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Dependence of T_c and transport properties on the Cu valence in $HgBa_2Ca_{n-1}Cu_nO_{2(n+1)+\delta}$ ($n=2,3$) superconductors

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We have determined the oxygen content and the Cu valence by iodometric titiration of single-phase $HgBa_2Ca_{n-1}Cu_nO_{2(n+1)+\delta}$ ($n=2,3$), Hg-1212 and Hg-1223, superconductors postannealed under various conditions in either a reducing or an oxidizing atmosphere. Their lattice parameters, T_c, resistivity, and the thermoelectric power have been systematically investigated as a function of Cu valence. Hg-1212 exhibits a parabolic or ''bell-shaped'' relationship between T_c and the Cu valence similar to that reported for $HgBa_2CuO_{4+\delta}$ (Hg-1201), while only a half of the parabola is observed for Hg-1223. The systematic variations in the resistivity and the thermoelectric power as well as the relationship between T_c and the Cu valence confirm that the Hg-1223 sample with the highest T_c of 135 K is almost optimally doped. Both Hg-1212 and Hg-1223 as well as Hg-1201 exhibit their maximum T_c values at the same nominal Cu valence of approximately 2.20 which is also comparable to those for other high-T_c cuprate superconductors. This coincidence of the Cu valence for optimally doped states suggests that the simple ionic model where each excess oxygen in the Hg-O_δ charge reservoir supplies two holes is appropriate in the present Hg-12$(n-1)n$ samples. [S0163-1829(97)06610-6]

I. INTRODUCTION

Since the discovery of the Hg-based superconductors,[1,2] their structural and physical properties have been extensively investigated. In particular, $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223) phase has attracted considerable attention, because it has the highest superconducting transition temperature T_c of 135.4 K under ambient pressure[3] and above 150 K under high pressure.[4,5] The structure of $HgBa_2Ca_{n-1}Cu_nO_{2(n+1)+\delta}$ is almost the same as that of Tl-based superconducting cuprates with a single Tl-O layer. Their structures consist of the $Ca_{n-1}Cu_nO_{2n}$ block (or the infinite layer block) and the Hg-O_δ ''charge reservoir'' block. It is noted that Hg in the Hg-O_δ block basically has a twofold coordination with oxygen since the occupancy of oxygen at the [1/2, 1/2, 0] site in the Hg-O_δ block is very small.[6] It has been established by neutron diffraction studies that ''excess'' oxygen occupying this site functions to dope holes into the CuO_2 plane and thus the doping state of the Hg-based superconductors can be varied by changing the excess oxygen content.

It is of particular importance to investigate the doping state or the hole concentration and their correlation with the superconducting properties of these superconductors because it may provide insight into the mechanism of high-temperature superconductivity. There have been several reports on the dependence of superconducting properties of $HgBa_2CuO_{4+\delta}$ (Hg-1201) on the hole concentration or the excess oxygen content. Wagner *et al.*[6] determined the excess oxygen content δ of two underdoped samples with $T_c=59$ K and 95 K to be 0.11 and 0.15, respectively, by neutron diffraction experiments. They also found that approximately 0.09 oxygen atoms per formula unit is located on the [1/2, 0, 0] chain site, which is associated with the substitution of Cu for the Hg site. Since the sample with $T_c=59$ K has the oxygen occupancy of only 0.02 on the [1/2, 1/2, 0] site, the contribution of oxygen at the chain site to hole doping is strongly suggested. On the other hand, Chmaissem *et al.*[7] found no chain site oxygen in their Hg-1201 sample. Thus the existence of chain site oxygen and its contribution to hole doping are still controversial.

Xiong *et al.*[8] determined the oxygen content of Hg-1201 by thermogravimetric analysis (TGA) combined with neutron diffraction experiments. They observed a parabolic relationship between T_c and the excess oxygen content δ. However, a δ value of 0.22 for the optimally doped sample was much larger than that reported by Wagner *et al.* and the value which was estimated from the actual hole concentration deduced from thermoelectric power (TEP) of their samples. Thus they suggested a significant deviation from the simple ionic model where one excess oxygen provides two holes into the CuO_2 plane. On the other hand, Fukuoka *et al.*[9] recently determined the excess oxygen content of single-phase Hg-1201 samples postannealed under various conditions by the iodometric titration method. The nominal copper valence values were calculated from the oxygen content data by assuming constant valence values of $+2.00$ and -2.00 for mercury and oxygen, respectively. The obtained correlation between T_c and the Cu valence exhibits a parabolic or ''bell shaped'' curve with the maximum in T_c at the Cu valence of $+2.18$. This Cu valence value is quite similar to those reported for other cuprate superconductors and rather supports the ionic model for the excess oxygen in the Hg-O_δ block.

For the $n=2$ and 3 phases, i.e., $HgBa_2CaCu_2O_{6+\delta}$ (Hg-1212) and Hg-1223, there have been less systematic studies on the relation between T_c and the excess oxygen content or the hole concentration. This is primarily because of the difficulty in synthesizing single-phase samples. Morosin *et al.*[10] reported the relation between T_c and conditions of annealing with various oxygen pressures for Hg-12$(n-1)n$ ($n=1$, 2, and 3). Although they succeeded in obtaining samples with various T_c values, their oxygen contents could not be determined. The oxygen content of some Hg-1212 and Hg-1223 samples were investigated by neutron diffraction experiments.[11–13] For instance, the oxygen content of the Hg-1212 sample with a maximum T_c of 127 K was determined to be 0.22.[11] Wagner *et al.*[13] also reported the results of neutron diffraction experiments for Hg-1223 samples with T_c values of 94, 107, and 135 K. Their excess oxygen content δ was determined to be 0.18, 0.22, and 0.27, respectively, and the occupancy of the chain site [1/2, 0, 0] was found to be almost constant ($\sim$0.09).

It has been an issue of particular interest whether the Hg-1223 sample with the highest T_c ($\sim$135 K) is optimally doped or underdoped. It has been pointed out that the dramatic increase in T_c of Hg-1223 above 150 K could be explained by either the optimization of hole concentration in the CuO_2 plane or the substantial change in the electronic structure. If the former hypothesis were correct, a T_c higher than 135 K could be achieved under ambient pressure by simply adjusting the hole concentration. Recently, Carrington *et al.*[14] reported the existence of the anomaly in the temperature dependence of the normal-state electrical resistivity ρ for a single crystal sample of Hg-1223 with $T_c=134$ K. This anomaly was similar to that observed in oxygen-deficient $YBa_2Cu_3O_y$ which was considered to be associated with the formation of the ‘‘spin gap’’ or psuedogap,[15] suggesting that the Hg-1223 sample is still underdoped.

Thermoelectric power of Hg-1223 with a T_c of 134–135 K has also been examined for both polycrystalline samples and single crystals to clarify the doping state.[14,16] By comparing their thermopower values at room temperature S(290 K) of typically 5–10 μV/K with the universal relationship proposed by Obertelli *et al.*,[17] it was suggested that these Hg-1223 samples were still slightly underdoped. On the other hand, Isawa *et al.*[27] reported a negative thermopower value at room temperature for Pb-doped Hg-1223 samples, suggesting that their samples postannealed in oxygen are overdoped. Since absolute values of the thermopower may contain some experimental errors, more systematic studies may be required.

In the present study, we carefully prepared nearly single-phase Hg-1212 and Hg-1223 samples with various oxygen contents by postannealing as-synthesized materials either in various oxygen pressures of 1–800 atm or in reducing atmosphere. The oxygen content of these samples have been determined by an iodometric titration method. T_c, electrical resistivity, and the thermoelectric power of these samples are systematically investigated as a function of excess oxygen content or the effective Cu valence. By comparing these properties for Hg-1223 with those for Hg-1212, it is confirmed that Hg-1223 with the highest T_c value of 135 K is actually optimally doped. The variable range of the excess oxygen content and the Cu valence to induce optimum T_c values in these superconductors are discussed in comparison with our previous results on Hg-1201.

II. EXPERIMENT

Samples were synthesized by direct solid state reaction of a mixed powder of high-purity HgO, BaO, CaO, and CuO. These starting monoxides were mixed to nominal compositions of $HgBa_2Ca_{n-1}Cu_nO_{2n+2}$ ($n=2$ and 3) in a glove box under an Ar atmosphere. The mixed powder was pelletized and encapsulated in a quartz tube under vacuum condition ($<10^{-4}$ Torr). Great care was taken to avoid exposing the pellets to air before they were encapsulated, because BaO easily absorbs moisture and CO_2. Hg-1212 and Hg-1223 samples were sintered at 665 °C for 49–100 h and at 665–710 °C for 100 h, respectively. As was previously reported by Isawa *et al.*,[3] sintering for a long time ($>$100 h) at a relatively low temperature ($\sim$700 °C) is necessary to obtain a nearly single-phase of Hg-1223. In order to prepare samples with various oxygen contents, the as-synthesized samples were then annealed either in reducing atmosphere or in high-pressure oxygen. The annealing conditions are summarized in Tables I and II. For reducing treatments, the sintered samples were encapsulated with Zr metal in an evacuated quartz tube. As was previously demonstrated for the case of Hg-1201,[9] the reduction level could be controlled by the amount of Zr metal. For oxidizing treatments, the oxygen pressure was varied between 1 and 800 atm to control the oxidation level. The annealing temperature was kept relatively low (270–400 °C), because it was found that annealing at higher temperatures resulted in decomposition of the phases. The annealing time was 12–48 h.

All the as-sintered and annealed samples were examined by powder x-ray diffraction (XRD) using Cu $K\alpha$ radiation and the lattice parameters of a and c axes were calculated from XRD data using the least-squares method. Figures 1(a) and 1(b) show the XRD patterns for as-sintered Hg-1212 and Hg-1223 samples, respectively. Most of the peaks can be indexed for the Hg-1212 and the Hg-1223 phases and impurity peaks, for example, from $Ba_2Cu_3O_y$ and $BaCuO_2$ are negligibly small in the patterns. After annealing under the conditions listed in Tables I and II, almost the same patterns as in Figs. 1(a) and 1(b) were observed, confirming that the annealing caused no substantial decomposition of the phases.

The metal compositions of as-sintered samples were analyzed by a scanning electron microscope equipped with an energy-dispersive x-ray analyzer (SEM-EDX). They were found to be Hg:Ba:Ca:Cu=0.96:2.05:0.96:2.00 for Hg-1212 and Hg:Ba:Ca:Cu=0.93:2.05:2.03:3.00 for Hg-1223, which are in good agreement with the nominal compositions. The oxygen contents of both the as-sintered and annealed samples were determined by a conventional iodometric titration method. The detailed procedure of the titration has already been published elsewhere.[18] The oxygen content was calculated on the assumption that the Hg valence is +2.00 and the Hg content is 1.00. The reproducibility for error between parallel experiments in the present iodometric titration method was found to be ±0.01 or less. The Cu valence was then obtained from the oxygen content considering that the valence of excess oxygen is −2.0.

Superconducting critical temperature T_c of the samples was determined by measuring dc magnetic susceptibility using a superconducting quantum interference device (SQUID) magnetometer in a field cooling mode with a field of 10 Oe.

TABLE I. Annealing conditions and observed properties of $HgBa_2CaCu_2O_{6+\delta}$ samples.

Sample	Zr amount[a] (mg)	P_{O_2} (atm)	T_{anneal} (°C)	T_c (K)	Lattice parameters a and c axes (Å)	Oxygen content	S (290 K) (μV)
2-1	188		400	93	3.8641(5), 12.712(2)	6.10	
2-2	250		300	92[b]		6.10[c]	29.7
2-3	63		400	102	3.8616(5), 12.698(3)	6.13	
2-4	125		300	105	3.8603(6), 12.690(3)	6.14	
2-5	62.5		300	121[b]		6.16[c]	11.7
2-6	13		400	122	3.860(1), 12.703(7)	6.19	
2-7	As sintered			127	3.860(1), 12.693(7)	6.21	4.8
2-8		1	300	122[b]		6.24[c]	−1.9
2-9		1	270	121	3.855(1), 12.684(7)	6.24	
2-10		10	270	110	3.854(1), 12.681(7)	6.27	
2-11		100	270	100	3.853(1), 12.675(7)	6.30	
2-12		100	300	100[b]		6.30[c]	−4.4
2-13		800	270	98	3.853(1), 12.683(7)	6.31	

[a] The amounts of annealed samples are 250 mg.

[b] T_c is estimated from the midpoint of resistive transition.

[c] Oxygen contents are estimated from the T_c values.

The electrical resistivity was measured using a conventional four probe method with a current density of approximately 0.02 A/cm^2. The thermoelectric power was measured using a temperature gradient of 0.3–0.5 K. The sample temperature was measured using a calibrated Si diode sensor and the temperature difference between the two ends of the sample was measured by two pairs of Cu-constantan thermocouples. The absolute thermoelectric power was corrected by the thermoelectric power of Cu.

III. RESULTS

A. Variation of lattice parameters and T_c

Figures 2 and 3 show the temperature dependence of dc magnetic susceptibility for some of the Hg-1212 and Hg-1223 samples listed in Tables I and II, respectively. Most of the samples exhibited one distinct superconducting transition with a Meissner volume fraction of 30–60% at low temperatures, indicating that excess oxygen is homogeneously distributed. A slight tail is observed prior to a distinct transition in a few samples. In this case, T_c is defined by the onset of the distinct transition.

Wide variations in T_c are observed for both the phases. For Hg-1212, the as-sintered sample exhibits the highest T_c of 127 K. With increasing the amount of Zr metal or the oxygen pressure in the postannealing process, T_c monotonically decreases to 91 and 98 K, respectively. This indicates that it is possible to vary the hole concentration of Hg-1212 by changing the amount of Zr metal as well as the oxygen pressure, as was demonstrated for Hg-1201.[9] For Hg-1223, the sample annealed in 1 atm oxygen has the highest T_c of 135 K. The T_c value also monotonically decreases to 92 K with increasing the amount of Zr metal. On the other hand, the annealing in oxygen at a higher pressure of 600–800 atm leads to a T_c decrease of only 1–2 K. These variations in

TABLE II. Annealing conditions and observed properties of $HgBa_2Ca_2Cu_3O_{8+\delta}$ samples.

Sample	Zr amount[a] (mg)	P_{O_2} (atm)	T_{anneal} (°C)	T_c (K)	Lattice parameters a and c axes (Å)	Oxygen content	S (290 K) (μV)
3-1	375		300	94[b]		8.17[c]	41.0
3-2	250		300	98		8.17	
3-3	63		400	101	3.8860(5), 15.887(3)	8.16	
3-4	125		300	105	3.858(1), 15.873(8)	8.20	
3-5	125		300	104[b]		8.20[c]	33.8
3-6	As sintered			132	3.8541(5), 15.855(4)	8.25	11.4
3-7		1	300	135	3.854(1), 15.855(8)	8.29	
3-8		1	300	135[b]		8.29[c]	5.2
3-9		600	300	134	3.8538(7), 15.865(4)	8.30	
3-10		800	300	133[b]		8.30[c]	1.9

[a] The amounts of annealed samples are 250 mg.

[b] T_c is estimated from the midpoint of resistive transition.

[c] Oxygen contents are estimated from the T_c values.

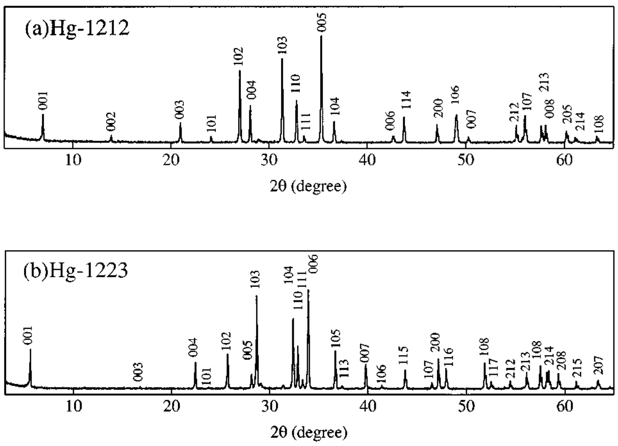

FIG. 1. Powder x-ray diffraction patterns for as-sintered $HgBa_2Ca_{n-1}Cu_nO_{2(n+1)+\delta}$ [(a) $n=2$ and (b) $n=3$] samples.

T_c for Hg-1223 as well as Hg-1212 induced by annealing in various oxygen pressures are comparable to those previously reported by Morosin *et al.*[10]

Figures 4 and 5 show the relations of the a-axis and c-axis lattice parameters with the oxygen content determined by the iodometric titration method for Hg-1212 and Hg-1223, respectively. Both the a-axis and c-axis lattice parameters of Hg-1212 are found to decrease monotonically with an increase in the oxygen content, similar to the case for Hg-1201.[9] This reinforces that excess oxygen is homogeneously distributed in these samples. A similar tendency is observed for Hg-1223, although the variations in a-axis and c-axis parameters are rather small for the samples annealed in oxidizing atmosphere.

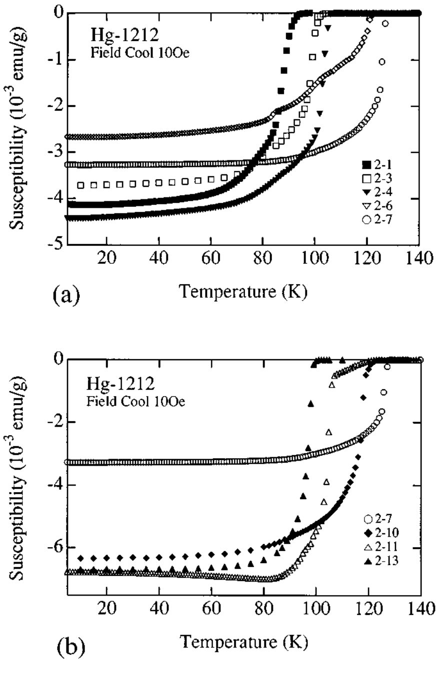

FIG. 2. Temperature dependence of the dc magnetic susceptibility for (a) reduced and (b) oxidized $HgBa_2Ca_{n-1}Cu_2O_{6+\delta}$ samples.

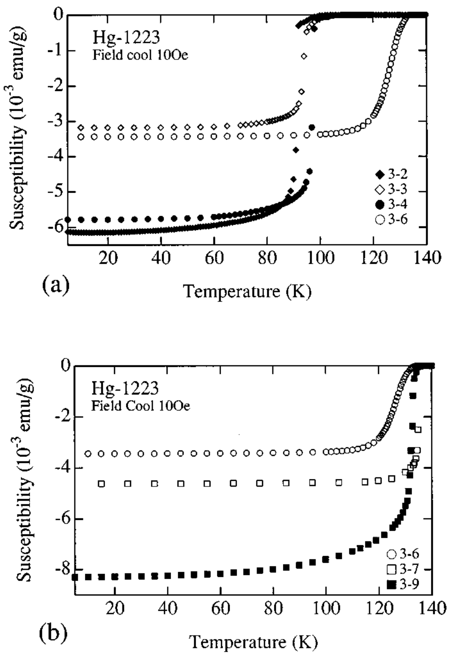

FIG. 3. Temperature dependence of the dc magnetic susceptibility for (a) reduced and (b) oxidized $HgBa_2Ca_2Cu_3O_{8+\delta}$ samples.

Figures 6(a) and 6(b) show the relations of T_c with the excess oxygen content δ and the a-axis lattice parameter for Hg-1212 and Hg-1223. The relations for Hg-1201 which has been published elsewhere[9] are also indicated. Parabolic or ''bell-shaped'' relations are observed in both figures for Hg-1212 as well as Hg-1201, indicating that their doping state can be extensively varied from underdoped to highly overdoped regimes. On the other hand, Hg-1223 seems to exhibit

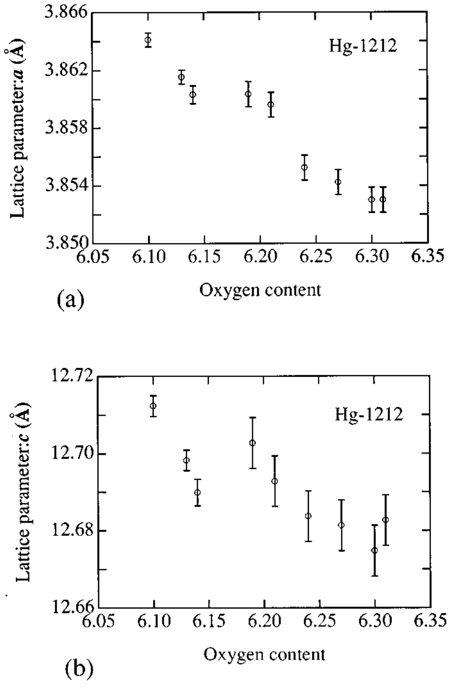

FIG. 4. Dependence on the oxygen content of (a) a-axis and (b) c-axis lattice parameters of $HgBa_2CaCu_2O_{6+\delta}$ samples.

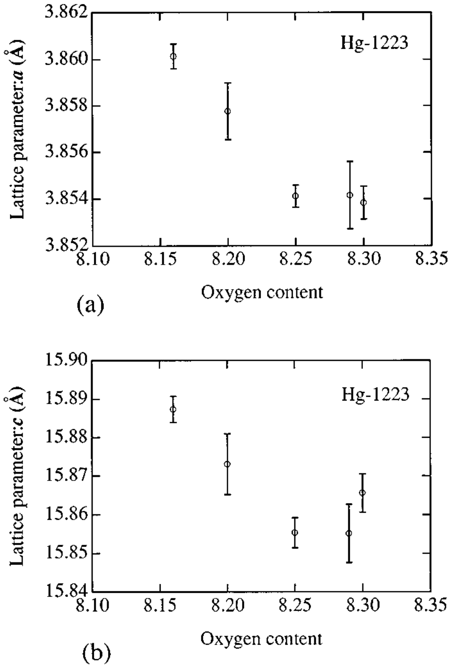

FIG. 5. Dependence on the oxygen content of (a) a-axis and (b) c-axis lattice parameters of $HgBa_2Ca_2Cu_3O_{8+\delta}$ samples.

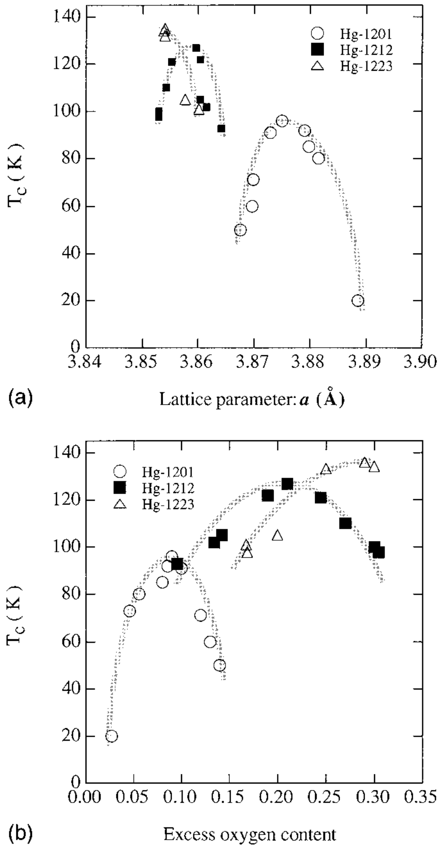

FIG. 6. Relation of T_c with (a) the excess oxygen content and (b) the a-axis lattice parameter for $HgBa_2Ca_{n-1}Cu_nO_{2(n+1)+\delta}$ ($n=1$, 2, and 3) samples. The data for $HgBa_2CuO_{4+\delta}$ is taken from Ref. 9. The shaded lines are a guide to the eye.

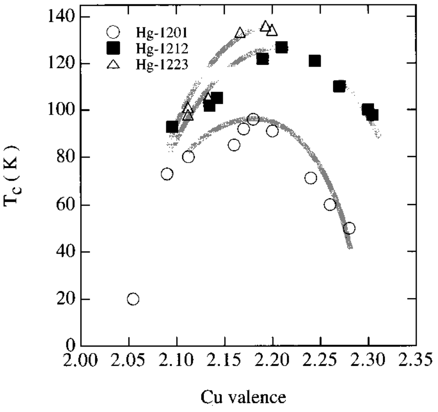

FIG. 7. Relation of T_c with the nominal Cu valence for $HgBa_2Ca_{n-1}Cu_nO_{2(n+1)+\delta}$ ($n=1$, 2, and 3) samples. The nominal Cu valence is obtained from the oxygen content under the assumption that hole carriers are homogeneously distributed to all the CuO $_2$ planes. The data of $HgBa_2CuO_{4+\delta}$ is taken from Ref. 9. The shaded lines are a guide to the eye.

only a half of the parabola. For the Hg-1223 sample annealed in high-pressure oxygen, only a slight increase in the oxygen content is observed. It is found that the maximum T_c of 127 K for Hg-1212 is realized at $\delta=0.21$ which is in good agreement with the value of 0.22 previously determined for a Hg-1212 sample with the same T_c by neutron diffraction (ND).[12] The excess oxygen content for the Hg-1223 sample with the maximum T_c of 135 K is 0.29, comparable to the value of 0.27 reported by Wagner *et al.*[13] in their ND study.

Figure 7 shows the relations between T_c and the nominal Cu valence for Hg-1212 and Hg-1223 as well as Hg-1201. The Cu valence was calculated on the assumption that hole carrier is homogeneously supplied to each CuO_2 plane. It is clear that all the phases exhibit their maximum T_c values at the same Cu valence of 2.18–2.21.[19] This value agrees well with those reported for other high-T_c superconductors.[20,21]

B. Variation of resistivity and thermoelectric power

Figure 8 shows the temperature dependence of electrical resistivity ρ for Hg-1212 samples. Although the resistivity

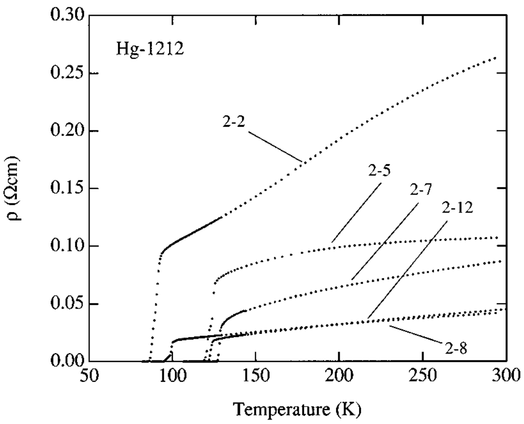

FIG. 8. Temperature dependence of the electrical resistivity for $HgBa_2CaCu_2O_{6+\delta}$ samples.

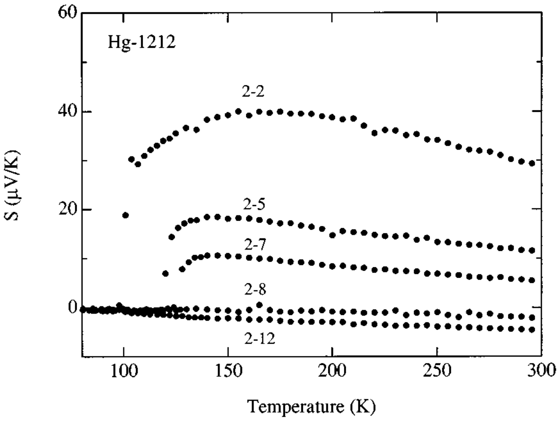

FIG. 9. Temperature dependence of the thermoelectric power for $HgBa_2CaCu_2O_{6+\delta}$ samples.

value of the order of 10^{-2} Ω cm is substantially larger than that of typically 10^{-3} Ω cm expected for good polycrystal samples of high-T_c superconductors, all the samples exhibit a positive temperature dependence. Moreover, the resistivity at room temperature systematically decreases with increasing the excess oxygen content, indicating that the resistivity actually reflects the variation in the in-plane resistivity ρ_{ab} in spite of substantial contribution of the grain-boundary resistance. For the most underdoped Hg-1212 sample, an apparent downward deviation from a linear ρ-T curve is observed. This anomaly appears similar to those reported in oxygen-deficient underdoped $YBa_2Cu_3O_{7-\delta}$ (YBCO) single crystals.[15] These anomalies have been considered to be caused by the opening of a pseudogap in the spin excitation spectrum (''spin gap'').

Figure 9 shows the temperature dependence of thermoelectric power S for Hg-1212 samples. The peculiar temperature dependence is similar to those reported for other high-T_c superconducting cuprates.[22,23] The thermoelectric power monotonically decreases with increasing the degree of oxidation and shows negative values in the overdoped region. It has been proven both experimentally[17] and theoretically[24] that the thermoelectric power at room temperature generally decreases with increasing the hole concentration in high-T_c superconducting cuprates. Obertelli *et al.*[17] proposed a universal relation curve between the thermoelectric power at 290 K, S(290 K), and the hole content or T_c normalized by the optimum T_c value. (The similar relation is also proposed by Matsuura.[25]) The universal relation curve shows that S(290 K) for optimally doped samples is slightly larger than zero, approximately 3 μV/K, and S(290 K) for underdoped and highly overdoped samples is positive and negative, respectively. In Fig. 10, S(290 K) and T_c are plotted as a function of the Cu valence for Hg-1212 samples. S(290 K) for the optimally doped Hg-1212 sample is approximately 5 μV/K which is close to the value by Obertelli *et al.*[17] It is evident that corresponding to the increase in the Cu valence, our Hg-1212 samples show the variation in S(290 K) similar to that of the universal relation. This reinforces that the doping state of Hg-1212 is actually controlled from the underdoped to the overdoped region. It is also noted that the highly overdoped Hg-1212 samples show negative S(290 K) values like other superconducting cuprates.

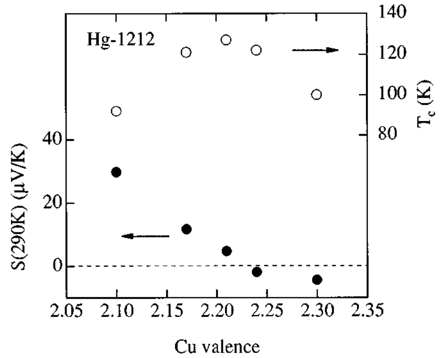

FIG. 10. Variation of thermoelectric power at 290 K, S(290 K), as well as T_c with the Cu valence for $HgBa_2CaCu_2O_{6+\delta}$ samples.

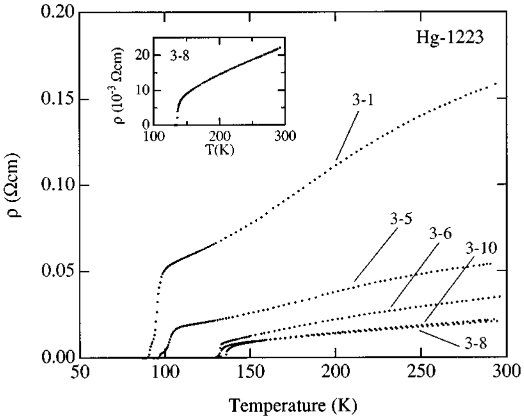

FIG. 11. Temperature dependence of the electrical resistivity for $HgBa_2Ca_2Cu_3O_{8+\delta}$ samples. The resistivity for the sample with $T_c = 135$ K is indicated in the inset.

Figure 11 shows the temperature dependence of the electrical resistivity for Hg-1223 samples with various oxygen contents. A systematic decrease in ρ at room temperature with increasing the oxygen content is also observed. Furthermore, the reduced samples as well as the as-sintered sample exhibit an apparent downward deviation from the linear ρ-T curve which is similar to that observed in underdoped Hg-1212. In order to clearly find the temperature at which the anomaly begins, $(\rho(T)-\rho(0))/\alpha T$ is plotted versus temperature in Fig. 12, as was proposed by Ito *et al.*[15] Here, $\rho(0)$ is the resistivity value at 0 K extrapolated from the T-linear part at higher temperatures and α is the slope of the T-linear part. It is found that the charasteristic temperature T_0 at which the anomaly starts monotonically decreases with increasing the oxygen content. This systematic variation in T_0 indicates that the observed anomaly has the same origin as that in oxygen-deficient YBCO, i.e., spin gap or psuedogap. The T_0 values of 220–280 K are slightly larger than those observed for YBCO with $\delta = 0.1$–0.3 and $T_c/T_c^{\max} = 0.95$–0.7.[15] These larger T_0 values seem consistent with the spin-gap opening temperature T^* which has recently been found to be much higher than that in YBCO by NMR measurements.[26] For Hg-1223 single crystals with $T_c = 134$ K, a much larger T_0 value of 370 K was previously reported by Carrington *et al.*,[14] although they did not observe a systematic T_0 variation. In contrast, no clear anomaly is

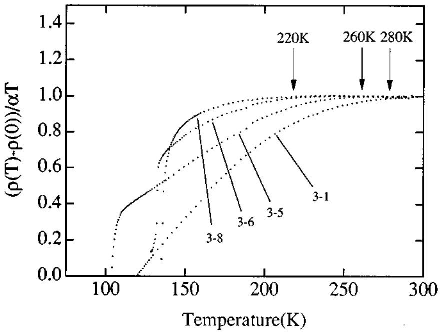

FIG. 12. $(\rho(T)-\rho(0))/\alpha T$ as a function of temperature for $HgBa_2Ca_2Cu_3O_{8+\delta}$ samples. Here, $\rho(0)$ is the resistivity value at 0 K extrapolated from the T-linear part at higher temperatures and α is the slope of the T-linear part.

observed for our sample with $T_c = 135$ K and the sample with a slightly larger oxygen content.

Figure 13 shows the temperature dependence of the thermoelectric power for Hg-1223 samples. The temperature dependence which is similar to that observed in Hg-1212 as well as other high-T_c cuprates is observed. In Fig. 14, S(290 K) as well as T_c is plotted as a function of the Cu valence. It is clear that S(290 K) systematically decreases with increasing the Cu valence, as observed for Hg-1212, suggesting that it also follows the universal relation proposed by Obertelli *et al.*[17] The sample with the highest T_c of 135 K shows an S(290 K) value of approximately 5 μV/K which is almost the same as the value observed for the optimally doped Hg-1212 sample in Fig. 10. A substantially smaller value of approximately 2 μV/K is observed for the sample with the largest oxygen content, although the value is still positive.

IV. DISCUSSION

It is found that T_c and the transport properties of Hg-1212 and Hg-1223 phases can be extensively varied by postannealing in either reducing or oxidizing atmosphere, as was previously demonstrated for Hg-1201.[9] The results of titration confirm that these variations result from the wide variations in the excess oxygen content δ or the Cu valence. The Hg-1212 samples exhibit a change in δ from 0.10 to 0.31. These lower- and upper-limit values are comparable to the values of 0.08 and 0.35 which were previously determined by ND for underdoped and overdoped samples, respectively.[12] The variation in δ from 0.16 to 0.30 for the Hg-1223 samples also well compares with the values of 0.19 and 0.27 reported in the recent ND study by Wagner *et al.*[13]

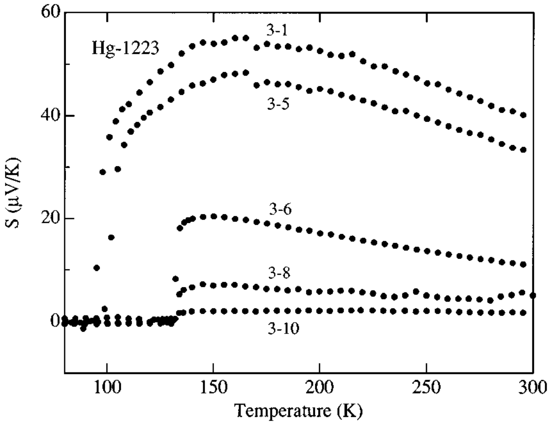

FIG. 13. Temperature dependence of thermoelectric power for $HgBa_2Ca_2Cu_3O_{8+\delta}$ samples.

It is clear in Fig. 6 that the δ value increases with the number of the CuO_2 plane n in the unit cell. A similar tendency has also been observed in previous ND studies on different phases.[6,12,13] From the results of Fig. 7, this tendency seems to result from the fact that almost the same range of the Cu valence is allowed for all the phases. In the Hg-1223 phase, the Cu valence is exceptionally limited below approximately 2.20. As indicated in Fig. 6, the a-axis parameter systematically decreases with increasing δ for each phase. However, the a-axis parameter for the Hg-1223 sample with $T_c = 135$ K of 3.853 Å is very close to the intrinsic size of the CuO_2 plane of 3.855 Å observed in the infinite layer compound $CaCuO_2$.[29] Thus the difficulty in further shrinking the a-axis parameter possibly limits the upper range of δ allowed for Hg-1223 as well as overdoped Hg-1212. Another reason for this upper limit may be the stability of the $Hg\text{-}O_\delta$ charge reservoir layer itself, because mercury favors twofold oxygen coordination rather than threefold coordination. This latter reason seems more plausible, since it was reported that Hg-1223 incorporates more oxygen by partially substituting cations with higher valences such as Pb and Re for the Hg site.[27,28]

The results of thermoelectric power measurements indicate that Hg-1212 follows the universal relation between S(290 K) and $T_c^{\max}/T_c$ or the hole concentration proposed by Obertelli *et al.*[17] That is to say, S(290 K) decreases monotonically with increasing the hole concentration and exhibits a slightly positive value of approximately 3–5 μV/K for optimally doped samples. Our Hg-1223 sample with the highest T_c of 135 K has almost the same S(290 K) value of approximately 5 μV/K as the optimally doped Hg-1212 sample. The anomaly in the electrical resistivity probably associated with the pseudogap or the spin gap is not observed for this sample as shown in Fig. 11. Considering these facts, we can conclude that the Hg-1223 sample with $T_c = 135$ K is actually optimally doped. The even smaller S(290 K) value for the Hg-1223 sample annealed in the highest oxygen pressure indicates that the doping state of Hg-

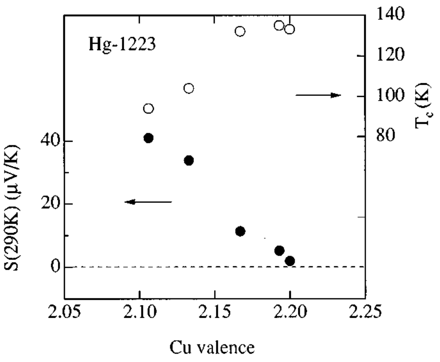

FIG. 14. Variation of S(290 K) as well as T_c with the Cu valence for $HgBa_2Ca_2Cu_3O_{8+\delta}$ samples.

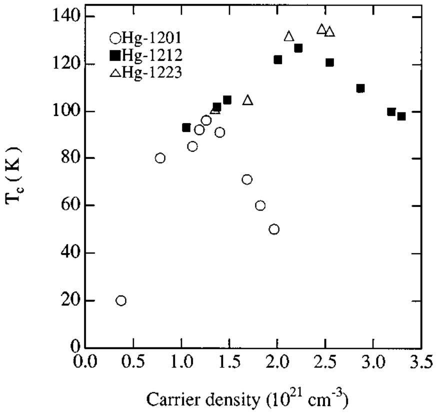

FIG. 15. T_c as a function of the normal carrier density calculated from the nominal Cu valence for $HgBa_2Ca_{n-1}Cu_nO_{2(n+1)+\delta}$ samples.

1223 can be varied to a slightly overdoped regime.

As mentioned earlier, previous ND studies on Hg-12($n-1$)n ($n=1$–3) indicated that there exists approximately 0.1 chain-site [1/2, 0, 0] oxygen associated with the Cu substitution to the Hg site.[6,13] Our previous titration measurements for Hg-1201 samples revealed that their excess oxygen content can be reduced to as small as 0.025,[9] suggesting a much smaller amount of chain-site oxygen. The EDX results for the present Hg-1212 and Hg-1223 samples suggest possible substitution of approximately 5% Hg-site by Cu and thus the existence of chain-site oxygen. However, it should be noted that all three systems, i.e., $n=1$, 2, and 3 in Hg-12($n-1$)n have similar parabolic T_c versus Cu valence curves as shown in Fig. 7 and exhibit optimum T_c values at the same Cu valence of 2.18–2.21 which is also comparable to the values for other cuprate superconductors. This fact suggests that the amount of chain-site oxygen in the present Hg-1212 and Hg-1223 samples is as small as that of our Hg-1201 samples. Furthermore it indicates that the chain-site oxygen, if any, supplies two holes as is the case for the oxygen at the interstitial [1/2, 1/2, 0] site. Xiong *et al.*[8] reported that their Hg-1201 samples have the excess oxygen much larger than that expected from the simple ionic model $p=2\delta$ (p: hole concentration). In contrast, the correlation in Fig. 7 clearly indicates that the assumption of $p=2\delta$ is appropriate in our samples.

One of the most remarkable universal correlations concerning T_c in high-T_c cuprate superconductors is the linear relation between T_c and the muon spin relaxation rate $\sigma(T\rightarrow 0)\propto n_s/m^*_{ab}$ (superconducting carrier density divided by in-plane effective mass) first reported by Uemura *et al.*[30] They demonstrated that the $n=1$, 2, and 3 compounds lie on the same linear line in the underdoped region, while T_c saturates near the optimally doped region. The higher optimum T_c values observed as n increases apparently correspond to larger n_s/m^*_{ab} values, although these compounds included those with different charge reservoir blocks. In Fig. 15, we plot T_c of the present Hg-12($n-1$)n ($n=1,2,3$) samples versus the normal carrier density estimated from the nominal Cu valence and lattice parameters. The underdoped and nearly optimally doped samples appear to lie on the same curve. Considering possible systematic deviation of the estimated carrier density from the actual normal carrier density which is basically equivalent to n_s in the underdoped region, this result seems consistent with Uemura's relation. Uemura interpreted the universal relation as evidence for superconductivity in the limit of Bose Einstein (BE) condensation for underdoped cuprate superconductors.[31] He also pointed out that the optimally doped state is given as the crossover point between BE condensation and conventional BCS condensation. The striking fact that this crossover point, i.e., the optimally doped state, is determined only by the same Cu valence in each CuO_2 layer of approximately 2.20 seems consistent with the picture of BE condensation in real space rather than BCS condensation in momentum space.[31]

V. CONCLUSIONS

We have determined the oxygen content and the Cu valence by iodometric titiration of single-phase $HgBa_2Ca_{n-1}Cu_nO_{2(n+1)+\delta}$ ($n=2,3$) superconductors post-annealed under various conditions in either reducing or oxidizing atmosphere. Hg-1212 is found to exhibit a parabolic or ''bell-shaped'' relationship between T_c and the nominal Cu valence similar to that observed for Hg-1201, while Hg-1223 exhibits only a half of the parabola. Systematic evolution of the temperature dependence of the resistivity and the thermoelectric power is observed for both Hg-1212 and Hg-1223. In particular, both the phases in the underdoped region clearly exhibit the anomaly in the resistivity probably associated with the formation of pseudogap or spin gap which is similar to that previously reported in oxygen-deficient YBCO. The absence of this anomaly as well as the S(290 K) value as compared with those of Hg-1212 samples with various doping states confirms that the Hg-1223 samples with the highest T_c of 135 K and even larger Cu valence are optimally doped and slightly overdoped, respectively.

The optimum T_c values for both Hg-1212 and Hg-1223 as well as Hg-1201 are attained at the same nominal Cu valence of approximately 2.20 which is also comparable to those reported for other cuprate superconductors. This coincidence of the nominal Cu valence for the optimally doped Hg-12($n-1$)n ($n=1$, 2, and 3) samples suggests that the simple ionic model where each excess oxygen supplies two holes is appropriate in the present Hg-12($n-1$)n samples, which contrasts the previous results on the oxygen content analysis for Hg-1201 reported by Xiong *et al.* The same Cu valence for optimally doped samples as well as the universal relation of T_c with the normal carrier concentration observed in underdoped Hg-12($n-1$)n samples seems consistent with the superconductivity in the limit of Bose Einstein condensation as previously pointed out by Uemura *et al.*

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