Higher T_C's by chemical substitutions in layered cuprates containing Hg in the reservoir blocks

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In order to explain why Tc of all Hg-12(n-1)n compounds increases with pressure and decreases with chemical substitutions, the variation of the Hg-1223 structure as a function of external pressure is compared to that induced in the same structure by total substitution of Ba with Sr and partial substitution of Hg with Re. The introduction of Sr in the structure seems to induce all the structural changes needed to simulate the structure stable under pressure except the thickness of the superconducting blocks, which decreases with pressure and increases by Sr substitution. The Re substitution does not seem to play an important role except for the stability of the structure and seems to contribute to produce overdoped samples.

1. INTRODUCTION

One of the strategies which may lead to the optimization of $T_{c'}$ for a given superconducting system, is the stabilization at ambient pressure of the phases responsible for the higher T_c's obtained by the application of external pressure. For example, resistance measurements under pressure on the Hg-12(n-1)n series show that T_c increases as a function of pressure for every compound studied, provided that it is optimally doped or underdoped. For example, at 35 GPa Hg-1223 exhibits the record highest T_c (164 K (onset)) ever recorded [1]. These in-situ high pressure studies, carried out together with in-situ structural studies, may indicate the strategy to obtain 'higher T_c' materials by appropriate chemical substitutions. The stabilization of the structure responsible for these higher T_c at ambient pressure might prove to be very rewarding. However, these substitutions have proved to cause more problems than anticipated as all of them have induced so far decreases of T_c. By comparing the structure of Hg-1223 at 8.5 GPa and that of a substituted Hg-1223 at

ambient pressure, the origin of these problems is discussed.

2. THE STRUCTURE OF Hg-1223 AS A FUNCTION OF PRESSURE

The tetragonal structures of Hg-12(n-1)n compounds contain the layer sequence: $(HgO_\delta)(BaO)\{(CuO_2)(Ca)\}_{n-1}(CuO_2)(BaO)$.
They have been refined by neutron powder diffraction data at ambient pressure and as a function of pressure up to 8 GPa. They all possess similar structural features. These are: nearly flat CuO_2 layers, long apical Cu-O distances, short Hg-O distances forming the dumbbell, and very long in-plane Hg-O distances. Another important feature is the partial oxygen-depleted HgO layer. This partial occupancy is actually the doping necessary to obtain the appropriate Cu valence. The optimal value of δ for each member, which increases with n, can be reached for n=1-3. For n>3 the maximum value of δ that can be inserted in the structure seems to be smaller than the optimal value to appropriately dope the CuO_2 layers. This might prevent the optimization of Tc of these compounds.

Table 1 gives the most important distances for Hg-1223 at ambient pressure and as a function of pressure [2]. The value of Tc at the pressure at which the structural refinement was carried out, was read from the Tc(P) curve for Hg-1223 [3]. The details of the structural determination as function of pressure are reported in reference [2]. From the values shown in Table 1 it can be seen that the decrease in both a and c lattice parameters is essentially linear, $da/dP \approx 0.011 Å/GPa$, $dc/dP \approx -0.090 Å/GPa$, with some deviation from linearity at very high pressures. Note that the decrease of the c parameter is 8 times that of the a parameter. At ambient pressure the Cu-O apical bond distance is very large (2.72 Å) and decreases to 2.44 Å at 8.5 GPa, which corresponds to a change of 10%, while the Hg-O apical bond distance reduces by only 2%. Both these two distance lie along the highly compressible c axis. The decrease in the Cu-O distance corresponds to 38% of the total decrease of the c axis. The Cu-O in-plane bond lengths for the square and pyramidal Cu cations as well as the in-plane Hg-O distance decrease by about 2%. This small decrease of the in-plane bond lengths is the source of the small contraction of the a lattice parameter. The shortening of the Cu-O in plane bond lengths should be regarded as the result of additional doping induced by pressure.

From this behavior it can be surmised that one could simulate the effect of pressure on the structure of Hg-1223 by substituting Ba by Sr. This substitution, being Sr smaller than Ba, would induce a shortening of the lattice parameters. At the same time, the Sr cation should move closer to the oxygen located in the middle of the Hg mesh with the consequent movement of the apical oxygen toward the pyramidal Cu cation, movement needed to readjust the electrostatic equilibrium.

An attempt to substitute Ba with Sr in Hg-1201 was made by Subramanian & Whangbo [4] who prepared samples of the series $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$ under a pressure of 0.1 GPa. These authors have been able to obtain single-phase samples up to x = 0.7; however, a decrease of T_C is obtained for increasing x while both lattice parameters decrease. Similar results have been obtained by Loureiro et al. [5] with Hg-1223. Since these measurements were not accompanied by structural refinements, it is not possible to single out the structural changes causing the T_C decrease.

3. THE STRUCTURE OF Re- AND Sr-SUBSTITUTED Hg-1223

Several other groups have used a double substitution in order to stabilize that of Ba with Sr. The second cation is either a 3d or 4d element, Ga, Pb, Bi, Tl, or Re. With the exception of Pb and Bi all the other elements are usually in their highest valence state. Every substituted sample of this type has exhibited a decrease of T_C. As in the case of the single substituted samples, no structural refinement has been carried out for these samples except for the (Re, Sr)-substituted Hg-1212 and Hg-1223 [6] and (Cr, Sr)-substituted Hg-1212 [7].

For the $(Hg_{0.75}Re_{0.25})Sr_2Ca_2Cu_3O_{8+\delta}$ samples Chmaissem et al. found that the as-prepared sample is orthorhombic with the Re cations ordered on the Hg layers. One of the two possible 1:3 orderings in the Hg layer is orthorhombic with a basal unit cell equal to (2a x 4a), whereas the other is tetragonal with a (2a x 2a) unit cell. Electron diffraction photographs showed reflections corresponding to the (2a x 4a x 2c) unit cell (a and c are those of the unsubstituted Hg-1223). All oxygen sites of the (Hg, Re) layer are occupied, but they are displaced from the ideal (1/2,1/2,0) position along the diagonal in order to form the appropriate octahedral coordination around the Re cations. This sample was found to become superconducting at 107 K. By vacuum-annealing it, an appreciable increase of T_C (from 107 to 120 K) was obtained. Table 2 gives selected interatomic distances found for the two phases by neutron powder diffraction. The values for the unsubstituted samples are given for comparison.

Table 1
Lattice parameters, interatomic distances (Å) and T_c (K) of Hg-1223 as a function of pressure

| | Applied Pressure (GPa) | | | | |
	0.0	0.5	3.5	6.0	8.5
a	3.8516(0)	3.8481(3)	3.8089(3)	3.7822(5)	3.7608(6)
c	15.7644(4)	15.740(3)	15.400(4)	15.180(6)	15.018(7)
Tc	135	138	142	144	146
Hg-O (dumbell)	1.98(1)	1.98(1)	1.95(2)	1.93(2)	1.97(2)
Hg-O (in-plane)	2.72(1)	2.72(2)	2.69(2)	2.67(3)	2.66(3)
Cu1-O (in-plane)	1.926(1)	1.924(1)	1.905(1)	1.891(1)	1.880(1)
Cu2-O (in-plane)	1.926(1)	1.926(1)	1.906(2)	1.892(2)	1.883(2)
Cu2-O (apical)	2.727(7)	2.70(2)	2.61(2)	2.57(3)	2.44(3)
Cu2-Cu2*	6.35(2)	6.38(3)	6.27(3)	6.18(3)	6.20(3)
(BaO)-(BaO)**	4.66	4.59	4.51	4.45	4.44

* Distance between two Cu cations of the same superconducting block, it gives its thickness.
** This represents the average distance between two BaO layers of the same reservoir block.
Reprinted from references [2, 3]

Table 2
Lattice parameters and interatomic distances in as-prepared and vacuum annealed $(Hg_{0.75}Re_{0.25})Sr_2Ca_2Cu_3O_{8+\delta}$ samples.

	Hg-1223	as prepared	vacuum annealed
a	3.8478(0)	3.8224 (av)	3.8265(1)
c	15.7782(3)	15.1709(6)	15.2126(5)
Cu2-O apical	2.741(6)	2.43 (av.)	2.406(6)
Cu2-O in plane	1.924(0)	1.914 (av)	1.914(0)
Hg-O dumbell	1.972(3)	1.99(1)	1.931(5)
Cu2-Cu2*	6.35(1)	6.54(1)	6.54(1)
(SrO)-(SrO)*	4.71 (av.)	4.53 (av.)	4.51 (av.)

*These distances are defined in Table 1.
Reprinted from reference [6].

4. DISCUSSION

It can be seen from the distances reported in Table 1 that the effect of pressure on the structure of Hg-1223 is the shortening of all cation-anion bond lengths. However, the compressibility of the unit cell is highly anisotropic. For example, the ratio of the compressibility along c and that along a has an average value greater than 2. Moreover, bonds along the same axis exhibit very different compressibility. For example, the compressibility of the apical Cu-O bond is more than 5 times that of the apical Hg-O bond. Both of the bonds lie along the c axis. One can state that the large increase of T_C observed in all Hg-12(n-1)n compounds is accompanied by the large decrease of the apical Cu-O bond length, whereas the apical Hg-O bond is only slightly compressible. Thus, in order to increase T_C one has to envisage a structure in which the c axis is shorter than that of unsubstituted Hg-1223 and as shown by Subramanian et al. [4] this is obtained by substituting Ba with Sr.

Gao et al. [1], from the Tc(P)-Tc(P=0) versus P plot, showed that the behavior of T_C for Hg-1201, Hg-1212, and Hg-1223 is nearly identical. The effect of pressure on the structures is also similar [2, 8]. For example, Subramanian et al. [4] found for $Hg(Ba_{1.3}Sr_{0.7})CuO_{4+\delta}$ a = 3.847 and c = 9.324 Å while the corresponding lattice parameters of the unsubstituted compound are a = 3.885 and c = 9.521 Å. The Sr substitution gives the appropriate variation of the lattice parameters, but the corresponding decrease of T_C strongly indicates that at least another structural feature must have changed inducing the observed T_C decrease.

A possible explanation for this behavior can be deduced from the data reported in Table 2 where some structural parameters for $(Hg_{0.75}Re_{0.25})Sr_2Ca_2Cu_3O_{8+\delta}$ are given. If we take into consideration the results of the vacuum annealed sample, we notice that, at least qualitatively, the a and c parameters and the two apical bond lengths decrease, so that the effect of the chemical substitution is equivalent to that

of the external pressure. The thickness of the reservoir block, (BaO)(HgOd)(BaO), also decreases with both the substitution and the application of pressure. The thickness of this block is the distance between two (BaO) layers and since Ba and O have different z parameters, the average of the two z's is considered. On the other hand, the Cu-Cu distance, which measures the thickness of the superconducting block, increases with the substitution whereas it decreases for increasing pressure. It should be this structural feature, that is the increase of the thickness of the superconducting layers, which is responsible for the decrease of T_C in the double substituted samples and by analogy in the single substituted samples.

5. CONCLUSION

From this analysis it is clear that a double substitution is needed for the simulation of the structure responsible for the high T_C's obtained by the application of external pressure. One substituant should be Sr. This cation induces all the structural changes needed, except one, that is the increase in thickness of the superconducting block. The second substituant should be chosen in such a way as to prevent this increase. Small cations such as Re, Mo, and Cr, likely in the 6+ state, seem to induce the wrong effect, and besides they tend to produce samples in the overdoped state as shown by the small values for the in-plane Cu-O distances (see Table 2).

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