JOURNAL OF MATERIALS SCIENCE **24** (1989) 2319–2323

Reproducibility of T_c in a $Bi_2Sr_2CaCu_2O_8$ superconductor

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The reproducibility of T_c in superconductive $Bi_2Sr_2CaCu_2O_8$ is known to be very poor. In our study, the reproducibility was found to depend greatly on preparation conditions. DTA, TGA and powder X-ray diffraction methods were used to study the $Bi_2Sr_2CaCu_2O_8$ superconductors prepared by different routes. Resistivity and diamagnetic susceptibility were taken as the measure of superconductivity. It was found that those superconductors prepared from the oxides/carbonates (one-step) process resulted in scattered T_c data which were less reproducible. The two-step synthesis from precalcined precursors of Bi-Sr-O and Sr-Ca-Cu-O containing mixtures, resulted in a much improved reproducibility with the predominant T_c = 80 K superconducting phase (more than 95%). It was also found that the amount of T_c = 115 K phase tends to decrease after repeated pulverization and sintering, leading to a single 80 K phase state. Compaction of the pulverized powder at a pressure $>4.5\,\text{ton cm}^{-2}$ was found to induce a preferred (0 0 *L*) orientation during sintering.

1. Introduction

Immediately following the discovery of high T_c in the Bi–Sr–Ca–Cu–O system with $BiSrCaCu_2O_x$ (1112 for short) [1], many other different stoichiometric compositions have been reported: $Bi_2Sr_2CaCu_2O_8$ (2212) [2–7], 2332 [8] and 4334 [9], etc. For the 2212 phase, T_c-onset ranges from 60 to 114 K [2–7]. One possible explanation is the formation of the multiple phases in the solid state reaction of this four-component system. In this paper we report the preparation of the 2212 phase through different routes, i.e. the one-step solid state reaction from the component carbonates and oxides (one-step for short), and through different precursors (two-step for short). The extensive powder X-ray diffraction (XRD) study, together with differential thermal analysis (DTA), thermogravimetric analysis (TGA), electrical resistivity and magnetic measurements were performed [10], in an attempt to attain better reproducibility in the 2212 superconducting phase.

2. Experimental procedure

The choice of precursor comes from the 2212 structural model [6]; Bi–Bi–Sr–O sandwiched layers located outside the pseudo-orthorhombic building block were chosen as the first precursor, while intermediate-layer Ca–Sr–Cu–O was chosen as the second. The precursors were first separately calcined and then mixed and sintered to form the 2212 phase.

Bismuth oxide, strontium carbonate, calcium carbonate and copper oxide, all with purity > 99.7% were used as starting materials. Weighed oxides (2 to 3 g) with cation ratio Bi : Sr : Ca : Cu kept at 2 : 2 : 1 : 2 were mixed in an agate pestle and mortar and calcined at 600° C for 6 h in the one-step synthesis. Bi–Sr–O (Bi : Sr = 2 : 1) and Sr–Ca–Cu–O (Sr : Ca : Cu = 1 : 1 : 2) precursors, were calcined consecutively at 600, 700, 800° C (and 900° C for the Bi–Sr precursor) for 3 h each, then mixed together. After calcination, the clinker was pulverized and compacted at different pressures, then sintered at 865 to 872° C for 12 to 72 h and air-quenched again. Alumina crucibles with 99.7% purity were used for both calcining and sintering in this work.

DTA and TGA (Rigaku 8078G) at a heating rate of $10°\,C\,min^{-1}$ from 100 to 1100° C were adopted to study the solid state reaction for the one-step mixtures and the two-step precursors.

XRD was used to investigate the phases formed after calcination and sintering. The diffractometer used was either a Rigaku DMAX-IIIB or DMAX-RB with Cu*Kα* radiation and a graphite monochromator. The lattice constants were determined by a modified Cohen's method [11].

The electrical resistance (or resistivity) was measured with an LR-400 four-wire resistometer using a constant current of 10 μA. The temperature was measured either with a GaAlAs or a silicon diode. The zero resistance

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was defined as smaller than 1 $\mu\Omega$. The diamagnetic susceptibility was measured with a PAR 155 vibrating sample magnetometer (VSM) under 50 G, with several milligrams of powder without demagnetization correction. Polarized light micrography was used to identify the second phases.

3. Results and discussion

The synthesized Bi–Sr–O precursor is most probably a single phase, as shown in Fig. 1a; however, it is an unknown one, and no available JCPDS data were available for indexing; trials to work out this structure are underway. Neither of the starting materials can be found in the XRD pattern of Bi_2Sr–O precursor shown in Fig. 1a. For the 800° C calcined Sr–Ca–Cu_2–O precursor, typically unreacted $SrCO_3$, CaO, CuO and a new phase corresponding to the 880° C reaction in the DTA curve marked "d", were identified (Fig. 1a). The precursors used in the subsequent two-step experiment were those calcined at 900° C for the Bi_2–Sr–O mixture and 800° C for the Sr–Ca–Cu_2–O mixture.

DTA and TGA results are shown in Fig. 2a. Fewer peaks in the DTA curve for the two-step process were observed. Those endothermic peaks in the two-step mixture below 840° C are due to reactions among the four oxides. The 850° C peak in the DTA curves for both processes (Fig. 2a) is very interesting. Because the Bi_2–Sr–O precursor was precalcined at 900° C, it is unlikely that the 850° C peak is related to the solid state formation of Bi_2SrO_4. The supplementary DTA analysis on the $SrCO_3$–$CaCO_3$–2CuO mixture showed the same but very large endothermic peak at 850° C (Fig. 2b, dashed line). Therefore, this 850° C peak in both DTA curves (Fig. 2a) might be related to the solid state formation in the Sr–Ca–Cu_2–O mixture. The 872° C (T1) peak in both DTA curves (Fig. 2a) is considered to correspond to the formation of the 2212 superconducting phase, while the 885° C (T2) peak denotes the melting point of the 2212 superconducting phase. These conclusions were verified independently by sintering. Both the 872 and 885° C peaks were also observed by Meng *et al.* [4]. The DTA data indicated that the positions of T1 and T2 are closely related to the stoichiometric ratio of Bi, Sr, Ca and Cu. The excess calcia would enhance the solid state reaction at T1, while excess cuporate shifts the melting point of the possible superconducting phase to a higher temperature. The 13° C temperature difference between the formation of superconducting phase and melting also reveals the importance of temperature control in the preparation of the 2212 superconducting phase.

The typical electrical resistivity and resistance against temperature curves are shown in Fig. 3. All samples showed a weak T_c-onset at 115, but one of them (one-step) tails off slowly to a T_c-zero at 60 to 70 K (Fig. 3, curves A, B); the other (two-step) tails off at 70 to 80 K (curves C, D). However, the reproducibility of the T_c-zero is very bad for the one-step specimens. Only one sample out of several tens shows a T_c-onset at 128 K and a T_c-zero at 92 K being observed

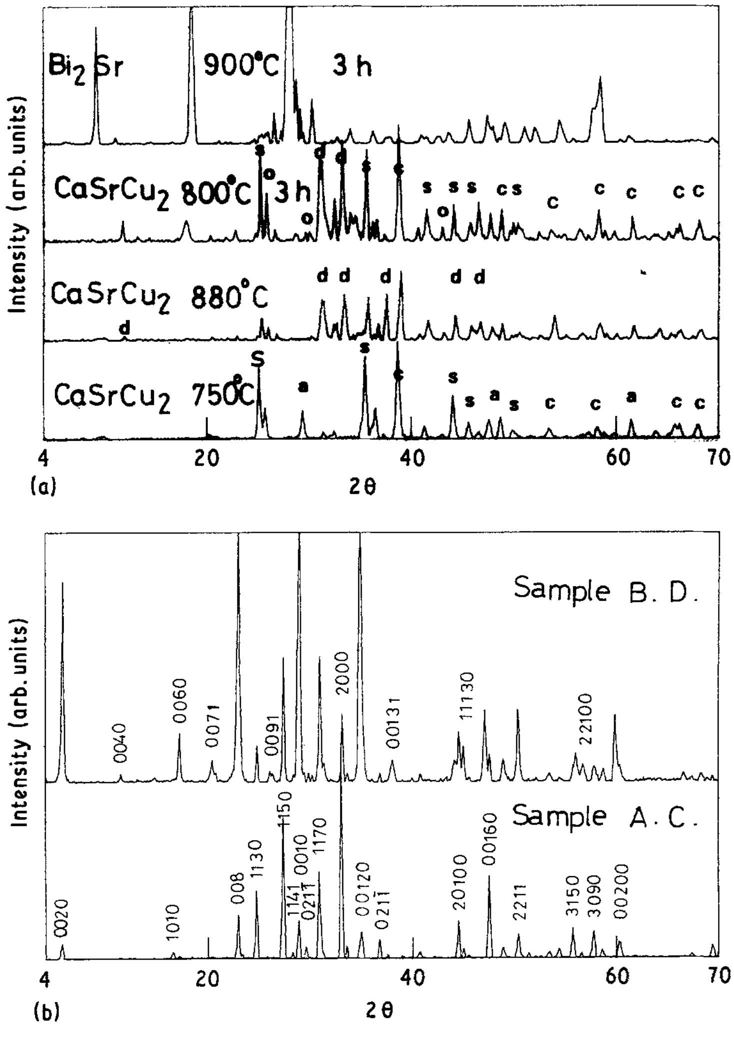

Figure 1 (a) Typical XRDs of the calcined two-step mixtures and those quenched from temperatures corresponding to endothermic peaks of DTA: d, 880° C; e, 1050° C. s, $SrCO_3$; o, CaO; a, $CaCO_3$; c, CuO. (b) Typical XRDs of the 80 K phase through two-step reaction, sample "B, D" is typical of PO (preferred orientation) with enhanced (0 0 *L*) peaks. Indexing of reflection planes is according to Onoda *et al.* [8].

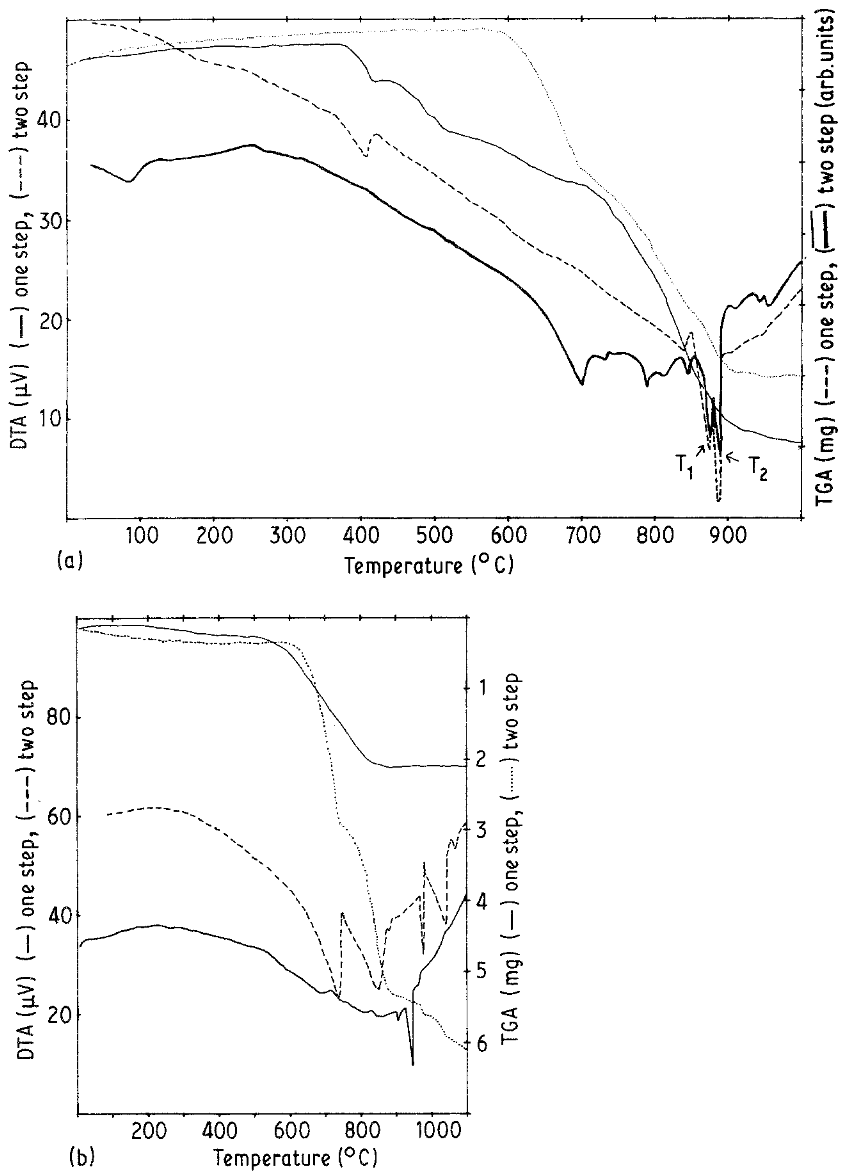

Figure 2 (a) Typical DTA and TGA curves of the one-step and two-step mixtures during heating at 10° C min^{-1}. Mass 25.0 mg, rate 10.0° C min^{-1}. Bi_2O_3 : $SrCO_3$: $CaCO_3$: CuO = 1 : 2 : 1 : 2, and (b) those of the respective precursors. (——) = Bi_2–Sr; (···) for Sr–Ca–Cu_2.

(curve E). The T_c-zero is extremely sensitive to the sintering temperatures and the quenching process, the air-quenched ones generally gave better results than the furnace cooled specimens. For the two-step specimens, the results are more reproducible and less sensitive to these parameters.

The difference in the T_c-zero was originally thought to arise from a varied phase or phase distribution. The 80 K phase was found to be the core phase with the 115 K phase covering the outside of the 80 K grains [9]. In this experiment the sintered products were pulverized and sintered again at higher temperatures (very near 872° C for a few hours or 865° C for a few days) in order to destroy the 115 K shell phase. The

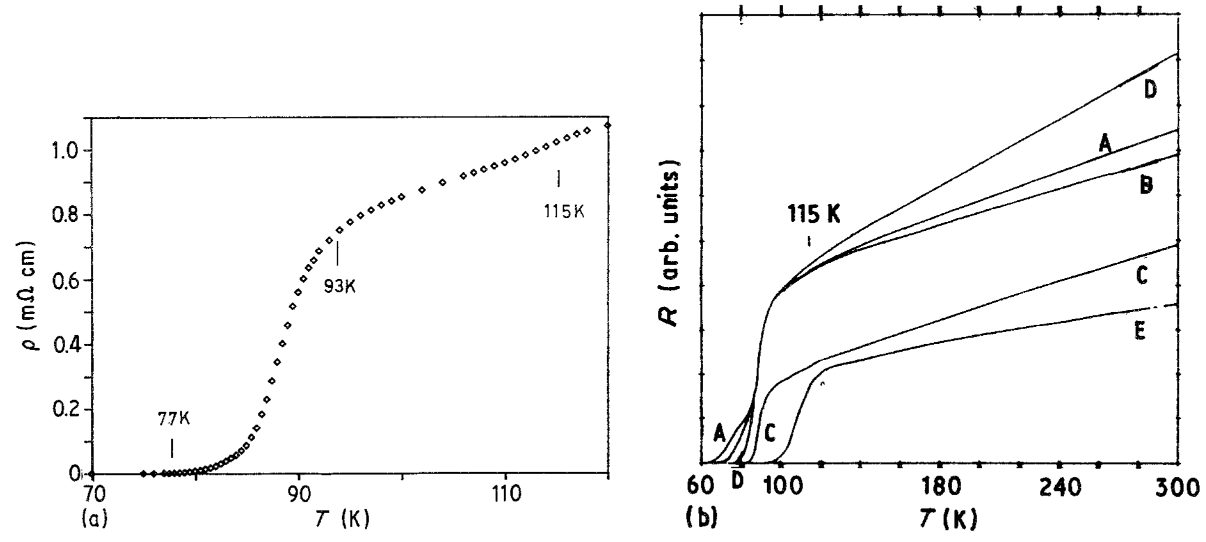

Figure 3 (a) Electrical resistivity of sample C and (b) resistance plotted against temperature curves of some typical specimens. "A", "B" and "E" are from the one-step process, "C" and "D" are from the two-step process. $Ba_2Sr_2CaCu_2O_8$.

outcome of a weaker 115 K T_c-onset transition in the electrical resistance curve indicates the possible instability of the 115 K phase at higher temperatures. It was found that a double sintering process improved the reproducibility of superconducting T_c of 80 K superconductivity for the two-step synthesis, but not for the one-step synthesis.

An interesting fact was noted after a close examination on XRD patterns as typically shown in Fig. 1b. It was found that some samples showed the preferred orientation (PO) of (0 0 L) which is substantial for the samples prepared with a compacting pressure higher than 4.5 ton cm^{-2}, while with a compacting pressure of 2.5 ton cm^{-2} or less, PO could not be found. However, T_c and T_c-zero are both independent of PO as shown in Fig. 3 (curves B and D). The reflections 1 1 4 1, 0 2 1 1, etc., in Fig. 1b did not originate from the impurity and can be readily indexed according to Onoda [8] showing the possible incommensurate modulation. The lattice constants were determined by a modified Cohen's method [11] as $a = 0.552(0)$ nm, $b = 0.551(8)$ nm and $c = 3.094(6)$ nm, similar to those reported by Sunshine *et al.* [6].

Fig. 4 shows the typical diamagnetic susceptibility measurement. The T_c-onset is 93 K instead of 115 K estimated from the resistance measurement (the same as curve C, Fig. 3); this difference could be attributed to a small volume fraction of the 115 K phase and the detection limit of the PAR 155 VSM. The drop at 115 K in susceptibility measurement was so weak to be significant in our measurement. The major phase is the 80 K phase (on-set at 93 K). The volume fraction of the 80 K phase is estimated from the susceptibility measurement at 50 G as 24%, lower compared to reports elsewhere [2–4, 6, 9]. However, no second phase can be identified in the XRD patterns of the two-step specimens. The amount of second phase can be estimated with polarized light microscopy to be less than 5% for the two-step specimens, while it is abundant for the one-step specimens. Hence, out of 95% 2212 phase (two-step synthesis) only a quarter is superconducting at 77 K. Much more work is needed to improve it.

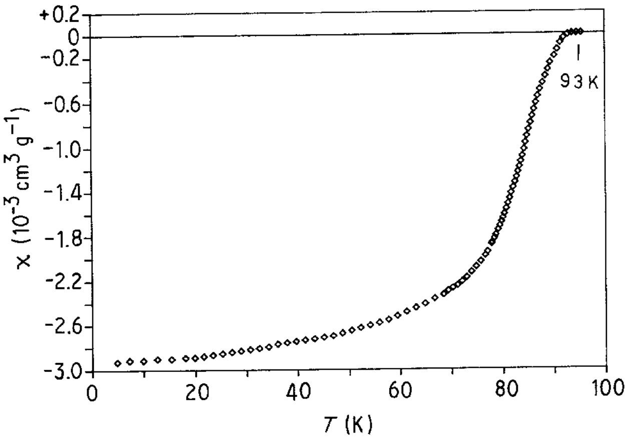

Figure 4 Typical diamagnetic susceptibility–temperature curve of a sintered two-step specimen "C" ($Bi_2Sr_2CaCu_2O_8$); $B_a = 50$ G, powder-cooled.

4. Conclusion

A two-step process using precalcined precursors of Bi_2–Sr–O and Sr–Ca–Cu_2–O mixtures was found to result in a much better reproducibility in the critical temperature of the 2212 superconductor compared to a conventional one-step calcined process from component carbonates and oxides. Detailed DTA studies showed fewer peaks with large endothermic peaks at 850 and 872° C indicating the easier solid state formation of the 2212 phase for the two-step precursors. The 885° C peak denotes the melting point of the 2212 phase.

A double sintering improved further the reproducibility of the 80 K superconductor for the two-step synthesis, but not for the one-step analysis. The outcome of a weaker 115 K T_c-onset transition in the electrical resistance curve and diamagnetic susceptibility measurement indicates the possible instability of the 115 K phase at higher temperatures (very near 872° C for a few hours or 865° C for a few days).

The sample prepared with a compacting pressure higher than 4.5 ton cm^{-2} showed a preferred (0 0 L) orientation, T_c and T_c-zero are both independent of preferred orientation.

The major phase is the 80 K phase (on-set at 93 K); the volume fraction of the 80 K phase is estimated to be 24% from susceptibility measurement, and greater than 95% from polarized light microscopy. Much more effort is required to improve it.

Acknowledgements

The authors are grateful for financial support from the National Science Council of the Republic of China, under the contract number NSC 77-0405-E006-11. Helpful discussions with Professor S. T. Lin are acknowledged.

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Received 23 June
and accepted 6 October 1988