Crystal Growth and Characterization of the Model High-Temperature Superconductor HgBa₂CuO_{4+ δ}**

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Since the discovery of high-transition-temperature (T_c) superconductivity in La_{2-x}Ba_xCuO₄ in 1986,^[1] the study of the lamellar copper oxides has remained at the forefront of condensed matter physics. Apart from their unusually high values of $T_{\rm c}$, these materials also exhibit a variety of complex phenomena and phases. This rich behavior is a consequence of the lamellar crystal structures, formed of copper-oxygen sheets separated by charge reservoir layers, and of the strong electron-electron correlations in the copper-oxygen sheets. After two decades of intensive research, which has stimulated many valuable new insights into correlated electron systems in general, there remains a lack of consensus regarding the correct theory for high- T_c superconductivity. The ultimate technological goal of room-temperature superconductivity might only be attained after the development of a deeper understanding of the mercury-based compounds HgBa₂Ca_{*n*-1}Cu_{*n*}O_{2*n*+2+ δ}, which currently exhibit the highest T_c values. One very important issue in this regard is the role of electronic versus chemical and structural inhomogeneities in these materials, and the associated need to separate material-specific properties from those that are essential to superconductivity.^[2-5] Unfortunately,

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[**] The authors acknowledge discussions with H. Eisaki and T. H. Geballe. This work was supported by the DOE under Contract No. DE-AC02-76SF00515 and by the NSF under Grant No. 0405655. there has been remarkably little scientific work on the mercury-based compounds because sizable crystals have not been available; quantitative measurements of any kind would be invaluable benchmarks for testing the theories of high- T_c superconductivity.

The compounds HgBa₂Ca_{*n*-1}Cu_{*n*}O_{2*n*+2+ δ} can be viewed as model systems not only because of their record high-*T*_c values, but also because of their high-symmetry crystal structures. Of particular interest is the simplest member of this materials family, HgBa₂CuO_{4+ δ} (Hg1201), which possesses only one copper–oxygen sheet per unit cell (*n* = 1), as shown schematically in Figure 1a. The largest crystals obtained by previous growth methods do not exceed 1 mm³, and hence are insufficient in size for detailed studies by many experimental tech-



Figure 1. a) Schematic of the tetragonal Hg1201 crystal structure. b) Photograph of a large Hg1201 crystal that was cleaved into two pieces of about equal size. The two pieces have a total mass of nearly 1 g, corresponding to a volume of approximately 100 mm³. c) a–b plane and d) a–c plane Laue patterns.

niques. Here we report a novel recipe for the growth of Hg1201 crystals as well as detailed sample characterization results, including initial inelastic magnetic neutron scattering data. We note that samples grown by the method described here have already enabled recent optical conductivity,^[6] inelastic X-ray scattering,^[7] and angle-resolved photoemission^[8] studies.

One of the major difficulties in growing Hg1201 crystals stems from the high vapor pressure of mercury oxide during

the crystal growth, which requires encapsulation or high-pressure techniques. In addition, sample preparation must be handled with special care because mercury is highly toxic. Various growth techniques are summarized in Table 1. The high-static-pressure synthesis technique (belt-type high-pressure apparatus) is very effective not only for Hg1201, but also for the four- and five-layer (n = 4, 5) compounds.^[9] However, this technique is not well-suited to the growth of single crystals. A relatively new technique, based on the application of high Ar gas pressure up to 11 kbar (1 bar = 100 000 Pa), allows the growth of single crystals.^[10] However, because of the small chamber size of the high-pressure apparatus (several cm³), the crystal size is limited. Conventional encapsulation also allow crystal growth.^[11-19] Based on this method, several improvements have been developed, including the use of a three-zone furnace to control the partial pressure of mercury; all these efforts resulted in either powder samples or crystals sized smaller than one cubic millimeter.^[18,20-23] In contrast to the sophisticated methods mentioned above, we adopted a conventional encapsulation approach. The problems usually associated with the high vapor pressure of mercury oxide were solved by using thick-walled high-quality quartz tubes, carefully dosing and mixing HgO with the precursor, and finding an adequate temperature profile for the crystal growth, thus allowing the tuning of the kinetics of the chemical reactions.

The synthesis of high-quality precursor material is a very sensitive initial step in the crystal growth. It is essential to produce a very clean precursor containing only barium, copper, and oxygen, with the correct stoichiometry of 2:1:3. Impurities tend to prevent proper chemical reaction, and thus influence the crystal growth. Therefore, any contamination should be eliminated, if possible. The different methods used to prepare precursors are also summarized in Table 1. A straightforward method is to simply mix BaO or BaO₂ with CuO.^[11,12] Unfortunately, at room temperature, barium oxide and peroxide

easily react with water or CO₂, forming Ba(OH)₂ or BaCO₃. For this reason, commercially available BaO is contaminated, and consequently not suitable for precursor preparation. Both types of contamination negatively affect the crystal growth: Ba(OH)₂ releases water during the synthesis, which increases the pressure and may cause an explosion of the sealed quartz tube, and BaCO₃ can act as an impurity, perturbing the crystal growth.^[9] An alternative method for preparing precursors involves heating a mixture of BaCO₃ and CuO to temperatures exceeding 1100 °C.^[15,16] A problem with this approach arises from the slow decomposition of BaCO₃, even at high temperature, and this method is therefore impractical. In order to improve the homogeneity of the precursor, a third approach, the sol-gel method, was employed by several groups.^[17,18,24] However, the use of an organic acid or polymer can easily contaminate the precursor with carbon. A fourth method uses a mixture of Ba(NO₃)₂ and CuO.^[13,14] Further improvements of this method involve reacting BaCO₃ with HNO₃ and drying the resulting aqueous solution by freeze- or spray-drying to synthesize a homogeneous precursor.^[19] We used this fourth method of precursor preparation, but found that the latter step was unnecessary, and that commercially available $Ba(NO_3)_2$ was sufficient.

We emphasize the importance of the calcination procedure. To avoid the gas back-flow commonly found in conventional tube furnaces, we designed a special precursor preparation system that employed a quartz kettle and continuous oxygen flow. After mixing and grinding of $Ba(NO_3)_2$ and CuO, the prepared powder was put into the kettle and heated to 920 °C. This method enabled us to obtain high-quality precursor material for the crystal growth.

For the reasons mentioned above, fresh precursor powder (which contains BaO) should be immediately mixed with mercury oxide, placed in a crucible, and sealed in the quartz encapsulation tube under vacuum. We used quartz tubes with

Table 1. Techniques for the preparation of Hg1201 and of precursor materials.

Technique used for the	Method used for the preparation	Product	Reference
preparation of Hg1201	of the precursor		
Encapsulation	Mixture of oxides or peroxides	Powder	[11, 12]
Encapsulation	Mixture of nitrates	Powder [13] or	[13, 14]
		Crystal (0.5 mm × 0.5 mm × 0.3 mm) [14]	
Encapsulation	Mixture of carbonates and CuO	Powder [15] or	[15, 16]
		Crystal (3 mm × 2 mm × 0.1 mm) [16]	
Encapsulation	Sol-gel method with citrates and tartrates	Powder	[17]
Encapsulation; Mn ₂ O ₃ /Mn ₃ O ₄	Sol-gel method with citrates	Powder	[18]
couple for oxygen partial			
pressure control			
Encapsulation	Drying of an aqueous nitrate solution	Powder	[19]
Three-zone encapsulation with Hg and oxygen	Sol-gel by polymerization	Powder	[24]
modulation			
High static pressure	Sol-gel by polymerization	Powder	[9]
High gas pressure	Mixture of BaCuO ₂ /CuO	Crystal (0.4 mm × 0.4 mm × 0.02 mm)	[10]
Encapsulation	Stoichiometric, contamination-free	Crystal size exceeding 100 mm ³	Present work
	mixture of nitrates		

dimensions of 15 mm (inner diameter), 2.5 mm (thickness), and 100 mm (height), and crucibles with typical dimensions of 10 mm (inner diameter) and 80 mm (height). Particular attention was devoted to the choice of crucible material. Crucibles containing silica are unusable because of the reaction between the silica and copper oxide. We also tried alumina crucibles, but found that at elevated temperatures CuO creeps up the crucible wall and eventually reacts with the quartz tube. This tendency also changes the composition of the material in the crucible. Furthermore, crystals tend to be contaminated with Al and to stick to the crucible walls, and hence are difficult to extract. We established that zirconia crucibles have the best overall characteristics and were best at containing the CuO solution during the crystal growth.

The precursor (mass 2.14 g) and HgO (1.20 g) were mixed in stoichiometric proportions. In addition, about 0.3 g of excess HgO was added in order to compensate for the vaporized Hg and to obtain a sufficiently high vapor pressure. By finetuning the amount of excess HgO, we were able to optimize growth conditions and avoid the explosion of the sealed quartz tube. The sealed quartz tube was placed in a conventional box furnace and heated up to 800 °C. At this temperature, solid-state reactions begin and the Hg1201 phase is formed. We benefited from this reaction as it lowers the HgO pressure in the encapsulation tube by keeping the furnace at this temperature for 10 h. Then, the temperature was gradually increased to 1020 °C, which melted the contents of the crucible and lead to a homogeneous precrystallization admixture. We found that slow-cooling at a rate of 2 °C h⁻¹ ensured equilibrium crystallization.

Figure 1b shows a picture of two halves of an as-grown Hg1201 crystal that was cut out of the crucible using a wire saw and subsequently cleaved parallel to the *a*-*b* planes. Its orientation was determined from the Laue patterns shown in Figure 1c and d. The fourfold pattern in Figure 1c is consistent with the known tetragonal crystal symmetry (space group P4/mmm). X-ray diffraction (XRD) characterization of smaller samples demonstrated that the crystals were typically single phase. The extracted room-temperature lattice parameters for the as-grown crystals were a = 3.886 Å and c = 9.517 Å, in agreement with previously published results.^[11,12,14]

A known feature of Hg1201 is the Hg off-stoichiometry, with a Hg deficiency that has been found to range from 8% to 20%.^[14,25-27] To determine the stoichiometry of a typical large crystal, we used inductively coupled plasma mass spectroscopy (ICP-MS). Small pieces were cut from different parts of the as-grown bulk: four pieces from near the top surface of the growth and five pieces from the middle section. The result obtained from the middle section indicated a rather uniform bulk distribution, with an average Hg/Ba/Cu ratio of 0.88:2.08:1.06, or a Hg deficiency of about 10%. However, we found a significant inhomogeneity and Hg deficiency near the top surface of the growth, with a Hg/Ba/Cu ratio ranging from 0.75:2.02:1.22 to 0.36:2.02:1.62. This result indicates that large segments in the middle of sizable crystals, such as the one shown in Figure 1b, are of good quality.

Magnetic susceptibility was measured on numerous samples and indicated a moderate sample dependence. As-grown samples are underdoped and, as shown in Figure 2, the mean value of T_c of a typical large as-grown sample is 75–80 K. The transition is fairly sharp, although the small slope above 80 K



Figure 2. Magnetic susceptibility measurements of as-grown and oxygenated samples. The magnetic susceptibility for a large as-grown (\bigcirc) and a small (6.2 mg) annealed (\blacksquare) sample as a function of temperature. (Susceptibility was measured with a Quantum Design MPMS-XL instrument.)

indicates a gradual doping change from underdoped to optimally doped (T_c onset of about 97 K). After annealing for five to seven days at 300-350 °C under an oxygen flow, smaller crystals typically became nearly optimally doped, with the onset T_c at 97 K and a very small transition width of ca. 2 K (Fig. 2). Our annealing tests show that the optimal annealing conditions depend strongly on crystal size and shape. The $T_{\rm c}$ onset can be as high as 97 K (very close to the maximum value of $T_c = 98$ K reported for powder samples^[12]) and the transition width is typically less than 5 K for small crystals (~10 mg) and 8 K for large crystals. Since impurity effects tend to lower and broaden the transition,^[2] this high value of $T_{\rm c}$ and the reasonably sharp transition suggest that large parts of our crystals are of the highest quality attained to date. Magnetic susceptibility measurements revealing a sharp transition in conjunction with a large superconducting volume fraction are often interpreted in terms of a homogeneous oxygen distribution. However, this conclusion can be misleading. Preliminary resistivity measurements indicate the presence of inhomogeneities near the surface of some of the small annealed crystals, which may be the result of partial decomposition or dopant oxygen disorder.

We now report on preliminary inelastic neutron scattering measurements which demonstrate that our Hg1201 crystals are suitable for detailed future studies of the structure of magnetic excitations. A central topic in the field of high- T_c superconductivity has been the role of the magnetic degrees of freedom and the question whether the cuprates exhibit universal magnetic excitations. Such studies require sizable single crystals. As a result, they have largely focused on single-layer (La,Sr)₂CuO₄ (T_c = 38 K at optimal doping) and two-layer YBa₂Cu₃O_{6+ δ} (T_c = 93 K at optimal doping), for which such crystals have been available for some time. It has been argued that the structures of the high-energy magnetic excitations in these two compounds are rather similar, although there also exist interesting differences at lower energies.^[28–30]

The neutron experiment was performed on an as-grown sample that consisted of five co-mounted crystals with total volume of ~110 mm³ mounted in the (H,H,L) zone, as shown in Figure 3a. Based on magnetic susceptibility measurements on small crystal pieces, we estimate a superconducting transition temperature of $T_c = (85 \pm 10)$ K for the entire sample. Bragg scattering at the (0,0,4) reflection indicated a total mosaic of ca. 1.5° (full width at half maximum (FWHM)) for the five co-mounted crystals. In an additional characterization test, we performed a constant-energy scan along [2,2,L] at an energy transfer of 3 meV. As shown in Figure 3b, this measurement revealed a well-defined transverse acoustic phonon branch.

To search for magnetic excitations, we performed constantmomentum scans at the antiferromagnetic wave vector $Q_{AF} = (0.5, 0.5, 4)$. Differences between scans at 10 K (superconducting state) and 110 K (normal state) indicate a maximum of 52 meV for the energy transfer (not shown). Momentum scans along [1,1,0] at 52 meV, both above (110 K) and well below (10 K) the T_c , reveal a relatively strong momentum dependence of the background scattering. After subtraction of the high-temperature data from those at 10 K, we



Figure 3. Hg1201 sample and inelastic neutron scattering measurements. a) Sample of five co-mounted crystals used for the inelastic neutron scattering measurements. b) Phonon characterization scan at 3 meV (r.l.u: reciprocal lattice units). c) Momentum scans (H,H,4) at an energy transfer of 52 meV at 10 K and 110 K. d) Intensity difference of the data in (c), suggesting the existence of a net magnetic signal, with fits to a possible commensurate (red) and incommensurate (blue) response. Initial crystal checks were performed at the National Institute of Standards and Technology (NIST) Center for Neutron Research. The inelastic experiment was performed at the 2T triple-axis spectrometer at Laboratoire Léon Brillouin, with 35 meV fixed final neutron energy and collimations set at 60–open–sample–open–open.

found a net positive signal in the vicinity of Q_{AF} . As demonstrated in Figure 3d, the net signal can either be described by a single broad peak centered at Q_{AF} , or by two sharper peaks centered at incommensurate positions shifted from Q_{AF} by ca. 0.13 r.l.u. (reciprocal lattice units).

We note that the signal rate is comparable to that obtained in a study of the single-layer compound $Tl_2Ba_2CuO_{6+\delta}$, which investigated an optimally doped ($T_c \sim 90$ K) sample that consisted of ca. 300 small co-mounted crystals with total volume close to that of our Hg1201 sample.^[31] Recent, thorough studies of $YBa_2Cu_3O_{6+\delta}$ have revealed that the spin excitations form an hourglass-shaped dispersion centered at $Q_{AF}^{[32-35]}$ At $Q_{\rm AE}$ the branches merge into a prominent feature, the socalled (π, π) resonance, observed in the superconducting state.^[33–38] The dispersions observed in YBa₂Cu₃O_{6+ δ} above and below the resonance cover a range of about 0.10-0.13 r.l.u.^[28,32] For nearly optimally doped $Tl_2Ba_2CuO_{6+\delta}$, the resonance energy was found to be 47 meV. The net response at 52 meV in our slightly underdoped Hg1201 sample is consistent with these prior results, and this energy may be at or slightly above the resonance in this material.

In summary, we significantly improved the conventional encapsulation method for the growth of Hg1201 in several ways: a new vertical kettle system was employed to prepare carbon-free high-quality precursor; careful dosing of HgO was adopted to control proper vapor pressure for crystal

> growth; Zirconia crucibles were employed to prevent CuO from creeping up the wall and to facilitate the extraction of crystals. Our method results in gram-sized Hg1201 single crystals, and it can likely be extended to the double- (n=2) and triple-layer (n=3) members of the series HgBa₂Ca_{n-1}Cu_nO_{2n+2+ δ}. The Hg1201 crystals were characterized by several experimental techniques, demonstrating their good quality. The present work provides the foundation for detailed experimental studies of this important family of transition metal oxides, such as inelastic neutron scattering, optical spectroscopy, and angle-resolved photoemission spectroscopy.

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