Enhancement of $T_c$ by Sr substitution for Ba in Hg-2212 superconductor

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Abstract

The Ba substitution by Sr has been studied in two Hg-2212 series: Hg$_2$(Ba$_{1-y}$Sr$_y$)$_2$YCu$_2$O$_{8-\delta}$ and Hg$_2$(Ba$_{1-y}$Sr$_y$)$_2$(Y$_{0.80}$Ca$_{0.20}$)Cu$_2$O$_{8-\delta}$. In both series a $T_c$ enhancement of about 40 K is observed when Sr substitutes Ba from $y = 0$ to $y = 1.0$.

The $y = 0$ compound of the first series is the non superconducting Hg$_2$Ba$_2$YCuxO$_{8-\delta}$ prototype. In the second series, this $y = 0$ compound is already superconducting at 21 K. Indeed the members of this series present a higher charge carrier density in their CuO$_2$ superconducting planes than their homologues of the first series due to the doping introduced by the substitution of 20% of Y by Ca. The compounds of both series were synthesized in high pressure (3.5 GPa) - high temperature (950 - 1050 °C) conditions. In both cases Sr substitution was successful up to the full replacement of Ba ($y = 1.0$). The Hg-2212 phases were characterized by XRD, SEM, EDX and a.c. susceptibility.

Key words: Mercury-based high-$T_c$ superconductors, Pressure effects on superconductivity, High-$T_c$ superconductors transition temperature, High pressure - high temperature synthesis

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1 Introduction

The double-Hg-layer superconductor Hg$_2$Ba$_2$YCuxO$_{8-\delta}$ (Hg-2212) was discovered in 1994 by Radaelli et al. This compound is an insulator. When doped

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with Ca in Hg\textsubscript{2}Ba\textsubscript{2}(Y\textsubscript{1-x}Ca\textsubscript{x})Cu\textsubscript{2}O\textsubscript{8-δ}, it becomes superconducting \(2; 3\). The \(T_c\) transition depends on the Ca content. It increases from 40 K for \(x \sim 0.15\) to 70 K for \(x \sim 0.40\). The optimal \(T_c\) in Hg-2212 system is 82-84 K \(4; 5; 6\). This value can only be reached by chemical stabilization of the oxygen-deficient double mercury layer. The oxygen vacancies content in Hg\textsubscript{2}Ba\textsubscript{2}YCu\textsubscript{2}O\textsubscript{8-δ} is already around \(δ = 0.4-0.5\) and increases by Ca doping, up to its solubility limit \(x = 0.40\). To further rise doping, stabilizing elements like Tl\textsuperscript{3+} \(7\) or Pb\textsuperscript{4+} \(8; 9\) have to be used in substitution of Hg\textsuperscript{2+}; these higher valency elements bring oxygen in the double (Hg/Pb or Tl)\textsubscript{2}O\textsubscript{2-δ} layer and then allow to further substitute Y by Ca.

The pressure effect on \(T_c\) in Hg-2212 is huge, over + 50 K under 20 GPa \(10\). The corresponding rate is always positive, independently of the doping state. Below 10 GPa, it decreases from 4.5 K/GPa for underdoped compounds \((T_c \sim 30-45\) K) to 2.7-3 K/GPa when \(T_c \sim 70\) K. In optimally doped (Hg,Pb)-2212 \((T_c \sim 82-84\) K) \(dT_c/dP \sim 1\) K/GPa below 20 GPa \(11\). By contrast, chemical pressure, for example when Ba is replaced by a smaller cation (Sr for instance), has a negative effect on \(T_c\) \(12; 13; 14\). However, strontium substitution does not reproduce the entire structural changes induced by mechanical pressure in superconducting cuprates \(15; 16\). Two exceptions have been reported up to now: the (La,Sr)\textsubscript{2}CuO\textsubscript{4} system \(17; 18; 19\) and the artificially stressed epitaxial (La,Sr)CuO\textsubscript{4} films \(20\), where a \(T_c\) increase is observed induced by a chemical pressure.

In this paper, we have studied Ba substitution by Sr in two Hg-2212 series of two different doping regimes (series I and II). The first one, series I, corresponds to the composition Hg\textsubscript{2}(Ba\textsubscript{1-y}Sr\textsubscript{y})\textsubscript{2}YCu\textsubscript{2}O\textsubscript{8-δ} and is built with Y in between the CuO\textsubscript{2} superconducting planes. The second one, series II, Hg\textsubscript{2}(Ba\textsubscript{1-y}Sr\textsubscript{y})\textsubscript{2}(Y\textsubscript{0.80}Ca\textsubscript{0.20})Cu\textsubscript{2}O\textsubscript{8-δ}, is doped with 20 % of Ca on the Y site. Each sample was synthesized at high pressure - high temperature (HP-HT) for \(0 \leq y \leq 1.0\). The effects of Sr/Ba replacement on superconductivity were analyzed using X-ray diffraction (XRD), scanning electron microscopy, EDX microanalysis and a.c. susceptibility measurements.

2 Experimental

The samples were prepared in a high pressure Conac-type apparatus. The reacting powders of each sample were mixed and compacted into a gold capsule which was submitted to a high pressure (3.5 GPa) - high temperature (1050 °C for the Ca free series and 950 °C for the Ca doped series) treatment. At this point, it is important to note that the chemical reactions take place into an inert and closed capsule, i.e. into a confined system. Thus, the average composition can not change during the HP-HT process, especially the oxygen
content of the sample, then the oxidation state of copper in the final Hg-2212 compound is principally fixed by the initial oxygen content of the starting mixture.

Two synthesis routes were tried, as explained in previous papers. The first one was used for series I (Ca-free). It consists in preparing two precursors, “Ba$_2$YC$_{u_2}$O$_z$” and “Sr$_2$YC$_{u_2}$O$_z$”, by reacting Y$_2$O$_3$ (Prolabo, 99.9 %) and CuO (Aldrich, 99 %) with BaO$_2$ (Merck, 95 %) or SrCO$_3$ (Aldrich, 99.9 %) at 850 °C or 950 °C respectively during 24 h under oxygen flow, followed by a quench to room temperature. Then, this pre-reacted precursor (a mixture of Y$_2$BaCuO$_5$, BaCuO$_2$, YBa$_2$Cu$_3$O$_7$−δ and YBa$_3$Cu$_2$O$_{6.5+x}$ for the Ba-based precursor) is mixed with HgO (Aldrich, > 99 %), inserted into the gold capsule and treated at HP-HT. For Hg$_2$(Ba$_{0.5}$Sr$_{0.5}$)$_2$YC$_{u_2}$O$_{8−δ}$, both precursors were mixed together with HgO in the ratio 1:1:2.

In the second route we attempted to better control the oxidation state of the sample by adjusting the oxygen content of the precursor introduced into the closed capsule to the desired value. This second method, used for series II, allows to control more precisely the oxygen stoichiometry before the HP-HT reaction and then the final doping state of the synthesized Hg-2212 compound. It consists in intimately mixing HgO directly in the right proportion with BaO$_2$, SrCuO$_2$, Y$_2$O$_3$, Ca$_2$CuO$_3$ oxides and metallic Cu (Ventron, 99 %) to have the nominal Hg$_2$(Ba$_{1−y}$Sr$_y$)$_2$(Y$_{0.80}$Ca$_{0.20}$)$_2$Cu$_2$O$_{7.50}$ composition, with y = 0 - 0.25 by step of 0.05, then 0.40, 0.50, 0.70 and 1.0. For example, in the case of Hg$_2$(Ba$_{0.75}$Sr$_{0.25}$)$_2$(Y$_{0.80}$Ca$_{0.20}$)$_2$Cu$_2$O$_{8−δ}$, to reach an oxygen content of 7.50, we used the mixture 2 HgO, 1.5 BaO$_2$, 0.5 SrCuO$_2$, 0.4 Y$_2$O$_3$, 0.1 Ca$_2$CuO$_3$ and 1.4 Cu. BaO$_2$ was chosen as the barium source instead of BaCuO$_2$ because it is very difficult to prepare BaCuO$_2$ without any trace of carbon contamination. The 95 % purity of the commercial BaO$_2$, which contains traces of barium carbonate, was also not considered sufficient. Our source of barium peroxide was prepared by precipitation of a solution of barium nitrate (more pure, Aldrich, 99 %) added with oxygenated water. The absence of barium hydroxide, carbonate or oxide hydrate was checked by XRD in the final BaO$_2$ product. SrCuO$_2$ was prepared by firing SrCO$_3$ and CuO under oxygen flow at 950 °C for 48 h followed by a second treatment at 980 °C for 36 h with an intermediate grinding. Ca$_2$CuO$_3$ was synthesized by reacting a mixture of 2 CaCO$_3$ (Aldrich, 99 %) + CuO at 1000 °C under oxygen flow for 15 h. The purity of these two oxides was checked by XRD before their mixing and the HP-HT treatment.

In the first set of syntheses, the obtained samples were multiphasic with mixtures of Hg-2212, Hg-1212 and others impurities. In this work, the HP-HT conditions (reaction time and temperature) were optimized in both series to avoid the formation of the analogue Hg-1212 phase (which appears for too long reaction time) and obtain the purest possible Hg-2212 samples.
XRD patterns were collected using a powder Siemens D-5000 diffractometer working in transmission mode at the wavelength $\lambda_{Cu, K\alpha_1} = 1.54056 \, \text{Å}$. The microstructure and composition of samples were investigated by scanning electron microscopy on a JEOL-840, equipped with a Kevex system for X-ray energy dispersive spectroscopy (EDX) analysis. A.C. susceptibility measurements were performed at 119 Hz using a home-made apparatus working at low magnetic field of 0.012 Oe, in the range 4.2 – 300 K (LEPES, CNRS, Grenoble, France).

3 Results and discussion

3.1 Phase purity and structural characterization

Figure 1 shows the XRD patterns of $y = 0$, 0.5 and 1.0 compounds of the series I. Figure 2 shows a zoom of 20-35° and 45-60° 2θ ranges for $y = 0$, 0.20, 0.40 and 0.70 compositions of the series II ($x = 0.20$). In both series the main phase is Hg-2212, without mono-Hg-layer Hg-1212 impurity. For the first time Sr-substituted Hg-2212 compounds are synthesized at HP-HT free of Hg-12(n-1)n type cuprates. Note also that full substitution of Ba for Sr is
Fig. 2. X-ray diffraction patterns of the 20% Ca doped Hg-2212 series.

reached in the Hg-2212 system.

For y = 0.0, traces of HgO or CuO are observed. For y > 0, an unknown phase appears in both series, whose amount increases with the Sr nominal content, it contains then Sr. The main XRD peak of this phase is close to 31° 2θ and its proportion increases with the Sr content. EDX microanalyses made systematically on samples of both series (SEM observations) show that this phase contains mainly Hg and Sr. It could also incorporate Cu or Ca in few amounts but the conclusion on this point is not definitive. Nevertheless, the list of its main Bragg peaks (indicated by tick marks in the bottom part of figure 1) corresponds to that of the Ca-Hg-O phase observed as an impurity in Ca-rich (Hg,Pb)-2212 compounds (8) and as an intermediate phase in the Hg-1223 formation (24). A structural model (space group I 4/mmm) and a composition (Ca$_{0.76}$Hg$_{1.24}$)O$_2$ were proposed for this new phase (24). This composition is close to that obtained from our microanalysis where Sr replaces Ca: (Sr$_{0.71}$Hg$_{1.29}$)O$_2$. These different observations suggest a common structure for both phases, Ca- or Sr-based, with the same stoichiometry.

The shift of the peaks towards higher 2θ values shows the shrinkage of the lattice due to the smaller Sr. It is particularly obvious on figure 2 for (107), (110) and (200) reflections. It proves that the Sr substitution on Ba site is effective. EDX microanalyses also show the Sr substitution and suggest that it reaches the nominal content, i.e. the measured Sr/(Sr+Ba) ratio is close to the
Fig. 3. Lattice parameters versus nominal Sr content in both Hg-2212 series (x = 0 and 0.20).

Table 1
Lattice parameters and $T_c$ for $\text{Hg}_2(\text{Ba}_{1-y}\text{Sr}_y)_{2}(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{8-\delta}$ samples (series I).

| Sr content | $y = 0.0$ | $y = 0.5$ | $y = 1.0$ |
|------------|-----------|-----------|-----------|
| $a = b$ (Å) | 3.8719(2) | 3.8327(3) | 3.8108(3) |
| $c$ (Å)    | 28.905(2) | 28.422(3) | 28.141(3) |
| $T_c$ onset | 0 K       | 32 K      | 42 K      |

nominal Sr stoichiometry. From EDX, the Ca doping is under-stoichiometric, in the 15-20 % range with respect to nominal stoichiometry (20 %). Lattice parameters were calculated by least square method (tables 1 and 2). In both series a decrease of the lattice parameters is observed, with a similar rate, i.e. $\sim 1.4$-1.6 % along the a-axis and $\sim 2.6$-2.8 % along the c-axis, as shown on figure 3. The lattice contraction is then not completely isotropic, it is larger for c-axis due to a larger compressibility along this direction than in the basal plane (i.e. the CuO$_2$ superconducting plane) which contains rather rigid bonds
Table 2
Lattice parameters and $T_c$ for Hg$_2$(Ba$_{1-y}$Sr$_y$)$_2$(Y$_{0.80}$Ca$_{0.20}$)Cu$_2$O$_{8-\delta}$ samples (series II).

| Sr content | y = 0.0 | y = 0.05 | y = 0.1 | y = 0.15 | y = 0.20 | y = 0.25 | y = 0.40 | y = 0.70 |
|------------|---------|---------|---------|---------|---------|---------|---------|---------|
| $a = b$ (Å) | 3.8589(3) | 3.8546(4) | 3.8514(3) | 3.8477(3) | 3.8454(4) | 3.8425(3) | 3.8333(4) | 3.8134(3) |
| $c$ (Å)    | 28.918(3) | 28.873(4) | 28.846(3) | 28.806(4) | 28.763(3) | 28.733(3) | 28.575(4) | 28.302(3) |
| $T_c$ onset | 21 K    | 27 K    | 32.5 K    | 39.5 K    | 38.5 K    | 41 K    | 51 K    | 60 K    |

of O-Cu-O type. The shrinkage of the a-axis is similar to that observed for the equivalent axis in Y-123 or Y-124 compounds (25, 26). The c-axis compression is around 0.76-0.82 Å for full substitution. This value is only slightly smaller than that predicted on considering the replacement of Ba by Sr in the four Ba-O planes of the structure and the difference of ionic radius between Ba and Sr (in coordination number 9). The full substitution would give a contraction of 1.28 Å. The a-axis for the two fully Sr-substituted samples is around 3.80-3.81 Å, which is typical of superconducting compounds containing only Sr, like Bi-based cuprates (27, 28). Moreover, no accident is visible on the variation of a-axis (and c-axis) which could indicate a brutal change of stoichiometry, on the oxygen composition for example. We can conclude that the variations of a and c lattice parameters are exclusively due to the Sr substitution for Ba.

3.2 Comparison of chemical pressure and mechanical pressure

Chemical pressure (by Sr) and mechanical pressure effects on lattice parameters are compared in figure 4. These data are reproduced from a previous high pressure experiment performed in a diamond anvil cell on the ID-09 beamline at the European Synchrotron ESRF (Grenoble, France) with a Hg$_2$Ba$_2$(Y$_{0.85}$Ca$_{0.15}$)Cu$_2$O$_{8-\delta}$ compound (21, 29). The scale of both X-coordinates (nominal Sr content and mechanical pressure) was chosen to have approximately the same decrease for a-axis in both cases.

We observe on the c-axis variations that the effect of mechanical pressure is not fully comparable with that of Sr chemical pressure. The pressure necessary to obtain the same shrinkage of the lattice corresponding to the full substitution Sr/Ba is not the same if one considers a-axis or c-axis. Along the a-axis it requires the application of an equivalent pressure of ~7 GPa whereas this value is higher along the c-axis, ~10 GPa. The difference is larger than experimental errors. In Y-123 and Y-124 systems, the complete substitution of Ba with Sr would induce a variation of the lattice parameters equivalent to the application of an external pressure of about 10-9.3 GPa (25, 26). This extrapolated value is consistent with what is observed here for the Hg-2212 system.
Fig. 4. Lattice parameters versus nominal Sr content for the Hg-2212 Ca-doped series (this work) and versus mechanical pressure for Hg$_2$Ba$_2$(Y$_{0.85}$Ca$_{0.15}$)Cu$_2$O$_{8-\delta}$ (ESRF ID-09 data, P. Bordet et al. (29), S. M. Loureiro (21)).

According to Acha et al. (10), a pressure of 10 GPa should increase $T_c$ by 30-45 K, depending on the doping state of the Hg-2212 compound. We will compare this value to the increase of $T_c$ obtained by chemical pressure of Sr in both series in the next paragraph.

3.3 Superconducting properties

The critical temperature $T_c$ was determined by a.c. susceptibility on fine powders which is a rather good method to determine the superconducting volume fraction (at 119 Hz with a low field of 0.012 Oe). Figures 5 and 6 show the measurements for series I and II. All the samples were superconducting, except the one for $y = 0.0$. The observed superconducting volume fractions (up to 70 %) do not correspond to the entire volume of the samples but are sufficient to attribute the transition to Hg-2212 which is the only cuprate detected by XRD.

The first compound of series I, Hg$_2$Ba$_2$YCu$_2$O$_{8-\delta}$, was not superconducting. This result is in agreement with previous measurements made by Radaelli et al. who did not observed superconductivity for this composition (11, 13).
Fig. 5. A.C. susceptibility versus temperature for \( y = 0.50 \) and 1.0 compounds of series I.

They showed that Ca doping on the Y site was necessary to induce superconductivity in Hg-2212. We show here, for the first time, that Ca doping on Y site is not necessary to reach the superconducting state. Indeed Hg\(_2\)(Ba\(_{0.5}\)Sr\(_{0.5}\))\(_2\)YC\(_2\)O\(_{8-\delta}\) and Hg\(_2\)Sr\(_2\)YC\(_2\)O\(_{8-\delta}\) are already superconducting without Ca doping, respectively at 32 K and 42 K (table 1). As a result of series I, \( T_{c \text{ onset}} \) increases regularly from 0 K (\( y = 0 \)) to 42 K (\( y = 1 \)) with the Sr content. In series II, the Hg\(_2\)Ba\(_2\)(Y\(_{0.8}\)Ca\(_{0.2}\))Cu\(_2\)O\(_{8-\delta}\) compound is superconducting at 21 K. This value is consistent with those reported previously. As for the previous case (table 2), the Ba replacement by Sr in series II also increases \( T_c \) continuously with the Sr content from 21 K (\( y = 0 \)) to 60-58 K (\( y = 0.7-1.0 \)).

To summarize, a 40 K increase is observed in Hg\(_2\)(Ba\(_{1-y}\)Sr\(_{y}\))\(_2\)(Y\(_{1-x}\)Ca\(_{x}\))Cu\(_2\)O\(_{8-\delta}\) (\( 0 \leq y \leq 1.0; x = 0, x = 0.2 \)), contrarily to other Sr-substituted families (Y-123 or Hg-12(n-1)n) where a decrease of \( T_c \) is shown \([12, 13, 14]\). This is a remarkable case where the Sr-chemical pressure has a positive effect on \( T_c \). This increase of 40 K is in the same order of magnitude than that obtained by applying a mechanical pressure of about 10 GPa in the Ba-based Hg-2212 compound \([10]\). In addition, the rate of \( T_c \) enhancement with Sr/Ba substitution is similar in both series, as illustrated in figure 7. As a consequence, it does not seem to be dependent of the doping level. Nevertheless, is the doping level constant among both series, i.e. equal to the doping regime of the \( y = 0 \) compound? This point is discussed in the next paragraph.
3.4 Discussion

Both EDX and lattice parameters variations agree to show that Sr substitutes to Ba nearly at the nominal content. A first consequence is that Y$^{3+}$ is not substituted by Sr$^{2+}$. This is discussed more carefully below.

If Sr$^{2+}$ would substitute Y$^{3+}$ on its site, then it would affect the hole doping of the CuO$_2$ planes. This does not happen for different reasons. First, the EDX results show that Sr and Ba contents vary in opposite way: the Sr content increases regularly when the Ba content decreases, and more precisely, the ratio of contents Sr/(Sr+Ba) determined by EDX is close to the nominal Sr content in all samples. Secondly, the $T_c$ rise is regular and continuous. If Sr$^{2+}$/Y$^{3+}$ site...
substitution would have been involved in this $T_c$ rise, this would have resulted in an over-stoichiometry of Sr. Moreover, this over-stoichiometry should have increased regularly to explain the $T_c$ increase. None of those phenomena is observed. Thirdly, if one assumes that Sr$^{2+}$ goes on the Y$^{3+}$ site and that its occupancy factor increases, for steric considerations one would observe an increase of the c-axis (the ionic radius of Sr$^{2+}$ being larger than Y$^{3+}$ in the eight-fold coordination), or at least a levelling of the shrinkage of the c-axis. This is neither observed.

As a consequence, because the substitution of Ba$^{2+}$ to Sr$^{2+}$ is isoelectronic, the doping is not changed in both series when the Sr content varies from $y = 0$ to 1.0. Probably the oxygen content in the Hg-2212 phase does not change significantly neither. This point is clearer in the series II, where the oxygen control was more accurate (mixture of oxides and metallic Cu with a total oxygen content of O 7.50) than in series I (mixture of HgO with precursors whose oxygen content is not well defined).

If the doping state is not changed and if the origin of this $T_c$ enhancement is structural, other experiments are necessary to precise its structural origin. We have performed neutron powder diffraction on both series to know exactly the changes induced locally into the 2212 structure. Refinements are underway and the corresponding results will be published elsewhere [30]. One significant result concerns the oxygen content determined from Rietveld refinements: it is almost constant in the whole range of Sr substitution for Ba [11]. It means that the $T_c$ enhancement observed in both series is not related to hypothetical oxygen content changes, but more likely a consequence of the Ba replacement by Sr.

4 Conclusion

The effects of chemical pressure were investigated in two Hg-2212 series: one based on yttrium, Hg$_2$(Ba$_{1-y}$Sr$_y$)$_2$YCu$_2$O$_{8-\delta}$ (series I), and the second one doped with 20% of Ca, Hg$_2$(Ba$_{1-y}$Sr$_y$)$_2$(Y$_{0.80}$Ca$_{0.20}$)Cu$_2$O$_{8-\delta}$ (series II). For the first time, Sr-substituted Hg-2212 superconductors were synthesized at high pressure - high temperature free from other analogue cuprate phases, i.e. members of the mono-Hg-layer family Hg-12(n-1)n.

We have shown that doping is not required to induce superconductivity in Hg-2212 system: Hg$_2$(Ba$_{0.5}$Sr$_{0.5}$)$_2$YCu$_2$O$_{8-\delta}$ and the full Sr-substituted Hg$_2$Sr$_2$YCu$_2$O$_{8-\delta}$ compounds of series I are already superconducting without Ca doping. In series II the Sr substitution enhances superconductivity that is already present in the Sr-free Hg$_2$Ba$_2$(Y$_{0.80}$Ca$_{0.20}$)Cu$_2$O$_{8-\delta}$ compound.
Fig. 7. Critical temperature versus nominal Sr content in both Hg-2212 series ($x = 0$ and 0.20).

In both series $T_c$ increases continuously from 0 K ($y = 0$) to 42 K ($y = 1.0$) for the first series and from 21 K to 60 K in the second one. In conclusion, contrarily to most superconducting cuprates, the Sr-chemical pressure has a positive effect on $T_c$ in the Hg-2212 system.

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