JOURNAL OF SOLID STATE CHEMISTRY 88, 183–187 (1990)

Single Phase High T_c Superconductors of the Bismuth Cuprate Family

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Received February 22, 1990; in revised form March 5, 1990

DEDICATED TO J.P.M. HONIG ON THE OCCASION OF HIS 65TH BIRTHDAY

The high-temperature superconducting phase of the Bi-2223 system, with and without Pb, was prepared by the sol–gel method. The material was characterized by X-ray powder diffraction and by magnetization. An almost pure phase was obtained on the addition of $Pb(NO_3)_2$ (0.2 *m*) in substitution for the Bi and less time for sintering was needed. © 1990 Academic Press, Inc.

Introduction

Since the discovery of superconductivity in the system Bi–Sr–Ca–Cu–O at least three phases with the compositions 2201, 2212, and 2223 have been identified. Maeda *et al.* (*1*) discovered bulk superconductivity at 85 K and evidence of superconductivity at 110 K. The preparation of single phase material with zero resistivity at 110 K has been shown to be extremely complicated; generally a mixture of all three phases is present in the bulk material. Since the initial discovery, there have been many publications detailing the existence of the high-temperature (HT) superconductor (SC) phase with $T_c \approx 110$ K and discussing the structure of the different phases of the system Bi–Sr–Ca–Cu–O (*2–6*). Within this class of compounds, Bi can be replaced by thalium and new phases of the general formula $Tl_2Ba_2Ca_{n-1}Cu_nO_y$ ($n = 1, 2, 3$) have been isolated (*7*); this substitution raises T_c to 125 K for $n = 3$. Obtaining the pure 110 K phase in the Bi system is one of the most challenging tasks: one usually obtains the low temperature (LT) phase ($T_c \sim 80$ K) or the high-temperature (HT) phase in multiphase mixtures (*1, 7–9*). Among other efforts, it was reported that the partial substitution of Pb and/or Sb facilitate and optimize the preparation of the 2223 phase (*11–16*). It should be stressed that the reason for preferring the HT bismuth cuprate SC is for its resistance to humidity and water, in contrast to $YBa_2Cu_3O_7$, and its much lower toxicity compared to the thallium cuprate SC.

The common procedure for obtaining ceramic superconductors is by the solid state time-consuming reaction: "shake 'n bake." Recently a new method for preparing $YBa_2Cu_3O_7$ (*17*) was published. This sol–gel method has been used for the preparation of glasses (see, e.g., Ref. (*18*)) and oxide perovskites (*19*). It is based on an initial mixture of organometallic precursors in solution at the suitable pH followed by drying

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and sintering. The solid obtained after drying is voluminous and the end product is finely powdered, mostly single phase and with improved SC properties. The high homogeneity is due to the initial solution mixture in contrast to solid oxide-grinded mixtures. The organic ligands used are diverse: citrates (*17*), amines (*20*), oxalates (*8*), etc.

The aim of this study was to prepare single phase HT bismuth cuprate SC, using the sol–gel method, and to characterize it structurally and magnetically.

Experimental

1. Preparation of Bi-2223

The appropriate stoichiometric amounts of metal nitrates were dissolved: 6.25 mmol Bi^{3+}, Sr^{2+}, Ca^{2+}, each, and 9.37 mmol $Cu(NO_3)_2$ in 70 ml water. To the solution, 6.25 g citric acid was added, followed by 30 ml ethyleneglycol. The solution was condensed at 120°C until a greenish colloidal precipitate was obtained. Continuation of the evaporation resulted in the formation of a dark gel. This gel was decomposed in a sand-bath to obtain the precursor. Gradual ignition to 500°C, grinding, and further calcination to 800°C followed by several hr at this temperature were needed to complete the decomposition and evaporate all the organic components. The powder was pressed into pellets (in a KBr die) and sintered overnight at 800°C. After slow cooling to room temperature in air, the sample was characterized by XRD and by a qualitative levitation experiment. Repeated annealing at 880°C was carried out until an optimal single phase was obtained.

2. Preparation of (Pb)Bi-2223

For this composition, 0.2 *m* Pb was substituted for the Bi and the same procedure as above was adopted; the only difference being lowering the annealing temperature to 870°C.

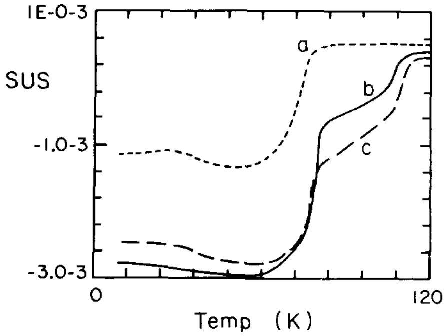

FIG. 1. Magnetic susceptibility vs temperature for $Bi_2Sr_2Ca_2Cu_3O_x$ initial stoichiometry. (a) After 33 hr annealing; (b) after 103 hr annealing; (c) after 148 hr annealing at 880°C.

3. Characterization

The phases were identified by XRD using a Philips Diffractometer with Cu*Kα* radiation. Magnetization was measured with a PAR 155 vibrating sample magnetometer cooled with He.

Results and Discussion

The bulk superconductivity of the samples was confirmed by susceptibility as a function of temperature during heating. An example of a Meissner curve is shown in Fig. 1 where the susceptibility was recorded by cooling the sample to liquid He temperature at a constant low magnetic field: tens of oersteds. Corresponding derivatives of these curves, with respect to temperature, yielded a single peak with maxima at ~85K for sample a which had been annealed for a total of 33 hr at 880°C. Further annealing at the same temperature for 70 hr and an additional 45 hr yielded the curves b and c, respectively. It is obvious that increasing the annealing time caused the formation of a second phase at ~110K. Whereas in a only the LT Bi-2212 phase

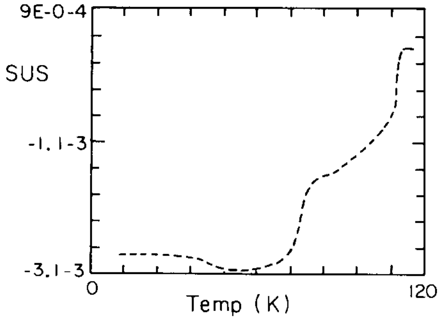

FIG. 2. Magnetic susceptibility vs temperature for $Bi_2Sr_2Ca_2Cu_3O_x$ after 263 hr total annealing.

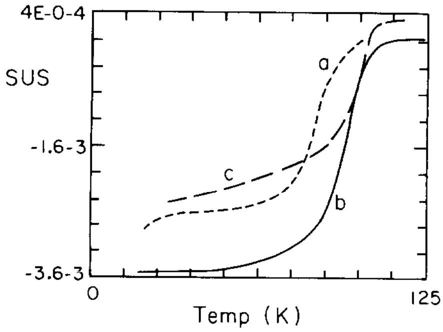

FIG. 3. Magnetic susceptibility vs temperature for $Bi_{1.8}Pb_{0.2}Sr_2Ca_2Cu_3O_x$ (a) after 56 hr annealing; (b) after 90 hr annealing; (c) after 95 hr annealing at 870°C.

was observed, in b and c, the 2223 phase grows. Continuation of the annealing process increases the amount of the 2223 phase at the expense of the 2212 phase (compare curves b and c. Further annealing for 115 hr increases the amount of the HT phase to more than 50% of the two-phase mixture (Fig. 2). Extending the annealing does not bring to the formation of a single 2223 phase.

Substituting Bi by Pb caused the formation of almost a SC phase after annealing for a comparatively short time (56 hr) at 870°C (Fig. 3a) with a considerable amount of the ~100K phase. Increasing the annealing time (total 90 hr) at the same temperature showed a sharp transition and a $T_c > 110K$ with no indication of two-phase character or impurity phases (Fig. 3b). It is generally accepted that the broadening of the superconducting transition usually reflects the presence of extraneous phases, therefore one can attribute the narrow (sharp) superconducting transition to the high structural homogeneity of the sample. Further short annealing of the sample (5 hr!) did not reduce T_c but decreased the content of the SC phase as seen from the shorter curve (Fig. 3c).

Preliminary results with Sb-substitution did not show the formation of single phase material. Changing the initial stoichiometry to 2332 yielded a phase mixture containing small amounts of 2212 phase.

A typical XRD diffractogram of Pb-substituted sample is shown in the 2θ range 20–40 (Fig. 4) with the two phases marked A

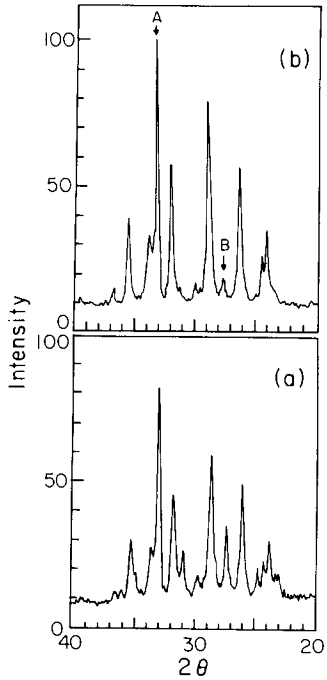

FIG. 4. XRD of $Bi_{1.8}Pb_{0.2}Sr_2Ca_2Cu_3O_x$ (a) after 56 hr annealing; (b) after 90 hr annealing. A : 2θ = 33.10; 100% of 2223 phase; B : 2θ = 27.50; 100% of 2212 phase.

TABLE I

LITERATURE AND OBSERVED d VALUES FOR THE Pb, Bi-HT PHASE

Literature (*21*, *22*)		Measured	
2θ	d	2θ	d
23.78	3.738	Sh	—
24.00	3.705	24.05	3.697
24.39	3.646	24.40	3.645
25.34	3.512	Sh	—
26.25	3.395	26.25	3.395
28.82	3.095	28.80	3.206
28.90	3.087		
31.95	2.799	31.90	2.803
33.13	2.702	33.10	2.704
33.85	2.646	33.75	2.653
34.55	2.594	V.W.	—
35.41	2.533	35.50	2.527
35.52	2.527		
38.87	2.315	V.W.	—
39.43	2.283	W	—

and B, corresponding to 2223 and 2212 phases, respectively. Figure 4a depicts the mixture after 56 hr annealing yielding A/B phase ratio of ca. 3; increasing the time of annealing to 90 hr raises this ratio to ca. 12 which is practically a single 2223 phase system (Fig. 4b). The ratio of the phases was estimated from the intensity of the diffraction lines at 27.50 and 33.10 (2θ) identifying the 2212 and 2223 phases, respectively. The pattern of the powder XRD of the longer annealing time process matches well with the face-center tetragonal structure reported earlier with the lattice parameters $a \approx b = 5.40$ Å and $c = 37.10$ Å (*21*, *22*). Table 1 shows the literature d values for the 2223 phase in the 2θ range 20–40 compared to the observed ones in this work.

The XRD pattern of the Bi-2223 systems with and without Pb (0.2 *m*) were found in this research to be very similar. As mentioned above, in the absence of Pb, a mixture of phases was always obtained. The best XRD pattern, viz., the one that contains a higher proportion of 2223 phase, corresponds to the magnetic data presented in Fig. 2. This pattern contains the 2212 phase (*23*, *24*) with the index (115), [2θ = 27.4, (I/I_0 = 100)] and the 2223 phase which is the major component in the mixture, with $I/I_0 = 100$ at $2\theta = 33.1$. There is some controversy concerning the XRD pattern, indexing, and lattice parameters of this latter phase. Since there are no good observed data for this Pb-free phase at this time, calculated data are available, presented by Shi *et al.* (*10*) and by Matheis and Snyder (*24*). Both data are indexed on a tetragonal basis but with slightly different lattice parameters: $a = b = 3.812$ Å, $c = 38.0$ Å and $a = b = 3.814$ Å, $c = 37.0$ Å, respectively. Lattice parameters were calculated from observed XRD data of Pb-substituted 2223 (*21*, *22*), viz., $a = 5.399$ Å, $b = 5.400$ Å, $c = 37.10$ Å and $a = 5.404$ Å, $b = 5.390$ Å, $c = 37.05$ Å, respectively. These parameters suggest an orthorhombic structure very close to the tetragonal. For this structure $I/I_0 = 100$ peaks at $2\theta = 33.1$ with the index (200). However, the calculated tetragonal Pb-free 2223 phase, the $2\theta = 33.2$, is indexed (110) with $I/I_0 = 40$; the 100% peak is at $2\theta = 4.7$ indexed (002). In this study, as mentioned earlier, the XRD pattern of Bi-2223 in the mixture with 2212 and the pattern of nearly pure single Pb, Bi-2223 phase are very similar and the $I/I_0 = 100$ peak at $2\theta = 33.1$ is in good agreement with the literature XRD for this phase (*21*, *22*). Our results suggest that the same XRD pattern exists for both Pb-substituted and Pb-free, Bi-2223 systems.

In summary a nearly pure Bi-2223 phase was obtained by the sol–gel reaction only in the presence of Pb. This phase was characterized by XRD and magnetic susceptibility. Due to the use of the sol–gel method, much shorter sintering and annealing periods were necessary to obtain the single phase material (see, e.g., Ref. (*14*) where 300 hr were needed).

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