### THE 120K-SUPERCONDUCTING PHASE IN Bi-Ca-Sr-Cu-O

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The formation of the high temperature superconducting phases in the quinary Bi-Ca-Sr-Cu-O compound system has been investigated. The 120K-superconducting transition appears in samples prepared between 850 and 900°C. A certain homogeneity range is found to exist in this superconducting system, suggesting that higher  $T_{\rm c}$  may be achievable in the same system.

In an attempt to gain insight into the occurrence of high temperature superconductivity and to raise the superconducting transition temperature  $T_i$ , we have carried out an intensive search for new superconducting oxides, immediately following the discovery of high  $T_c$  in oxide systems with the  $K_2NiF_2$  and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>2</sub> (1-2-3) structures. Based on existing results, we concluded that (1) both the trivalent element and the atomic size are crucial in stabilizing the oxides in a certain crystalline form favorable to high  $T_c$ , (2) the planar configuration of Cu-atoms appears to be strongly correlated with high  $T_c$ , and (3) enhanced complexity in crystal chemistry tends to be associated<sup>3</sup> with enhanced  $T_s$ , i.e. 30K-superconductivity in the single-layer ternaries and 90K-superconductivity in the imple-layer quaternaries. Indeed, superconductivity up to 120K has recently been observed<sup>4,5</sup> in the multiphase Bi-Ca-Sr-Cu-O (BCSCO) and Bi-Al-Ca-Sr-Cu-O systems. Later, Al was found to play only a negligibly small role in the observation. BCSCO is therefore a quinary superconducting compound system, consisting of the trivalent Bi. Our structural data showed<sup>6</sup> that the 90Ktransition in BCSCO is associated with the Bi<sub>2</sub>CaSr<sub>2</sub>Cu<sub>2</sub>O<sub>9-6</sub> (2:1:2:2) phase. Unfortunately, a single phase BCSCO sample with a  $T_c \sim 120$ K has yet to be obtained for detailed physical characterization. In this letter, we report the effects of synthesis conditions and compositions on  $T_c$ , the evolution of the superconducting phases, and the preparation of samples with the major 120K-supercon-

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### 544 R. L. Meng et al.

ducting phase. The results indicate that (1) the 120K superconducting-phase forms more easily in a Cu-rich environment at temperatures between 850 and 900°C, (2) there exists a certain homogeneity range for the formation of the superconducting phases with different  $T_c$ 's, and (3) higher  $T_c$  may be achievable in BCSCO homologous structures closely related to one another with greater crystal chemical complexity.

The chemical reactions and the physical properties of the quinary compound system of BCSCO over a wide range of compositions have been investigated. The differential thermal analysis (DTA), thermogravimetric analysis (TGA), and differential thermogravimetric analysis (DTG) were made on a Stanton Redcroft 781 Simultaneous Thermal Analyzer. The X-ray powder diffraction study was carried out by a Rigaku D/MAX IIIB automated diffractometer with a Cu-source. The resistance measurements were performed using the standard four-lead technique. The dc magnetization measurements were done employing the PAR M155 vibrating sample magnetometer. The magnetoresistance measurements were made in a superconducting magnet up to 6T. The temperature was determined by one or two of the following thermometers: chromel-clumel thermocouple, Au+0.07%Fe-chromel thermocouple, Pt-Rh thermocouple, Gethermometer, glass carbon thermometer, and diode thermometer, depending on the measurements and the temperature ranges examined. All thermometers within certain range have been calibrated against each other and against the standards. The uncertainty in temperature so determined was estimated to be less than  $\pm 1^{\circ}$ K above 500K, or  $\pm 0.3^{\circ}$ K below 400K.

The starting ingredients used in the present study were  $Bi_2O_3$  (99–99.999%),  $Bi(NO_3)_3 \cdot 5H_2O$  (99.99%).  $CaCO_3$ (99–99.995%),  $SrCO_3$  (99–99.999%) and CuO (99–99.009%). Although highly sensitive  $T_c$ -dependence on impurity was reported for the  $Bi_2Sr_2Cu_2O_7$ , no clear impurity effect on the  $T_c$  of BCSCO can be concluded from the present study. The initial powder materials of appropriate amounts were thoroughly mixed. The mixture was then heated and cooled in air. The DTA, TGA, and DTG results are shown in Fig. 1 for BCSCO-a and -b, with compositions of Bi:Ca:Sr:Cu = 1:1:1:1 and 1:1:1:2, respectively. Three reaction peaks at  $T_1$ ,  $T_2$ , and  $T_3$  are clearly evident below melting. This observation is typical for all compositions examined, provided that the Sr/Ca ratio is greater than 0.7. The increase of Cu tends to change  $T_1$ ,  $T_2$ , and  $T_3$  somewhat and to enhance the temperature difference between  $T_3$  and melting. This suggests possible greater chemical stabilities of BCSCO than 1-2-3 superconductors.

X-ray powder diffraction was carried out on more than 45 samples of different compositions prepared under different conditions. By comparing the X-ray data with the electrical and magnetic results, the diffraction pattern for the superconducting phase was therefore isolated as shown in Fig. 2. No difference has been detected yet within our resolution between samples with  $T_c$ 's between 60K and 120K. Results for BCSCO-b synthesized at various temperatures slightly higher than  $T_1$ ,  $T_2$ , and  $T_3$  are also displayed in the same figure. It is clear that the

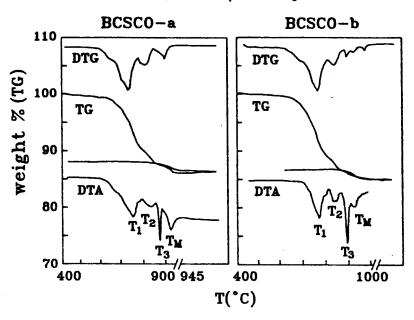


Fig. 1. DTA, TGA, and DTG results for BCSCO-a and -b in air with compositions Bi:Ca:Sr:Cu being 1:1:1:1 and 1:1:1:2. The scan speed for temperature is  $20^{\circ}$ /min.  $T_{\rm M}$  is the melting point.

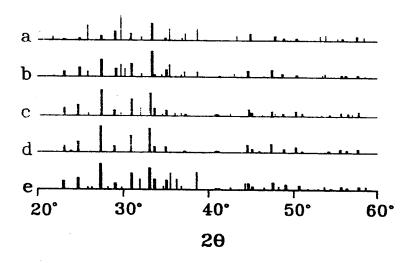


Fig. 2. X-ray results for BCSCO-b synthesized at different temperatures: a-820°C, b-864°C, c-880°C, d- the superconducting phase. Curve e is for BCSCO-c with composition ratio of 1:22:14:6.0 synthesized at 850°C.

#### 546 R. L. Meng et al.

superconducting phase starts to grow slowly at temperatures above  $T_1$ , then rapidly above  $T_2$ . The basic pattern of the superconducting phase appears in samples for Cu to Bi ratio varying from ~0.8 to 6.0 in the fashion mentioned above. For example, when the insulating Ca<sub>2</sub>CuO<sub>3</sub> was doped with only a few percent of Bi and Sr, the sample became completely superconducting resistively below 60K and the superconducting phase appeared in the X-ray diffraction pattern. We also found that an initial 2:1:2:2 composition ratio does not lead to the pure 2:1:2:2 structure<sup>6</sup> for the 90K-phase based on our synthesis conditions. The superconductivity 2:1:2:2 phase occurs more easily in the Cu-rich environment with Cu/Bi-ratio varying between 1 and 6. A Cu-rich sample BCSCO-c (with a composition ratio of 1:22:14:6:0) synthesized at 850°C was also studied. The X-ray data showed that a great majority of the sample belonged to the superconducting phase, in spite of the small amount of Bi and the rest associated with CuO. Synthesis in high oxygen atmosphere was found to be detrimental to the superconducting properties of BCSCO. Sometimes it even destroyed the 2:1:2:2 structure and made the sample paramagnetic.

Typical resistance (R) and magnetization (M) results are shown respectively in Figs. 3 and 4 for BCSCO-b, synthesized at different temperatures. It is clear that both the  $T_c$  and the Meissner effect grow as the synthesis temperature increases. The 120K transition occurs only when the sample is synthesized above ~850K, although lower  $T_c$  happens in samples prepared at lower temperatures. However,

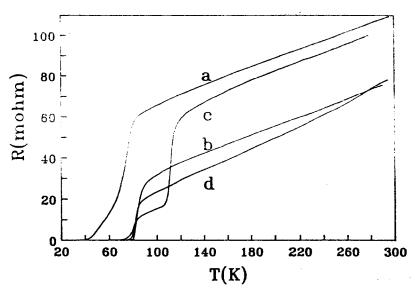


Fig. 3. Rvs. T for BCSCO-b synthesized at different temperatures a-820°C, b-864°C, c-880°C. Curve d is for BCSCO-c.

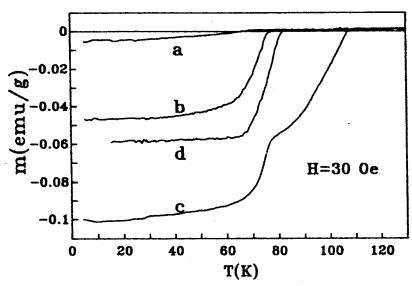


Fig. 4. M vs. T for BCSCO-b synthesized at different temperatures a-820°C, b-864°C, c-880°C. Curve d is for BCSCO-c.

the superconducting properties deteriorate when the sample is heated above the melting point. In these two figures, results for BCSCO-c are also shown. A trace of the 120K-transition is evident although the bulk of the sample is superconducting at ~85K. Totally unexpected is the relatively large Meissner effect (>50% of BCSCO-b) observed in BCSCO-c in spite of the small amount of Bi present. It should be noted that the porosity of our samples can be rather different. No effort has been made to extract resistivity or to calculate M per volume.

The magnetic field effect on R for a BCSCO-b sample is shown in Fig. 5. The transition is clearly suppressed to lower temperature and broadened in the presence of magnetic field. The broadening is similar to that observed in the 1-2-3 polycrystalline compounds due to the weak coupling between the highly anisotropic structure of the compounds. The upper critical field at 0°K for the 120K transition is estimated to be ~187T.

From the above R- and M-results, samples with a single superconducting transition at  $\sim 90\,\mathrm{K}$  or below can be obtained rather easily. However, no sample of ours has exhibited only one complete transition at  $\sim 120\,\mathrm{K}$ . In view of the large fraction of the Meissner effect associated with this 120K transition, the failure to achieve a complete resistive transition at this high temperature suggests that the high  $T_{\rm c}$  material must be enclosed by the low  $T_{\rm c}$  material. This is in strong contrast to the 1-2-3 compounds or even the low  $T_{\rm c}$  BCSCO superconductors. On the other hand, the appearance of two resistive superconducting transitions is similar to the A-15 superconducting compounds. There may exist a difference between the growth processes of the 90 and 120K-phases. Careful studies on the reaction kinetics andthe phase diagram of BCSCO is needed to achieve single transition

# 548 R. L. Meng et al.

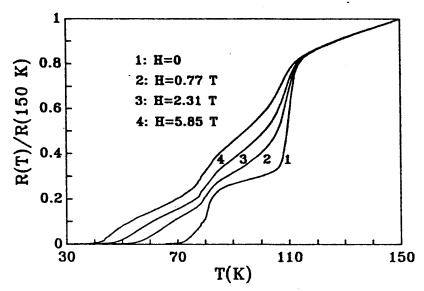


Fig. 5. R-T for BCSCO-b in different magnetic fields.

sample with  $T_c \sim 120$ K. High temperature annealing for more than 24 hours has not enhanced the signal size. The 120K-phase may be closely related to the 2:1:2:2 structure.

Recent structure study showed<sup>6</sup> that BCSCO with compositions 2:1:2:2 superconducting at  $\sim 90 \, \mathrm{K}$  has a four-layer structure, although the exact atomic arrangement is yet to be determined. Numerous structural defects have been observed in microcrystalites of this compound and have been suggested to be responsible for the existence of a certain homogeneity range in BCSCO. The high  $T_{\rm c}$  phase, i.e.  $\sim 120 \, \mathrm{K}$ , may have a homologous structure closely related to the 2:1:2:2 phase. This is consistent with our observation of similar X-ray diffraction patterns of samples with  $T_{\rm c}$  ranging from 40 to 120K. Single crystals with a  $T_{\rm c} \sim 90 \, \mathrm{K}$  have been obtained and investigated.

In conclusion, the  $T_c$  of BCSCO depends sensitively on the synthesis temperature but not on the Cu to Bi ratio. High  $T_c$  phase appears only for samples prepared at temperatures above 850°C but below melting. The present study indicates that there may exist a certain homogeneity range for the superconducting phase to form, preferably in a Cu-rich environment. This raises questions concerning the essential role of planar configuration of Cu-ions in BCSCO. The 120K-transition phase may possess a homologous structure of the newly identified 2:1:2:2 90K phase. Even higher  $T_c$  may be achievable in this system with increasing complexity in crystal chemistry. Attempt in obtaining samples with only one superconducting transition at ~120K or higher is being made.

## Acknowledgment

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