JOURNAL OF SOLID STATE CHEMISTRY 75, 207–211 (1988)

LETTERS TO THE EDITOR

Preparation of a High-Density Bi–Sr–Ca–Cu–O Ceramic with a Single Superconducting Phase

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Communicated by J. M. Honig, May 3, 1988

It is found that a high density ceramic of the Bi–Sr–Ca–Cu–O system with a single superconducting phase can be produced by quenching the specimen from the melt, and then annealing at an appropriate temperature in the oxygen atmosphere below the melting point. Here, a case of growing a superconducting material with T_c of 85 K with a nominal composition Bi : Sr : Ca : Cu = 2 : 2 : 1 : 2 is presented. The process thus has promise for producing high-quality, superconducting ceramic materials from the Bi–Sr–Ca–Cu–O system.

The Bi–Sr–Ca–Cu–O system has been reported to include several superconducting phases with T_c up to 120 K (*1–3*). After its discovery (*1*), a number of workers investigated this system and the existence of such superconducting phases was confirmed (*2–12*). Growth of single crystals of such superconducting phases have also been attempted, but its success has been limited to a material with T_c of 85 K (*13–15*).

A disturbing feature of this material is that the materials prepared by sintering apparently include several superconducting phases and the temperature at which the material has zero resistance is generally lower than liquid nitrogen temperature. In order to utilize this type of material for practical applications, it is desirable to have a single-phase material which can be prepared with relative ease without resorting to a sintering process. The present work is aimed at achieving this purpose.

Quenching of this material from the melt was found to produce an extremely tough material with high density. Therefore, if such quenched material is annealed at a temperature below the melting point, a specific structure characteristic of the annealing temperature is expected to nucleate and, hence, the production of single-phase materials would be possible at certain specific composition. The chance of obtaining a single-phase specimen with very high density therefore is expected to be high.

Here, we report one of our trials on preparing such high-quality superconducting ceramics with a nominal composition Bi : Sr : Ca : Cu = 2 : 2 : 1 : 2. The specimen was prepared from a mixture of Bi_2O_3 (99.9%), $SrCO_3$ (99.999%), $CaCO_3$ (99.999%), and CuO (99.9%) with the molar

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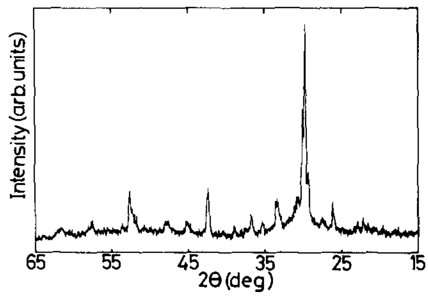


FIG. 1. X-ray (Cu$K\alpha$) powder pattern of the as-quenched specimen.

ratio of 2 : 2 : 1 : 2 as stated above. In order to ensure the proper composition of the melt, prereacted and well heat-treated powders were prepared for melting. First, the above mixtures were prereacted at 800°C. The prereacted powders were then repeatedly sintered and reground in order to make sure that the solid-state reaction was complete. The sintering treatment for this preparation process was carried out at 800°C in air for 16 hr, followed by that at 850°C in air for 24 hr. For melting, the reacted and sintered material was reground into a powder form, placed in a platinum crucible, and melted at 1000°C for 2 hr. For quenching, the melt was then poured on a heavy copper sheet and pressed by another copper sheet. This quenching process produced an extremely dense material of 100% theoretical density.

In Fig. 1, an X-ray powder pattern utilizing Cu$K\alpha$ of the as-quenched specimen is shown. A few number of peaks are observed, but their locations are found to be completely unrelated to structures which develop during the following annealing process. In Fig. 2 a bright field TEM image and a corresponding electron diffraction pattern obtained from crushed specimens are shown. The diffraction pattern shows haloes characteristic of the amorphous state. At least the strong, innermost diffuse ring

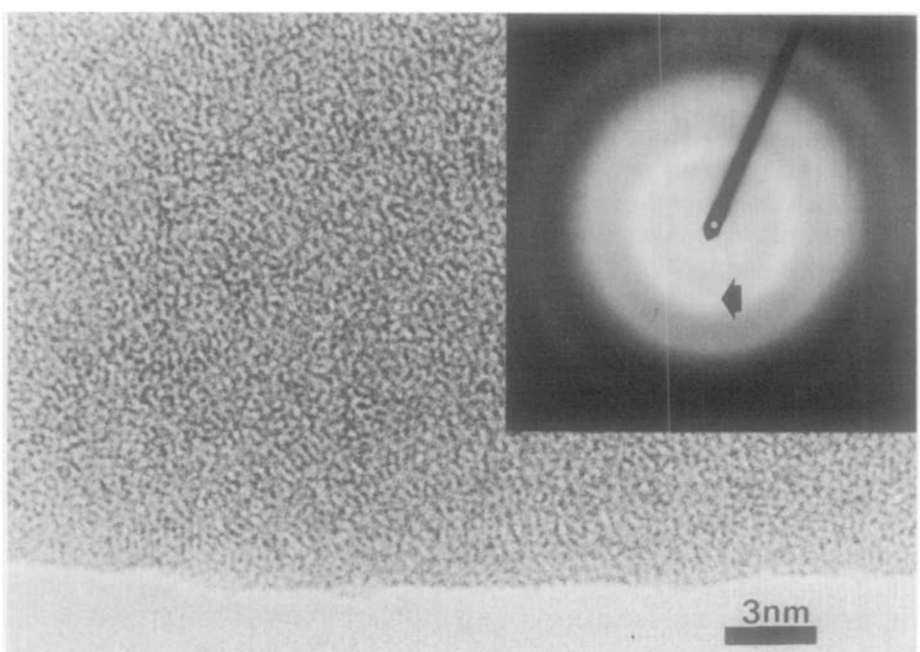


FIG. 2. A bright field image and a corresponding diffraction pattern of the as-quenched specimen. The strongest ring mentioned in the text is indicated by an arrow.

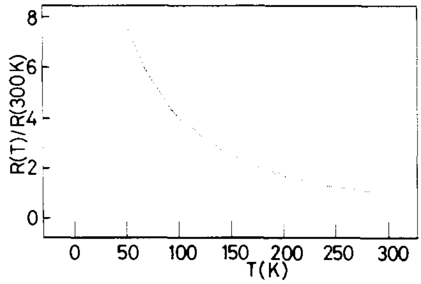


FIG. 3. Temperature dependence of the electrical resistivity of the as-quenched specimen.

coincides with the location of the strong peak of the X-ray powder pattern in Fig. 1. The micrograph also shows the characteristic features of amorphous materials, but some lattice fringes are also observable near the edge of the specimen, indicating the existence of crystalline materials. Based on these evidences, it seems that the material is at least partly glassy. Due to this situation, no specific effort was made to analyze the powder pattern in Fig. 1. In Fig. 3, the temperature dependence of the electrical resistivity of the quenched material is shown. The curve shows a strong increase in resistivity as the temperature is lowered, and there is no sign of the existence of superconducting phase down to 50 K. The specimen quenched from 1100°C shows practically the same behavior as the specimen quenched from 1000°C.

In order to obtain a single phase, it is necessary to choose a right temperature for annealing. For the material with the nominal composition 2:2:1:2, a superconducting phase with T_c of 85 K appears most commonly, and, therefore, we aimed at obtaining this phase as an isolated phase. Based on results of earlier experiments on sintered materials of similar compositions, several temperatures were chosen. In Fig. 4a, the powder pattern of the specimen annealed at 820°C in an O_2 atmosphere for 8 hr is shown. The pattern matches very well with that of Tarascon *et al.* (*12*) in which the powder used for X-ray diffraction was selected from the ceramic specimen with a similar composition by a magnetic separation process utilizing the Meissner effect. The pattern can be indexed as that of a tetragonal structure with the lattice constants $a_0 = 0.380$ nm and $c_0 = 3.05$ nm. It should be noted again that the peaks observed in the quenched specimen shown in Fig. 1 are practically unobserved in the pattern of the annealed specimen except for a trace of the strongest peak. The agreement of the powder pattern of the annealed specimen with that of the powder magnetically separated (*12*) indicates that the annealed specimen

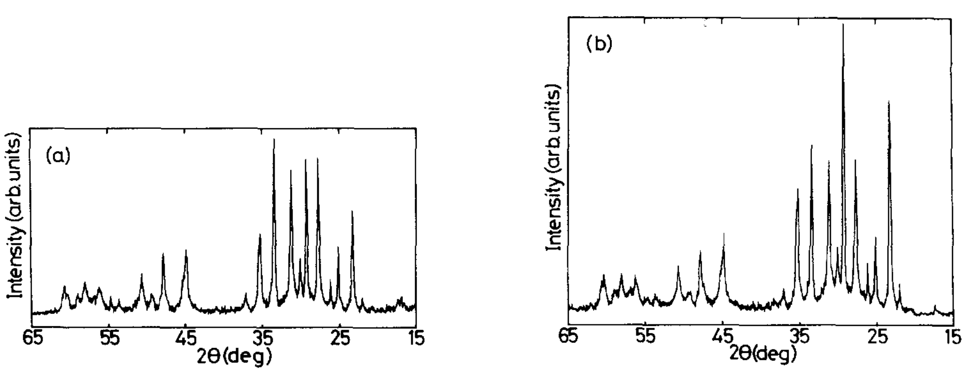
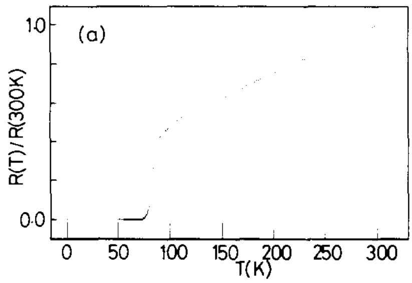


FIG. 4. X-ray powder pattern of a specimen annealed (a) at 820°C in an O_2 atmosphere for 8 hr and (b) at 820°C for 16 hr.



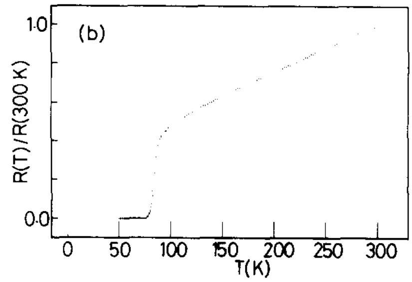


FIG. 5. Temperature dependence of the electrical resistivity of the specimen annealed (a) at 820°C in an O_2 atmosphere for 8 hr and (b) at 820°C for 16 hr.

has only a single superconducting phase. The resistivity–temperature curve of this specimen is shown in Fig. 5a. The characteristic of the R–T curve is typically metallic down to ~85 K and has a relatively sharp drop in resistivity from ~85 K to zero extrapolated to ~80 K but with a small tail which seems to extend to ~72 K. The measurement of the Meissner effect shown in Fig. 6 indicates that T_c is ~86 K. The small tail which extends for about 5–8 K is either due to the inhomogeneity in the oxygen distribution or to the imperfection of the crystal lattice. Further annealing of the specimen at 820°C in oxygen for 8 hr more gave an almost identical result but was found to reduce the tail somewhat so that the resistivity reaches zero at ~73 K as shown in Fig. 5b. The diffraction pattern of this specimen shown in Fig. 4b indicates the improvement in the crystallinity of the well-annealed specimen. The trace of the strongest peak in the quenched specimen is appreciably reduced by the annealing at 850°C for 19 hr. The resistivity–temperature curve of the specimen annealed at 850°C for 8 hr shows a further improvement in eliminating the tail which raises the temperature at which the resistivity reaches zero to ~76 K. Although an existence of a small amount of nonsuperconducting phase cannot be denied, the data indicates at least that the specimen consists primarily of a single superconducting phase. The research by means of high-resolution TEM of the structural development with annealing of the superconducting phase is under way.

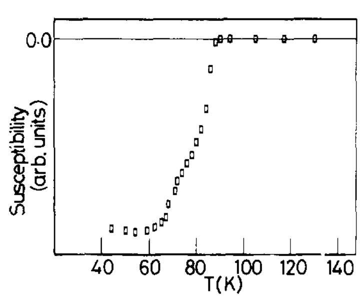


FIG. 6. Temperature dependence of the Meissner effect of a specimen annealed at 820°C for 8 hr under the magnetic field of 10 Oe.

The existence of a superconducting phase with T_c ~ 85 K in the Bi–Sr–Ca–Cu–O system has been well confirmed and even single crystals of this phase have been grown. In view of this situation, the investigation of structural development of this phase through solid-state reaction by annealing would be useful in understanding the relation between the structure and superconductivity of this material. Above all, the fact that a ceramic of a single-phase 85 K superconductor with a very high density is obtained from the melt-quenched specimen gives a promise of developing single-phase materials of a number of superconducting phases of very high quality in the Bi–Sr–Ca–Cu–O system. The effort of separating other superconductor phases other than that of 85 K is now under way based on similar processes.

Acknowledgments

The characterization of the specimen was assisted by a number of people of the superconductor research group at Purdue University. We specifically thank M. M. Miller and C. S. Calhoun for careful measurements of electrical resistivity and the Meissner effect and P. A. Metcalf for the measurement of the density of as-quenched materials. The work was supported by the Indiana Center for Innovative Superconductor Technology at Purdue University and National Science Foundation, Solid State Chemistry Program, Grant DMR-8619159, and we are thankful for discussions with members of the group, especially with A. I. Schindler, G. L. Liedl, and J. M. Honig.

References

1. H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, *Japan. J. Appl. Phys. Lett.* **27**, L209 (1988).
2. C. W. Chu, J. Bechtold, L. Gao, P. H. Hor, Z. J. Huang, R. L. Meng, Y. Y. Sun, Y. Q. Wang, and Y. Y. Xue, *Phys. Rev. Lett.* **60**, 941 (1988).
3. R. M. Hazen, C. T. Prewitt, R. Angel, N. L. Ross, L. W. Finger, C. G. Hadidiacos, D. R. Veblen, P. J. Heaney, P. H. Hor, R. L. Meng, Y. Y. Sun, Y. Q. Wang, Y. Y. Xue, Z. J. Huang, L. Gao, J. Bechtold, and C. W. Chu, *Phys. Rev. Lett.* **60**, 1174 (1988); D. R. Veblen, P. J. Heaney, R. J. Angel, L. W. Finger, R. M. Hazen, C. T. Prewitt, N. L. Ross, C. W. Chu, P. H. Hor, and R. L. Meng, *Nature (London)* **332**, 334 (1988).
4. R. L. Meng, P. H. Hor, Y. Y. Sun, Z. J. Huang, L. Gao, Y. Y. Xue, Y. Q. Wang, J. Bechtold, C. W. Chu, R. M. Hazen, C. T. Prewitt, R. J. Angel, and N. L. Ross, *Mod. Phys. Lett. B* **2**, 543 (1988).
5. M. A. Subramanian, C. C. Torardi, J. C. Calabrese, J. Gopalakrishnan, K. J. Morrissey, T. R. Askew, R. B. Flippen, U. Chowdhry, and A. W. Sleight, *Science* **239**, 1016 (1988).
6. S. S. P. Parkin, E. M. Engler, V. Y. Lee, A. I. Nazzal, Y. Tokura, J. B. Torrance, and P. M. Grant, submitted for publication.
7. S. Jin, R. C. Sherwood, T. H. Tiefel, G. W. Kammlott, R. A. Fastnacht, M. E. Eavis, and S. M. Zahurak, *Appl. Phys. Lett.* **52**, 1628 (1988).
8. G. Xiao, M. Z. Cieplak, D. Musser, and C. L. Chien, submitted for publication.
9. J. P. Zhang, H. Shibahara, D. J. Li, L. D. Marks, J. B. Wiley, S. J. Hwu, K. R. Poeppelmeler, S. N. Song, J. B. Ketterson, and B. Wood, submitted for publication.
10. T. M. Shaw, S. A. Shivashankar, S. J. La Placa, J. J. Cuomo, T. R. McGuire, R. A. Roy, K. H. Kelleher, and D. S. Yee, preprint.
11. H. W. Zandbergen, Y. K. Huang, M. J. V. Menken, J. N. Li, K. Kadowaki, A. A. Menovsky, G. Van Tendeloo, and S. Amelinckx, *Nature (London)* **332**, 620 (1988).
12. J. M. Tarascon, Y. Le Pge, P. Barboux, B. G. Bagley, L. H. Greene, W. R. McKinnon, G. W. Hull, M. Giroud, and D. M. Hwang, submitted for publication.
13. J. Z. Liu, G. W. Crabtree, L. E. Rehn, Urs Geiser, D. A. Young, W. K. Kwok, P. M. Baldo, J. M. Williams, and D. J. Lam, *Phys. Lett. A* **127**, 444 (1988).
14. L. F. Schneemeyer, R. B. Van Dover, S. H. Glarum, S. A. Sunshine, R. M. Fleming, B. Batlogg, T. Siegrist, J. H. Marshall, J. V. Waszczak, and L. W. Rupp, *Nature (London)* **332**, 422 (1988).
15. S. A. Sunshine, T. Siegrist, L. F. Schneemeyer, D. W. Murphy, R. J. Cava, B. Batlogg, R. B. Van Dover, R. M. Fleming, S. H. Glarum, S. Nakahara, R. Farrow, J. J. Krajewski, S. M. Zahurak, J. V. Waszczak, J. H. Marshall, P. Marsh, L. W. Rupp, Jr., and W. F. Peck, preprint.