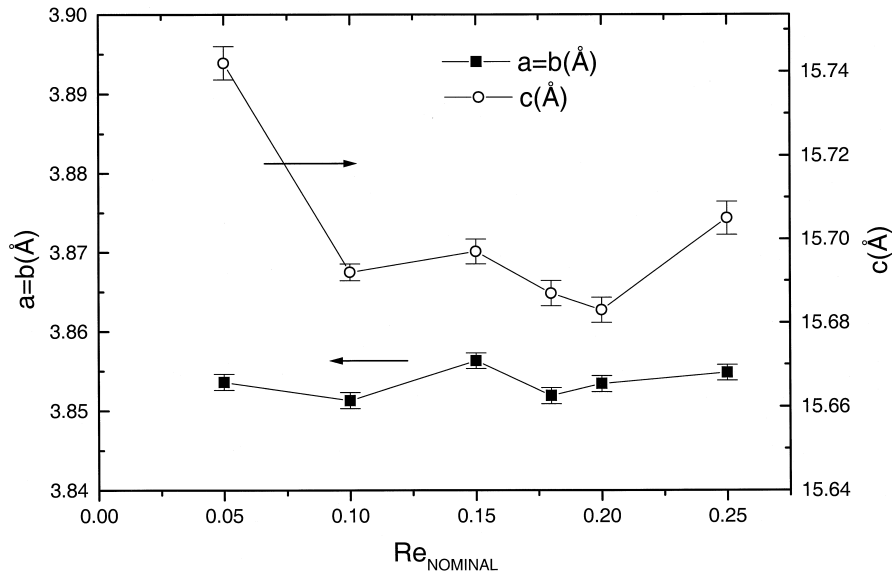


Fig. 2. Evolution of the cell parameters of $(\text{Hg,Re})\text{-1223}$, with different nominal Re content $x = 0.05, 0.10, 0.15, 0.18, 0.20$ and 0.25 .

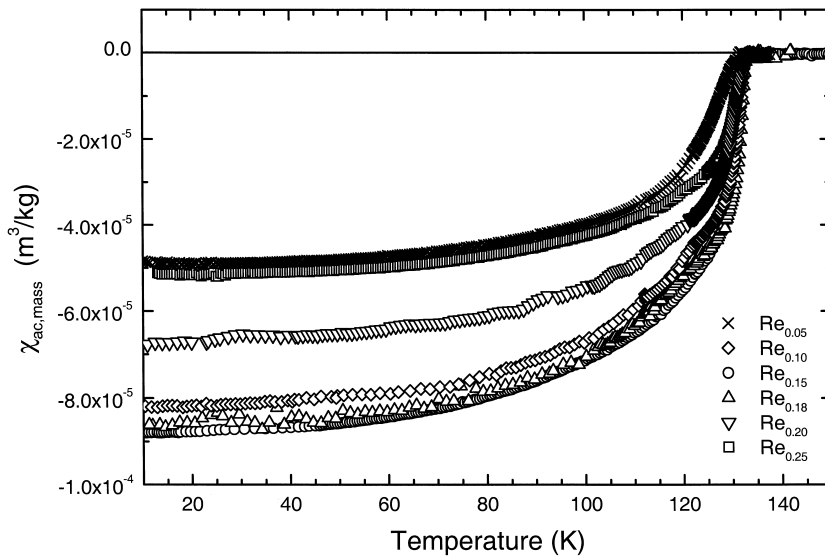


Fig. 3. AC susceptibility measurements of (Hg,Re)-1223, with different nominal Re content $x = 0.05, 0.10, 0.15, 0.18, 0.20$ and 0.25 .

It is interesting to point out that the value of T_c is the same for all the samples (Fig. 4). It seems that the value of T_c does not depend on the Re content. However, the superconducting volume fraction is directly influenced by the Re content used in the

synthesis. In addition, the irreversibility line position is influenced by the Re concentration.

In Fig. 5, the irreversibility line derived from the χ''_{ac} of the intragrain peak is shown [27]. Above 115 K all samples behave similarly. However, around 77

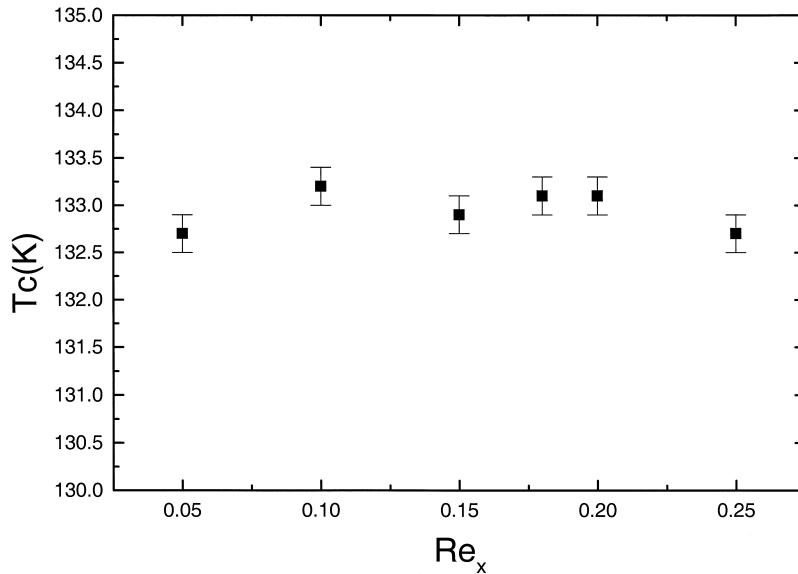


Fig. 4. Evolution of $T_{c(\text{onset})}$ of (Hg,Re)-1223, with different nominal Re content $x = 0.05, 0.10, 0.15, 0.18, 0.20$ and 0.25 .

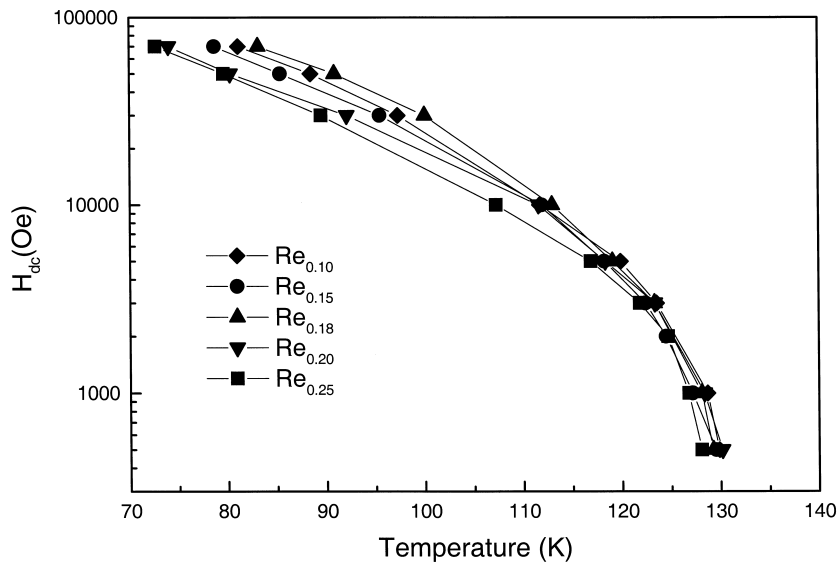


Fig. 5. Irreversibility line from χ''_{ac} measurements of (Hg,Re)-1223, with different nominal Re content $x = 0.10, 0.15, 0.18, 0.20$ and 0.25 .

K, the nominal Re concentration of $x = 0.18$ has the highest value while the lowest corresponds to $x = 0.25$. The behaviour of the magnetic shielding derived from AC susceptibility is in agreement with this observation because both magnetic shielding and the irreversibility line are linked with the critical current. From these results we can conclude that the sample having the best superconducting properties is obtained with a Re composition of $x = 0.18$.

3.3. Thermobaric analysis

The measurements of pressure–temperature give an important information concerning the stability of the superconducting phase vs. Re content (for the same thermal treatment). In Fig. 6, the maximum pressure of synthesis for each nominal Re concentration is shown. This pressure corresponds to the maximal reached temperature.

A decrease of the pressure with the increase of the Re content is noticeable. This fact may indicate that the Re substitution, for Re concentration in the range $0.10 \leq x \leq 0.20$, favours the incorporation of the mercury in the solid phase instead of being vaporised. Then the stabilisation of the structure of the superconductor phase is promoted by Re, as was also observed by others. Nevertheless, an increase of the pressure for $x = 0.25$ occurs, which might be indica-

tive of some synthesis problem for this Re content in our present conditions.

Moreover, the homogenisation degree of the cations present in the precursor phase affects directly the formation of the superconducting phase [20,26]. Therefore, the lower pressure achieved for the samples with $0.10 \leq x \leq 0.20$ may be due to a high degree of cationic homogenisation in the precursor compared with other stoichiometries. Then the reactivity of these precursors for forming the superconducting phase from the solid–gas reaction, [22,28,29] is higher in these stoichiometries than both extremes ($x = 0.05$ and 0.25). Therefore, the precursor synthesis used in this work is becoming more optimal for a nominal rhenium content in the range of $0.10 \leq x \leq 0.20$.

3.4. Energy-dispersive X-ray analysis

In order to have a better understanding of the phase distribution present in the samples, the energy-dispersive X-ray measurements have been done. The first thing to point out is the presence of different phases in the superconductor ceramics in all the superconducting samples observed. Secondly, the Re concentration found by EDX analysis shows a different value than the nominal one; a similar behaviour is found by Reder et al. [17]. If we focus our

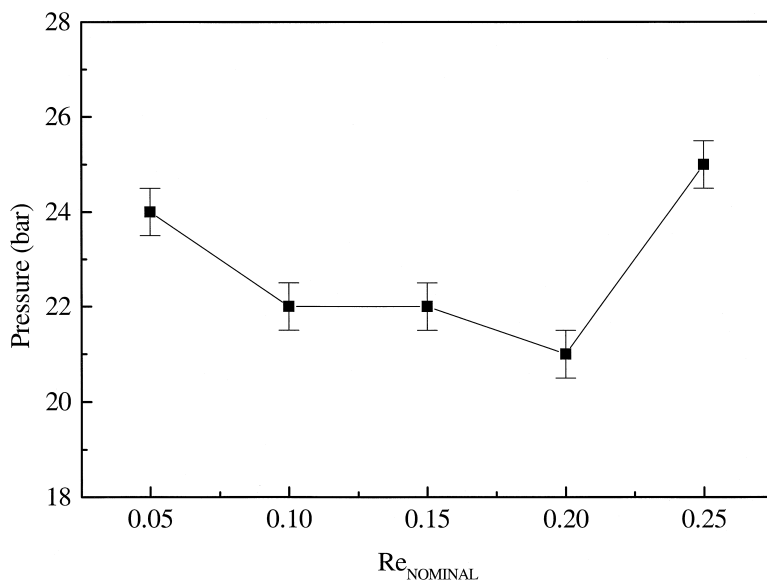


Fig. 6. Evolution of the maximum synthesis pressure of (Hg,Re)-1223, with different nominal Re content $x = 0.05, 0.10, 0.15, 0.20$ and 0.25 .

attention on the Re content obtained from the EDX analysis in the superconducting phase, two different sets of samples are observable: one is with a Re concentration $x \approx 0.25$, and the other set corresponds to the samples having concentrations larger or smaller than the former. The first group of samples corresponds to a nominal concentration of Re of $x = 0.15, 0.18$ and 0.20 , and the second group corresponds to a nominal concentration of Re of $x = 0.05, 0.10, 0.25$.

Fig. 7 shows a microphotograph of backscattered electrons for a sample with a nominal Re concentration of $x = 0.10$. We can observe the presence of several impurity phases in a matrix of superconducting phase (Hg,Re)-1223. The main impurity phases are HgCaO_2 , Ca_2CuO_3 , (Hg,Re)-1212 and Ba–O (which may be Ba(OH)_2 , BaO_2 or $\text{Ba(CO}_3\text{)}_2$). Then, by analysing the Re content in the (Hg,Re)-1223 phase in different zones in the superconducting matrix, we obtain a Re concentration around $x \approx 0.15$.

It is interesting to point out that the measured concentration of Re is higher than the nominal one used in the preparation of the precursor phase. This can be explained if we take into account the presence of these impurities. First, since we do not observe impurity phases such as barium perhenates in the

superconductor rhenium phases, we suggest that all Re remain in the form of (Hg,Re)-1223 only, as commented before. Thus, the presence of the impurities makes an off stoichiometry and impedes obtaining 100% of (Hg,Re)-1223. Thus, the change of the initial stoichiometry and the assumption that the Re reacts preferentially to form (Hg,Re)-1223, make it possible to find superconducting phases with a higher Re concentration than the nominal Re concentration introduced. This fact seems to be a common characteristic of all the samples investigated for $0.05 < x < 0.25$.

In Fig. 8, a microphotograph of backscattered electrons for a sample with a nominal Re concentration of $x = 0.18$ is shown. We also analysed the samples with a nominal Re concentration of $x = 0.15$ and $x = 0.20$ with similar results with $x = 0.18$ samples. We can observe an increase of the (Hg,Re)-1223 matrix phase content than the sample with a nominal concentration of $x = 0.10$. The impurity phases present in these ceramics are HgCaO_2 , CaCu_2O_3 , and Ba–O (which may be Ba(OH)_2 , BaO_2 or $\text{Ba(CO}_3\text{)}_2$). Nevertheless, the sample with an initial Re stoichiometry of $x = 0.20$ shows a little more amount of these impurities, mainly CaCu_2O_3 . The second important detail concerns the Re content in the super-

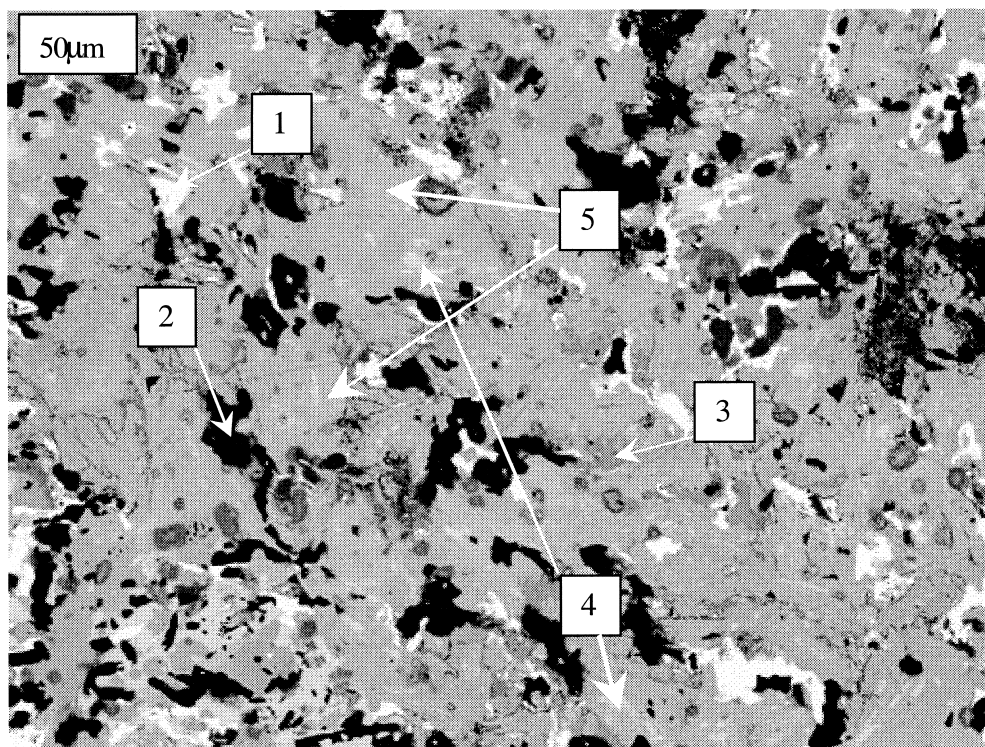


Fig. 7. Micrography of backscattered electrons of $\text{Hg}_{0.90}\text{Re}_{0.10}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ where 1: HgCaO_2 , 2: CaCu_2O_3 , 3: Ba-O (which may be Ba(OH)_2 , BaO_2 or $\text{Ba(CO}_3\text{)}_2$), 4: $(\text{Hg,Re})\text{-1212}$, 5: $(\text{Hg,Re})\text{-1223}$.

conducting $(\text{Hg,Re})\text{-1223}$ phase: The EDX analysis reveals that the samples with a nominal Re concentration of $x = 0.15$, 0.18 and 0.20 have a Re EDX content around $x \approx 0.25$.

From these results, we can say that the superconducting phase $(\text{Hg,Re})\text{-1223}$ has a tendency to form a stoichiometry of $1/4$ Re and $3/4$ Hg in the HgO_8 plane. Some authors suggested that this cationic stoichiometry tends to be the ideal ratio between both cations [11,12,14,15], due to the octahedral oxygen coordination of the Re.

In Fig. 9, a microphotograph of backscattered electrons for a sample with a nominal Re concentration of $x = 0.25$ is shown. Its Re content reaches $x = 0.28$, which is a little higher than the nominal. It is observable that the superconducting matrix is not as homogeneous as the sample with $x = 0.18$. A large number of nucleation points of impurity phases such as CaCu_2O_3 and $(\text{Hg,Re})\text{-1212}$ are detected.

If we assume that in the mercury plane, the maximum Re content is $x = 0.25$ in the HgO_8 plane

as commented before, then we must suppose that another cation site is susceptible of being substituted by the Re such as the Cu site [9,11]. This way, we can understand the substitution of Re content higher than $x = 0.25$.

In Fig. 10, the nominal Re concentration versus the measured Re content is shown. It is easy to see that an increase of the concentration of Re in the superconducting phase exists up to the point where the nominal value of $x = 0.15$ is reached. Above this point a plateau is observed up to $x = 0.20$. The best superconducting samples are obtained in this region. For $x > 0.20$, another increase of Re content in the superconductor phase starts. However, it is harmful for the superconducting properties.

3.5. Micro-Raman analysis

Fig. 11 shows the Raman spectra of different $\text{Hg}_{1-x}\text{Re}_x\text{-1223}$ samples with increasing nominal Re content, from $x = 0.05$ to $x = 0.25$. The Raman

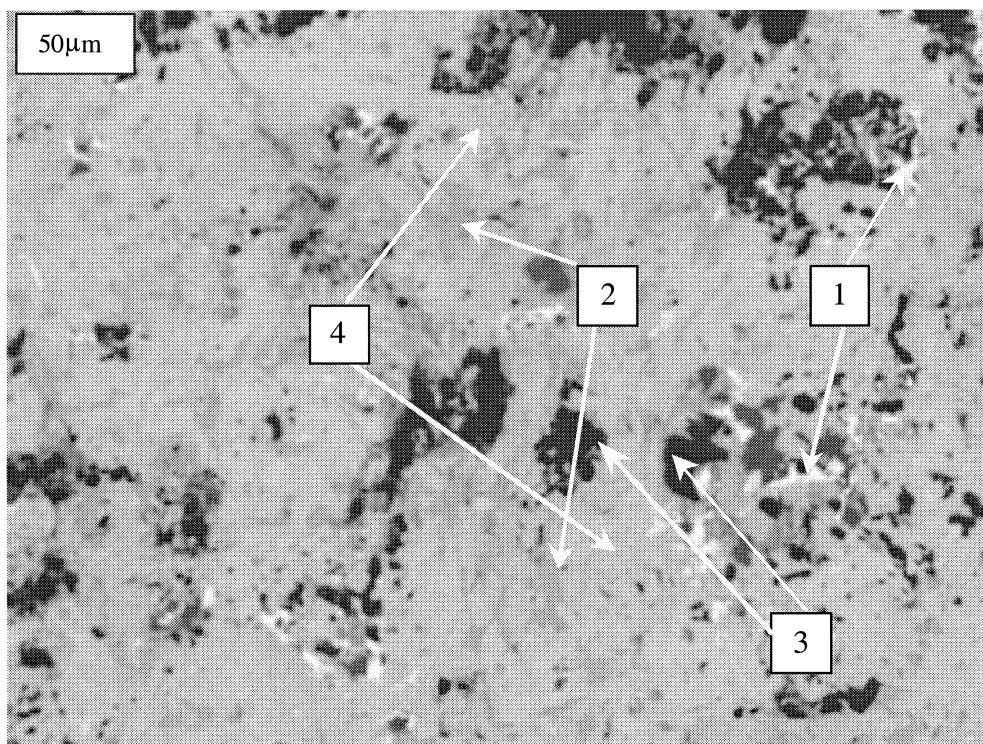


Fig. 8. Micrograph of backscattered electrons of $\text{Hg}_{0.82}\text{Re}_{0.18}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ where 1: HgCaO_2 , 2: Ba-O (which may be Ba(OH)_2 , BaO_2 or $\text{Ba(CO}_3\text{)}_2$), 3: CaCu_2O_3 , and 4: $(\text{Hg,Re})\text{-1223}$.

spectrum corresponding to the sample with the lower Re concentration ($x = 0.05$) displays a strong peak at 590 cm^{-1} and a shoulder at 570 cm^{-1} . Based on previous mode assignment for Hg-1223 [30–32], the peak at 590 cm^{-1} can be readily assigned to the A_{1g} mode vibrations concerning the apical oxygen in the $\text{Hg-O}_A\text{-Cu}$ bond. The peak at 570 cm^{-1} has been assigned to the A_{1g} mode of the apical oxygen modified by the presence of interstitial oxygen. The presence of the neighbouring interstitial oxygen, O_δ , gives rise to a downward shift (by about 20 cm^{-1}) of the apical oxygen vibration at 590 cm^{-1} producing the double peak like structure commonly observed in $\text{Hg-12}(n-1)n$ superconductors [30–32]. The peak intensities were obtained from the least-squares fits using Lorentzians. The relative peak intensity of the 570 cm^{-1} mode over that of the 590 cm^{-1} mode grows steadily as the amount of the Re substitution in $\text{Hg}_{1-x}\text{Re}_x\text{-1223}$ increases (see Fig. 12), and for $x = 0.18$ and 0.25 , the 570 cm^{-1} Raman peak becomes the dominant spectral feature. This change in

intensity can be understood by taking into account the fact that an enhancement of the Re content increases the O_δ content. Doping Re in the Hg-site of Hg-1223 is regarded as increasing the occupancy of the O_δ site in the Hg-1223 structure [13]. Consequently, the number of O_A sites with O_δ neighbours increases relative to that of O_A without O_δ neighbours, as the O_δ content increases. Similar behaviour has been found in $(\text{Hg}_{1-x}\text{Tl}_x)\text{Ba}_2(\text{Ca}_{0.86}\text{Sr}_{0.14})_2\text{-Cu}_3\text{O}_{8+\delta}$ where the amount of oxygen in the Hg/Tl-O plane is controlled by the doping level of Tl ions [30].

Furthermore, we can also observe in Fig. 11 that the sample with a 10% nominal Re content shows a weak Raman signal at high energy (635 cm^{-1}). This signal increases in intensity increasing nominal Re content. We assign this mode to the A_{1g} vibrations of the apical oxygen in the $\text{Re-O}_A\text{-Cu}$ bond. The Re-O_A bond has to be much stronger than the Hg-O_A bond, due to the higher valence ($n = 6, 7$) and the smaller radii of the Re ions compared to Hg

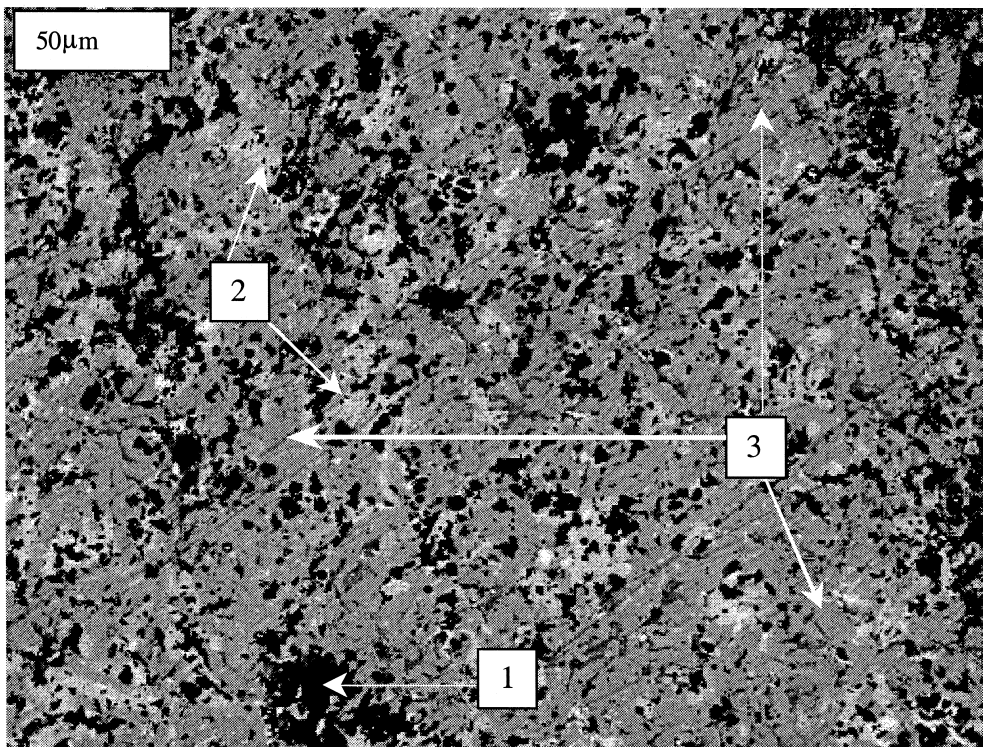


Fig. 9. Micrograph of backscattered electrons of $\text{Hg}_{0.75}\text{Re}_{0.25}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ where 1: CaCu_2O_3 , 2: (Hg,Re)-1212, 3: (Hg,Re)-1223.

ions [13,17]. It is then reasonable that the stretching motion of the $\text{Re}-\text{O}_A$ appears at higher energies.

Attempts to modify the interstitial oxygen content, O_δ , in the $\text{Hg}/\text{Re}-\text{O}_\delta$ planes have been made

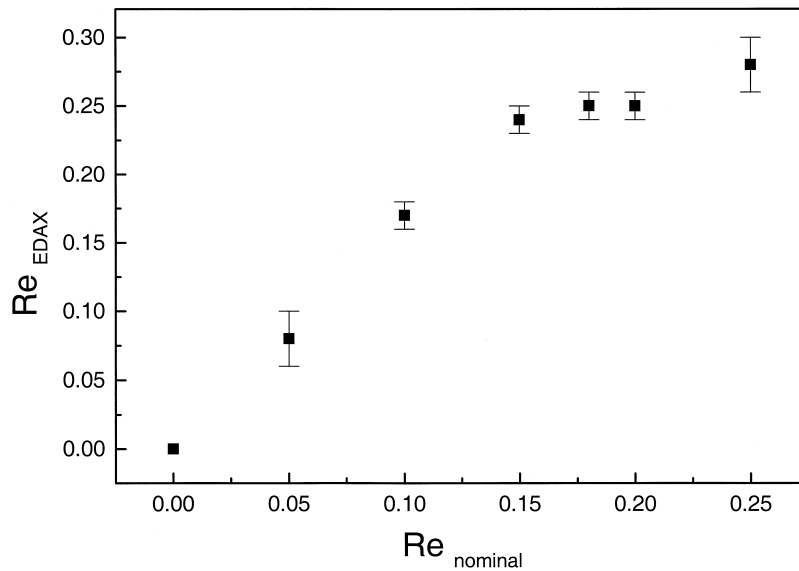


Fig. 10. Comparison between the nominal Re concentration vs. the EDX analysis Re content in the (Hg,Re)-1223 phase.



Fig. 11. Raman spectrum from $\text{Hg}_{1-x}\text{Re}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y$, where $x = 0.05, 0.10, 0.18$ and 0.25 .

by post-annealing the samples in vacuum at elevated temperatures. Samples have been annealed up to 550°C for 48 h in vacuum (1×10^{-2} bar). In contrast with the Hg-1223 and Hg/Tl-1223 compounds,

no variation in the relative intensity of the Raman peaks has been observed up to this temperature, before some of the crystallites start to decompose due to Hg segregation. The Re substitution brings an

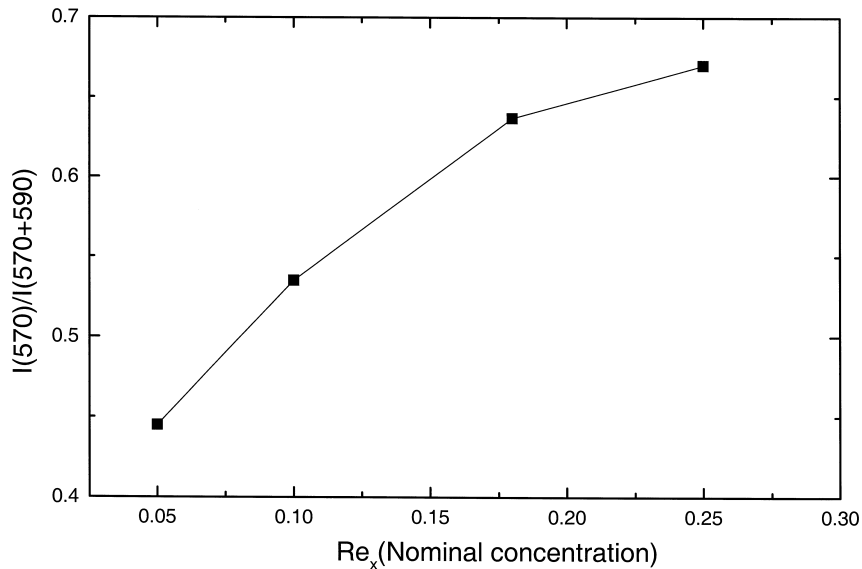


Fig. 12. Relative Intensity of the Raman signal at 570 cm^{-1} as function of Re nominal concentration.

additional oxygen atom into the unit cell at the crystallographic site $(x\ x\ 0; x \approx 0.34)$ [13]. In this model, the Re atom is octahedron coordinated with oxygen atoms. The fact that the Raman spectra do not substantially change with sample annealing indicates that the additional oxygen atoms introduced by Re substitution form a very stable structure, probably originated again by the high state of valence for Re and to its smaller ionic radius.

4. Conclusion

We can conclude that using the same route of synthesis by solid state reaction for the synthesis of (Hg,Re)-1223, an optimal superconducting ceramic is obtained when a nominal concentration of Re between $0.15 \leq x \leq 0.20$ is used. The superconducting phase formed has a tendency to adopt the stoichiometry of $1/4$ Re and $3/4$ Hg in the mercury layer. This can be the ideal coordination to stabilise the crystal cell in agreement with other authors. On the other hand, a clear influence of the rhenium content on the oxygen amount of the HgO_δ layer is noticeable; Re brings additional oxygen in this site. These additional oxygen atoms are very stable and stabilise the mercury layer. Nevertheless, the Re content and its related oxygen content in the HgO_δ layer, do not influence significantly the T_c value.

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