Thermal Expansion of $\text{Bi}_2.2\text{Sr}_{1.8}\text{CaCu}_2\text{O}_x$ Superconductor Single Crystals


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Using a low-temperature stage X-ray diffractometer, we have investigated the temperature dependence of the lattice parameters of single crystal superconductors $\text{Bi}_2.2\text{Sr}_{1.8}\text{CaCu}_2\text{O}_x$. The experimental results show that (i) the lattice constants increase linearly with increasing temperature above about 100 K; (ii) the c-axis lattice parameter shows a kink in the superconducting transition region, while the a, b-axis parameters do not show any anomalous behavior in this region; (iii) both a, b, and c show negative thermal expansion coefficients below 40–50 K, which may be related to the characteristics of the Cu–O bond.

KEY WORDS: $\text{Bi}_2212$ high-temperature superconductor; lattice parameter.

1. INTRODUCTION

Thermal expansion is an important thermodynamic property of superconductors, and a number of experimental results have been reported [1–12] for the high-$T_c$ materials. Since $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7-\delta$ (Y123) was the first high-$T_c$ superconductor with $T_c > 77$ K, most reports [1–7] have focused on the Y123 materials. However, a few experimental studies [10–12] on the thermal expansion of Bi-based high-$T_c$ superconductors have appeared in the literature. Of particular relevance, the following investigations have been reported. Arendt et al. [10] measured the temperature dependence of the lattice parameters above room temperature for $\text{Bi}_{2}2\text{Bi}_{2}2\text{Bi}_{2}$ and $\text{Bi}(\text{Pb})2\text{Bi}_{2}2\text{Bi}_{2}$ powder samples. Using a three-terminal capacitance dilatometer, Braun et al. [11] measured the coefficient of thermal expansion in the superconducting transition region for a $\text{Bi}(\text{Pb})2\text{Bi}_{2}2\text{Bi}_{2}$ powder sample. Misra et al. [12] measured the thermal expansion, also in the transition region, for a $\text{Bi}_{2}2\text{Bi}_{2}$ single crystal sample grown by the flux method, although they did not specify the crystal orientation of the measurements. For geometric reasons we assume that their results were obtained for the $a, b$-direction. For various reasons, the float zone technique has many advantages over with the flux method for the growth of high-quality $\text{Bi}_{2}2\text{Bi}_{2}$ single crystals. In fact, the lack of high-quality single crystals limits the ability of many experiments to measure reliable intrinsic properties of the superconducting phase. To our knowledge, there is no previous report of thermal expansion measurements on $\text{Bi}_{2}2\text{Bi}_{2}$ single crystals grown by the float zone technique. The availability of high-quality single crystals prepared by the float zone technique allows for a more meaningful investigation of the physical properties of these materials than has been previously possible.

In the present paper, we report the results of an investigation of the thermal expansion of high-quality single crystals of $\text{Bi}_2.2\text{Sr}_{1.8}\text{CaCu}_2\text{O}_x$ as a function of temperature in the range of 4 to 300 K by low-temperature X-ray diffraction methods. This is the first report of thermal expansion measurements made on single crystals of this material grown by the float zone technique.

2. EXPERIMENTAL DETAILS

High-purity $\text{Bi}_2\text{O}_3$, $\text{SrCO}_3$, $\text{CaCO}_3$, and CuO powders were mixed in the stoichiometric ratio of...
Bi: Sr: Ca: Cu = 2.2: 1.8: 1: 2. There are two reasons for using these ratios: First, single crystals prepared from this starting composition have an identical structure to the ideal 2:2:1:2 phase, and show almost the same physical properties as the Bi2212 material. Second, this starting composition more readily produces high-quality single crystals than the ideal 2212 stoichiometry. The mixed powder was calcined at 780°C for 24 h. After grinding, it was sintered at 850°C for 72 h. The sintered material was shown to be the superconducting phase on the basis of its X-ray diffraction patterns. The superconducting powder was pressed into rods of 5 mm diameter, and sintered at 800°C for 24 h in order to enhance its mechanical strength. The sintered rod was melted at a rate of 50 to 60 mm/h to obtain a dense polycrystalline feed rod, which was used for growing the single crystal by the float zone technique. The float zone furnace (Nichiden Machinery, Ltd.) was equipped with a pair of half ellipsoidal mirrors which reflected the radiation from two 1.5-kW halogen infrared lamps. The focused infrared light melted a small portion of the rod, which was the floating zone. The growth of the single crystal was performed at a rate of 0.4 to 0.5 mm/h in 1 atm of flowing oxygen. Individual single crystals could be cleaved from the zone-melted rods.

The single crystals grew along the a, b-direction (i.e., along the “symmetry” axis of the rod). Electron diffraction patterns showed the existence of a substantial number of 90° domains in many pieces of single crystals. Disk-shaped sections were cut from the rod to provide samples for the present investigation. By this technique, crystals with typical dimensions of 0.05 to 0.1 mm in the c-direction were obtained. Each section of the rod had many pieces of single crystals bound by the solvent. The c-axes from different pieces of single crystal are in the same plane, which is perpendicular to the growth direction and parallel to the disk-shaped section. After breaking each section along its axis, single crystals with well-defined (i.e., shiny) cleavage planes in the a-b direction could be obtained. Crystal orientation was then confirmed by X-ray diffraction patterns.

The magnetic susceptibility ($\chi'$ and $\chi''$) was measured by a standard ac susceptometer which used a two-phase lock-in amplifier (Princeton Applied Research, Model 129A) to separate the in-phase and quadrature components of the signal. The superconducting transition temperature, $T_c$, determined by the location of the cusp in $\chi'$, was found to be 83 K as illustrated in Fig. 1.

An X-ray (Cu Ka radiation) scanning diffractometer (Siemens D-500) with a low-temperature sample stage was utilized to measure lattice constants. The sample was mounted in a continuous flow cryostat (Oxford CF1100) and the temperature was controlled by regulating the flow of helium gas and electrically heating the sample holder using an Oxford ITC4 controller. Temperature stability was ±1 K below 40 K, ±0.1 K in the range of 40 to 150 K, and ±0.5 K above 150 K. The measurements were performed during a warming cycle from 4.2 to 300 K.

Since the crystal orientations were easily found, the sample could be readily aligned on the cold stage of the X-ray diffractometer. For a well-aligned single crystal, only specific characteristic reflections are observed in the scanning diffractometer pattern. Figure 2 shows two wide-angle diffraction patterns obtained at room temperature for the two sample orientations used in this experiment. In order to precisely determine changes of the peak positions, diffraction patterns were obtained over a small range of angles ($\Delta 2\theta = 0.5^\circ$) around selected peaks with a step size of 0.005°. As illustrated by the patterns in Fig. 2, the sample oriented along the a, b-axis showed only a single strong peak in the diffraction pattern (200)/(020), while the c-axis oriented showed several peaks. Measurements for the latter orientation were made...