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High Pressure Synthesis of Hg1223 Superconductor under Highly Oxidizing Atmosphere

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Abstract

We tried to prepare the mercury-based superconductor, $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg1223), under highly oxidizing atmosphere using a high pressure technique. Samples containing Hg1223 as the main phase with $T_C = 90$–122 *K were obtained. CuO and* a new phase *were included in the samples as impurities. The* a-*axes of the samples were shorter than the values ever reported for Hg1223 with* $T_C = 135$ *K. These results suggest that our Hg1223 samples had excess hole concentrations, i.e. they are over-doped. The irreversibility field (*B_{irr}*) was measured for two samples with* $T_C = 118$ *and 94 K. They had almost the same normalized temperature (*$1-T/T_C$*) dependence of* B_{irr}*.* © *1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

Extensive studies have been carried out so far on the synthesis and physical properties of the high temperature cuprate superconductors. Their structures are constructed by alternating stacks of the infinite layer block and the charge reservoir block. It is considered that the latter block supplies hole carrier to the CuO_2 plane in the former block. This covalent CuO_2 plane, embedded within a lattice of ionic charges, can be expressed as $[CuO_2]^{+p-2}$. The obtained correlation between T_C and p exhibits a parabolic or 'bell-shaped' curve with the maximum in T_C at $p \sim 0{\cdot}2$.[1] The carrier concentration range with $p > 0{\cdot}2$, $p \cong 0{\cdot}2$ and $p > 0{\cdot}2$ are called as under-doped, optimally doped and over-doped regions, respectively. From the viewpoint of practical application, not only T_C but also magnetic properties should be concerned. Particularly, the irreversibility field (B_{irr}) is an important characteristic. It is proved that B_{irr} versus the normalized temperature ($1-T/T_C$) is improved by hole-doping, i.e. the increase of p.[2] On the other hand, T_C in the over-doped region decreases with increasing p. Thus the main concern comes to the p region slightly larger than 0·2.

$HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg1223) exhibits the highest T_C (= 135 K) of all currently known superconductors.[3] Preparation of Hg1223 with p larger than 0·2 is difficult under ambient pressure.[1] Fujinami *et al.*[4] reported that the over-doped Hg1223 with $p > 0{\cdot}2$ was successfully obtained by utilizing a high pressure technique. They prepared Hg1223 with $T_C = 97$ K from the highly oxidized precursor. For the cuprate superconductors, it is generally known that the size of the CuO_2 plane tends to decrease with an increase of hole concentration,[5] and an over-doped sample exhibits a negative thermoelectric power.[6] They claimed that the doping state of the sample was located in the over-doped region from the observation of a shrinkage in the lattice parameter a and a negative thermoelectric power.

In the present work, we tried to investigate the magnetic property of over-doped Hg1223 in detail. Hg1223 samples were prepared in highly oxidizing atmosphere using a high pressure technique. The partial oxygen pressure during synthesis was systematically controlled by changing the composition of starting materials in a closed system.

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2 Experimental

The starting materials, HgO, BaO_2, CaO, CuO and Cu, were mixed with a nominal composition of $HgBa_2Ca_2Cu_3O_y$ in an agate mortar. The nominal oxygen content, y, was controlled by varying the ratio Cu/CuO. The mixture was pressed into a pellet. Then the pellet was tightly packed into a gold capsule covered by a NaCl sleeve and placed into a pyrophyllite container equipped with an internal carbon heater. Since the sample during high-pressure heat-treatment is closed in the NaCl sleeve which confines oxygen, the nominal oxygen content, y, influences the phase formation. The high-pressure synthesis was carried out in a cubic-anvil-type apparatus at 1000°C and 6 GPa for 4 h. Some as-prepared samples were subjected to post-annealing treatment in flowing argon gas at 250°C for 10 h in order to further tune the hole-doping level.

Identification of crystallized phases and structural analysis were carried out by X-ray powder diffraction (XRD) using CuK_α radiation and the lattice parameters of a and c axes were calculated from XRD data using the least-squares method. Microstructure was analyzed with a scanning electron microscope (SEM). DC magnetic susceptibility was measured using a superconducting quantum interference device (SQUID) magnetometer in a magnetic field of 20 Oe. Magnetic hysteresis loop was taken using a vibrating sample magnetometer (VSM) with a sweep rate of $0{\cdot}7\ T\,\mathrm{min}^{-1}$ at various temperatures.

3 Results and Discussion

Figure 1 shows the XRD patterns of the samples with the nominal composition of $HgBa_2Ca_2Cu_3O_y$ ($8{\cdot}0 \leq y \leq 8{\cdot}5$). In the case of $y = 8{\cdot}0$, $HgBa_2Ca_3Cu_4O_{10+\delta}$ (Hg1234) phase is mainly observed. In the range of $8{\cdot}1 \leq y \leq 8{\cdot}5$, Hg1223 as the main phase and a relatively small amount of impurity phases are seen. The lattice parameters of Hg1223 are listed in Table 1. The a parameter decreased with increasing y. These lattice parameters are comparable with the reported values.[4,7] The peaks of the impurity phases grow with increasing y. The peaks due to CuO were marked by the open circles in Fig. 1. It is considered that the peaks at $2\theta = 20.5$, 31.0, 37·5 and 51·2° (marked by the crosses) come from *a new phase*, denoted as 'X-phase', which is stabilized in a highly oxidizing atmosphere. Structural and composition analysis of this new phase is now in progress.

The samples with $y = 8{\cdot}1-8{\cdot}5$ showed large Meissner signal with a single-step transition (>20% full Meissner at 5 K). It indicates that the

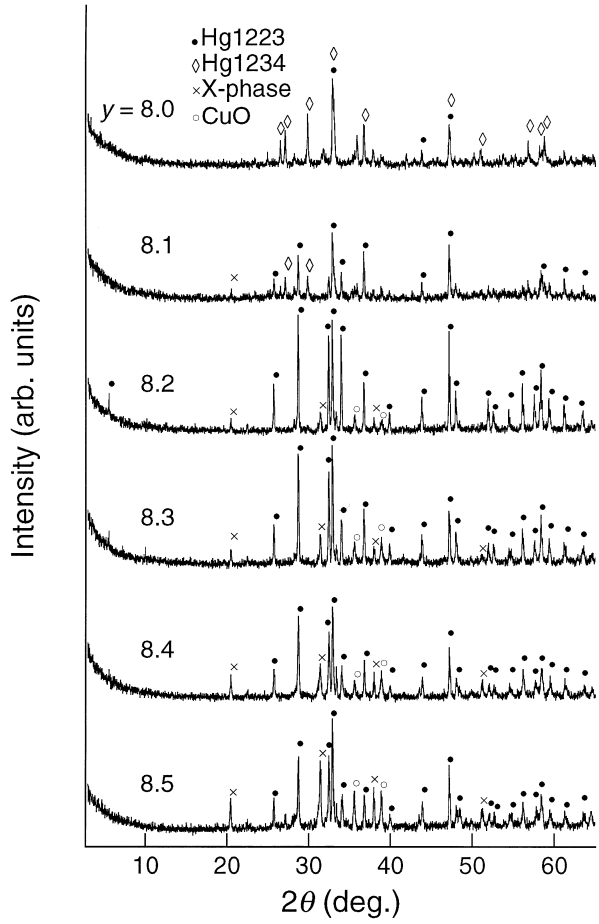

Fig. 1. XRD patterns of the prepared samples. The numbers in the graph indicate the nominal oxygen content, y, of the starting materials.

observed superconductivity surely comes from the main phase in the samples. The observed T_C is also listed in Table 1. T_C decreases with increasing y. For the sample with $y = 8{\cdot}1$, T_C and the a parameter are smaller than the values reported for Hg1223 with highest T_C (= 135 K).[1] It is likely that 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 CuO_2 planes and the incorporation of holes into the planes.[5] Therefore, the shrunk a-axis and lowered T_C in our sample with $y = 8{\cdot}1$ suggest that the sample is over-doped. The sample with $y = 8{\cdot}4$, which has much lower T_C and shorter a-axis than the $y = 8{\cdot}1$ sample, is supposed to be further over-doped.

The samples with $y = 8{\cdot}2$ and 8·4 were post-annealed in flowing argon gas. The temperature dependence of the magnetic susceptibility for as-prepared and Ar-annealed samples are shown in Fig. 2. The Ar-annealed samples have a T_C of 132 K, implying that oxygen ions were removed by the post-annealing and subsequently the hole concentration decreased to the optimal level. In the XRD patterns of the post-annealed samples, the main phase had the 1223 structure, indicating that

decomposition of Hg1223 did not occur during the post-annealing. The lattice parameters of the post-annealed samples are listed in Table 1. The *a*-axis parameter increased by the post-annealing. The observed increases in T_C and the *a*-axis parameter for the post-annealed samples support that the as-prepared samples with $y = 8{\cdot}2$ and 8·4 were over-doped.

Table 1. Nominal oxygen content, y, T_C, and the lattice parameters of the Hg 1223 phase in the prepared samples

	As-prepared			*Ar-annealed*		
y	T_C (K)	a (Å)	c (Å)	T_C (K)	a (Å)	c (Å)
8·1	122	3·853(2)	15·823(9)	—	—	—
8·2	118	3·853(1)	15·833(6)	132	3·853(1)	15·828(5)
8·3	100	3·852(2)	15·818(9)	—	—	—
8·4	94	3·850(2)	15·787(10)	132	3·853(1)	15·829(5)
8·5	90	3·847(4)	15·784(10)	—	—	—

Magnetic hysteresis loop was measured for the as-prepared samples with $y = 8{\cdot}2$ and $y = 8{\cdot}4$. The field dependence of ΔM [magnetization difference; defined as $M^+ - M^-$ (emu cm^{-3})] as a function of applied field at various temperatures are shown in Fig. 3. The critical current density J_C was calculated using the Bean model.[8] The grain size, which was estimated from the SEM observation of fractured surface, was approximately 10 μm for both cases of $y = 8{\cdot}2$ and 8·4. B_{irr} was determined as the field where ΔM fell below 0·03 emu cm^{-3}, corresponding to $J_C \cong 10^3$ A cm^{-2}. Figure 4 shows B_{irr} versus $(1 - T/T_C)$ for the as-prepared samples. The normalized temperature dependence of B_{irr} of the samples were almost the same. Karppinen *et al.*[10] previously compared B_{irr} of their as-prepared sample (over-doped; $T_C = 107$ K) with their Ar-annealed

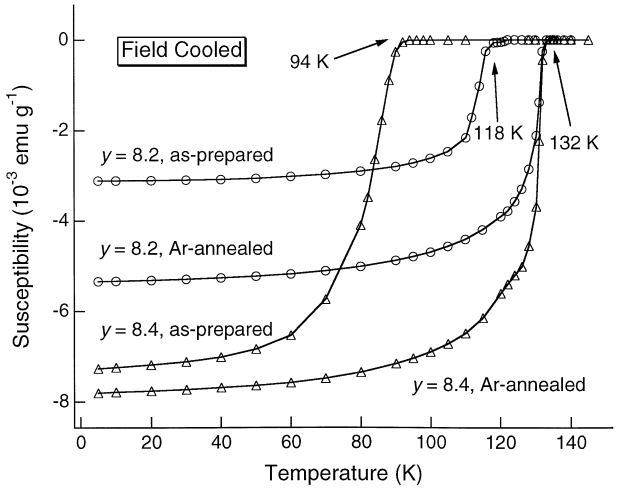

Fig. 2. Temperature dependence of the magnetic susceptibility of as-prepared and Ar-annealed Hg1223 samples measured in the applied field of 20 Oe.

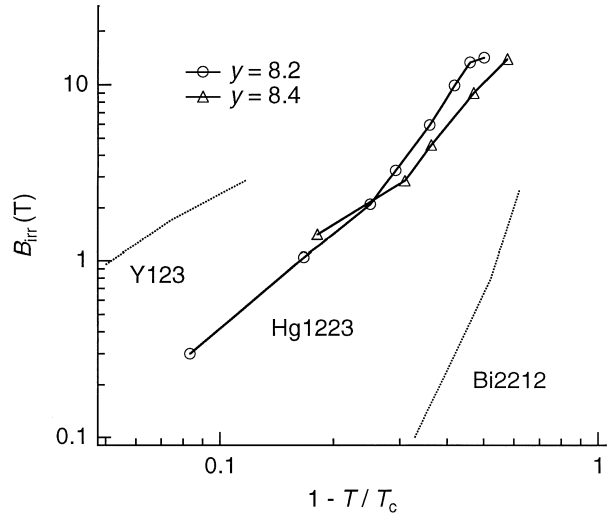

Fig. 4. Irreversibility field (B_{irr}) as a function of normalized temperature $(1 - T/T_C)$ for the present as-prepared Hg1223 samples, $Bi_2Sr_2CaCu_2O_8$ (Bi2212) and $YBa_2Cu_3O_{6.9}$ (Y123).[9]

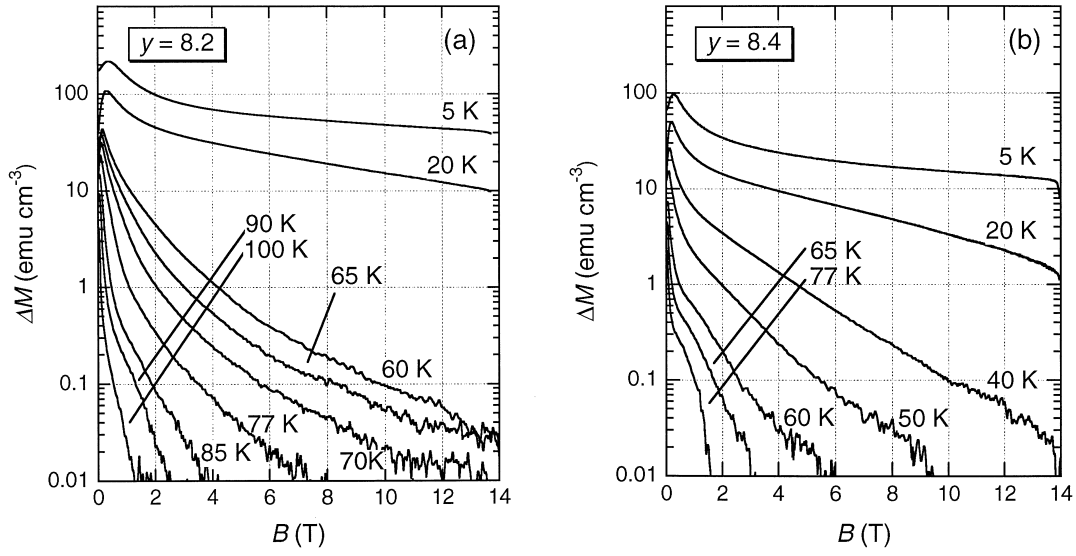

Fig. 3. Field dependence of ΔM at various temperatures for as-prepared samples with (a) $y = 8{\cdot}2$ and (b) $y = 8{\cdot}4$.

one (under-doped; $T_C = 118$ K) and reported that B_{irr} of the former sample was higher than that of the latter in the B_{irr} versus $(1-T/T_C)$ characteristics. They explained that no cation removal occurred during Ar-annealing and the variation of B_{irr} came from variation in the hole concentration, that is, the oxygen content. If the difference in the doping level for our samples with $y = 8{\cdot}2$ and $8{\cdot}4$ only comes from the different oxygen content, it is expected that the sample with $y = 8{\cdot}4$ should be better than the $y = 8{\cdot}2$ sample in the B_{irr} versus $(1-T/T_C)$ characteristics. However, no difference was observed in our experiments. Probably, the doping level is changed not only by the oxygen content. Other factors should be taken into consideration. For example, it could be possible that deviation in the cation composition from stoichiometry, i.e. Hg:Ba:Ca:Cu = 1:2:2:3, brings about a change in the doping level. Actually, the growth of peaks due to impurities such as CuO and 'X-phase' with the increase in y was seen in the XRD patterns, as shown in Fig. 1. The formation of impurities might be an implication of the deviation in the composition of the Hg1223 phase.

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