

# An optimum heating program for fabricating MTG $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ superconductors

Z. L. Du

Physics Department, The University of Zhongshan, Guangzhou, China

T. F. Yu, J. C. L. Chow, and P. C. W. Fung

Physics Department, The University of Hong Kong, Hong Kong

(Received 16 September 1993; accepted 20 April 1994)

Following our recent report on the successful fabrication of "stationary" MTG  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  pellets in a simple tube furnace, we have tried many heating programs with various "crystal growth starting temperatures",  $T_s$ , and sintering temperatures,  $T_e$ ; the samples are sintered for 20–40 h before quenching in air. It is found that  $T_s$ - $T_e$  should be rather narrow to produce good MTG samples, and the typical value of  $J_c$  is enhanced from  $100 \text{ A cm}^{-2}$  (for a polycrystalline sample) to about  $3 \times 10^3 \text{ A cm}^{-2}$  for our good ones. SEM and TEM results indicate that the samples are full of packs which contain highly oriented mica-like layers.

## INTRODUCTION

There are several crucial aspects to make fabrication of the Bi-class MTG samples a success. The first technical problem one faces is the loss of sample material when the sample is heated to melt. We have to find a substrate that reacts with the melt liquids to form crystals basically of the Bi-class members at a slow rate. The "unwanted layer" can be ground off after sintering, leaving a substantial amount of desired superconducting material. We have found in our previous investigation of this project that pellet made of Sr with the same composition as the sample will serve the stated purpose.<sup>1</sup> The

second problem one faces is to find the right temperature for crystal growth to commence. Of course, the cooling temperature has to be within a (narrow) range to sustain the growth of single crystal-like layers or lumps. It is also anticipated that nuclei should exist inside the sample to help the growth process. While  $\text{Y}_2\text{BaCuO}_5$  is guessed to be the nuclei for the Y-123 specimens,<sup>2-6</sup> the CaO particles are conjectured to be possibly the nuclei in the Bi-class samples, and the solid-state reaction method consists of two steps as described in Ref. 1.

The MTG heating program for stationary sample(s) placed near the ends of a simple tube furnace can be

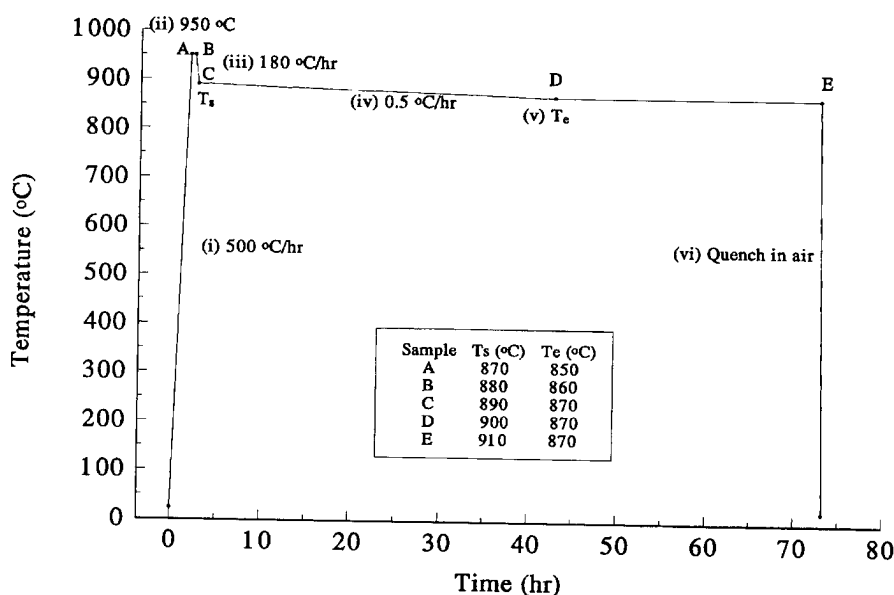


FIG. 1. Diagram showing the heat-treatment profile of the MTG  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  superconductors.

TABLE I. Heating programs for  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  superconductor.

Program	$T_s$ (°C)	$T_e$ (°C)
A	870	850
B	880	860
C	890	870
D	900	870
E	910	870

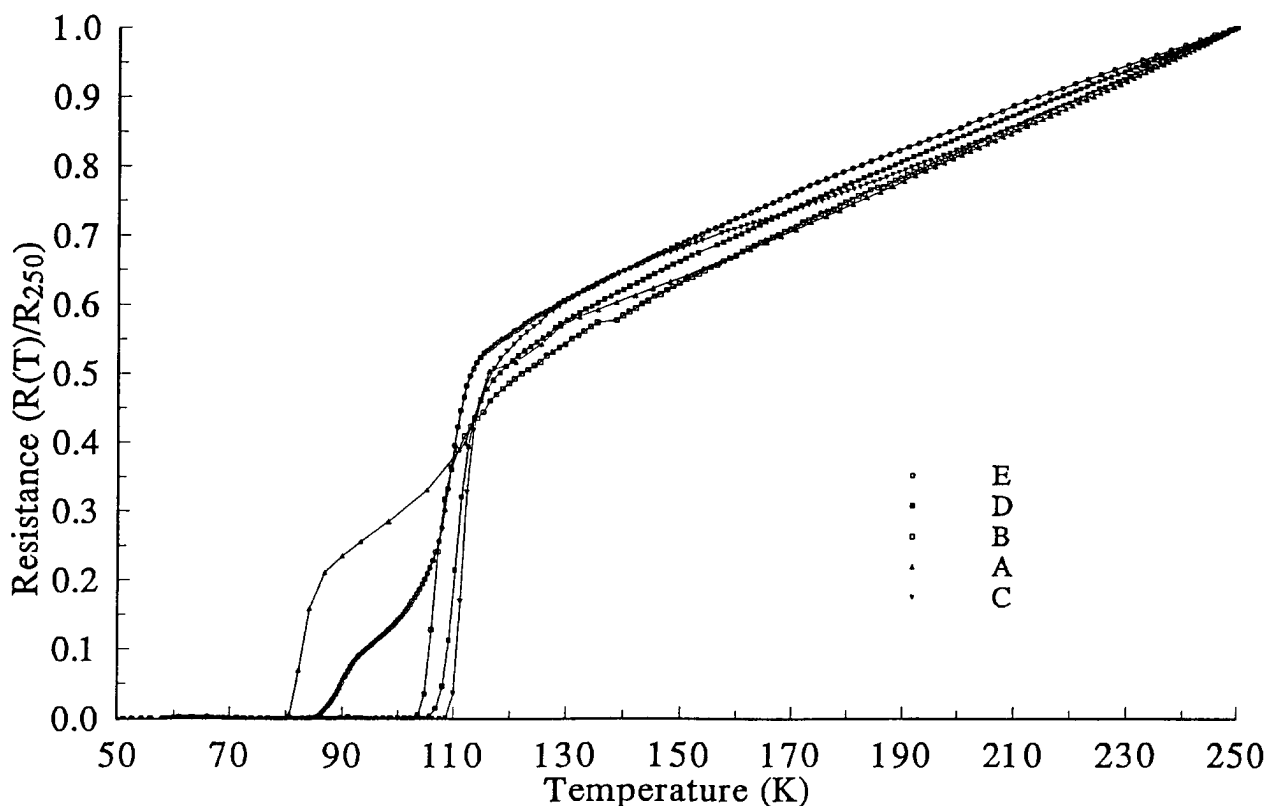
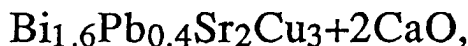
considered to be made of six heating stages. In stage (i), the tube is heated to the maximum temperature  $T_m$  of the heating program with a rate that is not at all critical (Fig. 1). It is believed that some particles must act as nuclei for crystal growth, and one natural theory is to make  $T_m$  higher than the melting temperatures of all compounds except perhaps one. Since the melting temperature of CaO powder is 2614 °C,  $T_m$  is chosen to be 950 °C at which compounds of Bi, Sr, and Cu have already melted and CaO is the "added ingredient" after preheating the precursor BiSrCuO.<sup>1</sup> The sample is left in

the melt state for a brief period of a few tens of minutes. It is then suddenly cooled, again with a rate that is not critical, to a crucial temperature  $T_s$  which may be called the "crystal growth starting temperature".

A slow cooling begins with a crucial rate of say  $D$  °C/h, until the temperature is  $T_e$ , the sintering temperature. The sample is sintered for tens of hours at  $T_e$  and is either quenched (in air, liquid nitrogen) or cooled in a furnace. In Ref. 1, we have found out that a workable program is specified by  $T_m = 950$  °C,  $T_s = 890$  °C,  $T_e = 870$  °C, and  $D = 0.5$  °C/h. We have tried many programs since then, and we report in this paper the results of some typical ones, leading to the establishment of an optimum heating program for samples with the prescribed stoichiometric ratio.

## II. FABRICATION AND CHARACTERIZATIONS

First, we preheated the mixture of  $\text{Bi}_2\text{O}_3$ , PbO, SrO, and CuO according to the stoichiometric ratio  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  at a temperature of 750 °C for 40 h. The partially crystallized material was then ground

FIG. 2.  $R$ - $T$  relationships of the five samples A, B, C, D, and E with different heat treatments.

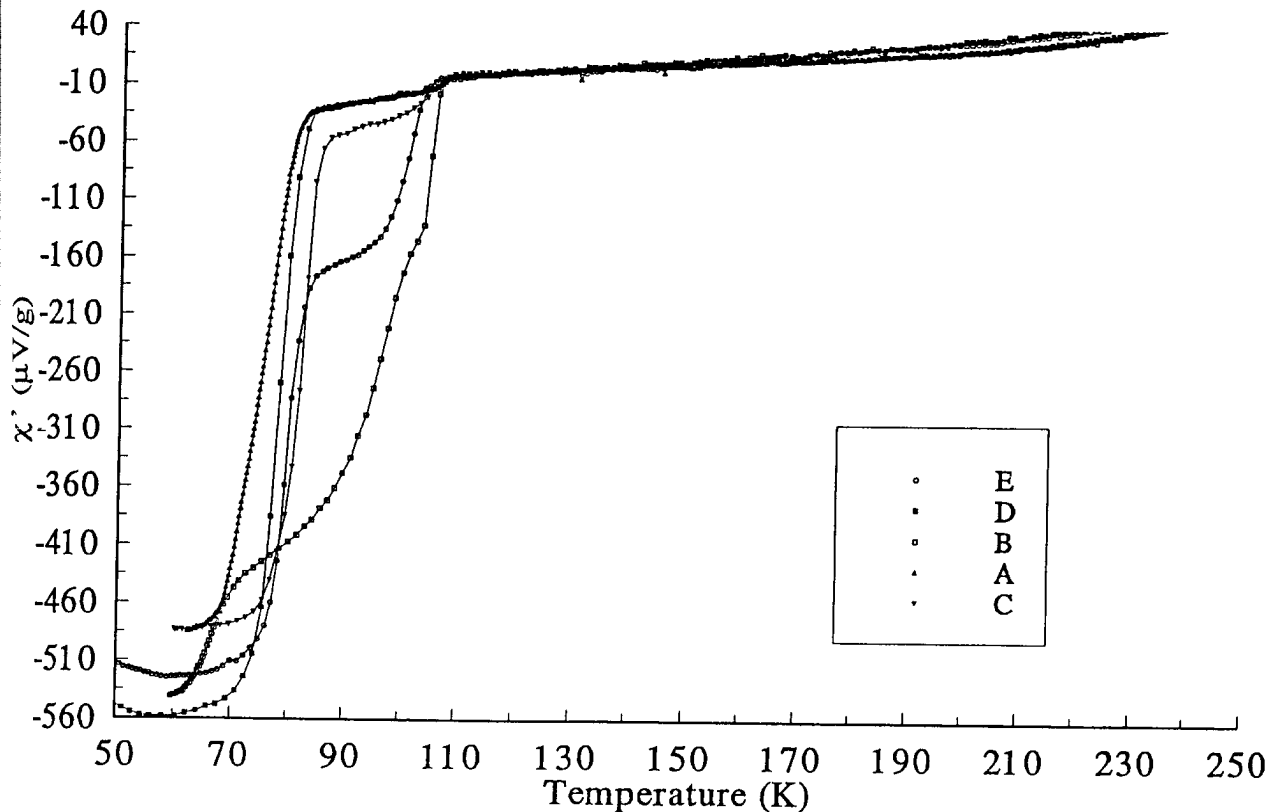
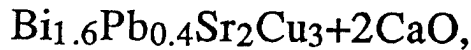


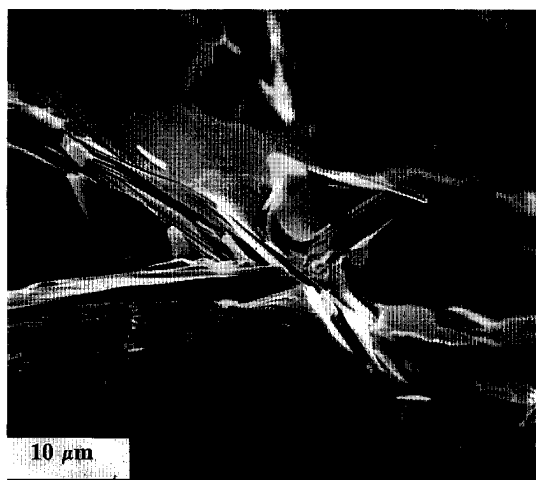
FIG. 3.  $\chi$ - $T$  relationships of the five samples A, B, C, D, and E with different heat treatments.

with CaO powder based on the nominal composition  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ , and a pellet of size  $11 \times 5 \times 1 \text{ mm}^3$  was made under a pressure of 8 tons. Another pellet of the same size was made of SrO powder and the two pellets were stacked and placed on a common crucible; the middle of the sample was adjusted to be at a location where the temperature gradient was  $10 \text{ }^\circ\text{C/cm}$  at  $950 \text{ }^\circ\text{C}$ . We specified the heating program by the four parameters  $T_m$ ,  $T_s$ ,  $T_e$ , and  $D$  described in the last section. We shall not list all the trials, but will introduce among these five special programs one that was found to be the optimum. In these programs,  $D$  was fixed to be  $15 \text{ }^\circ\text{C/h}$ ,  $T_m$  to be  $950 \text{ }^\circ\text{C}$ , and  $T_s$  and  $T_e$  satisfy numbers specified in Table I. The heating programs A, B, C, D, and E correspond to the specimens fabricated A, B, C, D, and E, respectively.

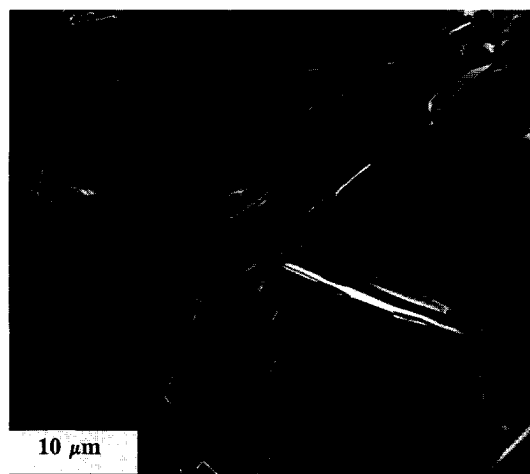
The other parameters are depicted in Fig. 1. After fabrication, the five samples were tested with the usual four-probe techniques, and Fig. 2 depicts these five  $\chi$ - $T$  curves. The usual  $\chi$ - $T$  curves were measured with a commercial APD SSC characterization set (see Fig. 3). TEM morphology using our Cambridge Stereoscan S150

microscope operated with a magnification of  $2000\times$  revealed that the crystals did grow to form stacks of layers, though spaces were found between such stacks [Figs. 4(a)–4(e)]. As the mass density of these samples is only about  $3.1\text{--}3.9 \text{ g cm}^{-3}$  (cf. over  $5.4 \text{ g cm}^{-3}$  for the good Y-123 MTG samples), we should expect that there must be empty space around the interior of each sample. Mechanical pressing has been used to fabricate the Bi-class of SSC wires by others,<sup>7–11</sup> and we must improve the mass density of the MTG Bi-class samples at a slightly later stage. It suffices to develop a suitable MTG process for the Bi-class samples now. Increasing the SEM magnification to  $5000\times$ , we observed mica-like structure of the crystals in the micron scale [Figs. 5(a)–5(e)]. Thus, within one stack of “crystal sheets”, the layers in the  $1 \text{ }\mu\text{m}$ – $10 \text{ }\mu\text{m}$  scale are tightly packed indeed.

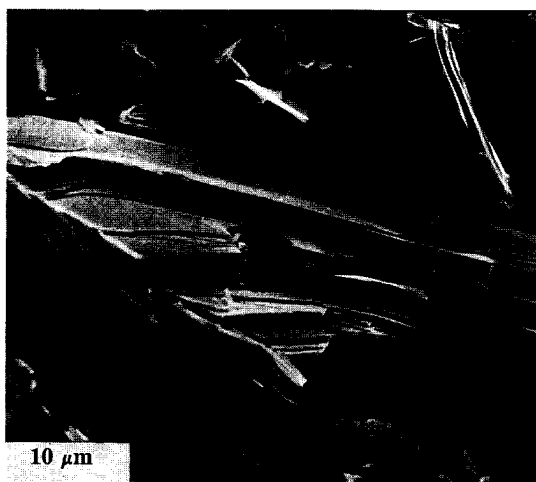
A small portion of sample C was ground, and films of thickness  $\sim 70\text{--}80 \text{ nm}$  were prepared in the manner stated in Ref. 12 for TEM (Model: JEM JEOL 2000FX) observation. Figure 6(a) is a typical TEM micrograph that shows massive dislocation in the grain. Since the



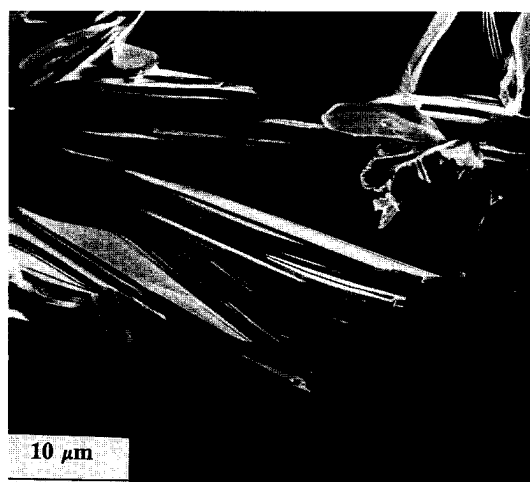
(a)



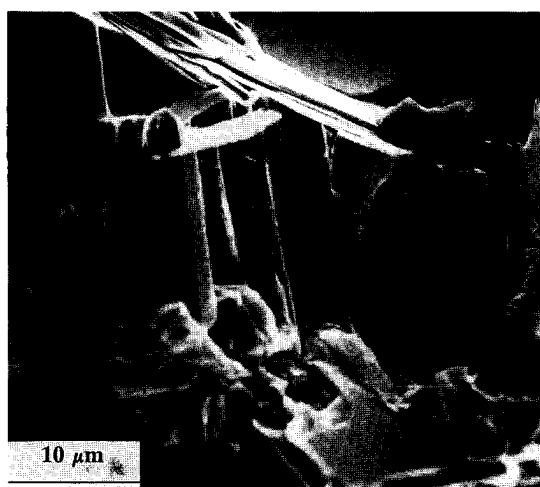
(b)



(c)



(d)

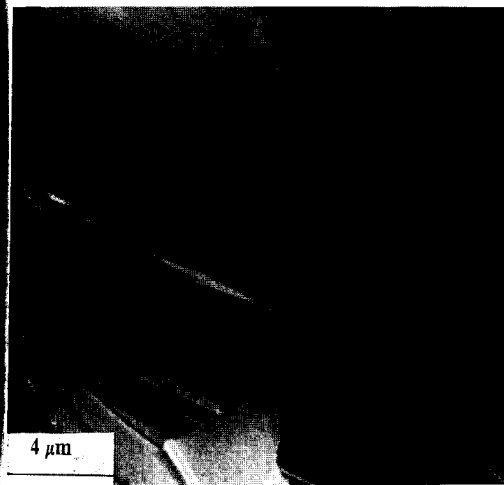


(e)

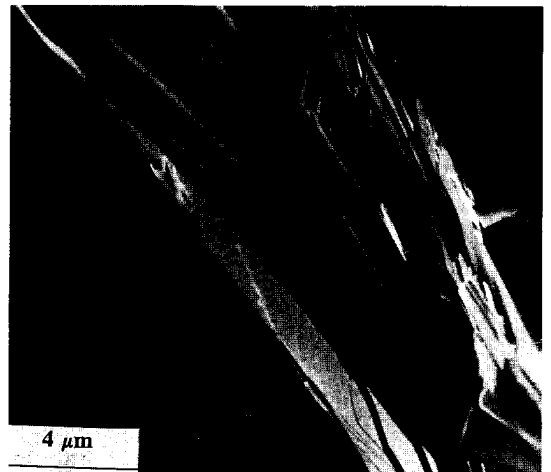
FIG. 4. (a–e) SEM morphology with a magnification of 2000 $\times$  of samples A, B, C, D, and E, respectively.

*c*-axis of a Bi-sample (either the 2212 or 2223 phase) is relatively large, the dislocation energy is smaller in a MTG sample as compared to that of a solid-state reaction

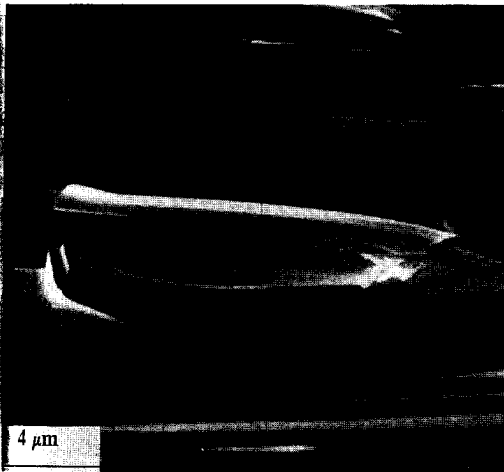
sintered sample. Moreover, in Fig. 6(b), we can observe parallel lattice fringes which are believed to represent the (001) planes of the orthorhombic crystals. The av-



(a)



(b)



(c)



(d)



(e)

FIG. 5. (a–e) SEM morphology with a magnification of 5000 $\times$  of samples A, B, C, D, and E, respectively.

crage apparent spacing between two adjacent lines is about 43 Å. We have found many such observations, indicating that the MTG method is rather effective in forcing crystals to grow along parallel directions. Our recent calibration of the TEM<sup>12</sup> indicates that the physical length between the lattice fringes is  $43 \text{ Å} \times 86\% \approx 37 \text{ Å}$ , indicative of the *c*-axes of aligned 2223 crystals. To find the critical current  $J_c$  of the sample, we measured the dc magnetization  $M$  for external magnetic field  $H$  varying from 0 to 1000 G and reversed the direction in the manner described in Ref. 2. The loops are basically similar to those of Fig. 6 in Ref. 2 and will not be produced here. Employing the Bean model, we can calculate

$$J_c = \frac{2\Delta M}{d\left(1 - \frac{d}{3w}\right)}$$

where  $\Delta M$  is the change of  $M$  in the hysteresis at  $H = 0$ ,  $d$  is the thickness, and  $w$  the width of the sample. The  $J_c$  value for our samples is found to be around  $3 \times 10^3 \text{ A cm}^{-2}$ .



(a)

### III. ANALYSIS AND CONCLUSIONS

(1) We have reported five heat programs that will produce successful MTG Bi-samples, satisfying the stated stoichiometric ratio. The melting point of the precursor  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  is lower than 870 °C so that we can operate  $T_s$  at or slightly above 870 °C. From  $R$ - $T$  and  $\chi$ - $T$  results, it appears that program B is the optimum one; i.e., it is suitable to choose  $T_s = 880 \text{ °C}$ .  $T_e$  has to be about the temperature at which the 2223 phase is formed, which is 860 °C. If we choose a lower  $T_e$  value, surely more 2212 phase crystal will be formed. Thus, the ranges of  $T_s$  and  $T_e$  are rather restrictive, and the best one so far found for the specimen ( $\text{Bi}_{1.6}\text{Pb}_{0.4}$ ) is simply program B:  $T_s = 880 \text{ °C}$ , and  $T_e = 860 \text{ °C}$ .

(2) Though we have not fabricated MTG samples with pure 2223 phase, we believe it is not difficult to make such samples if we proceed with a similar systematic analysis of the thermal treatment and the characteristics of the consequential samples. In particular, the sintering time is only 40 h at  $T_e$ . It is well established that by elongating the sintering time to about seven days,<sup>13-15</sup> close to pure 2223 phase can be obtained. In fact,



(b)

FIG. 6. (a) TEM morphology of the sample C showing massive dislocation in the grain. (b) TEM morphology of the sample C showing parallel lattice fringe.

several years ago we fabricated 95% pure 2223 phase polycrystalline samples with Pb and V doping.<sup>16,17</sup> The main objective here is to report the workable values of  $T_s$ ,  $T_e$ , and  $D$  from which an optimum program is deduced by experiment.

(3) That the heating program can be considered as a successful one is based on revelation of MTG characteristics. We have learned from experiment that crystals grow along the direction of negative gradient of temperature.<sup>5</sup> Single crystal-like layers are formed, and a majority of the weak links are eliminated. Such features are shown directly and indirectly in the SEM micrographs. Figures 5(a)–5(e) can be considered very good ones according to the SEM of Bi-class samples so far published. We must note that the highly oriented crystal layers form stacks that may show somewhat random orientation directions while good MTG YBCO samples show layered structure stretching over the mm scale.<sup>2–4</sup> We have not achieved such large scale crystal alignment for the Bi-class yet. However, our technology developed so far will definitely help us to make MTG Bi-samples with better texture and microstructure; the macroscopic features are related in our analysis. With measured  $J_c$ , SEM, TEM morphology, etc., we can confidently fabricate MTG Bi-samples with a mass density much higher than  $3.9 \text{ g cm}^{-3}$  and  $J_c$  much greater than the present values of several times  $10^3 \text{ A cm}^{-2}$ .

#### IV. SUMMARY

We have successfully found an optimum heating program for fabricating MTG  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  superconductors in a simple tube furnace. In this paper, different parameters including crystal growth starting temperature ( $T_s$ ) and sintering temperature ( $T_e$ ) were varied with the cooling rate ( $D$ ) and maximum temperature ( $T_m$ ) fixed to  $0.5 \text{ }^\circ\text{C/h}$  and  $950 \text{ }^\circ\text{C}$ , respectively, in our heating program. Through a lot of trials, five typical programs, namely A, B, C, D, and E, with  $T_s$  and  $T_e$  values corresponding to Table I were reported here. According to the  $R$ - $T$  and  $\chi$ - $T$  relationships, as

well as the SEM and TEM morphology of the above five specimens, it appears that program B with  $T_s = 880 \text{ }^\circ\text{C}$  and  $T_e = 860 \text{ }^\circ\text{C}$  is the optimum one. Using this program, we can make MTG BSCCO specimens with better texture as well as good microstructure and macroscopic characteristics compared with that of polycrystalline BSCCO specimens.

#### REFERENCES

1. Z. L. Du, P. C. W. Fung, J. C. L. Chow, Z. H. He, and T. F. Yu, unpublished research.
2. Z. L. Du, P. C. W. Fung, Z. H. He, G. H. Zhou, M. J. Li, Y. Lu, and J. X. Zhang, *J. Supercond.* **6**, 27–35 (1993).
3. P. C. W. Fung, Z. L. Du, J. C. L. Chow, Z. H. He, T. F. Yu, Y. Y. Luo, Q. Y. Li, and Y. Lu, *Physica C* **212**, 279–291 (1993).
4. Z. L. Du, P. C. W. Fung, J. C. L. Chow, T. F. Yu, Z. H. He, Y. Li, Y. Y. Luo, and J. X. Zhang, *Physica C* **215**, 319–328 (1993).
5. P. C. W. Fung, J. C. L. Chow, T. F. Yu, and Z. L. Du, *J. Supercond.* **6**, (4), 247–254 (1993).
6. F. Young, Z. Lian, Z. Pingxiang, W. Keguang, J. Ping, W. Xiaozu, L. Changxun, and X. Mianrong, *Supercond. Sci. Technol.* **5**, 432–434 (1992).
7. S. X. Dou, H. K. Liu, J. Wang, and W. M. Bian, *Supercond. Sci. Technol.* **4**, 21–26 (1991).
8. Y. C. Guo, H. K. Liu, and S. X. Dou, *Appl. Supercond.* **1** (1/2), 25–31 (1993).
9. T. S. Chin, L. H. Perng, and C. H. Lin, *Supercond. Sci. Technol.* **4**, 294–300 (1991).
10. C. T. Wu, K. C. Goretta, and R. B. Poeppel, *Applied Supercond.* **1** (1/2), 33–42 (1993).
11. K. Nomura, M. Seido, H. Kitaguchi, H. Kumakura, K. Togano, and H. Maeda, *Appl. Phys. Lett.* **62** (17), 2131–2133 (1993).
12. P. C. W. Fung, J. C. L. Chow, and J. Gao, *J. Supercond.* **6** (5), 327–334 (1993).
13. T. Matsushita, A. Suzuki, K. Teramoto, M. Okuda, and H. Naito, *Supercond. Sci. Technol.* **4**, 721–724 (1991).
14. M. Vlasse, J. Golben, and T. Mitchell, *Supercond. Sci. Technol.* **5**, 236–239 (1992).
15. Qing-rong Feng, H. Zhang, Sun-qi Feng, X. Zhu, K. Wu, Zun-xiao Liu, and Li-xin Xue, *Solid State Commun.* **78** (7), 609–613 (1991).
16. Y. Xin, Z. Z. Sheng, F. T. Chan, P. C. W. Fung, and K. W. Wong, *Solid State Commun.* **76** (12), 1347–1350 (1990).
17. P. C. W. Fung, Z. C. Lin, Z. M. Liu, Y. Xin, Z. Z. Sheng, F. T. Chan, K. W. Wong, Y.-N. Xu, and W. Y. Ching, *Solid State Commun.* **75** (3), 211–216 (1990).