

# Establishment of strongly overdoped states in the $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ superconductor

K. Fujinami

*Materials and Structures Laboratory, and Department of Innovative and Engineered Materials,  
Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Yokohama 226, Japan*

T. Ito and H. Suematsu

*Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226, Japan*

K. Matsuura

*Hokkaido Electric Power Co., Ebetsu, Hokkaido 067, Japan*

M. Karppinen

*Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226, Japan  
and Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology, FIN-02015 HUT, Finland*

H. Yamauchi

*Materials and Structures Laboratory, and Department of Innovative and Engineered Materials,  
Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Yokohama 226, Japan*

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Strongly overdoped  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  (Hg-1223) samples with superconducting transitions as low as 97 K were successfully obtained by using  $\text{HgO}$ ,  $\text{Ca}_2\text{CuO}_3$ ,  $\text{CuO}$ , and mixtures of highly oxidized  $\text{BaCuO}_{2+\epsilon}$  ( $\epsilon \approx 0.13$ ) and/or  $\text{BaO}_2$  powders as starting materials for the high-pressure synthesis at 5 GPa and 950 °C. The overdoped state was confirmed by observing negative values for the Seebeck coefficient throughout the temperature range from  $T_c$  to 320 K in a thermoelectric power measurement. Also, both of the cell parameters  $a$  and  $c$  were found to decrease with decreasing  $T_c$ , reflecting, respectively, an increase in hole concentration in the  $\text{CuO}_2$  planes and the incorporation of oxygen into the  $\text{HgO}_\delta$  layer. The oxygen excess  $\delta$  as determined by the  $\text{Cu}(+I)/\text{Cu}(+II)$  coulometric titration method, was  $\sim 0.19$  in the overdoped sample with  $T_c = 107$  K. Subsequent reducing annealing in an Ar atmosphere at 280 °C increased the  $T_c$  to 131 K. Consistently, only positive Seebeck coefficient values were observed up to 320 K for the Ar-annealed sample. A clearly underdoped material with  $T_c = 118$  K was obtained by annealing the same sample in Ar at a higher temperature ( $\sim 400$  °C). Finally, high-pressure synthesis starting from less-oxidized  $\text{BaCuO}_{2+\epsilon}$  ( $\epsilon \approx 0.06$ ) yielded a Hg-1223 material with  $\delta \approx 0.10$  and  $T_c = 132$  K. [S0163-1829(97)04945-X]

## I. INTRODUCTION

The  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  (Hg-1223) superconducting cuprate phase exhibits the highest values until now recorded for the superconducting transition temperature  $T_c$ , i.e., the already highest ambient value of  $\sim 135$  K increases even above  $\sim 150$  K under high pressure.<sup>1,2</sup> The pressure-induced rise in  $T_c$  should stimulate attempts to facilitate also in ambient conditions the structural features<sup>3,4</sup> responsible for the record-high  $T_c$  values under high pressures. In other words, either the ambient-pressure structure is not yet optimally doped or the charge is unfavorably distributed within one single  $\text{CuO}_2$  plane.<sup>5</sup> In this respect, extensive studies on the physical properties in a wide hole-doping range are indispensable. Furthermore, excess oxygen/overdoping in the charge-reservoir block is supposed to lower the anisotropy of magnetization and raise the irreversibility field by making the  $\text{HgO}_\delta$  layers more conductive along the  $c$  axis, in a similar way as the  $\text{CuO}$  chains are “metalized” in the fully oxidized Cu-1212 structure.<sup>6,7</sup> Thus, overdoped  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  would be the best candidate for the highest- $T_c$ , highest- $H_{\text{irr}}$  and highest- $J_c$  material for applications.

Even though the hole concentration can be easily tuned

from the underdoped region far to the overdoped side both in the  $n=1$  and 2 members of the Hg-12( $n-1$ ) $n$  homologous series,<sup>8-10</sup> only very few indications of clearly overdoped Hg-1223 samples have been obtained so far. The first high-pressure synthesis of the Hg-1223 phase resulted in single-phase material with a  $T_c$  of 102–115 K.<sup>11,12</sup> However, even though the normal-state resistivity increased along with the increase in  $T_c$  (to  $\sim 131$  K) upon low-temperature annealing in oxygen, it is difficult to verify whether the as-synthesized sample was in an overdoped state or not, since the annealing was also found to increase the amount of impurity phases. On the other hand, the Pb-doped Hg-1223 sample of Isawa *et al.*<sup>13</sup> with a nominal stoichiometry of  $(\text{Hg}_{0.8}\text{Pb}_{0.2})\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  and  $T_c \approx 122$  K was shown to exhibit a negative value for the room-temperature (RT) Seebeck coefficient ( $S_{290\text{K}}$ ) in thermoelectric power measurements. This fact is generally considered as an indication of the overdoped state in superconducting cuprates.<sup>14,15</sup> Recently, Bordet *et al.*<sup>16</sup> reported an overdoped state in Au-substituted Hg-1223. Up to the solubility limit of Au on the Hg-site ( $\sim 30\%$ ) both the  $a$  and  $c$  cell parameters and the  $T_c$  (down to  $\sim 121$  K) were found to decrease with increasing Au content. The overdoped state was confirmed by observing a higher  $T_c$  ( $\sim 125$  K) after annealing the sample in Ar.

Thus, cationic substitution has been so far the most successful way to synthesize (lightly) overdoped Hg-1223 samples. In the present contribution, a strongly overdoped state in the Hg-1223 phase was achieved by excess-oxygen doping. In a high-pressure synthesis of the samples, mixtures of oxidized  $\text{BaCuO}_{2+\epsilon}$  ( $\epsilon \approx 0.13$ ) and/or  $\text{BaO}_2$  powders were utilized for providing the excess oxygen. Also reduced  $\text{BaCuO}_{2+\epsilon}$  ( $\epsilon \approx 0.06$ ) powder was tested as a starting material. With postannealings performed in a thermobalance in well-controlled conditions the oxygen stoichiometry of as-synthesized samples was further altered. Besides extensive chemical analyses for the oxygen content both in the precursors and in the superconducting products, the synthesized samples were characterized by XRD, SQUID, and thermoelectric power measurements.

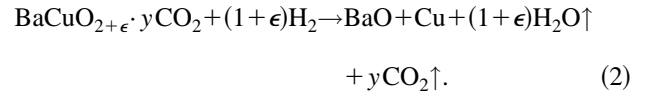
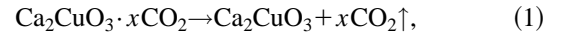
## II. EXPERIMENTAL

The  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  samples were synthesized by a high-pressure technique from stoichiometric (in terms of metal composition) amounts of HgO,  $\text{BaO}_2$ , CuO,  $\text{Ca}_2\text{CuO}_3$ , and two types of  $\text{BaCuO}_{2+\epsilon}$  precursors with different oxygen contents. The  $\text{Ca}_2\text{CuO}_3$  and  $\text{BaCuO}_{2+\epsilon}$  precursors were first prepared with repeated heat treatments under the following conditions: (i)  $\text{Ca}_2\text{CuO}_3$  from  $\text{CaCO}_3$  and CuO powders at 950 °C in  $\text{O}_2$ , (ii) the oxidized form of  $\text{BaCuO}_{2+\epsilon}$  from  $\text{BaO}_2$  and CuO powders at 850 °C in  $\text{O}_2$ , and (iii) the reduced form of  $\text{BaCuO}_{2+\epsilon}$  from the oxidized  $\text{BaCuO}_{2+\epsilon}$  material by quenching directly from 800 °C to RT after 12-h Ar annealing. For the high-pressure high-temperature treatments the desired mixtures of the above-described raw materials were tightly packed into gold capsules. Each gold capsule was then covered by a NaCl sleeve and placed into a pyrophyllite container equipped with an internal graphite tube heater. The high-pressure syntheses were carried out in a cubic-anvil-type apparatus at 5 GPa and 950 °C for 1 h.

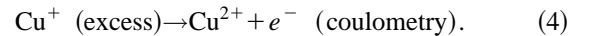
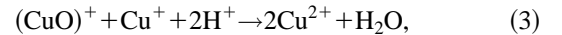
After being characterized the high-pressure synthesized  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  samples were subjected to post-annealing treatments in Ar at 280–400 °C in order to further tune the hole-doping level. These postannealings were carried out in a thermobalance (MAC Science TG/DTA 2000 S) to be able to *in situ* detect the changes in the weight/oxygen stoichiometry. The mass of the TG samples varied from 10 to 80 mg, and the heating and cooling rates were 2 °C  $\text{min}^{-1}$ . The isothermal heating period was 5 h for powder samples and 12–24 h for bulk samples. In some of the postannealing experiments the thermobalance was connected to a mass spectrometry (MAC Science TG/DTA 2000 S/MS) to carry out evolved gas analysis, especially for the oxygen evolution.

Both the  $\text{Ca}_2\text{CuO}_3$  and  $\text{BaCuO}_{2+\epsilon}$  precursors may contain variable amounts of carbonate. Prior to use, the carbonate content of  $\text{Ca}_2\text{CuO}_3$  was checked by thermogravimetric (TG) measurements performed in an Ar atmosphere up to 700 °C. By this temperature all carbon is released from  $\text{Ca}_2\text{CuO}_3$  [Eq. (1)]. In the case of Ba-containing compounds, the carbonate group is more stable and can not be removed from the sample under the above conditions. Therefore, in order to estimate the amount of carbonate in the two  $\text{BaCuO}_{2+\epsilon}$  precursors, the powders were reduced in a thermobalance by heating up to 1000 °C in a 5%  $\text{H}_2$ /95% Ar atmosphere. Under these conditions copper is reduced to metallic state,

while barium is maintained in an oxide form. The possible carbonate ( $y\text{CO}_2$ ) present in the  $\text{BaCuO}_{2+\epsilon} \cdot y\text{CO}_2$  powders is released as carbon dioxide [Eq. (2)]. This reaction was confirmed using  $\text{BaCO}_3$  as a reference compound.<sup>17</sup> As seen in Eq. (2), the observed weight loss is a sum of contributions from both the excess oxygen and the amount of carbonate. Consequently, the carbonate content can be calculated only after the oxygen content is analyzed separately. On the other hand, in the case of  $y=0$  the  $\text{H}_2$ /TG reduction would reveal the oxygen content of the sample:<sup>18</sup>



The amount of excess oxygen both in the two  $\text{BaCuO}_{2+\epsilon} \cdot y\text{CO}_2$  precursors and in the synthesized  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  samples could be analyzed by a coulometric titration method, using the experimental setup and principles described in details in Refs. 19 and 20. Upon dissolving the sample in a 1 M HCl solution containing CuCl both trivalent copper and peroxide-type oxygen, i.e.,  $(\text{CuO})^+$ , are reduced by Cu(+I) according to Eq. (3), and then a coulometric backtitration of the excess Cu(+I) is applied as a final analysis step [Eq. (4)]. Using  $\text{BaCO}_3$  and HgO as reference materials it was confirmed that at least in the present experimental conditions carbonate and divalent mercury do not participate in the reactions concerned:



The samples were also characterized for the phase-purity and lattice parameters by powder x-ray diffraction (XRD; MAC Science M18XHF;  $\text{CuK}_\alpha$  radiation), and for the superconducting properties by SQUID measurements (Quantum Design MPMSR) carried out down to 5 K in the field-cooling mode with a magnetic field of 10 Oe. The reported  $T_c$  values are onset temperatures of the diamagnetic signal.

Finally, three of the synthesized samples, one supposed to be over-doped, the second being close to optimized and the third under-doped, were characterized by a two channel thermoelectric power (TEP) measurement apparatus in the temperature range of 80 and 320 K, employing two pairs of copper-constantan thermocouples. The temperature gradient was kept at  $\sim 1$  K. The absolute Seebeck coefficient ( $S$ ) values were calculated from the relative measurement data by subtracting the contribution from the copper reference wires. The uncertainty in the measurements was  $\pm 0.2 \mu\text{V K}^{-1}$ .

## III. RESULTS AND DISCUSSION

First, the carbonate contents and the amounts of excess oxygen in the used precursor materials were determined by combined TG and titration analyses. The results are summarized in Table I. The carbonate content in  $\text{Ca}_2\text{CuO}_3$  was found to be quite low, corresponding approximately to the formula of  $\text{Ca}_2\text{CuO}_3 \cdot 0.02\text{CO}_2$ . The  $\text{BaO-CuO}_{1+\epsilon} \cdot y\text{CO}_2$  system, on the other hand, was supposed to be more complicated. The  $\text{BaCuO}_2$  phase has been reported to exist as a

TABLE I. Chemical analysis results for the carbonate content and oxygen excess in the nonstoichiometric precursor materials used for the high-pressure synthesis. All the numbers are calculated as an average of at least three parallel analysis results.

Precursor	Carbonate content $x/y$	Oxygen excess $\epsilon$
$\text{Ca}_2\text{CuO}_3 \cdot x\text{CO}_2$	$0.020 \pm 0.005$	
Oxidized $\text{BaCuO}_{2+\epsilon} \cdot y\text{CO}_2$	$0.01 \pm 0.02$	$0.13 \pm 0.01$
Reduced $\text{BaCuO}_{2+\epsilon} \cdot y\text{CO}_2$	$0.00 \pm 0.02$	$0.06 \pm 0.01$

“barium-deficient/rich, oxygen-rich carbonate-cuprate” with a stoichiometry, if expressed by  $\text{Ba}_z\text{CuO}_{2+\epsilon} \cdot y\text{CO}_2$ , varying approximately in the limits of  $0.9 \leq z \leq 1.1$ ,  $0 \leq \epsilon \leq 0.15$ , and  $0 \leq y \leq 0.125$ .<sup>21,22</sup> The strong affinity between the cuprate and carbonate groups, seen, e.g., as a continuous solubility of  $\text{CO}_3^{2-}$  into  $\text{CuO}_\delta$  chains in Ba-based superconducting cuprate structures,<sup>23</sup> was recently shown to result in a solid solution of carbonate and cuprate groups even in  $\text{BaCO}_3$  up to the stoichiometry of  $\text{Ba}(\text{CO}_3)_{0.5}(\text{CuO}_\delta)_{0.5}$ .<sup>24</sup> In the present study, however, the carbonate contamination was found to be negligible, since both the coulometric titration and  $\text{H}_2/\text{TG}$  reduction analyses gave within the estimated error limits the same values for the oxygen excess, i.e.,  $\epsilon = 0.13$  and  $0.06$  for the oxidized and reduced  $\text{BaCuO}_{2+\epsilon}$  precursors, respectively. In Fig. 1, examples of the obtained TG curves are shown. In both  $\text{BaCuO}_{2+\epsilon}$  precursors the weight loss is stepwise and starts around 400 °C. The onset temperature for the reduction is comparable to that observed for the  $\text{CuBa}_2\text{YCu}_2\text{O}_{6+\delta}$  compound.<sup>17,20</sup> Furthermore, it seems that as in the case of  $\text{CuBa}_2\text{YCu}_2\text{O}_{6+\delta}$  the first step in the reduction curve of the  $\text{BaCuO}_{2+\epsilon}$  precursors correspond to the removal of the excess oxygen  $\epsilon$ . Therefore, this step alone could be used for determining the oxygen stoichiometry, supposing that slow enough ( $\sim 1 \text{ }^\circ\text{C min}^{-1}$ ) heating rates were applied. In the present reduction experiments (heating rate  $20 \text{ }^\circ\text{C min}^{-1}$ ), however, the different reduction steps slightly overlapped, and the oxygen contents were calculated according to Eq. (2) from the overall weight loss in between 250 and 1000 °C.

The different Ba sources, i.e.,  $\text{BaCuO}_{2.06}$ ,  $\text{BaCuO}_{2.13}$ , and  $\text{BaO}_2$ , were then tested in terms of the resulting doping level

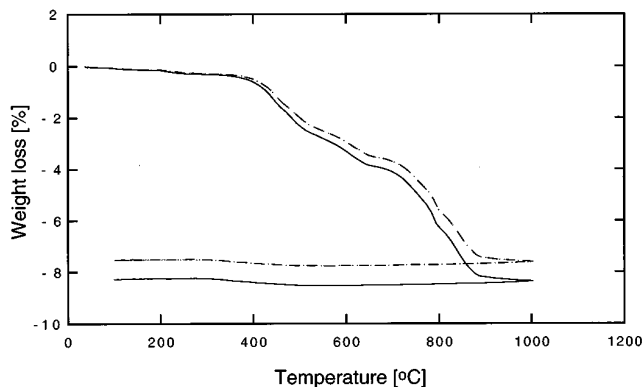


FIG. 1. Typical  $\text{H}_2/\text{TG}$  reduction curves obtained for the  $\text{BaCuO}_{2.13}$  (solid line)  $\text{BaCuO}_{2.06}$  (chain line) precursors.

in the  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  product in otherwise fixed conditions during the high-pressure synthesis. For each studied Ba source, the high-pressure synthesis was repeated several times, with quite consistent results in the parallel experiments. By using  $\text{BaCuO}_{2.06}$  and  $\text{BaCuO}_{2.13}$  precursors, the synthesis yielded essentially single phase material, although traces of  $\text{CuO}$  as well as small unknown impurity peaks at  $2\theta \approx 20.5^\circ$ ,  $31.4^\circ$ , and  $51.3^\circ$  were always detected, as indicated, e.g., in the XRD pattern recorded for the product in the case of the  $\text{BaCuO}_{2.13}$  precursor (Fig. 2). The SQUID data (Fig. 3), however, showed only one superconducting transition with a Meissner volume fraction of 40–50%. When employing  $\text{BaO}_2$  as an oxidizing agent in the high-pressure synthesis, the phase purity of the  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  phase decreased considerably. With the  $(\text{BaCuO}_{2.13} + \text{BaO}_2)$  mixture, the Hg-1223 phase was still the main phase, but in the case of  $\text{BaO}_2$  as the only Ba source the high-pressure synthesis product consisted mainly of the starting materials (Table II).

The resulting oxygen content in the synthesis product, established by two parallel  $\text{Cu}(+I)/\text{Cu}(+II)$  coulometric titrations, seems to depend on the nominal oxidation power of the starting material (Table II). The oxygen excess in the  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  samples synthesized from  $\text{BaCuO}_{2.06}$  was found to be  $\delta \approx 0.10$  (nominal value 0.12), while the synthesis starting from the more oxidized  $\text{BaCuO}_{2.13}$  yielded Hg-1223 material with  $\delta \approx 0.19$  (nominal value 0.26). The facts that (i) the samples were not totally of single phase but (ii) no other superconducting (i.e., oxidized) phases were detected suggest that the actual oxygen contents in the superconducting  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  phase may be somewhat higher than these “overall average” values, however. For the samples synthesized from the  $(\text{BaCuO}_{2.13} + \text{BaO}_2)$  mixture or from  $\text{BaO}_2$ , no estimation for the oxygen content was even tried because of the multiphase character of the samples.

In general, the present oxygen content values are quite small if compared, e.g., to the result of  $\delta \approx 0.30$  obtained by iodometry by Tokiwa-Yamamoto *et al.*<sup>25</sup> for optimally doped samples (synthesized under normal pressure) with  $T_c = 135 \text{ K}$ . Basically,  $\text{Cu}(+I)/\text{Cu}(+II)$  coulometry and iodometry detect exactly the same quantity, i.e., the sum of trivalent copper and peroxide-type oxygen in the whole sample, and in both methods the oxygen content is then calculated supposing (i) single-phase character for the sample, (ii) nominal metal composition in the whole sample, (iii) nominal metal occupancies in the superconducting structure, and (iv) the divalent oxidation state for mercury. On the other hand, neutron diffraction studies by Wagner *et al.*<sup>26</sup> and Finger *et al.*<sup>27</sup> suggested a coupled substitution of Cu on the Hg-site and oxygen on an otherwise unoccupied O site along the  $a$  axis, the situation of which would be better described by the formula  $(\text{Hg}_{1-\delta_1}\text{Cu}_{\delta_1})\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta_1+\delta_2}$  rather than by  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ . For example, in the normal-pressure synthesized sample with  $T_c = 135 \text{ K}$  Wagner *et al.*<sup>26</sup> found the following occupancies for  $\delta_1$  and  $\delta_2$ , respectively: 0.09 and 0.18. Furthermore, in terms of hole-doping the  $\text{CuO}_2$  planes the excess oxygen atoms by  $\delta_1$  and  $\delta_2$  may act with quite different efficiencies, as was shown by bond-valence

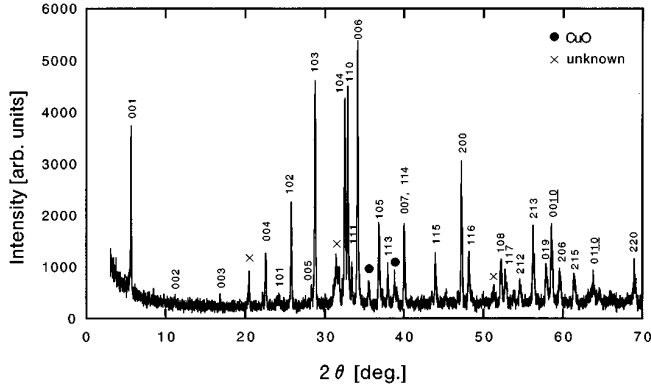


FIG. 2. XRD pattern recorded for the sample synthesized at 5 GPa and 950 °C from HgO,  $\text{Ca}_2\text{CuO}_3$ , and  $\text{BaCuO}_{2.13}$ . The reflections due to the Hg-1223 phase are indicated.

calculations given in Ref. 28. As a conclusion, it is possible that samples synthesized by different methods in different laboratories may have different systematic deviations from the above assumptions (i)–(iv), and the absolute oxygen content values when determined by chemical analysis may therefore differ quite much, but comparison between the values obtained for sample series prepared in consistent conditions should reveal correct trends at least.

For the  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  samples synthesized from the  $(\text{BaCuO}_{2.13} + \text{BaO}_2)$  mixture and from the oxidized  $\text{BaCuO}_{2.13}$  ( $\delta \approx 0.19$ ),  $T_c$  values of 97 and 107 K were, respectively, obtained (Table II). These samples were supposed to be overdoped, since the less-oxidized sample synthesized from the reduced  $\text{BaCuO}_{2.06}$  ( $\delta \approx 0.10$ ) was found to have a much higher  $T_c$  of 132 K. The overdoped state of the  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.19}$  sample was further confirmed by observ-

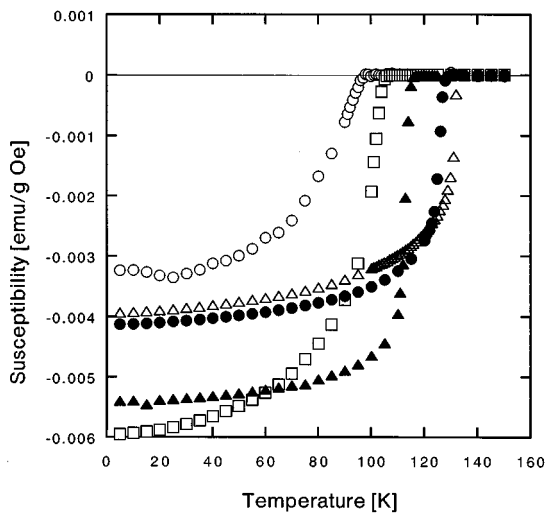


FIG. 3. SQUID data (field-cooling curves) for the following powder samples: as-synthesized from the  $(\text{BaCuO}_{2.13} + \text{BaO}_2)$  mixture ( $\circ$ ) ( $T_c = 97$  K), as-synthesized from  $\text{BaCuO}_{2.13}$  ( $\square$ ) ( $T_c = 107$  K), as-synthesized from  $\text{BaCuO}_{2.06}$  ( $\triangle$ ) ( $T_c = 132$  K), synthesized first from  $\text{BaCuO}_{2.13}$  and postannealed in Ar at 280 °C ( $\bullet$ ) ( $T_c = 131$  K), and synthesized first from  $\text{BaCuO}_{2.13}$  and postannealed in Ar at 400 °C ( $\blacktriangle$ ) ( $T_c = 118$  K).

ing negative values for the Seebeck coefficient at temperatures higher than  $T_c$  in a thermoelectric power measurement (Fig. 4). The obtained  $S_{290\text{K}}$  value of  $-3.0 \mu\text{V K}^{-1}$  is slightly lower than that reported by Isawa *et al.*<sup>13</sup> for the Pb-doped Hg-1223 phase ( $T_c = 122$  K;  $S_{290\text{K}} \approx -2.8 \mu\text{V K}^{-1}$ ). Subsequent reducing annealing of the present  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.19}$  sample in an argon atmosphere at 280 °C increased the  $T_c$  to 131 K. Consistently, above  $T_c$  the Seebeck coefficient remained positive throughout the whole temperature range measured ( $S_{290\text{K}} \approx +5.8 \mu\text{V K}^{-1}$ ). Further reduction of the same overdoped  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.19}$  sample by annealing in Ar at 400 °C resulted in a clearly underdoped material with  $T_c = 118$  K (Table II). On the other hand, the as-synthesized  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.10}$  sample possessing  $T_c = 132$  K and  $S_{290\text{K}} \approx +1.6 \mu\text{V K}^{-1}$  is supposed to be close to optimized. Even though the RT Seebeck coefficient is positive as generally observed for underdoped superconducting cuprates, the material might be slightly overdoped, since the  $S$ -vs- $T$  curve is located at much lower  $S$  values than that of the underdoped sample possessing a  $T_c$  only 1 K higher (Fig. 4). If this were the case the empirical rule of overdoped cuprates exhibiting negative  $S$  values above RT would not then precisely apply to the Hg-1223 phase. In order to clarify this point, the possible contribution from the  $\text{HgO}_\delta$  layer to the TEP of the Hg-1223 samples should be understood.

The  $S$ -vs- $T$  curve for the sample annealed in Ar at 280 °C (Fig. 4) shows, after the sharp rise just above  $T_c$ , an overall decrease with increasing temperature in the normal state with the rate of decrease being slower at higher temperatures. This resembles the behavior previously reported for underdoped Hg-1212 and Hg-1223 samples.<sup>29–31</sup> On the other hand, the temperature dependence of TEP of the as-synthesized  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.19}$  sample possesses typical features, i.e., an immediate drop to negative values above  $T_c$  and a linear negative slope up to RT, established in general for strongly overdoped cuprate superconductors and seen, e.g., for oxidized Hg-1201 samples.<sup>32</sup> Recently, Chen *et al.*<sup>33</sup> reported of an anomaly in the  $S_{290\text{K}}$ -vs- $T_c/T_{c,\text{max}}$  behavior observed for strongly overdoped Hg-1201 and Hg-1212 samples. For many other high- $T_c$  cuprates  $S_{290\text{K}}$  decreases monotonically with increasing hole concentration and thus with decreasing  $T_c$  in the overdoped region,<sup>15</sup> but for both the Hg-1201 and Hg-1212 phases a minimum was found at a certain amount of overdoping (for Hg-1212 at  $T_c/T_{c,\text{max}} \approx 0.8$  and  $S_{290\text{K}} \approx -3 \mu\text{V K}^{-1}$ ). The present overdoped  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.19}$  sample with  $T_c/T_{c,\text{max}} \approx 107/135 \approx 0.8$  and  $S_{290\text{K}} \approx -3.0 \mu\text{V K}^{-1}$  would be located exactly at the minimum point in the  $S_{290\text{K}}$ -vs- $T_c/T_{c,\text{max}}$  curve of the Hg-1212 phase. In order to test whether these values would correspond to a minimum, if existed, also in the case of the Hg-1223 phase, TEP data for more strongly overdoped samples are needed. Unfortunately, the  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  sample with  $T_c = 97$  K ( $T_c/T_{c,\text{max}} \approx 97/135 \approx 0.7$ ) was not considered pure enough for revealing reliable TEP results.

All the reducing postannealing treatments (in Ar at 280 and 400 °C) of the high-pressure synthesized samples were carried out in a thermobalance in order to ensure a good control of the temperature profile and to *in situ* detect the changes in the oxygen stoichiometry/weight. In all these annealings, despite the initial amount of excess oxygen in the

TABLE II. Summary of the used synthesis conditions and the obtained characterization results for the synthesized samples. Most of the syntheses were repeated several times, with reproducible results. The summarized results for the oxygen excess, cell parameters, and  $T_c$  are average values of the parallel experiments.

Synthesis conditions	Oxygen excess $\delta$ analyzed/nominal	Cell parameters [ $\text{\AA}$ ] $a/c$	$T_c$ [K]	$S_{290\text{ K}}$ [ $\mu\text{V K}^{-1}$ ]
High $p$ from $\text{BaCuO}_{2.06}$ → Ar-annealed at 280 °C	0.10/0.12	3.850/15.79 3.854/15.81	132 132	+1.6
High $p$ from $\text{BaCuO}_{2.13}$ → Ar annealed at 280 °C → Ar annealed at 400 °C	0.19/0.26	3.847/15.76 3.850/15.77	107 131 118	-3.0 +5.8
High $p$ from ( $\text{BaCuO}_{2.13} + \text{BaO}_2$ )	/1.00	3.841/15.73	97	
High $p$ from $\text{BaO}_2$	/2.00	multiphase		

sample, quite a constant total weight loss of 0.4–0.6 wt % was observed. If this weight loss were attributed only to the oxygen depletion, it would correspond to 0.2–0.3 oxygen atoms per  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  formula unit. On the other hand, if it were only due to mercury loss, it would correspond to 0.02–0.03 Hg atoms. However, it seems that both oxygen and mercury losses occurred, since two overlapping processes with slightly different activation energies were seen in the TG curves. The lower temperature weight loss ( $\sim 200$  °C) originates most probably from the evaporation of Hg from the grain boundaries/HgO impurity phase,<sup>34</sup> while the higher temperature ( $\sim 250$  °C) weight loss is believed to correlate with the amount of released oxygen from the  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  structure. Consistently, only the higher temperature weight loss was accompanied with detectable oxygen evolution in the TG/MS experiments. The two processes, even though being somehow distinguished in a quali-

tative way, could not, however, be totally separated. Therefore, only the following semi-quantitative conclusion could be made: the oxygen loss upon the Ar annealings is less than  $\Delta\delta \approx 0.2$ . Finally it is noted that according to the careful TG experiments of Tokiwa-Yamamoto *et al.*,<sup>25</sup> no loss of mercury from the Hg-1223 structure occurs below  $\sim 500$  °C.

Most of the high-pressure syntheses and the subsequent postannealing experiments were repeated several times with well-reproducible results. Besides the oxygen content analysis performed for some of the samples, all the samples were characterized by XRD and SQUID measurements for the cell parameters and the superconducting properties. In Table II, the used synthesis conditions as well as the average values obtained from the parallel experiments for the oxygen contents, cell parameters, and  $T_c$ 's are summarized. The decrease in  $T_c$  seems to correlate with the decrease in both the cell parameters  $a$  and  $c$ . The decrease in the  $a$  parameter, i.e., the shortening of the in-plane Cu-O bond, originates from the removal of antibonding electrons from the  $\text{CuO}_2$  planes,<sup>35</sup> while incorporation of excess oxygen atoms into the  $\text{HgO}_\delta$  charge-reservoir block is supposed to shorten the distance between the Ba and  $\text{HgO}_\delta$  planes, and thereby be seen as a shortening of the  $c$  axis.<sup>28</sup>

Lokshin *et al.*<sup>36</sup> describe the high-pressure synthesis of overdoped Hg-1223 samples using  $\text{BaO}_2$  as an oxygen generator. In Fig. 5, based on both their data and the present results the  $T_c$  is plotted against the  $a$  and  $c$  cell parameters for the overdoped Hg-1223 samples. From these plots, as well, it is clearly seen that the present samples, obtained from the oxidized  $\text{BaCuO}_{2.13}$  precursor and from the mixture of  $\text{BaCuO}_{2.13}$  and  $\text{BaO}_2$  in the high-pressure synthesis, are strongly overdoped.

#### IV. CONCLUSIONS

Strongly overdoped  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  samples with  $T_c$  as low as 97 K were successfully obtained by using highly oxidized  $\text{BaCuO}_{2+\epsilon}$  ( $\epsilon \approx 0.13$ ) and  $\text{BaO}_2$  powders as excess oxygen sources in the high-pressure synthesis. The overdoped state was confirmed by thermoelectric power measurements. Also, both the  $a$  and  $c$  cell parameters were found to decrease with increasing oxygen content and decreasing  $T_c$ .

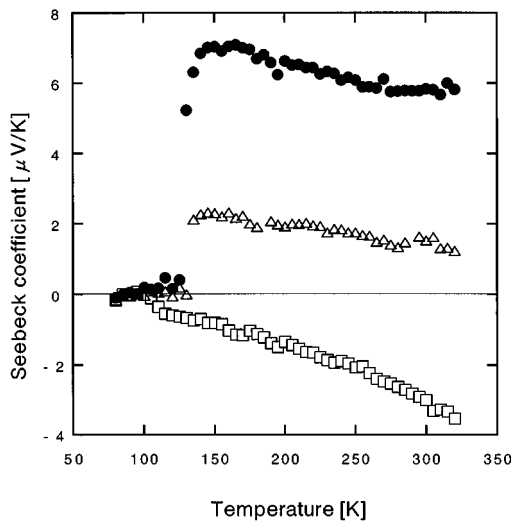


FIG. 4. Temperature dependence of Seebeck coefficient for the following samples: as-synthesized from  $\text{BaCuO}_{2.13}$  ( $\square$ ) ( $T_c = 107$  K), as-synthesized from  $\text{BaCuO}_{2.06}$  ( $\triangle$ ) ( $T_c = 132$  K), and synthesized first from  $\text{BaCuO}_{2.13}$  and postannealed in Ar at 280 °C ( $\bullet$ ) ( $T_c = 131$  K).

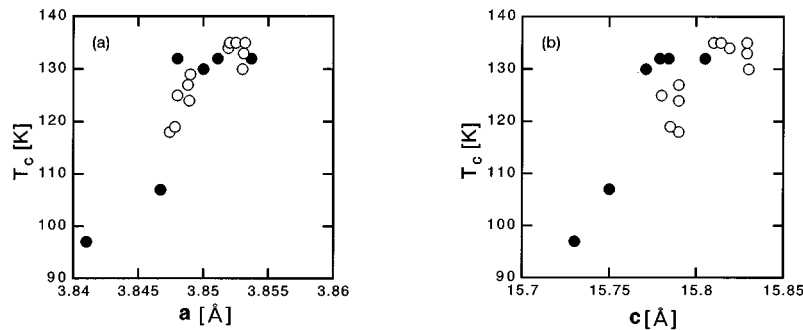


FIG. 5.  $T_c$ -vs- $a$  (a) and  $c$  (b) cell parameters for the present samples (●) and for the samples in Ref. 36 (○).

On the other hand, by subsequent postannealings in an argon atmosphere the hole concentration in the high-pressure synthesized samples was reduced so that the hole-doping state reached the underdoped side.

In order to control the hole-doping level in the high-pressure synthesized Hg-1223 phase, the use of  $\text{BaCuO}_{2+\epsilon}$  precursors, exhibiting two different oxygen stoichiometries of  $\epsilon \approx 0.06$  and  $0.13$ , was found to be extremely fruitful. In the present contribution, the synthesis conditions as well as methods of chemical analysis were established to control and determine the oxygen content and carbonate contamination in the oxidized and reduced forms of  $\text{BaCuO}_{2+\epsilon}$ . Furthermore, oxygen content analysis of superconducting mercury cuprates by the coulometric titration method was reported.

The methods developed and demonstrated in this contri-

bution for controlling the oxygen stoichiometry in Hg-1223 are believed to be most useful in the subsequent studies on the characterization of the physical properties in a wide range of hole doping in the superconducting cuprate phase exhibiting the highest  $T_{c,\text{max}}$ .

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