JOURNAL OF MATERIALS SCIENCE **33** (1998) 5359–5363

Successful synthesis of $Hg_{0.80}Re_{0.20}Sr_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ (n = 1, 2) by the sealed quartz tube technique

A. CALLEJA*, A. SIN, L. FÀBREGA, J. L. GARCÍA-MUÑOZ, S. PIÑOL,
J. FONTCUBERTA, X. OBRADORS
Institut de Ciència de Materials de Barcelona–C.S.I.C., Campus de la UAB, E-08193, Bellaterra, Spain
E-mail: calleja@icmab.es

Ba-free Hg,Re-1201 and -1212 were prepared by the sealed quartz tube technique. The starting materials were nominal precursor $Re_{0.20}Sr_2Ca_nCu_{n-1}O_x$ ($n = 1, 2$) and HgO. The unreacted pellets were annealed at 750 °C for 12 h for the $n = 1$ member and 850 °C for 12 h for the $n = 2$ member. Rietveld structural refinement was performed with the X-ray diffraction patterns, including impurity phases if needed. Both phases showed SG P4/mmm (nr. 123). Fitted tetragonal cell parameters were $a = b = 3.7822(1)$ Å, $c = 8.8776(5)$ Å and $a = b = 3.8205(3)$ Å, $c = 12.0438(8)$ Å for the $n = 1$ and $n = 2$ members, respectively. DCSQUID (Superconducting Quantum Interference Device) magnetometry and AC susceptibility were used to measure the superconducting properties of the samples. We also studied the effect of post-treatments in oxygen and argon. No superconductivity was found for the $n = 1$ in any case. However, $T_{c,\mathrm{onset}}$ as high as 107 K was determined for the Hg,Re-1212.

1. Introduction

The superconductor family $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ has caused considerable interest since its discovery [1], and one of the reasons for this is the elevated transition temperatures: 97 [2], 127 [3], 135 [4], and 127 K [5] for the $n = 1$, 2, 3, and 4 members, respectively. Higher members of the series have been found ($n < 8$) with gradually lower T_c's. In an early stage, the samples were synthesized under high pressures (GPa) due to the marked instability of the HgO_δ layer, formed by Hg divalent ions in dumb-bell coordination with the oxygen atoms. It was later shown that adding high-valence cations of a similar ionic radius stabilized the crystal lattice by incorporating extra oxygen atoms in the HgO_δ layer. Doping elements such as Bi, Pb, Tl, W, Mo, Re, V, Cr, etc. [6–8] have proved effective in aiding the synthesis of these compounds. Accordingly, the reduced synthesis pressure allowed the use of the sealed quartz tube technique, which is simpler and permits preparing larger amounts of the ceramic superconductors.

Structurally, these phases are related to the Bi- and Tl-12 (n–1)n series. A common feature of these compounds is their pancake-like structure of the vortices at relatively low temperatures. This lack of vortex stiffness results in low irreversibility lines. From the point of view of the superconducting performance, it is desirable to raise these lines. In fact, it has been recently demonstrated that metallization of the c-axis by using cations with high oxidation states is beneficial [9]. In this way, the intrinsic anisotropy of these materials is strongly reduced so that three-dimensional vortex behavior is preserved at higher temperatures and the flux pinning becomes more effective. Consequently, the irreversibility line should be markedly enhanced. Fàbrega *et al.* [10] discussed the presence of surface barriers in the Hg,Re-1223 compound.

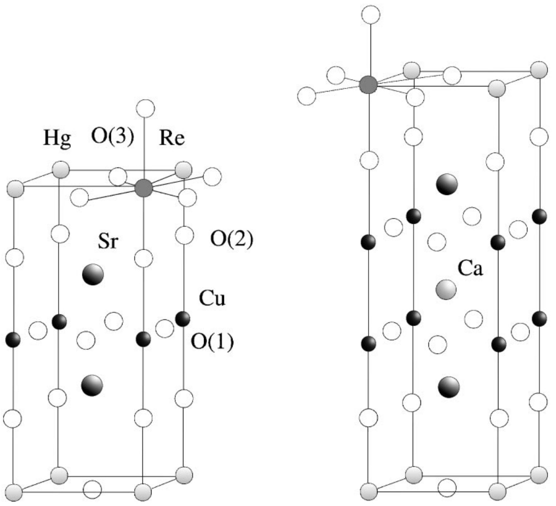
Another approach for decreasing anisotropy in the Hg series is substituting Ba^{2+} ($R_{\mathrm{ionic}} = 1.3$ Å) for the smaller Sr^{2+} ($R_{\mathrm{ionic}} = 1.1$ Å). Tallon *et al.* [9] estimated the value of the irreversibility field for Sr-based Hg,Re-1212 prepared under high pressure and found that it should be close to the value observed in the well-known $YBa_2Cu_3O_{7-\delta}$.

Under high pressures, it has been possible to obtain Ba-free samples of the Hg-family series, even with dopants such as rhenium [11, 12]. Kuzmicheva *et al.* [13] exposed the crystallochemical instability for such substitution and proposed the partial replacing of strontium by lanthanide cations to match the crystallographic requirements leading to the superconducting crystallographic cell. Moreover, strontium should improve the resistance to degradation at ambient conditions so that the need for atmosphere-control equipment such as the dry-box is minimized, if not eliminated.

---

* Author to whom all correspondence should be addressed.

0022–2461



(a) (b)

Figure 1 Squematic representation of the unit cells of (a) Hg,Re-1201 and (b) Hg,Re-1212.

Subramanian *et al.* [14] studied the undoped $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$ compounds, finding that superconductivity vanished for $x \geq 0.5$, but they failed to prepare the pure Sr-substituted phase. Recently, S. Lee *et al.* [15] reported the formation of $(Hg,Pb)(Ba_{1-x}Sr_x)_2Ca_2Cu_3O_{8+\delta}$ with $x = 0.0$–2.0 by encapsulating a spray-dried nitrate solution in a quartz tube. The T_c of the Ba-free Hg,Pb-1223 was 110 K. However, lead does not reduce the c-axis appreciably, and so, the blocking layer distance [9] in such a large extent as rhenium. Fig. 1 shows the squematic representation of the rhenium-doped $n = 1$ and 2 members.

In summary, there is current interest in the Sr-based Hg-superconductors, especially the $n = 2$ and 3 members, and it seems that the sealed quartz tube technique is suitable for producing such materials. In the present work, we report the synthesis of Ba-free Hg-1201 and -1212 with no lanthanide additions. The preparation was carried out by the vacuum sealed quartz tube technique.

2. Experimental procedure

A solid-state process was carried out to prepare the precursor $Re_{0.20}Sr_2Ca_{n-1}Cu_nO_{5+x}$ ($n = 1, 2$). Starting reagents were $SrCO_3$ (Baker, 99.9%), $CaCO_3$ (Aldrich, 99.9%), CuO (Aldrich, 99.98%), and ReO_2 (Aldrich, 99.9%). The raw powders were homogenized in an agate mortar, uniaxially pelletized under 0.1 GPa, and calcined at 850 °C for 15 h in an oxygen flow. In a second step, the precursor material was crushed, homogenized again, and treated at 930 °C for 15 h in an oxygen flow. The absence of carbonates was checked by X-ray powder diffraction. The brownish powder so obtained was mixed with HgO (Aldrich, 99%) in an agate mortar and pelletized as in the previous case. The compact was then introduced in a fused quartz tube ($\varnothing_{int} = 8$ mm, $\varnothing_{ext} = 10$ mm) held by an alumina boat crucible to avoid contact with the fused quartz, which reacts with the green pellet to form low-melting alkaline-earth silicates. A quartz rod ($\varnothing = 8$ mm) was also placed inside the tube to raise the filling factor to 0.7 g/cm^3 (sample mass-to-capsule volume ratio). This parameter has been demonstrated to be extremely important in this superconductor family synthesis [16]. The tube was sealed under vacuum with an acetylene-oxygen torch so that the final length was 90 mm.

The quartz capsule was placed in a tubular furnace at 750 and 850 °C for 12 h, for Hg,Re-1201 and Hg,Re-1212, respectively. The heating and cooling rates were 120 °C per h. In the case of the $n = 2$ member, a quick ramp of 300 °C per h up to 650 °C was implemented to minimize the $HgCaO_2$ formation [17].

X-ray powder diffractometry was performed in Rigaku Rotaflex RV-200. CuK_α radiation (not monochromized) was used. Rietveld refinement was applied to the X-ray diffraction patterns by means of the FULLPROF v.2.5 program.

DC magnetization was measured as a function of temperature and magnetic field in a commercial SQUID magnetometer. AC susceptibility was analyzed at different AC frequencies and amplitudes with a Quantum Design PPMS susceptometer. In both types of measurements, the temperature was varied in the range 5–120 K, and the DC applied field ranged between 0 and 5 T.

3. Results

3.1. $Hg_{0.80}Re_{0.20}Sr_2CuO_{4+\delta}$ ($n = 1$)

The X-ray diffraction (XRD) pattern corresponding to the sample with the $n = 1$ stoichiometry is shown in Fig. 2. The 2θ-interval was 5–60°. Some unreacted $SrCuO_2$ and Sr_2CuO_3 are present minoritarily together with the one-copper-layered superconductor. The Rietveld analysis of the phase is displayed in Table I. (0 0 1) preferential orientation had to be introduced in the refinement. This is due to anisotropic growth leading to platy habit growth of the grains. The occupancy factor of mercury and rhenium ions were fixed at 0.80 and 0.20, respectively, while their

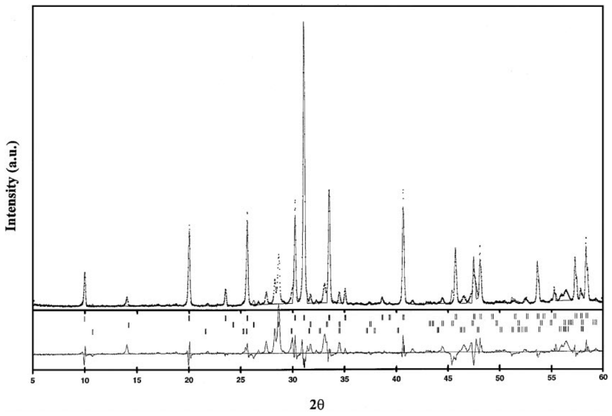


Figure 2 Best-fit Rietveld refinement (lines) and experimental XRD pattern (dots) for $Hg_{0.80}Re_{0.20}Sr_2CuO_{4+\delta}$. $R_p = 7.22\%$ $\chi^2 = 15.0$. Marks below indicate the reflections, from top to bottom, of Hg, Re-1201, Sr_2CuO_3, and $SrCuO_2$. The last line is the difference between experimental and calculated intensities. The impurity phases were excluded from the refinement. The synthesis conditions were 750 °C for 12 hours.

TABLE I Refined structural parameters for the as-prepared $Hg_{0.8}Re_{0.2}Sr_2CuO_{4+\delta}$ sample

Atom	X	y	z	B_{iso}	n
Hg	0	0	0	5.0(2)	0.80
Re	0	0	0	5.0(2)	0.20
Sr	0.5	0.5	0.3024(4)	2.6(2)	2.00
Cu	0	0	0.5	0.8(2)	1.00
O(1)	0.5	0	0.5	1.7(5)	2.00
O(2)	0	0	0.242(1)	1.7(5)	2.00
O(3)	0.33(1)	0.33(1)	0	1.7(5)	0.80

Space group P/4 mmm (123). Lattice constants $a = b = 3.7822(1)$ Å, $c = 8.8776(5)$ Å. Agreement factors $R_p = 7.22\%$ and $\chi^2 = 15.0$. Constraints $B_{iso}(Hg) = B_{iso}$ (Re), $n_{O(3)} = 4n_{Re}$ and B_{iso} equal for all oxygen atoms.

isotropic temperature factors were equaled [10]. In addition, the impurities were excluded from the refinement. The fitted SG was P4/mmm with lattice parameters $a = b = 3.7822(1)$ Å and $c = 8.8776(5)$ Å. These values are clearly lower than the Ba-based Hg-1201 but slightly higher than Cr-doped samples. In Table II, values taken from literature have been selected for comparison.

From the results, the refinement is consistent with full occupancy of the (0, 0, 0) site by Hg and Re, accepting a rather high value of B_{iso} for both atoms. This anomalous value of the thermal coefficient was also observed in early work [1]. Among several reasons for this, presence of copper or planar CO_3^{2-} groups in the HgO_δ layer has been proposed [11, 18]. Hg deficiency was reported by Chmaissen [11] for the $n = 2$ and 3 Sr-substituted members. It is also interesting to note the obtained large value of B_{iso} for Sr.

Regarding oxygen atoms, B_{iso} was constrained to be equal for all positions. Otherwise, some values became negative at the expense of the others, with no improvement of the refinement. The O(3) occupancy was fixed at four times the occupancy of rhenium according to the model in which octahedral ReO_6 clusters arrange in the HgO_δ, adding four extra oxygen atoms per (0, 0, 0) site. In addition, efforts were made to allow for interstitial oxygen atoms in the (0.5, 0.5, 0) position but the implementation resulted in negative occupancies in all cases and thus was discarded. The position of O(3) was also allowed to vary, which converged to $x = y = 0.33(1)$. The coordinates are comparable to values found in literature for high-pressure samples [11]. Orthorhombic distortion of the cell did not lead to better fits. Moreover, the derived apical O(2)-Cu distance of 2.29(1) Å is shorter than in $Hg_{1-x}Cr_xSr_2CuO_{4+\delta}$ (2.52 Å) and, as expected, is fairly shorter than in $HgBa_2CuO_{4+\delta}$ (2.78 Å) [19]. In addition, the z coordinate of Cu and O(1) was allowed to differ from 0.5 to dilucidate any buckling between CuO_2 units as reported by Chmaissen *et al.* [20]. Unfortunately, no meaningful improvement in the fit allowed to determine the buckling. Superstructure peaks corresponding to ReO_6 arrangement were not observable in the X-ray diffraction pattern.

The as-prepared Hg,Re-1201 did not display superconductivity down to 4.2 K if the sample was post-treated in flowing oxygen or in argon at 300 °C per h for 20 h. To enhance oxygen diffusion, the sample was pulverized in an agate mortar in both cases.

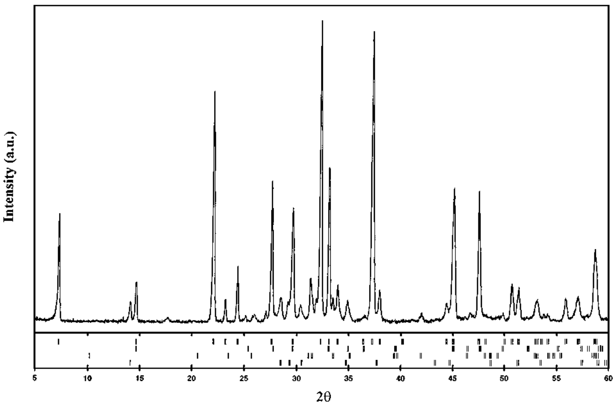


Figure 3 XRD pattern of $Hg_{0.80}Re_{0.20}$ $Sr_2CaCu_2CuO_{6+\delta}$. The marks represent, from top to bottom, Hg,Sr-1212, Hg,Sr-1201, $(Sr,Ca)CuO_2$, and $HgCaO_2$. The synthesis conditions were 850 °C for 12 hours.

3.2. $Hg_{0.80}Re_{0.20}Sr_2CaCu_2O_{6+\delta}$ ($n = 2$)

The XRD pattern is displayed in Fig. 3. There still remains some unreacted $HgCaO_2$ ($n = 1$), and precursor phases (mainly $(Ca,Sr)_2CuO_3$).

Rietveld analysis of the Ba-free Hg,Re-1212 posed some problems because it was not possible to lower the R_p agreement factor below 12%, the value of which is not appropriate to extract reliable structural information. We tried including the impurity phases or possible orthorhombicity with no improvement. Again, the data adjusted to tetragonal SG P4/mmm with lattice constants $a = b = 3.8205(3)$ Å and $c = 12.0438(8)$ Å.

The AC susceptibility diagram of the Hg,Sr-1212 powder is displayed in Fig. 4. The transition temperature onset was 107 K while the superconducting volume fraction was estimated to be about 80%. Upon oxygenation at 300 °C for 20 h (in powder), the transition onset moved to 103 K together with an important increase of the superconducting volume fraction.

Fig. 5 displays the hysteresis cycle of the as-grown Hg,Sr-1212 powder at 5 K. A critical current density at

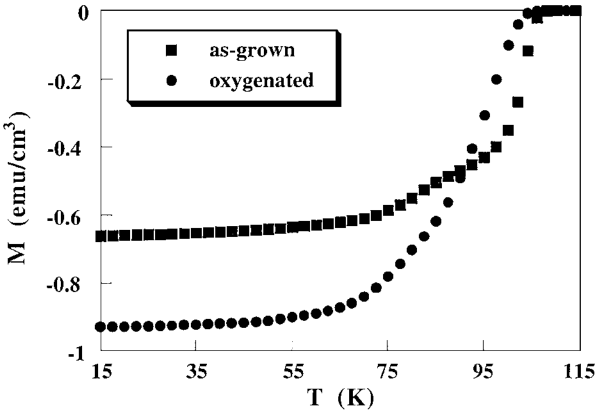


Figure 4 AC susceptibility diagram for the as-prepared and oxygenated $Hg_{0.80}Re_{0.20}Sr_2CaCu_2O_{6+\delta}$ ($n = 2$). Note that, upon oxygenation at 300 °C for 20 h, T_c is slightly lowered to 103 K while the superconducting volume fraction is clearly enhanced.

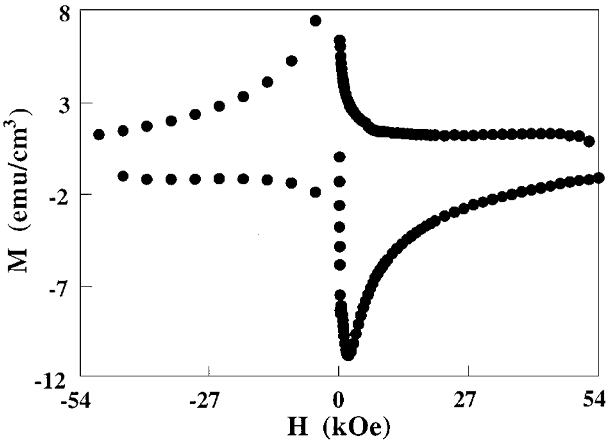


Figure 5 DC magnetization hysteresis loop at 5 K for the as-prepared Hg,Sr-1212 powders.

3 T of about $5 \cdot 10^5$ A/cm^2 can be estimated, assuming a grain size of about 2 μm. This value is somewhat lower than j_c estimated for the Ba-based Hg,Re-1223 [10]. The hysteresis cycles narrow very fast for increasing temperatures, indicating low bulk pinning.

4. Discussion

4.1. $Hg_{0.80}Re_{0.20}Sr_2CuO_{4+\delta}$ ($n = 1$)

First, the possibility of preparing the Sr-based Hg,Re-1201 by such a simple technique as the sealed quartz tube should be stressed. In our case, some unreacted impurities still remained.

A list of Hg-1201 phases with lattice constants and optimized T_c has been selected from the literature and is displayed in Table II. The reduction in the axis is clear when strontium appears. The same effect of shortening is seen when high-polarizing dopants are added (Re, Cr, Pr, etc.). Lanthanide additions strongly depress T_c so that it is desirable to eliminate them. Shorter c-axis derives in reduced blocking layer thicknesses so that, in principle, irreversibility lines are improved [9].

The fact that no oxygen atoms in the (0.5, 0.5, 0) position were found to improve the refinement may be a signal of steric hindrance due to the high occupancy of O(3) atoms coming from ReO_6 clusters. There must be interstitial oxygens in a different site because Chmaissen *et al.* [11] recovered the superconductivity in their high-pressure samples by annealing in vacuum.

Finally, the suppression of the superconductivity in our system is believed to be a consequence of an excessive oxygen doping due to the extra oxygens brought in by ReO_6 clusters. On the assumption that rhenium displays a +7 oxidation state [11], a simple charge balance states that copper valence is

$$v_{\mathrm{Cu}} = 4.80 \times 2 - 0.8 \times 2 - 0.20 \times 7 - 2 \times 2 = +2.6$$

Optimally doped $n = 1$ phase should display a value around +2.16, following the universal hole dependence of T_c [26]. Thus, it should be concluded that the structure is strongly overdoped in the as-prepared stage. However, these extra oxygen atoms are extremely difficult to eliminate by post-treatments in different atmospheres as they are covalently bonded to Re. It is worthwhile to mention the fact that Shimoyama *et al.* [27] found decreasing values of T_c with increasing rhenium doping for the Ba-based Hg,Re-1201. In this way, T_c for the composition $Hg_{0.80}Re_{0.20}Ba_2CuO_{4+\delta}$ was 15 K, compared to the value of 98 K for the rhenium undoped compound. Because Ba-free Hg-12(n–1)n materials exhibit lower T_c's, it might turn out that the corresponding Sr-based phase does not become superconducting, at least down to 4.2 K.

It should be desirable to compare these X-ray results with neutron diffraction data to clarify, with as much accuracy as possible, the oxygen coordinates and occupancies, which are of major interest for the superconducting properties.

4.2. $Hg_{0.80}Re_{0.20}Sr_2CaCu_2O_{6+\delta}$ ($n = 2$)

First of all, the formation of Hg,Re-1212 by the sealed quartz tube technique is quite remarkable mainly because as the number of copper layers increases so does the pressure needed to synthesize the phases [16], especially if no lanthanide cations are present. Indeed, in our case, there still remained impurities such as Hg,Re-1201, $HgCaO_2$, and other unreacted compounds. The overlapping of reflections from these residual phases with that of the main phase makes refining oxygen positions and occupancies very difficult.

In Table III, we selected some Hg-1212 synthesis in the literature both with and without barium along with their lattice constants and optimized T_c. Compared to the homologue barium phase, the c-axis is clearly shortened by 0.51 Å [20], while T_c moves from 120 to 107 K. Again, the addition of lanthanide cations greatly reduces the c-axis, but, in contrast, greatly lowers T_c [13]. In [11], shorter a- and c-axis are found for high-pressure samples of similar composition, only the rhenium doping was higher than in the present work. Interestingly, T_c is markedly higher in our case: 107 versus 90 K.

Additionally, the fact that T_c is slightly decreased while the superconducting volume increases may be due to some kind of oxygen inhomogeneity in the

TABLE II

Composition	$a = b$ (Å)	c(Å)	T_c(K)	Reference
$HgBa_2CuO_{4+\delta}$	3.87711(2)	9.49814(8)	97	[21]
$(Hg,Cr)Sr_2CuO_{4+\delta}$	3.840	8.639	58	[22]
$Hg_{0.6}Cr_{0.4}Sr_2CuO_{4+\delta}$	3.8500(7)	8.6961(2)	60	[19]
$Hg_{0.3}Pb_{0.7}Sr_{2-x}La_xCuO_{4+\delta}$	3.7493(3)	8.986(1)	41	[13]
$Hg_{0.80}Re_{0.20}Sr_2CuO_{4+\delta}$	3.7822(1)	8.8776(5)	Not superconducting	This work

TABLE III

Composition	$a = b$ (Å)	c(Å)	T_c	Reference
$Hg_{0.84}Re_{0.16}Ba_2CaCu_2O_{6+\delta}$	3.8580(4)	12.5524(2)	$\cong 120$	[20]
$(Hg,Pb)Sr_2(Ca_{0.5}\ Y_{0.5})_2Cu_2O_7$	3.8159(6)	11.950(2)	90	[25]
$Hg_{0.4}Pr_{0.6}Sr_2(Sr_{0.7}Pr_{0.3})Cu_2O_{6+\delta}$	3.8385(4)	12.264(1)	85	[24]
$HgSr_2LaCu_2O_x$	3.824	11.56	28	[13]
$HgSr_2(Ca_{0.5}Ce_{0.5})Cu_2O_x$	3.891	12.62	54	[13]
$Hg_{0.5}Bi_{0.5}Sr_2Ca_{1.4}Nd_{1.6}Cu_2O_{6+\delta}$	3.8259(4)	12.0029(6)	94	[23]
$Hg_{0.75}Re_{0.25}Sr_2CaCu_2O_{6+\delta}$	3.8014(1)*	12.0029(6)	90	[11]
$Hg_{0.8}Re_{0.2}Sr_2CaCu_2O_{6+\delta}$	3.8205(3)	12.0438(8)	107	This work

*SG Pmmm $b = 3.8101(1)$.

as-prepared material. Nevertheless, this should be confirmed by more accurate structural refinements like neutron diffraction.

5. Conclusion

We have demonstrated the possibility of preparing Ba-free Hg-superconductors ($n = 1$ and 2) by the sealed quartz tube technique. While no superconductivity was found in the Hg, Re-1201, due probably to excessive rhenium doping, $T_{c,\text{onset}}$ as high as 107 K was obtained for the as-prepared Hg, Re-1212 but with a small superconducting volume fraction. Upon oxygenation at 1 atm at 300 °C, $T_{c,\text{onset}}$ was slightly reduced to 103 K but the superconducting volume fraction raised considerably. Oxygen inhomogeneity in the as-prepared material is believed to be responsible.

The present work opens the way to production of more stable and less anisotropic Hg,Sr-1212 by an inexpensive technique such as the sealed quartz tube. Work is now in progress to study the superconducting performance of the Ba-free Hg,Re-1212, which could be very promising from a practical point of view.

Acknowledgements

The authors gratefully acknowledge financial support from CICYT (MAT96-1052), Generalitat de Catalunya (GRQ95-8029) and DIOPMA.

References

1. S. N. PUTILIN, E. V. ANTIPOV, O. CHMAISSEN and M. MAREZIO, *Nature* **362** (1993) 226.
2. V. A. ALYOSHIN, D. A. MIKHAILOVA and E. V. ANTIPOV, *Physica C* **271** (1996) 197.
3. S. M. LOUREIRO, E. V. ANTIPOV, J. L. THOLENCE, J. J. CAPPONI, O. CHMAISSEN, Q. HUANG and M. MAREZIO, *ibid.* **217** (1993) 253.
4. M. PARANTHAMAN, *ibid.* **222** (1994) 7.
5. B. A. SCOTT, E. Y. SUARD, C. C. TSUEI, D. B. MITZI, T. R. MCGUIRE, B. H. CHEN and D. WALKER, *ibid.* **230** (1994) 239.
6. S. HAHAKURA, J. SHIMOYAMA, O. SHIINO, T. HASEGAWA, K. KITAZAWA and K. KISHIO, *ibid.* **235–240** (1994) 915.
7. D. PELLOQUIN, A. MAIGNAN, S. MALO, M. HERVIEU, C. MICHEL and B. RAVEAU, *J. Mater. Chem.* **5** (1995) 701.
8. B. RAVEAU, C. MICHEL, M. HERVIEU and A. MAIGNAN, *ibid.* **5** (1995) 803.
9. J. L. TALLON, C. BERNHARD, CH. NIEDERMAYER, J. SHIMOYAMA, S. HAHAKURA, K. YAMAURA, Z. HIROI, M. TAKANO and K. KISHIO, *J. Low Temperature Physics* **105** (1996) 1379.
10. L. FÀBREGA, B. MARTÍNEZ, J. FONTCUBERTA, A. SIN, S. PIÑOL and X. OBRADORS, *Physica C* **296** (1998) 29.
11. O. CHMAISSEN, J. D. JORGENSEN, K. YAMAURA, Z. HIROI, M. TAKANO, J. SHIMOYAMA and K. KISHIO, *Phys. Rev. B* **53** (1996) 14647.
12. K. YAMAURA, J. SHIMOYAMA, S. HAHAKURA, Z. HIROI, M. TAKANO and K. KISHIO, *Physica C* **246** (1995) 351.
13. G. M. KUZMICHEVA, E. P. KHLYBOV, V. N. KOCHETKOV, T. PALEWSKI, J. WARCHULSKA and I. N. AFANASIEVA, *Cryst. Res. Technol.* **30** (1995) 451.
14. M. A. SUBRAMANIAN and M. H. WHANGBO, *J. Solid State Chem.* **109** (1994) 410.
15. S. LEE, M. KUZNETSOV, N. KIRYAKOV, D. EMELYANOV and Y. TRETYAKOV, *Physica C* **290** (1997) 275.
16. A. SIN, A. G. CUNHA, A. CALLEJA, M. T. D. ORLANDO, E. M. EMMERICH, E. BAGGIO-SAITOVICH, M. SEGARRA, S. PIÑOL and X. OBRADORS, *Adv. Mat.*, in press.
17. A. SIN, A. G. CUNHA, A. CALLEJA, M. T. D. ORLANDO, E. M. EMMERICH, E. BAGGIO-SAITOVICH, J. XIMENOS, S. PIÑOL and X. OBRADORS, *Physica C* **306** (1998) 34.
18. D. PELLOQUIN, V. HARDY, A. MAIGNAN and B. RAVEAU, *Physica C* **273** (1997) 205.
19. O. CHMAISSEN, D. N. ARGYRIOU, D. G. HINKS, J. D. JORGENSEN, B. G. STOREY, H. ZHANG, L. D. MARKS, Y. Y. WANG, V. P. DRAVID and B. DABROWSKI, *Physical Review B* **52** (1995) 15636.
20. O. CHMAISSEM, P. GUPTASARMA, U. WELP, D. G. HINKS and J. D. JORGENSEN, *Physica C* **292** (1997) 305.
21. A. ASAB, A. R. ARMSTRONG, I. GAMESON and P. P. EDWARDS, *ibid.* **255** (1995) 180.
22. J. SHIMOYAMA, S. HAHAKURA, K. KITAZAWA, K. YAMAFUJI and K. KISHIO, *ibid.* **224** (1994) 1.
23. D. PELLOQUIN, M. HERVIEU, C. MICHEL, G. VAN TENDELOO, A. MAIGNAN and B. RAVEAU, *ibid.* **216** (1993) 257.
24. M. HERVIEU, G. VAN TENDELOO, A. MAIGNAN, C. MICHEL, F. GOUTENOIRE and B. RAVEAU, *ibid.* **216** (1993) 264.
25. S. F. HU, D. A. JEFFERSON, R. S. LIU and P. P. EDWARDS, *J. Solid State Chem.* **103** (1993) 280.
26. J. L. TALLON, C. BERNHARD, H. SHAKED, R. L. HITTERMAN and J. D. JORGENSEN, *Phys. Rev. B* **51** (1995) 12911.
27. J. SHIMOYAMA, K. KITAZAWA and K. KISHIO in “Proceedings of the 10th Anniversary HTS Workshop on Physics, Materials and Applications, 1996,” edited by World Scientific, p. 85.

Received 14 July
and accepted 17 August 1998