Effect of optimum thermal treatment on BiSrCaCu$_2$O$_y$

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BiSrCaCu$_2$O$_y$ compositions have been subjected to different atmosphere treatments and cooling schedules after initial calcination and firing in air. The large variation in properties has been explained on the basis of oxygen disorder effects and possible insertion of oxygen in different planes.

1. Introduction

Since the first observation of high temperature super-conductivity in a Bi–Ca–Sr–Cu–O system [1], a large number of investigations have been carried out to synthesize various superconducting phases exhibiting transitions between 110 and 10 K [2–4]. It has been reported by many authors that with small changes in heat-treatment conditions, there could be significant variations in the properties of these bismuth-based superconductors. To our knowledge, however, no detailed or systematic attempts have been reported on 1112 composition, therefore, we considered it worthwhile to investigate a variety of thermal treatment schedules for 1112 composition. The resultant samples have been characterized using X-ray diffraction, a.c. susceptibility and d.c. resistivity measurements the results of which are reported here.

2. Experimental procedure

The stoichiometric proportions of Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$ and CuO for composition BiSrCaCu$_2$O$_y$, were mixed and calcined at 820°C for about 20 h. The resultant was again mixed and the final heat-treatment schedule given after pelletizing. The different heat-treatment and cooling schedules and the label of the samples are given in Table I. X-ray diffraction were recorded using a Rich Seifert Isodebyeflex 2002 diffractometer with CuKα radiation. The electrical resistivity and a.c. susceptibility were measured using a four-probe method and mutual inductance bridge, respectively, in conjunction with a closed cycle helium refrigerator (CTI Make).

3. Results and discussion

Fig. 1 gives the X-ray diffraction patterns of a set of samples QA, FA, SA, FO and F1A. The X-ray diffraction patterns of other samples in Table I were recorded and each was found to be similar to one of the samples in Fig. 1. For example, the diffraction patterns of samples QL, QA and FN are very similar and they all are typical semiconductors down to 10 K. The characteristic line of semiconducting phase [5] at d =

0.405 nm is fairly strong in these samples which are either absent or very weak in other samples which exhibit superconducting characteristics at low temperatures. Also, the lines at d = 0.383 (008) and 0.356 nm (113) which are typical of the 80 K superconducting phase [5] are absent in all the semiconducting samples. Similarly the line at d = 0.287 nm (200) is absent in samples QA and FA but present in others of Fig. 1, hence, distinct differences could be observed between samples which are semiconductors and superconductors, respectively. Therefore, faster quenching or oxygen deficient atmosphere does not appear suitable for the growth of the superconducting phase. In both cases, Bi–O layers become oxygen deficient whereas in slow cooling there is sufficient time for diffusion and ordering of oxygen atoms. Perhaps, in the case of quenched samples, superconducting and semiconducting phases remain mixed randomly. During the furnace cooling, these mixed structures tend to separate from each other in order to construct a superconducting passage. If we compare the X-ray diffraction patterns of the samples which exhibit superconducting characteristics, the following observations are worth mentioning.

(a) The lines at d = 0.385, 0.323 (115) and 0.356 nm which appear characteristic of the 80 K phase are present in all the samples which exhibit diamagnetism and zero resistance. These lines are, as mentioned above, absent in all semiconducting samples and sample FA.

(b) The line at d = 0.298 nm which is characteristic of the 20 K phase are present in samples FO and SA.

(c) The line characteristic of the 110 K phase (at d = 0.372 nm) is not seen in any X-ray diffraction pattern though there is evidence of this phase (small amount) through resistivity measurements.

(d) Lines at d ~ 0.232 and 0.250 nm which are characteristic of CuO are present in all the samples except sample FO. The sample FO, however, shows zero resistivity at 20 K and has a small volume fraction (~ 20%) of superconducting phase. The presence, therefore, of a secondary phase such as CuO appears
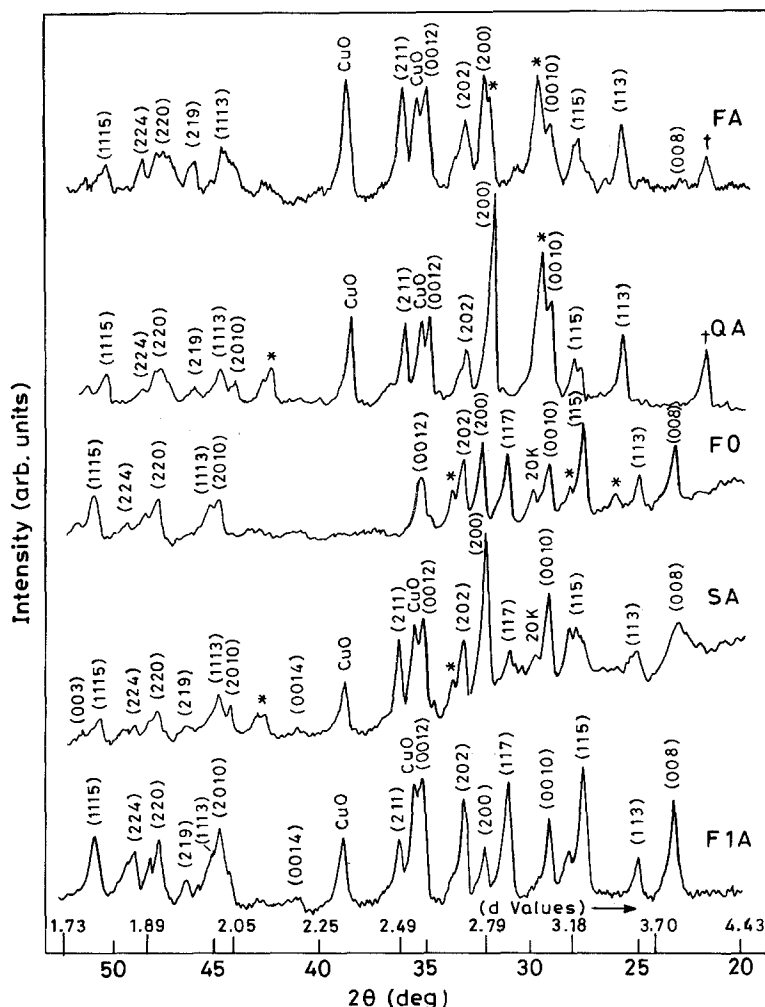
Figure 1 X-ray diffraction patterns of a set of samples QA, FA, SA, FO and FlA. The lines marked * could not be indexed. The line marked + at $d = 0.405$ nm is characteristic of semiconducting phase.

to help in improving the superconducting properties. A similar observation has been made by us in 214 (LSCO) system and has been explained on the basis of fluctuations in superconducting wave functions due to interpenetrating grains of two or more phases [6].

Fig. 2 gives the plot of a.c. susceptibility against temperature for all the samples which showed onset of superconductivity within the temperature range studied. Fig. 3 gives the corresponding plot of normalized resistivity against temperature. Table II summarizes the important parameters derived such as onset temperature, volume fraction estimated and temperature at which zero resistance is achieved. Since, the sample QL, QA and FN are semiconductors throughout the temperature range studied their data are not included.

It is interesting to note that there is a large variation in superconducting characteristics as a function of

heat-treatment and quenching conditions. We have observed similar results for 214 (LSCO) or 123 (YBCO) system [6, 8]. Besides the semiconducting samples, sample FA which was fast cooled in furnace in air did not exhibit zero resistance up to 10 K, though there was evidence of onset of superconductivity at 70 and 75 K in χ_{ac} and ρ measurements. The volume fraction of the superconducting phase is also small ($< 10\%$) and before the onset, it behaves as a semiconductor. The samples FO (oxygen annealed and furnace cooled) and SO (oxygen annealed and cooled slowly) also behaved as a semiconductor before the onset and volume fraction in these samples is $\sim 20\%$. It appears, therefore, that oxygen plays an important role in transition from a superconducting to a semiconducting behaviour without going through a non-superconducting metallic state. Similar results have been reported in 123 or bismuth compositions

TABLE I Different heat-treatment schedules and labels of the samples

Heat treatment	Cooling schedule*	Label
820° C/20 h + 864° C/24 h	Quenched in liquid nitrogen	QL
	Quenched in air	QA
	Furnace fast cooled in air	FA
	Furnace slow cooled in air	SA
	Nitrogen annealed and furnace cooled	FN
	Oxygen annealed and furnace cooled	FO
	Oxygen annealed and cooled slowly	SO
880° C/20 m + 865° C/60 h	In air and furnace cooled	F1A
880° C/60 m + 870° C/36 h	In air and furnace cooled	F2A

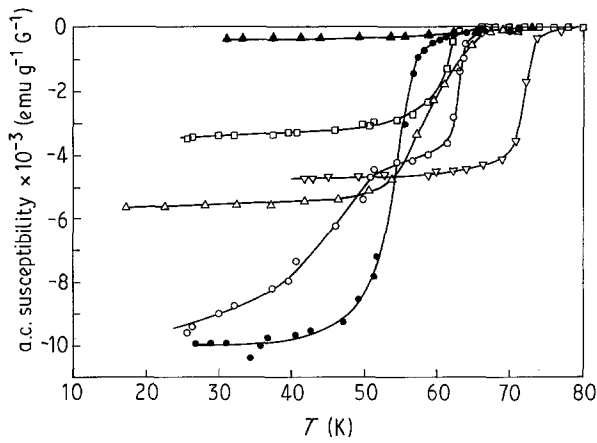*Heating and cooling have been done in air unless specified otherwise.

Figure 2 Plot of a.c. susceptibility against temperature for different samples. (▽ FO, △ F1A, ○ F2A, □ SO, ● SA, ▲ FA.)

Figure 3 Plot of normalized d.c. resistivity against temperature for different samples. (● FO, ▲ F1A, ○ F2A, △ SO, ▽ SA, □ FA.)

with varying oxygen content [3, 7, 8]. In fact measurements on single crystal YBCO and bismuth composition show semiconductor-like behaviour in the c direction and metallic in the (a, b) plane. The above results could be in some way related to this phenomenon. It is, therefore, possible that in one case, non-homogeneous oxygen vacancy distribution occurs for c-axis electronic states, hence, the material is metallic in all directions. On the other hand, for samples FO and SO, the non-homogeneity perhaps starts appearing in the ab plane and ρ_{ab} increases and perhaps become comparable to ρ_c resulting semiconductor-like behaviour. For these samples (FO and SO), zero resistance is achieved at 20 and 10 K respectively. It is noteworthy that the X-ray diffraction of these two samples exhibited fairly strong line characteristic of 20 K phase such as $Bi_2Sr_2CuO_6$ ($d = 0.298, 0.268$ nm) [4]. For some other samples (SA, F1A and F2A), zero resistance were recorded between 50 and 65 K. There is also an evidence of 110 K phase in these samples which is indicated by a drop in resistivity at about this temperature. All three samples are furnace cooled in air. SA has been cooled rather slowly, whereas F1A and F2A have undergone normal cooling inside furnace. Secondly, F1A and F2A have been differently heat-treated before furnace cooling. They have been

heat treated close to melting point for short intervals before treating them for longer duration at slightly lower temperature. This presumably helps in stabilization of Cu–O layer structure over much longer regions along c-axis. All the three samples have evidence of 110 K phase in their resistivity plots. Obviously, the volume fraction of 110 K phase is small. The volume fraction of the superconducting phase is around 50% in these three samples. 80 K phase appears to be the major one.

One thing is intriguing: annealing in air is more favourable than annealing in oxygen for growth of high T_c phase in bismuth-based superconductors and is in contrast to yttrium-based 123 superconductors. It looks like an optimum concentration of oxygenation is required for better superconducting properties in bismuth-based superconductors. A naive interpretation given below is based on insertion of oxygen in different planes. Initially oxygen perhaps goes as an interstitial O_2^- ion in line joining Bi–Bi atoms in BiO plane. This insertion of an extra oxygen in Bi–O layers causes distortion of the lattice and produces the carriers (as oxygen holes) which are responsible for better superconducting properties [9]. On the other hand, when excess of oxygen is there, it may enter Sr–Ca atom layers. It is envisaged that square planar like arrangements around copper ions are characteristic for d^9 or d^8 ions and apparently provide optimum two-dimensional current paths for high T_c superconductivity [10]. This is possible only by removing oxygen atoms from (Sr–Ca) atom layers, hence, excess oxygen in these layers may destroy square planar like arrangement around copper ions and in turn the superconducting property degrades.

Acknowledgements

TABLE II Superconducting properties of differently heat-treated samples

S. No.	Sample	T_c^{onset} (χ_{AC}) (K)	T_c^{onset} (ρ) (K)	T_c^{zero} (ρ) (K)	Volume (%)
1	QL	Semiconductor			—
2	QA	Semiconductor			—
3	FA	70	75	*	< 10
4	SA	65	75	65	50
5	FN	Semiconductor			—
6	FO	76	110† 70	20	20
7	SO	65	110† 80	10	20
8	F1A	70	110† 75	60	55
9	F2A	70	110† 85	55	49

*Zero resistance not achieved down to 10 K.
† Deviation from linearity is indicated suggesting a small fraction of 110 K phase.
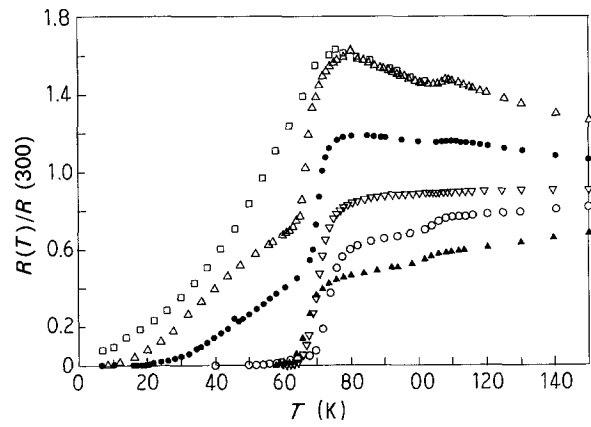
References

1. H. MAEDA, Y. TANAKA, M. FUKUTOMI and T. ASANO, *Jpn J. Appl. Phys.* **27** (1988) L209.
2. U. BALACHANDRAN, D. SHI, D. I. DOSS SANTOS, S. W. GRAHAM, M. A. PATEL, B. TANI, K. VANDERVOORT, H. CLAUS and R. B. POEPPEL, *Physica* **C156** (1988) 649.

3. D. BAHADUR, A. BAJERJEE, A. DAS, K. P. GUPTA, A. MITRA, M. TEWARI and A. K. MAJUMDAR, *Mater. Res. Bull.* **24** (1989) 1405.

4. C. N. R. RAO, L. GANAPATHI, R. VAJAYRAGH-VAN, G. R. RAO, K. MURTHY and R. A. MOHAN-RAM, *Physica* **C128** (1988) 827.

5. S. KOYAMA, U. ENDO and T. KAWAI, *Jpn J. Appl. Phys.* **27** (1988) L1861.

6. A. K. RASTOGI, A. BANEERJEE, MANJU TEWARI and D. BAHADUR, *Phase Transitions* **10** (1987) 123.

7. J. M. TARASCON, L. H. GREENE, W. R. MCKIN-NON, G. W. HULL and T. M. GEBALLE, *Science* **235** (1987) 1373.

8. D. BAHADUR, A. BANERJEE, A. DAS, K. P. GUPTA, T. MATHEWS, A. MITRA, M. TEWARI and A. K. MAJUMDAR, *Rev. Solid State Sci.* **2** (1988) 177.

9. Y. L. PAGI, W. R. McKINNON, J. M. TARASCON and P. BARBOURE, preprint, 1989.

10. Y. SYONO, K. HIRAGA, N. KOBAYASHI, M. KIKU-CHI, K. KUSABA, T. KAJITANS, D. SHINDO, S. HOSOYA, A. TOKIWA, S. JERADA and Y. MUTO, *Jpn J. Appl. Phys.* **27** (1988) L569.