High-\(T_c\) Superconductivity in the Multi Phases Sr–Bi–Ca–Cu–O

C. Politis

Kernforschungszentrum Karlsruhe, Institut für Nukleare Festkörperphysik, Postfach 3640, D–7500 Karlsruhe, Fed. Rep. Germany and University of California, San Diego, Dept. of Electrical and Computer Engineering, Mail Code C–014, La Jolla, CA 92093, USA

Received 12 February 1988/Accepted 16 February 1988

Abstract. High-\(T_c\) superconductivity with \(T_c\) onsets up to 120 K (midpoint: 90 K, zero resistance: 85 K) is observed in the multi phase Sr–Bi–Ca–Cu–O with the nominal composition of Sr\(\text{BiCaCu}_2\text{O}_6\). We report the synthesis and the superconducting temperature of the multi phase Sr\(\text{BiCaCu}_2\text{O}_{6+x}\), Sr\(\text{BiCaCu}_2\text{O}_{6-\delta x}\) and Sr\(\text{BiCaCu}_3\text{O}_{7+x}\) (0≤x≤1) compounds.

PACS: 74.70 Vy

In the last two years, three structural families of mixed-valence high-\(T_c\) superconducting copper oxides have been discovered: La\(_{2-x}\)A\(_x\)Cu\(_{4-y}\) (A=Ca,Sr,Ba), LnBa\(_2\)Cu\(_4\)O\(_7\) (Ln=Y,La,Nd,Sm,Eu, Gd,Dy,Ho,Er,Tm,Yb and Lu) and Sr\(_2\)Bi\(_2\)Cu\(_2\)O\(_7\). La\(_{2-x}\)A\(_x\)Cu\(_{4-y}\) were synthesized and studied for the first time by the Raveau group [1]. The superconductivity in La–Ba–Cu–O with \(T_c\) of 35 K was discovered by the Zürich group [2]. Superconductivity in the multi phases Y–Ba–Cu–O with \(T_c\) above the boiling temperature of liquid nitrogen (77 K) was observed both in Houston and Alabama [3]. LnBa\(_2\)Cu\(_3\)O\(_7\) and LnBa\(_2\)Cu\(_3\)O\(_7-x\)F\(_x\) with \(T_c\)'s above 100 K have already been reported [4–8]. The recently [9] discovered class of mixed-valence copper oxides, Sr\(_2\)Bi\(_2\)Cu\(_2\)O\(_7\) with superconductivity at temperatures of 22 K have opened the door for new high-\(T_c\) compounds for the first time without rare earths and the enhancement of the superconducting transition temperature by substituting Ca and Bi for Sr [10]. Recent studies of such compounds with no rare earth have also been reported [11,12]. \(T_c\) onsets up to 120 K and zero resistance at 77 K were found in the multi phases SrBiCaCu\(_2\)O\(_x\) [11]. Recently, one superconducting phase with onset temperatures near 120 K and zero resistance at 85 K has been identified with the composition Sr\(_2\)Bi\(_2\)CaCu\(_2\)O\(_9\) [12]. We report here the synthesis and the superconducting temperatures of various Sr–Bi–Ca–Cu–O samples.

1. Experimental Procedure

For these studies, fine powders of SrCO\(_3\), Bi\(_2\)O\(_3\), CaO and CuO (all of them with 99.999% purity) were mixed in appropriate proportions, pulverized, and pressed into 4 g pellets with 20 mm diameter (3 mm thickness) at 4 kbar. The pellets were first repeatedly heated at 780° C for 3 h (with intermediate grinding) in air; then for 12 h at 800–950°C in air. Depending on the composition, different heat treatments and quenching or cooling conditions between 300° and 800° C were carried out in vacuum, air or in oxygen.
The superconducting transitions were measured resistively using calibrated platinum resistors. The samples were cut into 10x3x2 mm bars. Their resistivity was determined by four probes attached with silver paste and gold wires. The dc currents were kept very low (1 μA-10mA) to avoid any possible suppression of $T_c$ in the samples.

2. Results

The colour of the sintered superconducting pellets, depending on composition and heating conditions, changed between dark-grey and black-metallic. For all the samples a metallic thermal and electrical conductivity was found. The normal room-temperature resistance of the samples was between 10 and 2000 Ω. Figure 1 shows the transition into the superconducting state for three Sr-Bi-Ca-Cu-O compounds after 12 h annealing at 800°C in air and quenching. The zero resistivity increases from 70 K for SrBiCaCuO$_6$ (a) to 75 K for SrBiCaCu$_2$O$_6$ (b) and 79 K for SrBiCaCu$_3$O$_7$ (c). For the nominal composition SrBiCaCu$_2$O$_6$, a clear onset at 120 K is observed. Figure 2 shows the superconducting behaviour of various SrBiCaCu$_2$O$_6$ samples. After rapid quenching from 450°C in air an onset at 120 K, midpoint of 90 K and zero resistivity at 85 K, have been measured. We have observed in many SrBiCaCu$_2$O$_6$ samples two transitions in the superconducting state. Such steps have been observed in many samples after heat treatment at different temperatures in oxygen and air, by slow cooling but also by rapid quenching ($10^3$ K/s). Only after heat treatment under vacuum conditions ($10^{-3}$ mbar) was no step found. But it is still not clear under which conditions the step in the resistivity with onset at 115 K does exist. There are, in principle, two explanations: a phase transition at 115 K due to stabilization by defects, or the presence of a high-$T_c$ superconducting phase with clear onset at 115 K. In fact, according to magnetic measurements [13] the onset of superconductivity in high-$T_c$ SrBiCaCu$_2$O$_x$ occurs at 113 K.

3. Conclusion

We have described the preparation and superconducting measurements of high-$T_c$ multi-phase Sr-Bi-Ca-O compounds. The highest $T_c$ onset recorded for our specimens was 120 K in SrBiCaCu$_2$O$_6$. It is hoped that still higher $T_c$'s can be obtained by suitable substitution and preparation conditions.

References