Journal of Alloys and Compounds, 209 (1994) 225–229
JALCOM 1085

Preparation and superconducting properties of high-quality Bi-2212 ceramics

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(Received November 22, 1993)

Abstract

High-quality Bi-2212 ceramic samples were obtained by a solid-state reaction method. At the starting composition $Bi_{2.12}Sr_{1.90}Ca_{1.02}Cu_{1.96}O_y$, X-ray diffraction, optical micrographs and scanning electron microscopy investigations show that the level of impurity phases is less than 1% by volume. Synthesis at a few degrees below the melting point favours grain growth. A final annealing treatment at controlled temperature and oxygen pressure, followed by rapid quenching, yields sharp superconducting transitions, as observed by measurement of the a.c. susceptibility and Meissner effect, and specific heat experiments. The Meissner fraction in 2 mT approaches 50%.

1. Introduction

In the Bi_2O_3–SrO–CaO–CuO quaternary diagram, three superconducting phases have been found: $Bi_2Sr_2Ca_nCu_{n+1}O_{2n+6+\delta}$ with $n=0$, 1, 2. Depending on hole doping, the non-congruent Bi-2212 phase ($n=1$) has a critical temperature T_c that ranges from 50 to 94 K [1]. Since the discovery of this material [2], a tremendous effort has been expended in the production of high-quality samples. A large volume fraction of superconducting phase and a sharp transition are prerequisite for any significant investigation of the anomalies at T_c, notably by specific heat techniques. Recently, several groups have reported the limits of the non-stoichiometric Bi-2212 single-phase region [3–5], which is slightly enriched in Bi. However, at sintering temperatures above 870 °C, these limits are still unclear. Based on these phase diagrams and on an additional earlier report [6], we tried to produce Bi-2212 ceramics with large grains. Most samples were found to contain impurity phases, and we were led to re-investigate the synthesis conditions. In this paper, we describe explicitly the method used to obtain pure and large grained Bi-2212 samples. These ceramics were characterized by X-ray diffraction, optical micrographs, scanning electron microscopy, a.c. susceptibility, Meissner effect and specific heat measurements.

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2. Sample preparation

High purity (99.999%) Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO powders were mixed at various starting compositions and calcined in two stages, first at 600–750 °C for 20–36 h, and subsequently at 750–800 °C for 32–60 h, to avoid the formation of a transient liquid phase. After grinding, the calcined powder was pressed into a disk (7 mm in diameter and 2–4 mm thick) under a pressure of about 640 MPa, and sintered at 860 °C for 30–60 h. In order to increase the homogeneity, this process was repeated twice with intermediate grindings for some batches. The pellets were then pulverized, compacted under a pressure of about 900 MPa, and sintered above 880 °C. The temperature of the furnace was controlled by a Pt–Pt10%Rh thermocouple, allowing an accuracy of ±2 °C. Calcination and sintering were always carried out in pure oxygen flow. Table 1 summarizes the parameters of sample preparation.

Finally, in order to ensure better homogeneity of the oxygen concentration, samples of batch N were annealed at selected temperatures T_a and oxygen pressures $p(O_2)$ in a vertical furnace, and rapidly quenched into liquid gallium. Some samples were annealed in a closed high-pressure furnace. In the latter case, quenching occurred by convection. The annealing times ranged from 8 to 520 h. Table 2 summarizes the annealing conditions and superconducting properties for samples from batch N. Each sample code is formed by a letter indicating the batch, followed by two numbers. The first number represents the oxygen pressure during annealing.

0925-8388/94/$07.00
SSDI 0925-8388(93)01085-I

TABLE 1. Sintering conditions

Purity	Batch	Composition	First sintering (°C, h)	Intermediate sintering (°C, h)	Last sintering (°C, h)
X	A	$Bi_{2.03}Sr_{1.94}Ca_{0.97}Cu_{2.06}O_y$	860, 48		882, 36
O	B	$Bi_{2.15}Sr_{1.85}Ca_{1.00}Cu_{2.00}O_y$	860, 48		880, 48
O	C	$Bi_{2.15}Sr_{1.85}Ca_{1.00}Cu_{2.00}O_y$	860, 24	860, 24	880, 36
O	D	$Bi_{2.15}Sr_{1.85}Ca_{1.03}Cu_{1.97}O_y$	860, 60		883, 66
O	E	$Bi_{2.15}Sr_{1.85}Ca_{1.03}Cu_{1.97}O_y$	860, 60		883, 132
O	F	$Bi_{2.15}Sr_{1.85}Ca_{1.05}Cu_{1.95}O_y$	860, 30		880, 60
X	G	$Bi_{2.15}Sr_{1.85}Ca_{1.07}Cu_{1.93}O_y$	860, 60		883, 60
X	H	$Bi_{2.16}Sr_{1.95}Ca_{0.95}Cu_{1.94}O_y$	860, 30		880, 60
X	I	$Bi_{2.12}Sr_{2.00}Ca_{0.93}Cu_{1.95}O_y$	860, 30		880, 60
X	J	$Bi_{2.13}Sr_{1.95}Ca_{0.97}Cu_{1.95}O_y$	860, 60		880, 60
P	K	$Bi_{2.12}Sr_{1.90}Ca_{1.02}Cu_{1.96}O_y$	860, 60		880, 60
P	L	$Bi_{2.12}Sr_{1.90}Ca_{1.02}Cu_{1.96}O_y$	860, 60	880, 60	883, 84
P	M	$Bi_{2.12}Sr_{1.90}Ca_{1.02}Cu_{1.96}O_y$	860, 30	860, 30 880, 60	883, 84
P	N	$Bi_{2.12}Sr_{1.90}Ca_{1.02}Cu_{1.96}O_y$	860, 30	860, 30 880, 30	900, 120

Pellets were pulverized and pressed between sintering stages. X impurities observed by X-ray diffraction (more than 5% by volume); O impurities observed by optical micrography (1%–5%); P less than 1% impurities.

TABLE 2. Annealing conditions and superconducting properties of batch N samples

Code	$p(O_2)$ (bar)	T_a (°C)	Time (h)	T_c (K)	ΔT_c (K)	$-4\pi\chi_v$ (10 K) (%)
N/+3.1/3	1300	300	8	46.9	1.8	27
N/+3.1/4	1300	400	8	51.0	2.4	32
N/0/3	1	300	520	64.9	1.2	27
N/0/4	1	400	240	74.0	1.1	32
N/0/6	1	600	65	84.9	0.9	45
N/0/7	1	700	24	88.1	1.1	45
N/−2/6	10^{-2}	600	65	91.2	0.8	48
N/−2/7	10^{-2}	700	26	91.8	0.9	47
N/−4/5	10^{-4}	500	238	92.0	0.7	46
N/−4/5.5	10^{-4}	550	102	92.5	0.7	44

T_c is defined as the temperature at which $|\partial\chi'/\partial T|$ is maximum. ΔT_c is defined as the full width at half height of $|\partial\chi'/\partial T|$.

$-2 \equiv 10^{-2}$ bar, $0 \equiv 1$ bar and $+3 \equiv 10^{+3}$ bar. The second number indicates the annealing temperature. For example, N/−2/6 was annealed under 10^{-2} bar oxygen pressure at 600 °C.

3. Metallurgical studies

The crystal structure was studied at room temperature by X-ray diffraction, using a Guinier camera with Cu Kα radiation. Silicon was added to the powdered samples as an internal standard. After polishing using diamond paste, the sample surface was examined both in an optical microscope and in a scanning electron microscope (Cambridge Instruments Stereoscan 360).

X-ray diffraction patterns indicated the presence of impurity phases in samples from batches A, G, H, I and J, which contain less than 1.00 or more than 1.05 calcium per formula unit, the latter being normalized to seven cations. Microprobe analysis showed that the impurities in batch A are $Sr_2CaCu_4O_7$, $(Sr,Ca)_1CuO_2$ and SrO. Based on X-ray diffraction studies, samples from the other batches (B, C, D, E, F, K, L, M and N) appeared to be single phase. We could however detect small amounts of impurity phases for batches B, C, D, E and F by using the more sensitive technique of optical micrography. Microprobe analysis showed that the impurity in batch C is essentially CuO. Only batches K, L, M and N contain no observable secondary phases. We conclude that the most appropriate starting composition is $Bi_{2.12}Sr_{1.90}Ca_{1.02}Cu_{1.96}O_y$. Quite recently, Knížek *et al.* studied the single-phase region of the Bi-2212 superconductor [7]. Although they used a lower sintering temperature (850 °C), our metallurgical results are roughly consistent with theirs. The melting point depends critically on the initial stoichiometry and the surrounding atmosphere. $Bi_{2.12}Sr_{1.90}Ca_{1.02}Cu_{1.96}O_y$ melts at approximately 904 °C in flowing oxygen. Therefore, the largest grains appear in batch N samples annealed at 900 °C, very close to the melting point. In the following, we discuss the purity and superconducting properties of samples taken from this batch (Table 2).

Figure 1 shows the X-ray diffraction pattern of an as-sintered sample before annealing. Except for two spurious camera peaks at $4\Theta = 84.84°$ and 98.83°, and the peaks of the silicon standard, all diffraction peaks can be indexed in the Bi-2212 orthorhombic structure with lattice parameters $a = 5.405$ Å, $b = 5.413$ Å and

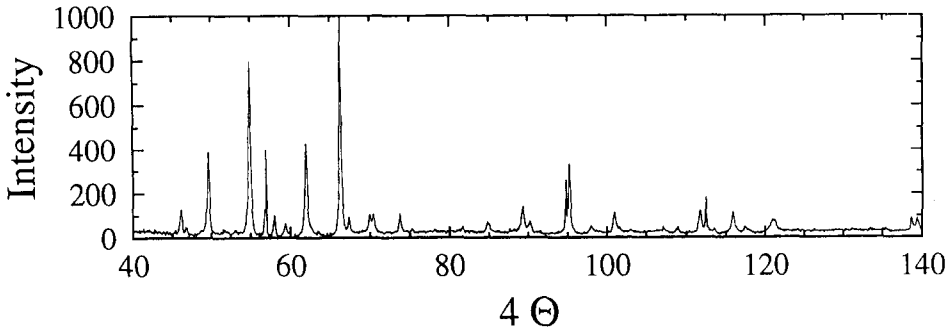

Fig. 1. X-ray diffraction pattern of a sintered sample before annealing, batch N.

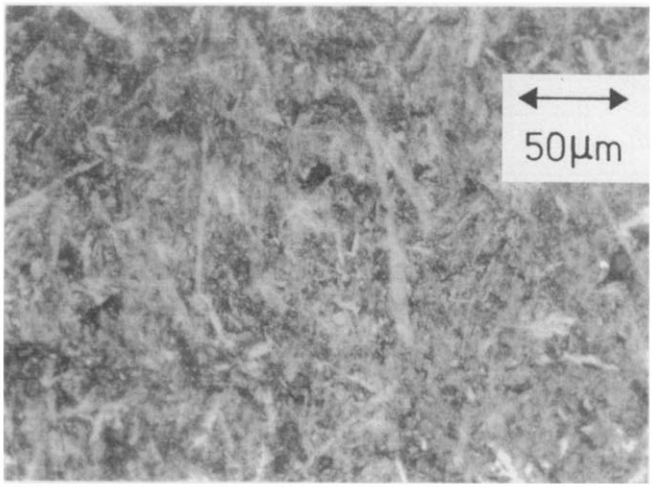

Fig. 2. Optical micrograph of the sample in Fig. 1.

$c = 30.80$ Å. These cell parameters are determined by least-squares fits to 15 lines indexed according to the space group $A2aa$. The peaks at $4\Theta = 59.37°$ and 73.76° are satellite reflections due to the modulated structure [8–12].

An optical micrograph of an as-sintered sample under polarized light is presented in Fig. 2. The sample consists of plate-like crystals, which appear generally as needles as a result of random cuts. The grain size in batch N, approximately 100 μm length, is about twice as large as that of batch M. The latter was sintered at a lower temperature, 883 °C instead of 900 °C. Micrographs show that impurity phases amount to less than 1% by volume. The macroscopic density is about 65% of the theoretical value (6.66 g cm^{-3}). The quality of the samples produced by the process described above is very reproducible.

4. Superconducting properties

The a.c. susceptibility was measured in a magnetic field of 10 μT rms at a frequency of 81 Hz. Figure 3 shows the a.c. susceptibility *vs.* temperature for one quenched bulk sample (N/−2/6). The typical two transitions of a granular system are observed in the temperature dependence of the real component χ'. The first transition at $T_c^{onset} \approx 92$ K is associated with the bulk intragrain superconducting transition. T_c, defined as the temperature at which $|\partial\chi'/\partial T|$ is maximum, is 91.2 K. The second transition at $T \approx 18$ K is due to the expulsion of flux from the apparent geometrical volume when the critical current of the weak links joining the grains becomes equal to the required macroscopic shielding current. The presence of the dissipation peak and the strong dependence on low magnetic fields are characteristic of the latter intergrain transition, which involves an exceedingly low mass fraction. The main bulk superconducting transition shown in Fig. 3 has a width ΔT_c of 0.8 K (full width at half height of $|\partial\chi'/\partial T|$). This result indicates good homogenities of both the oxygen content and the cation distribution.

Depending on the oxygen concentration that results from the final annealing condition (T_a, $p(O_2)$), we obtained a wide range of T_c values extending from a maximum 92.5 K (N/−4/5.5) to a minimum 46.9 K (N/+3.1/3). Owing to fast quenching, the transitions remain sharp (see Table 2). These results confirm the strong influence of the oxygen content on the superconducting transition. In the present study, the T_c values differ slightly from those obtained when the starting composition was $Bi_2Sr_2Ca_1Cu_2O_y$ [1]. For example, the onset T_c values of $Bi_{2.12}Sr_{1.90}Ca_{1.02}Cu_{1.96}O_y$ and $Bi_2Sr_2Ca_1Cu_2O_y$ under $T_a = 600$ °C and $p(O_2) = 1$ bar are 85.4K and 83.1 K respectively.

A SQUID magnetometer was used to measure the Meissner effect. The external magnetic field, 1.98 mT, was calibrated using a lead sample in the superconducting state. The susceptibility was corrected by a demagnetizing factor which was estimated from the aspect ratio of the bulk sample. Figure 4 shows the temperature dependence of the Meissner flux expulsion for samples N/−2/6 and N/+3.1/4. The shape of the curves reveals that each sample undergoes one single

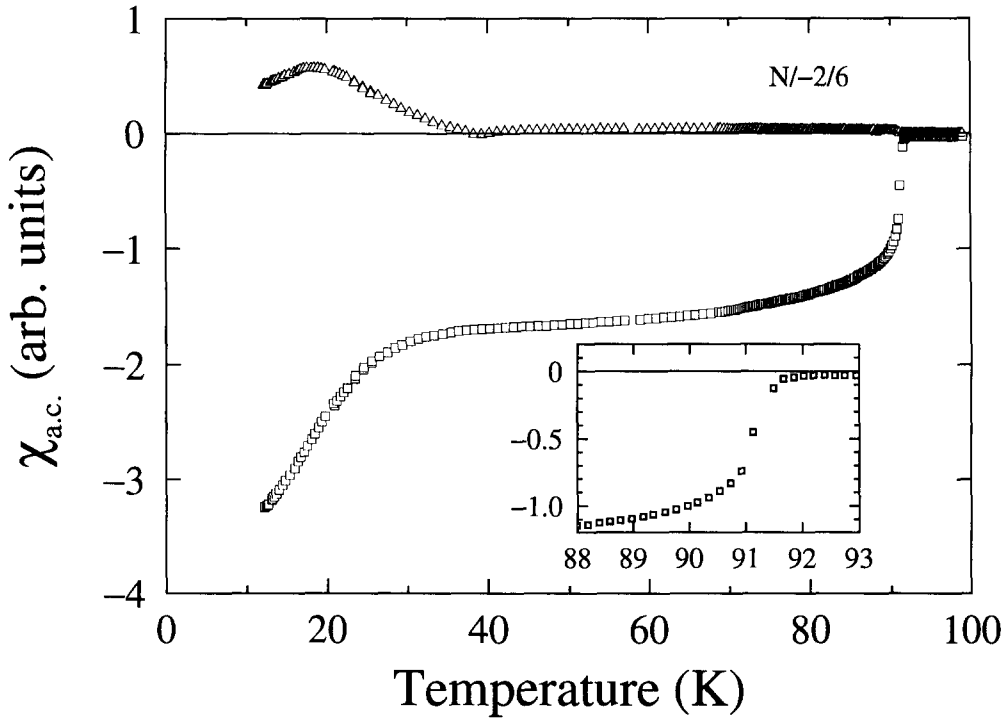

Fig. 3. Temperature dependence of the real χ' and imaginary χ'' parts of the a.c. susceptibility for sample N/−2/6.

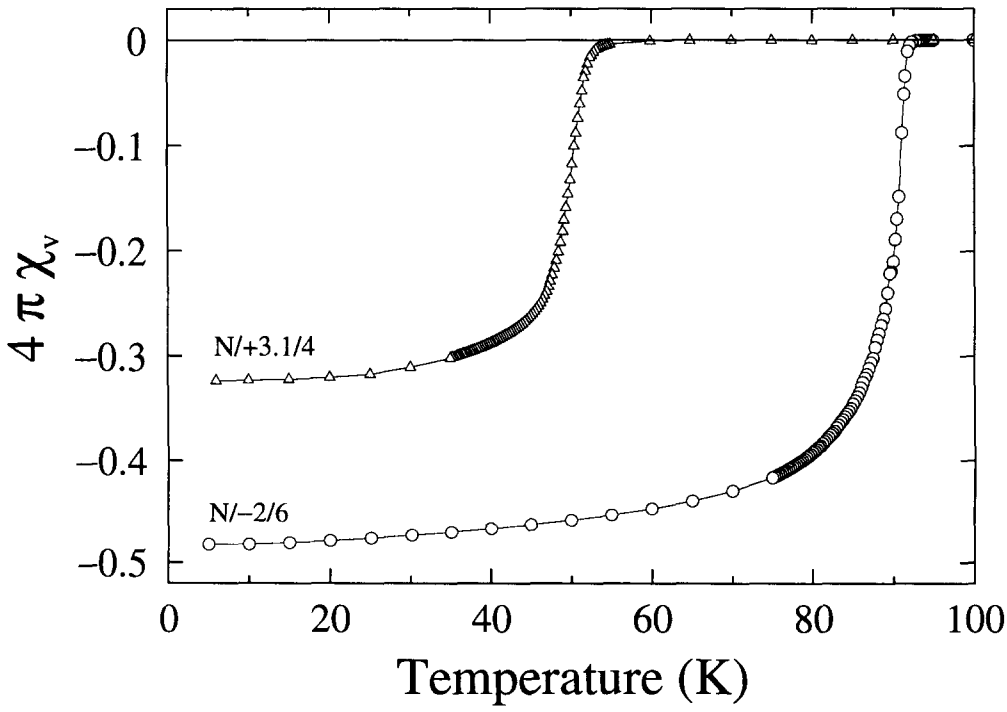

Fig. 4. Field cooling susceptibility (Meissner effect) in $B = 1.98$ mT, sample N/−2/6 (see Fig. 3). Ideal diamagnetism corresponds to $4\pi\chi_v = -1$.

bulk transition. As expected, the weak-link transition below 30 K is not observed. The onset temperatures of the Meissner and a.c. susceptibilities coincide for both samples. The Meissner fraction exceeds 45% below 60 K for sample N/−2/6 (Fig. 4), a value that is larger than most published data. The Meissner fraction decreases rapidly when the doping is such that T_c is not optimal, a very general feature of high temperature superconductors. The data of Table 2 suggest that this fraction is more closely correlated with the annealing

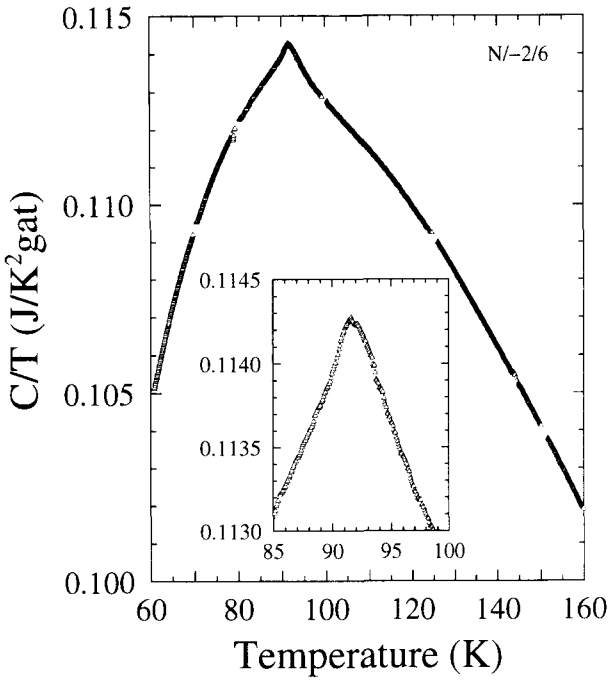

Fig. 5. Specific heat C/T *vs.* temperature, sample N/−2/6 (see Figs. 3 and 4). One gat is 60.02 g.

temperature than with the oxygen pressure or the critical temperature.

The specific heat was measured in an adiabatic, continuous heating type calorimeter using platinum thermometry [13]. The result for one quenched sample N/−2/6 is shown in Fig. 5; the sample mass was 0.37 g. A λ-like anomaly is observed at T_c. The distinct positive curvature just below the peak confirms that the broadening due to inhomogeneities is very limited; consequently the conspicuous absence of a specific heat jump at T_c appears to be an intrinsic feature of this typical two-dimensional superconducting system. The critical temperature T_c corresponding to the maximum of C/T is 91.56 ± 0.1 K, to be compared with 91.2 ± 0.2 K for the maximum of $|\partial\chi'/\partial T|$ in 10 μT rms. The peak of C/T coincides within experimental accuracy with the onset of the shielding transition. The temperature interval between the upper and the lower inflection points of C/T is 2.86 K. This is sharper than the best results obtained so far in our laboratory [14] and other representative published data [15]. The bulk homogeneity of the sample resulting from quenching is thus confirmed. Analysis of the specific heat in magnetic fields up to 14 T is under way.

5. Summary

High quality Bi-2212 superconducting ceramics were prepared by a solid-state reaction method. It was found that the most appropriate starting composition for samples sintered close to the melting point is $Bi_{2.12}Sr_{1.90}Ca_{1.02}Cu_{1.96}O_y$. Under these conditions, the impurity phases contribute to less than 1% of the volume. After sintering at 900 °C, the grain length increases to approximately 100 μm. The Meissner fraction attains 48%. The quenched samples with various T_c values all show sharp superconducting transitions. The λ-like anomaly at T_c can be clearly observed in the temperature dependence of specific heat, and the absence of a jump at T_c is confirmed.

Acknowledgments

The authors are grateful to F. Liniger, A. Naula and J.A. Fernandez for their technical assistance. This work was partially supported by the Fonds National Suisse de la Recherche Scientifique and the Ministry of Education, Science and Culture of Japan.

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