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Laser fabrication of Pb doped Bi–Sr–Ca–Cu–O superconductor

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It has been shown that the addition of Pb enhances the formation of 110 K (2223) phase in Bi–Sr–Ca–Cu–O system due to kinetic reasons. With the premise that a local temperature spike, exceeding the melting temperature of the compound, might enhance the nucleation and growth of the 110 K phase, we have conducted laser calcination experiments of Pb doped Bi–Sr–Ca–Cu–O compound by using a high energy Nd:YAG laser. It is found that laser calcination of this material indeed enhances kinetics of formation of the 110 K phase. Nearly 100% 2223 phase has been obtained in laser processed samples in much shorter sintering time compared with the conventional sintering.

1. Introduction

The high T_c Bi–Sr–Ca–Cu–O superconducting compound has a number of phases with different critical temperatures, T_c. The three major phases are referred to by their cation ratios as 2201 (T_c below 77 K), 2212 ($T_c \sim 85$ K), and 2223 ($T_c \sim 110$ K) phases [2]. Since the discovery of superconductivity in this compound [3], many efforts have been made to maximize the amount of high T_c-2223 (110 K) phase. A major enhancement in the formation of high T_c-2223 phase was made by doping Bi–Sr–Ca–Cu–O compound with Pb [1, 4–7]. However, with Pb doping, about 200 h of total processing time is required to obtain a single or nearly a single high T_c phase. In this study, a new laser processing technique was developed with an objective to enhance the kinetics of formation of the high T_c phase of a Pb doped Bi–Sr–Ca–Cu–O superconductor. With laser calcination process, we were able to fabricate a near single-phase high T_c Bi–Pb–Sr–Ca–Cu–O superconductor in about 100 h of sintering, following the laser calcination. The on-set critical temperature of the laser calcined sample was found to be about 110 K. However, the zero resistance temperature was about 98 K.

2. Experimental procedure

Starting materials of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, and CuO were weighed and mixed to have Bi:Pb:Sr:Ca:Cu cation ratio of 1.5:0.5:2:2:3. This powder was thoroughly ground with a pestle and mortar to ensure thorough mixing. The fine mixed powder was then placed in a specially designed slow rotating pan and irradiated with a de-focused pulsed Nd:YAG laser beam at two different power levels, (Table I).

During laser irradiation, the powder was constantly stirred by a stationary vane attached to the rotating pan. Periodically, calcining powder was re-ground to ensure uniform laser–powder interaction. The average linear speed of the rotating pan with respect to laser beam was about 2.5 cm s^{-1}. A 400 W Nd:YAG pulse laser with a pulse rate of 100 pulses per second and a pulse width of 2.2 ms was used during all the experiments.

For comparison, an identical batch of powder mixture was also calcined conventionally in a furnace set at 830 °C for 7 h. The laser and conventionally calcined powders were pelletized and these pellets were sintered at 865 °C in air for different durations up to 240 h, then cooled at a rate of 100 °C h^{-1}. A Scintac-XDS-2000 X-ray diffractometer (XRD) with a Cu target, a Hitachi S-2500C scanning electron microscope (SEM) with Link energy dispersive X-ray spectroscopy (EDS), were used to characterize these superconductors. Resistivity was measured by using an auto-balancing alternating current (a.c.) bridge with a lock-in amplifier (Linear Research) using a standard four-probe technique. The mutual inductance, which is proportional to the a.c. magnetic susceptibility of the in-phase component, χ', was measured directly using an autobalancing Hartshorn bridge.

3. Results and discussion

It has been shown by other researchers that formation of the high T_c phase can be enhanced by the melt-quench method with Ca and Cu rich starting composition [1]. A similar melt-quench effect was obtained when Bi–Pb–Sr–Ca–Cu–O powder mixture was exposed to high energy and short duration laser pulses. Coarse particles were formed by localized melting. Due to a localized rapid heating and quenching, chemical homogeneity of the well mixed starting powder was preserved. Therefore, we were able to greatly increase the rate of formation and volume fraction of

0022–2461

TABLE I Calcining conditions

	Laser power (W)	Time (h)	Pulse energy density ($J\,cm^{-2}$)
Sample A	90	0.5	1.8
Sample B	50	1.5	1.0
Sample C	conventionally calcined (830 °C, 7 h)		

the high-T_c phase ($T_c \sim 110$ K) without using any excess Ca and Cu in the starting powder.

The mechanism of formation of high T_c phase by laser and conventional processes appeared to be quite different by observation of the XRD data. As seen in Fig. 1, the conventionally processed sample initially showed a mixture of low T_c-2212 phase and Ca_2PbO_4. As the duration of sintering increased, the amount of Ca_2PbO_4 decreased, and a phase cycling behaviour was observed [2]. The high T_c-2223 phase was then formed by reaction of low T_c phase with Ca_2PbO_4 and Ca_2CuO_3 [8, 9].

Different results were observed for two laser processed samples, see Figs 2 and 3. At an early stage of sintering, predominately a low T_c-2212 phase was formed. After prolonged sintering, the high T_c phase, $Bi_2Sr_2Ca_2Cu_3O_x$, was formed via an unbalanced reaction of the following form [10]

$$2Bi_2Sr_2CaCu_2O_x \rightarrow Bi_2Sr_2Ca_2Cu_3O_y + Bi_2Sr_2CuO_z$$

The initial formation of 2212 phase leaves some excess Ca and Cu ions of the starting stoichiometric 2223 composition. The 2201 ($Bi_2Sr_2CuO_z$) phase formed, then combines with the unused Ca and Cu ions to form the low T_c-2212 phase. Therefore, compared to the high T_c-2223 phase, the amount of retained 2201 phase in laser calcined samples was not

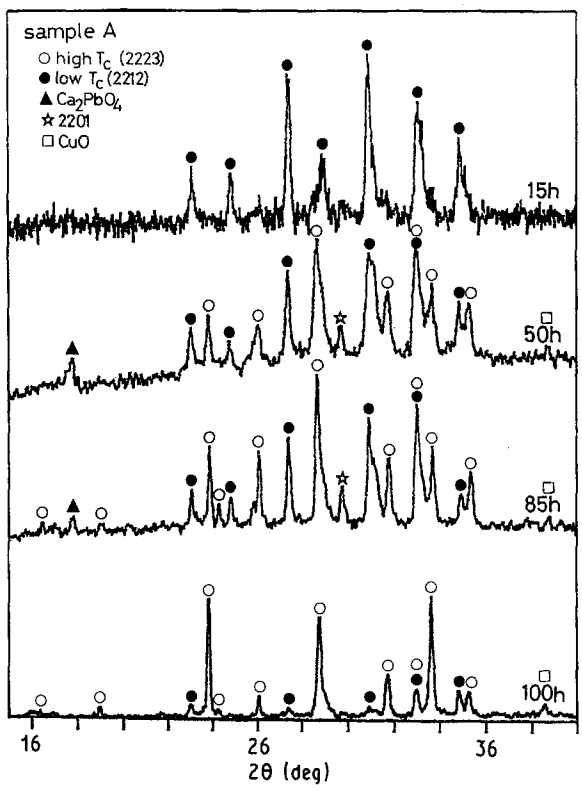


Figure 2 X-ray diffraction diagrams of $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ sample processed with 90 W laser power during various stages of sintering.

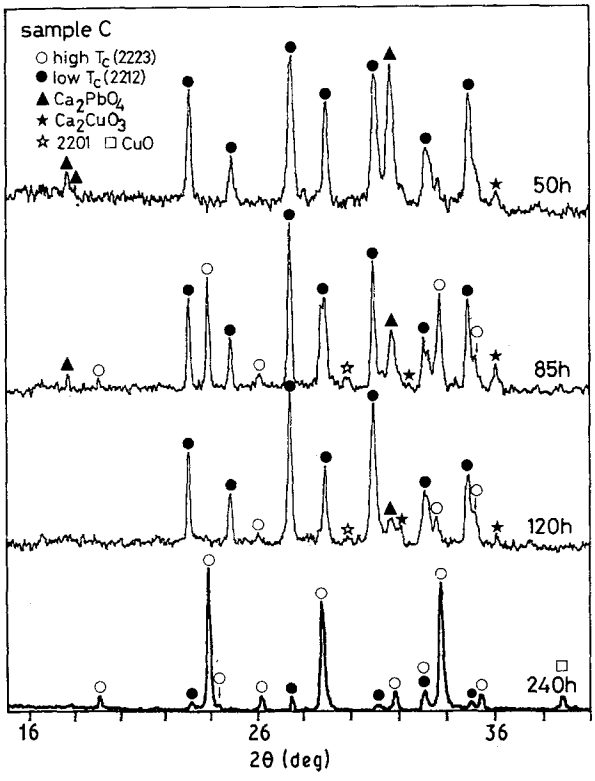


Figure 1 X-ray diffraction diagrams of conventionally processed $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ sample during various stages of sintering.

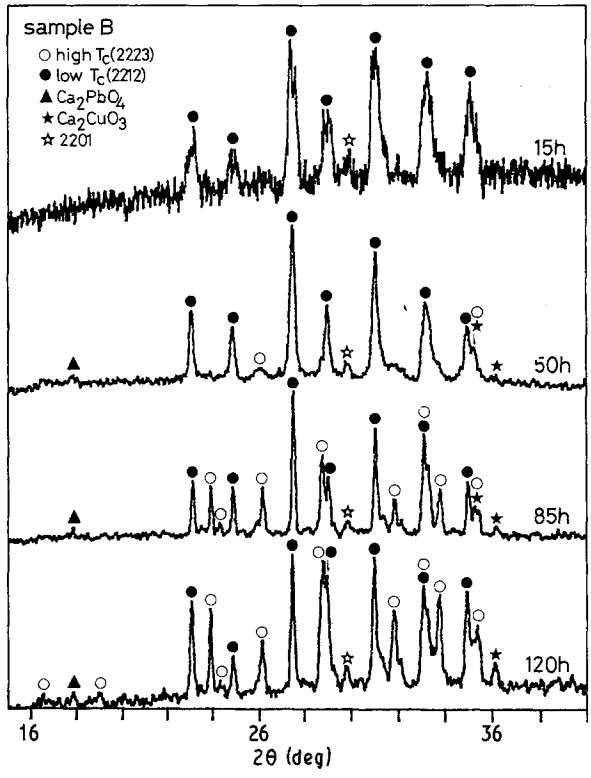


Figure 3 X-ray diffraction diagrams of $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ sample processed with 50 W laser power during various stages of sintering.

large. A considerable amount of Ca_2CuO_3 was also formed in sample B after prolonged sintering. Due to the complexity of this sample, it is difficult to determine how much Ca_2CuO_3 was present. EDS analysis were performed on fractured surfaces of this sample. The EDS and XRD data support the assumption that Ca was in fact trapped in the form of Ca_2CuO_3 in the sample B [6]. Thus, a low volume fraction of high T_c phase and the zero resistance temperature below 77 K were observed for this sample. Due to the high energy density of the laser beam some weight loss, in the form of particulate ejection, of the starting powder is unavoidable during laser calcination process. Thus, the final compositions of laser and conventionally calcined samples were analysed by EDS rather than by a weight loss measurement. No significant compositional difference was found through the chemical analysis.

Scanning electron micrographs shown in Fig. 4a and b indicate a characteristic plate-like grain structure. The laser processed sample (see Fig. 4a) showed well-grown plates of 10–30 micrometres wide and about 1 micrometre thick. The plate size of laser processed sample was about 2–3 times as large as the conventionally processed one.

The measurements made on the resistance and the magnetic susceptibility of laser and conventionally processed samples are plotted as a function of temperature in Fig. 5a and b. All these samples show superconducting on-set temperature about 110 K. The zero resistance temperature of laser processed sample, after 100 h sintering, is about 98 K. The second inflections (marked by arrows in Fig. 5b) in the a.c. susceptibility curve were observed for sample A, sintered for 100 h, and sample C, sintered for 240 h. The second inflection in these two samples is likely due to Josephson-like weak coupling between the high T_c grains [11]. A sharp drop in magnetic susceptibility for sample A, sintered for only 85 h, can therefore be attributed to the absence of Josephson-like weak coupling. Though, the laser and conventionally processed samples show similar on-set transition temperatures and over-all trends. Our initial results showed that depending on processing conditions the laser processed samples can have a significantly large resistance transition width.

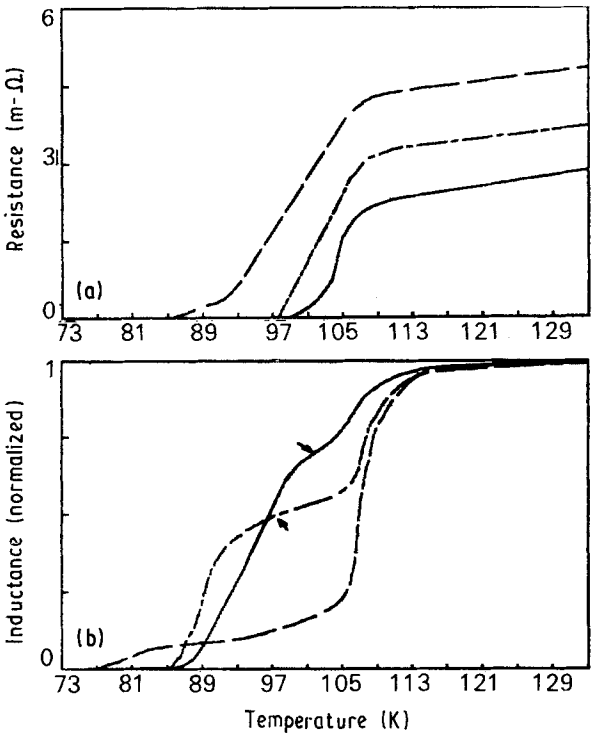
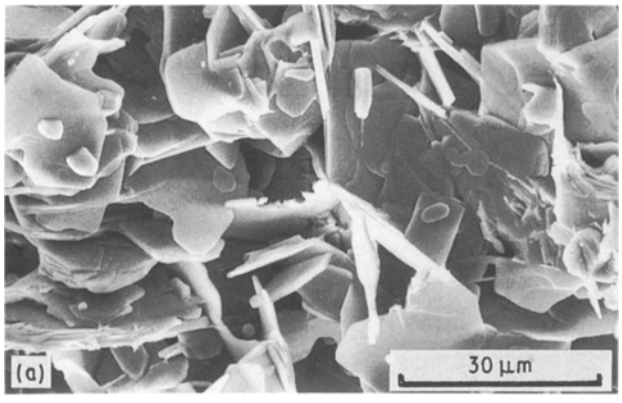


Figure 5 (a) Resistance versus temperature curves and (b) magnetic susceptibility versus temperature curves of conventionally and laser processed samples, respectively: (– –) sample A, 865 °C for 85 h; (– – –) sample A, 865 °C for 100 h; (—) sample C, 865 °C for 240 h.



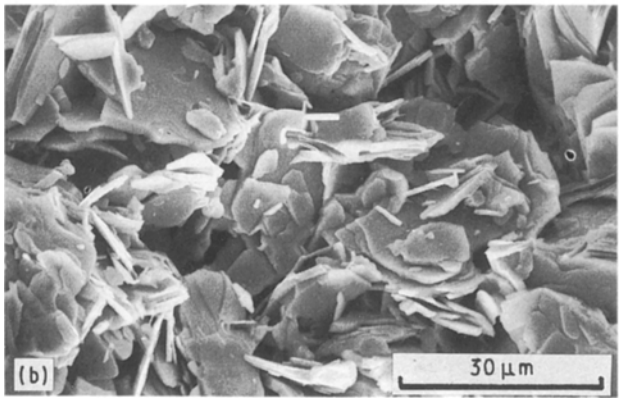


Figure 4 Scanning electron micrographs of (a) sample A, laser calcined and sintered at 865 °C for 85 h; (b) sample C, conventionally calcined and sintered at 865 °C for 240 h.

4. Conclusions

Superconductors of Bi–Pb–Sr–Ca–Cu–O system of near single high T_c phase were made by using a new laser calcining process. The total processing time was reduced to about 100 h. Both resistance and magnetic susceptibility data showed an on-set of superconducting transition at about 110 K. A sharp magnetic susceptibility drop was observed above 106 K. The zero resistance temperature was about 98 K. High T_c phase was formed via a different kinetic path in laser calcined sample compared with the conventionally processed sample.

References

1. D. SHI, M. S. BOLEY, J. G. CHEN, M. XU, K. VANDERVOORT, Y. X. LIAO, A. ZANGVIL, J. AKUJIEZE and C. SEGRE, *Appl. Phys. Lett.* **55** (1989) 699.

2. J. M. TARASCON, W. R. McKINNON, P. BARBOUX, D. M. HWANG, B. G. BAGLEY, L. H. GREENE, G. HULL, Y. LePAGE, N. STOFFEL and M. GIROUD, *Phys. Rev.* **B38** (1988) 8885.
3. H. MAEDA, Y. TANAKA, M. FUKUTOMI and T. ASANO, *J. Appl. Phys.* **27** (1988) L209.
4. 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. MARCH, L. W. RUPP, Jr. and W. F. FECK, *Phys. Rev.* **B38** (1988) 893.
5. Y. YAMADA and S. MURASE, *Jpn. J. Appl. Phys.* **27** (1988) L996.
6. M. TAKANO, J. TAKADA, K. ODA, H. KITAGUCHI, Y. MIURA, Y. IKEDA, Y. TOMII and H. MAZAKI, *ibid.* **27** (1988) L1041.
7. M. MIZUNO, H. ENDO, J. TSUCHIYA, N. KIJIMA, A. SUMIYAMA and Y. OGURI, *ibid.* **27** (1988) L1225.
8. T. UZUMAKI, K. YAMANAKA, N. KAMEHARA and K. NIWA, *ibid.* **28** (1989) L75.
9. H. ENDO, J. TSUCHIYA, N. KIJIMA, A. SUMIYAMA, M. MIZUNO and Y. OGURI, *ibid.* **27** (1988) L1906.
10. N. KIJIMA, H. ENDO, J. TSUCHIYA, A. SUMIYAMA, M. MIZUNO and Y. OGURI, *ibid.* **27** (1988) L1852.
11. A. SUMIYAMA, H. ENDO, J. TSUCHIYA, N. KIJIMA, M. MIZUNO and Y. OGURI, *ibid.* **28** (1989) L373.

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