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INVESTIGATIONS ON THE PHASE FORMATIONS, PROPERTIES AND SINGLE CRYSTAL GROWTH IN THE HIGH- T_c SUPERCONDUCTING Ca–Sr–Bi–Cu–O SYSTEM

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We have performed investigations on the Ca–Sr–Bi–Cu–O system with respect to high- T_c superconductivity and structural properties. It is shown that there are two high- T_c superconducting phases in the system, i.e. a 110 K and an 85 K phase. The 85 K phase has a body-centred tetragonal structure with a stoichiometry of $\text{CaSr}_2\text{Bi}_2\text{Cu}_2\text{O}_8$. The 110 K phase is closely related to the 85 K phase. It is formed only in a very narrow temperature range and easily deteriorates to the phase with the lower T_c by quenching. Although some samples show a large diamagnetic signal at 110 K in ac-susceptibility measurements, there is still evidence of the presence of the 85 K phase. X-ray diffraction studies, especially in the low-angle region, show a structural relation between these two superconducting phases. The procedures of the preparation and the characterization of the 85 K and 110 K polycrystalline superconducting phases as well as the single crystal growth of the 85 K superconducting phase are described.

1. Introduction

Since the discovery of high- T_c superconductivity around 110 K in the multiphase Ca–Sr–Bi–Cu–O system by Maeda et al. [1], much effort has been concentrated on the identification and characterization of the phases responsible for the high- T_c superconductivity [2, 3]. Single crystal growth of the 85 K phase and its composition, structure and physical properties have also been reported [4–6]. At the early stage of our investigations [7], we have reported results on the high resolution electron microscopy of samples with the nominal composition of $\text{CaSrBiCu}_2\text{O}_x$. These samples exhibit nearly zero resistance at 107 K. At least two major phases in the sample were found with the approximate composition ratio of Ca:Sr:Bi:Cu equal to 0.8:1.7:2:2 (corresponding to the c -axis about 31 Å) and

1.2:1.4:2:3 (corresponding to the c -axis about 37 Å). The c -axis in the latter phase is about 6 Å longer than that of the former one. Consequently, it is proposed that the latter phase is formed by inserting two additional atomic layers, probably Ca and CuO_2 layers, into the 31 Å phase, and may be responsible for the 110 K transition. Similar results were found in the Ca–Ba–Tl–Cu–O system, which also exhibits two superconducting phases [8].

In this paper we mainly describe our preparation methods and characterizations of the 85 K and 110 K superconducting phases in the Ca–Sr–Bi–Cu–O system from the nominal starting compositions 1112, 1222, 2223. The single crystal growth and the characterization of the 85 K phase are also presented.

Samples were analysed by DTA, TGA, electron microprobe, X-ray and electron microscopy. Superconductivity was characterized by ac-susceptibility

and four-point ac- and dc-resistivity measurements. The temperature dependence of the magnetization in a low magnetic field was measured and the Meissner effect was determined with a SQUID magnetometer for some samples.

2. Sample preparation

All samples were prepared by the standard solid state reaction method similar to that used for the preparation of $\text{YBa}_2\text{Cu}_3\text{O}_7$. The starting ingredients (CaCO_3 , SrCO_3 , Bi_2O_3 and CuO , Johnson Matthey, Specpure) were well-mixed, pressed into pellets and heated in an alumina crucible for 15 hours. The heating temperature is varied from 800 to 880°C, according to the different compositions of the samples. After milling, the powder products were pressed into pellets again and subsequently heated at the same temperature. This procedure may be repeated to ensure the homogeneity. The final products were further processed using different heat-treatments and quenching procedures, as described below. A large number of samples with various nominal compositions we prepared and examined. Here we describe the methods of the preparation for those samples with the nominal starting composition 1112, 1222 and 2223, which show the highest superconducting transition temperature.

2.1. 1112 starting composition

Samples with this nominal composition showed the highest superconducting transition temperature at 110 K among the samples measured so far. One of the experimental procedures was as follows. The pellets from the reacted products as described above were annealed at 850°C for 22 hours, and quenched into liquid nitrogen, then pulverized and pressed into pellets again. The pellets were sintered at 880°C for 60 hours and quenched into liquid nitrogen. As a final procedure the samples were annealed at 890°C for 20 minutes, then at 880°C for 9 hours and furnace-cooled to room temperature. The result of the ac-susceptibility measurement for this sample is shown in fig. 1 (open circles). The amplitude of the diamagnetic signal is normalized by the weight of the sample. From fig. 1, two step-wise transitions are

Fig. 1. Temperature dependences of ac-susceptibility for samples of starting composition 1112 (○) and 2223 (●).

clearly seen at 110 K and at 80 K, indicating two different superconducting phases. It is noted that the amplitude of the diamagnetic signal for the 110 K transition is much larger than that for the 85 K transition and that the ratio of the diamagnetic signal between these two phases is not influenced by the pulverization of the sample. These facts imply that the 110 K phase in the sample is a major superconducting phase and has bulk superconductivity.

The temperature dependence of the magnetization of the sample was measured with a SQUID magnetometer in a magnetic field of 10 G. Two distinct jumps in the magnetization were observed, as seen in fig. 2. The first onset of diamagnetism occurs at 106 K and the second at 77 K. These steps clearly

Fig. 2. Temperature dependence of the magnetization of the sample with starting composition 1112 measured by a SQUID magnetometer in a magnetic field of 10 G (●) and without magnetic field cooling (○).

correspond to the presence of two superconducting phases in the sample, as previously seen in the ac-susceptibility measurements. The Meissner effect is about 50% of the total shielding effect for both phases. About 65% of the total Meissner effect is attributed to the 110 K phase in this case, indicating again the bulk nature of superconductivity.

Several samples which were heated only 880°C for 3 or 4 days and were furnace-cooled also show a large diamagnetic signal with the onset temperature around 110 K. It is noted that in all cases a mixture of the 80 K and the 110 K phases is present in the sample.

We have recognized that the 110 K superconducting transition can easily be suppressed to 85–95 K by quenching the sample into liquid nitrogen after a short time annealing at any temperature between 850°C and 880°C. The quenching effect on ac-susceptibility of the sample is illustrated in fig. 3.

The samples which were not annealed at 880°C for a long time, show a T_c near or below 80 K. It is observed that the T_c of these samples can be enhanced to 85–95 K by a short time heating at 840°C to 880°C and then by quenching into liquid nitrogen.

It was found that 1112 samples have no phase transitions below 880°C by DTA, which measures were performed in air with a heating rate of 10°C/min. An endothermic peak starts at 880°C, followed by two other peaks at 930 and 970°C, as seen in fig. 4. These peaks indicate three different melting stages.

The TGA experiments show that there is no weight

Fig. 3. The quenching effect on the ac-susceptibility of the sample with starting composition 1112. Solid circles (●) indicate the results before quenching. The sample shows the onset of T_c at 110 K. After quenching the sample from 880°C into liquid nitrogen, the onset of T_c is suppressed to 85 K (■). The amplitude of the signal after quenching is reduced.

Fig. 4. Chart of the differential thermal analysis in air for the sample with starting composition 1112. The heating rate was 10°C/min.

change in the sample up to 880°C, which is in contrast to the case of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ system.

2.2. 1222 starting composition

According to Zandbergen et al. [7], the composition of $\text{CaSr}_2\text{Bi}_2\text{Cu}_2\text{O}_x$ corresponds to the 85 K phase. So far we have not observed the 110 K transition in the samples of this composition. We have obtained this 85 K phase as follows. The samples were reacted at 820°C for 15 hours. The already reacted samples were heated again at 880°C for 60 hours with intermediate milling and pressing into pellets and were finally furnace-cooled.

Superconductivity at 85 K is also obtained by quenching the samples into liquid nitrogen from 850°C without a long time heat treatment at 880°C.

In general, the 85 K phase is easily obtained in a wide range of the starting compositions. However, a homogeneous single phase, starting from this stoichiometric composition, has not been achieved yet. Grains with a wide range of Ca:Sr:Bi:Cu composition ratios, such as 1:1.8:1.7:1.9 and 1:1.8:1.3:1.6, were found in the electron microprobe analyses.

2.3. 2223 starting composition

Although the composition of $\text{Ca}_2\text{Sr}_2\text{Bi}_2\text{Cu}_3\text{O}_x$ is suggested by Zandbergen et al. [7] to be the phase responsible for the superconductivity at 110 K, we have not succeeded in obtaining the 110 K single

phase in the samples with this starting composition. If samples are heated at 850°C for 20 hours and are furnace-cooled, the superconducting transition at 75–80 K is found. The X-ray powder diffraction pattern shows an almost single phase character as an 85 K phase (with the c -axis of 30.6 Å). By quenching the sample from 850°C into liquid nitrogen, the T_c is enhanced to about 90–95 K. The X-ray diffraction pattern of the quenched sample shows almost the same pattern as before, only with a slight shift to higher angle in 2θ and with the intensity change of some peaks.

After heated at 880°C for a few days and furnace-cooled, the samples show the 110 K superconducting transition. However, the lower T_c phase is always present together with the 110 K phase (shown in fig. 1), similar to the 1112 samples.

3. Single crystal growth of the 85 K phase

In the course of our investigations we have succeeded in growing single crystals of the 85 K superconducting phase by the following procedure. A mixture of the starting components of CaCO_3 , SrCO_3 , Bi_2O_3 and CuO (Johnson Matthey, Specpure) in the Ca:Sr:Bi:Cu ratio of 1:2:2.5:2.5 was placed in an alumina crucible and heated at 890°C for several hours. The mixture was melted completely at this temperature. The molten sample was then cooled with a rate of 3°C/h to 790°C and finally to 340°C with the rate of 30°C/h. The crucible was crushed and crystals were separated from the matrix. The platelike crystals, normally sitting at the center of the crucible, congregated together with some unknown phases. Some yellowish materials, which have a higher melting point, adhere to the wall of the crucible. The separated single crystals have typical dimensions of $0.5 \times 0.5 \times 0.01 \text{ mm}^3$ and have a well developed lamellar structure with a metallic luster. A SEM picture of the single crystal is shown in fig. 5.

Electron microprobe analyses show that the composition ratio of Ca:Sr:Bi:Cu:O in a platelike single crystal is about 0.89:2.11:2.10:2.9.44, with less Ca and an excess of the Sr and Bi contents comparing to the stoichiometric ratio of 1222.

The X-ray powder diffraction analyses of the col-

Fig. 5. Photograph of the 85 K single crystal taken by a scanning electron microscope. The scale in the picture represents 100 μm .

lection of single crystals show a body-centered tetragonal structure with lattice parameters of 3.843 Å and 30.79 Å for the a - and c -axes, respectively.

The temperature dependence of the ac-susceptibility measured on an as-grown crystal is shown in fig. 6. The onset of superconductivity is as high as 86 K and the total diamagnetic signal is larger than that of polycrystalline samples. In fig. 6, a curve of the ac-

Fig. 6. Temperature dependences of the ac-susceptibility and ac-resistivity (inset) for the 85 K single crystal.

Fig. 7. Temperature dependences of the magnetization for the 85 K single crystal by a SQUID magnetometer in magnetic fields of 3 G (circles) and 10 G (triangles). The open symbols indicate the magnetization due to the shielding effect, while the solid symbols show the Meissner effect in the corresponding magnetic fields. The magnetic field is applied parallel to the *c*-axis of the crystal.

resistivity of the single crystal is shown in the inset. In this case, a zero resistivity state ($< 10^{-9} \Omega \text{ cm}$) is reached at 82 K.

A sharp onset of diamagnetism at 87 K is also found with a SQUID magnetometer, as shown in fig. 7. A plateau is reached around 50 K. The Meissner effect is field dependent and is about 30% of the total

shielding effect for 3 G and about 25% for 10 G.

Besides the very thin platelike crystals, very thin whiskers with a typical length of several millimeters were found. It turned out by electron microprobe analyses to be a bismuth-rich phase with an approximate composition ratio of Ca: Sr: Bi: Cu: O equal to 0.96: 2.70: 4.40: 2: 14.85.

4. Discussion

From the various experiments performed here, it is empirically recognized that the 110 K phase is formed only when the samples are annealed at a temperature very close to the first partial melting point for a long time. If the temperature exceeds the partial melting point, some unknown phases occur and the superconducting properties of the sample are severely degraded.

Without long time heating at 880°C, the samples exhibit the 80–85 K superconducting transition only. The X-ray diffraction patterns for these samples show that the major phase has a body-centered tetragonal structure with lattice constants of 3.81–3.84 Å and 30.5–30.8 Å for the *a*- and *c*-axes, respectively. As we mentioned above, the quenching procedure can enhance T_c to about 90 K, while the X-ray pattern does

Fig. 8. X-ray powder diffraction patterns of the 1112 samples from 20 to 60 degrees in 2θ with Cu $K\alpha$ radiation. Top: the spectrum for the sample with T_c onset at 80 K. The peaks marked by circles can be indexed by a body-centered tetragonal structure with $a = 3.818 \text{ Å}$ and $c = 30.64 \text{ Å}$. Bottom: the spectrum for the sample with T_c onset at 110 K. Several new peaks are marked by arrows.

not change drastically except for the intensities of some peaks. This fact suggests that there is no phase transition below the quenching temperature, which is consistent with the DTA results. The quenching effect on T_c as well as the wide range of lattice parameters in the different samples with different heat treatments may be due to the wide solubility range of some elements in this phase.

So far, we have not succeeded in obtaining the 110 K superconductor as a single phase. In all of our samples, the 110 K superconducting phase coexists with the 85 K phase. However, we have observed an interesting correlation between these two superconducting phases in the X-ray powder diffraction patterns. In fig. 8, the X-ray powder diffraction patterns of two samples from 1112 starting composition with different heat treatments are presented. The spectrum shown in the top of the figure represents the samples with the onset of T_c at 80 K. Most of the diffraction lines in this spectrum can reasonably be indexed to a body-centered tetragonal structure with lattice constants of 3.818 Å and 30.64 Å for the a - and c -axes, respectively. The rest of the weak diffraction lines indicate that some unknown minor phases exist in the sample. The spectrum shown in the bottom of the figure represents the samples with the superconducting onset at 110 K. Comparing this spectrum with the upper one, several new peaks are found, as marked by arrows in fig. 8. These additional peaks can consistently be explained by assuming a body-centered tetragonal structure, similar to the 85 K phase, but with a longer c -axis of about 37 Å.

In order to confirm the long periodicity of the 110 K phase, low-angle X-ray powder diffraction analyses were performed between 4 and 6.5 degrees in 2θ (Cu $K\alpha$ radiation). The results are depicted in fig. 9. Comparing these spectra with the ac-susceptibility results, the correlation between the structural feature and the onset of the superconductivity is clearly seen. The 85 K single crystal described above shows a sharp peak at 5.81 degrees (see curve A in fig. 9), which corresponds to the (002) reflection of this phase with $c = 30.79$ Å. Curves B to E represent the low-angle X-ray diffraction patterns for the samples with 1112 starting composition after different heat treatments. The samples which only show the 80 K transition have a similar pattern (curve E) to the 85 K single

Fig. 9. Low-angle X-ray powder diffraction spectra of the 85 K single crystal (curve A) as well as the 1112 samples with different heat treatments (curves from B to E). A relatively broad peak around 4.85 degree in 2θ is closely related to the appearance of the 110 K phase. All samples with the onset of T_c at 110 K show this peak.

crystal. In curves B to D in fig. 9, a new peak between 4.81 and 4.87 degrees in 2θ , in addition to the (002) diffraction of the 85 K phase at about 5.5–5.8 degrees, is observed. It is noted that the intensity ratio of the two peaks increases from curves B to D, which is remarkably in correspondence to the fraction of the 110 K superconducting transition indicated by ac-susceptibility measurements. According to the high resolution electron microscopy results [7], the 110 K phase has a structure related to the 85 K phase and probably has a c -axis of about 37 Å. This implies that the new peak around 4.85 degrees may be due to the (002) reflection of the 110 K phase. In fact, among the samples investigated, all samples which clearly show a 110 K transition have this peak, while all other samples which have only the 85 K transition do not show this peak. In general, this peak is broader than that of the 85 K phase, which means that the 110 K phase in the samples does not crystallize properly. It is highly probable that the 110 K phase is formed in a short-range ordered manner, either by decomposition of the 85 K phase at a temperature very close to the partial melting point or by an additional inclusion of Ca and CuO_2 layers in the 85 K phase through a long distance diffusion. Difficulties of the preparation of the 110 K superconducting single phase may be due to the large unit cell, especially in the c -direction, which makes a long distance diffusion necessary, as well as due to

the apparent slow thermodynamical kinetics of the 110 K phase formation.

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