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Sintering period dependence of composition and superconducting properties of (BiPb)SrCaCu$_{1.8}$O$_x$ system

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The material system $(Bi_{0.7}Pb_{0.3})Sr_1Ca_1Cu_{1.8}O_x$ forms, at 840° C, two major phases having a high T_c (100 K) and a low T_c ($\sim$70 K) both of which consist of platelets and a non-superconducting minor phase which has a rod-like shape and is isolated by the major phases. As the sintering period increases, the amount of high T_c phase increases accompanying the decrease in low T_c phase while the amount of the non-superconducting phase is independent of sintering period, resulting in a superconductor with T_c of 100 K. Changes in compositions of each phase also occur during sintering due to evaporation of bismuth and lead.

1. Introduction

Since the discovery of superconducting properties with a critical temperature (T_c) of $\sim$40 K in the $(LaBa)_2CuO_4$ system [1], great efforts have been directed toward the development of new materials with better properties. Existence of oxide superconductors with T_c higher than 100 K has been reported in Bi–Sr–Ca–Cu–O [2], Tl–Ba–Ca–Cu–O [3] and Th–Ba–Ca–Cu–O [4] systems. Among these new families of materials, the Bi–Sr–Ca–Cu–O system appears to be attractive from the consideration of material cost since it does not contain any rare earth elements. It was also reported that Bi–Sr–Ca–Cu–O superconductors are more stable. However, superconductors made by usual ceramic fabrication techniques from this material system contain two major phases: one with T_c of $\sim$105 K and the other with T_c $\sim$80 K.

Recently, Takano *et al.* [5] reported the fabrication of lead substituted Bi–Sr–Ca–Cu–O ($Bi_{0.7}Pb_{0.3}$-$Sr_1Ca_1Cu_{1.8}O_x$) superconductor with T_c of 107 K, starting from co-precipitated oxalates containing the relevant cation in various ratios and sintering the pellet for a long time (244 h).

Therefore, there is an ample interest in investigating the effects of powder preparation and sintering conditions on the compositions after the sintering and superconducting properties of the lead substituted Bi–Sr–Ca–Cu–O system. As the sintering period increases for this system, not only the changes in relative amounts of the high and low T_c phases occur as reported by Takano *et al.* [5] but also significant evaporation of bismuth and lead occur causing changes in the composition of the various phases present in the superconductor.

In this paper we report the results of an investigation of changes in composition and superconducting properties as a function of sintering period.

2. Experimental procedure

A conventional ceramic powder compacting method was used for sample preparation. A powder with a composition of $Bi_{0.7}Pb_{0.3}Sr_1Ca_1Cu_{1.8}O_x$ was prepared by dry mixing bismuth oxide, lead oxide, strontium carbonate, calcium carbonate and copper oxide in a plastic bottle with zirconia balls. Differential thermal analysis (DTA) data of this mixed powder showed two endothermic peaks: one near 745° C which was probably associated with the decomposition of carbonates and the other at 850° C which could possibly be associated with the melting of Bi_2O_3. Thus the mixed powder was calcined at 800° C for 12 h in air, and was then crushed and ground with a mortar and pestle. Discs with diameter 11 mm and height 5 mm were obtained using a press and die set. Final pressing was carried out using a cold isostatic press with pressure of 4000 kg cm^{-2}. Disc samples were sintered at 845° C for 24, 96, 168 and 240 h in an air atmosphere and then quenched in air. Photographs of surfaces were taken using a scanning electron microscope (SEM) to study the microstructure. X-ray diffraction patterns were taken to analyse structure and phases. Energy dispersive analysis of X-ray (EDAX) data and X-ray

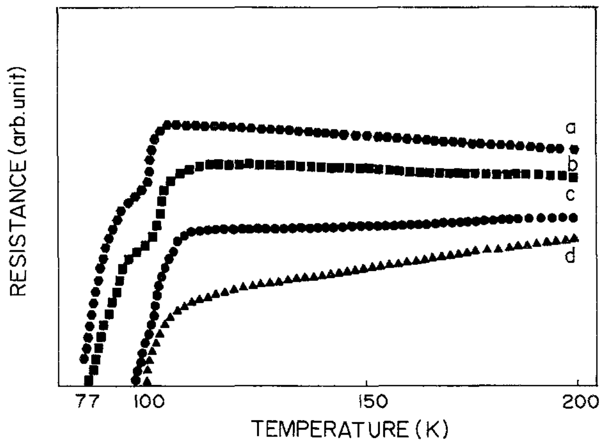

Figure 1 Electrical resistance as a function of temperature for $(Bi_{0.7}Pb_{0.3})Sr_1Ca_1Cu_{1.8}O_x$ sintered at 845° C in air for various sintering periods. (a) 24 h; (b) 96 h; (c) 168 h; (d) 240 h.

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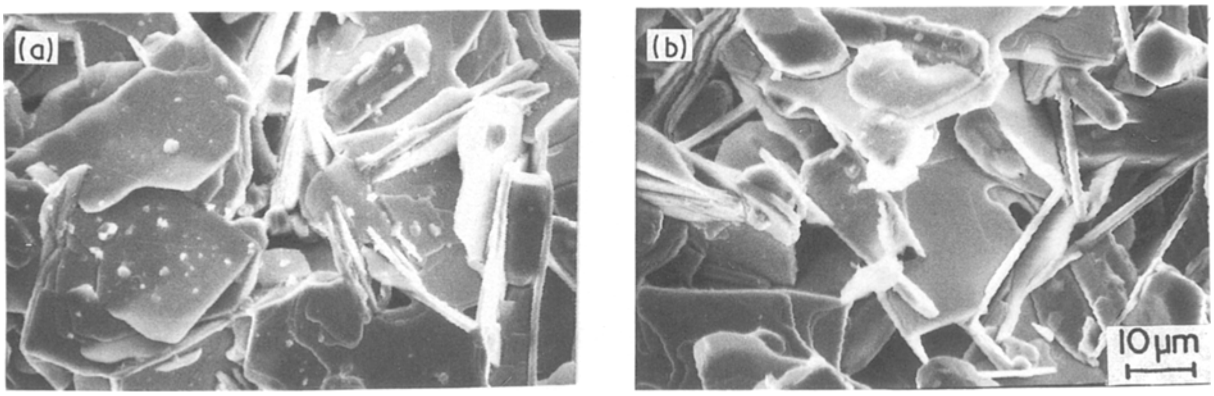


Figure 2 SEM photographs of $(Bi_{0.7}Pb_{0.3})Sr_1Ca_1Cu_{1.8}O_x$ sintered for (a) 24 h and (b) 240 h.

mapping data were also taken to investigate the macroscopic and microscopic variations of composition. The electrical resistance was measured by an a.c. 4-point probe method using silver contacts and diamagnetic property was observed by the levitation method.

3. Results and discussion

The electrical resistances of the $(Bi_{0.7}Pb_{0.3})Sr_1Ca_1Cu_{1.8}O_x$ sintered at 845° C for various periods of sintering as a function of temperature are shown in Fig. 1. For the specimens sintered up to 96 h (a and b) the electrical resistances decrease sharply in two steps as the temperature decreases. This fact obviously indicates that there exist at least two phases in the sintered specimens, namely one with high T_c and another with low T_c. These curves are similar to those observed in sintered $Bi_1Sr_1Ca_1Cu_{1.8}O_x$ superconductors [2] except the temperatures at which the sharp decrease in resistance occurs are lower by several degrees. It appears that the amount of the phase with low T_c decreases as the sintering period increases, and for the specimen that was sintered for 240 h (d) the resistance decreased by one step with T_c of 100 K. The curve (d) is similar to the one reported by Takano *et al.* [5] for the sintered $(Bi_{0.7}Pb_{0.3})Sr_1Ca_1Cu_{1.8}O_x$ whose powder was prepared by the oxalate method. Again a difference in T_c is observed since their sample showed a T_c of 107 K. The absence of the second sharp decrease in resistance against T curve does not, of course, necessarily mean complete absence of the phase with a low T_c. It means, however, that the amount of the phase with low T_c decreased and became isolated so that it does not contribute to electrical conductivity. The sample (a) did not float on a magnet at 77 K whereas the samples (b), (c) and (d) did. This fact indicates that not only the phase with low T_c but also the phase with high T_c increases as the sintering period increases.

Figure 2 shows the microstructures of $(Bi_{0.7}Pb_{0.3})$-$Sr_1Ca_1Cu_{1.8}O_x$ superconductors which were sintered at 845° C for 24 and 240 h. It appears that the sintered specimens consist of two major phases, i.e. second phase grains are imbedded in a major phase matrix. It can be seen that the amount of the isolated grains does not significantly depend on the sintering period. Since they are not connected, their contribution to the electrical conductivity should be negligible. This fact combined with the fact that there exist two sharp decreases in the resistance against T curve (Fig. 1a and b) indicated that the majority phase consists of, at least, two phases both contributing to the electrical conductivity. The relative amount of these phases appears to depend on the sintering period even though it is difficult to observe with SEM.

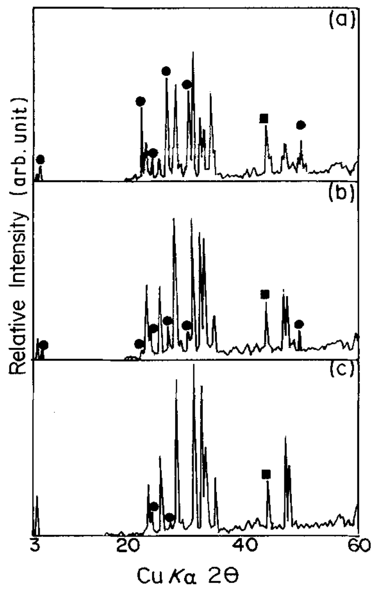


Figure 3 X-ray diffraction patterns for $(Bi_{0.7}Pb_{0.3})Sr_1Ca_1Cu_{1.8}O_x$ sintered at 845° C in air for (a) 24 h, (b) 96 h and (c) 240 h.

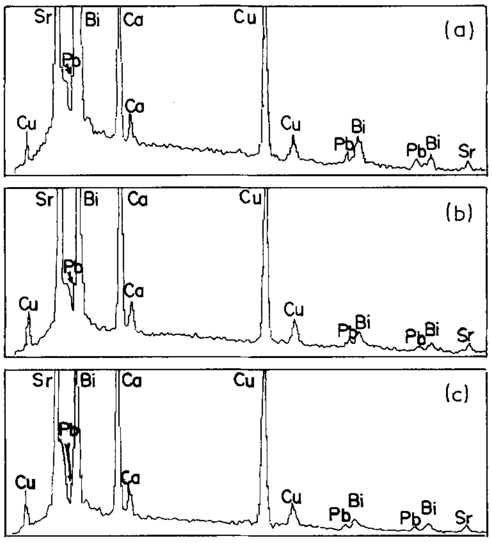


Figure 4 EDAX energy spectra for the specimens of Fig. 3.

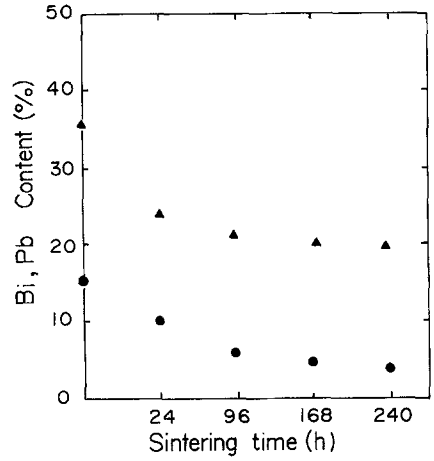


Figure 5 Variations of (▲) bismuth and (●) lead content against sintering period.

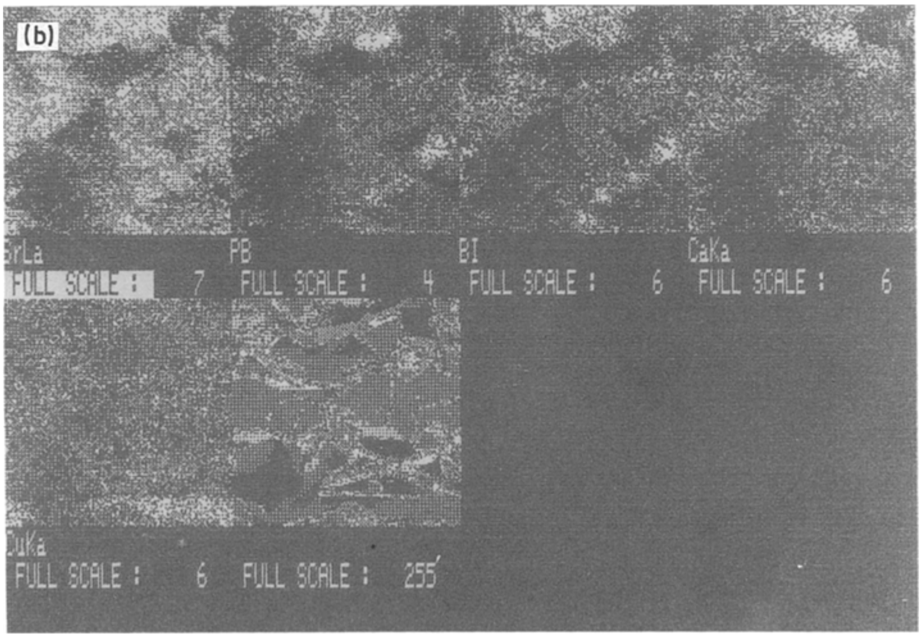
Figure 3 shows the X-ray diffraction patterns of the $(Bi_{0.7}Pb_{0.3})Sr_1Ca_1Cu_{1.8}O_x$ superconductors sintered at 845° C for various periods of sintering. The diffraction pattern for the specimen that was sintered for 24 h (a) is similar to that for the Bi–Sr–Ca–Cu–O system reported by Takayama-Muromachi *et al.* [6].

It mainly consisted of diffraction peaks due to the low T_c phase (●) and high T_c phase. Unlike the Bi–Sr–Ca–Cu–O system, however, the amplitudes of the diffraction peaks due to the high T_c phase in the lead substituted system, increase and those due to the low T_c phase decrease as the sintering time is increased, as can be seen in Fig. 3(a–c). The diffraction peaks due to a third phase (■) appear to be sintering period independent, and it appears that these peaks are associated with the isolated grains observed in the microstructure of Fig. 2.

EDAX data of the specimens with an initial composition of $(Bi_{0.7}Pb_{0.3})Sr_1Ca_1Cu_{1.8}O_x$ sintered at 845° C for various sintering periods are shown in Fig. 4. Since basic information, such as the phase diagram for this system, is not reported, it is difficult to determine the exact composition of the various phases present in each specimen. But it is rather surprising to note that the amounts of bismuth and lead decrease drastically with the increase in the sintering period. For the specimens which were sintered more than 196 h and for which the resistance against temperature curves showed only one sharp decrease (Fig. 1c and d), the final contents of bismuth and lead were less than half of the initial contents when the EDAX data were taken on as-sintered surface.

Figure 5 shows the variations of the bismuth and lead contents measured on an inside area (fractured and polished surface) as a function of sintering period. The weight per cent with respect to total cation bismuth and lead are 35 and 16 respectively. The bismuth and lead content decrease sharply up to 96 h sintering and then decrease slowly with further sintering. For the sample that was sintered for 240 h the bismuth and lead content decreased to 20 and 4 wt % respectively. Not only the macroscopic composition changes as shown in Fig. 5, but also the compositions of various phases change with the sintering period as shown in the X-ray mapping of Figs 6 and 7. Figure 6a and Fig. 7a show microstructures of the specimens

Figure 6 (a) Microstructure and (b) X-ray mapping of $(Bi_{0.7}Pb_{0.3})$-$Sr_1Ca_1Cu_{1.8}O_x$ sintered at 845° C in air for 24 h.



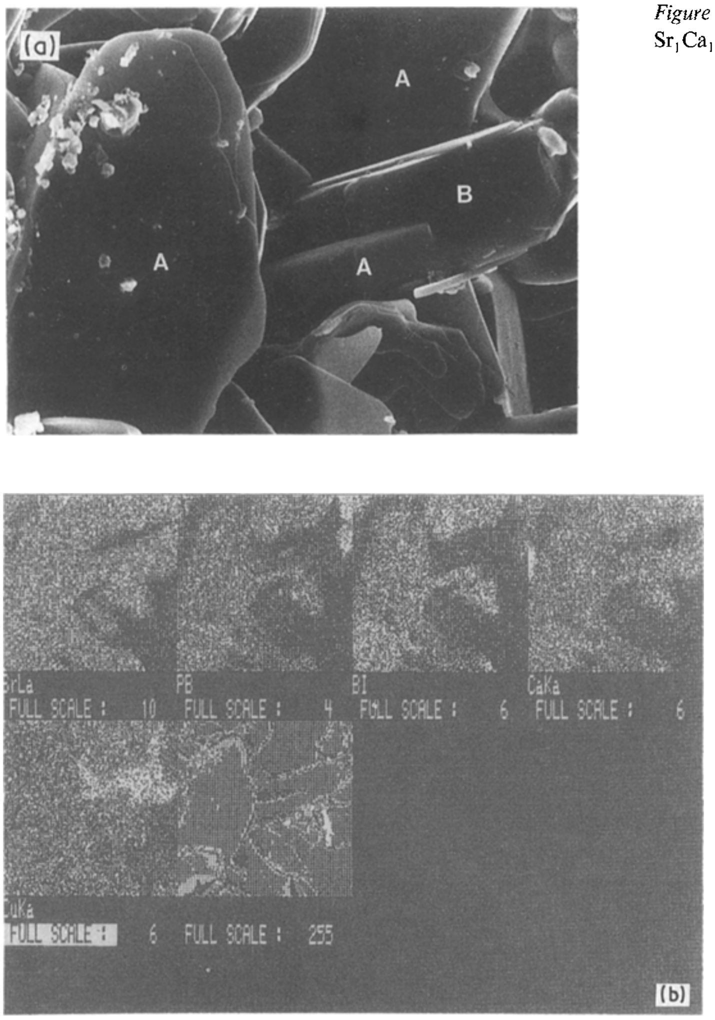


Figure 7 (a) Microstructure and (b) X-ray mapping of $(Bi_{0.7}Pb_{0.3})$-$Sr_1Ca_1Cu_{1.8}O_x$ sintered at 845° C in air for 240 h.

sintered for 24 and 240 h, respectively, and corresponding X-ray mappings are shown in Figs 6b and 7b. For the specimen sintered for 24 h (Fig. 6), there is no significant difference in the distribution of all elements between the platelet grains (A) and the rod-like grain (B), but the distribution of all elements is not quite uniform. The distribution appears to be more uniform for the specimen that was sintered for 240 h, but the concentration of lead and bismuth were reduced and the copper concentration was increased in rod-like grain (B). Point EDAX data indicated the presence of only 2 ~ 3 wt % of lead and bismuth in rod-like grain for the specimen sintered for 240 h. Thus it appears that the long sintering causes uniform distribution of all elements in the plate-like grains which are the superconducting phase and deplete bismuth and lead of rod-like grain which is non-superconducting phase through evaporation.

4. Conclusions

Based on the results of analysis of composition, microstructure and electrical properties of superconductors in the material system $(Bi_{0.7}Pb_{0.3})Sr_1Ca_1Cu_{1.8}O_x$ system, prepared from oxides and carbonates and sintered at 845° C for various sintering periods, the following conclusions can be drawn:

1. The $(Bi_{0.7}Pb_{0.3})Sr_1Ca_1Cu_{1.8}O_x$ forms two major phases having a high T_c of 100 K and a low T_c of ~ 70 K both of which consist of platelets and a non-superconducting phase which is rod-like in shape and does not contribute to electrical conductivity, being isolated.
2. The microstructures of the major phases and the non-superconducting minor phase do not change significantly with increasing sintering time from 1 day to 10 days.
3. As the sintering period increases, the amount of the phase with high T_c increases while the phase with low T_c decreases resulting in a superconductor with the high T_c (100 K).
4. The amount of the non-superconducting phase is sintering period independent.
5. The composition of each phase changes during sintering in an open tray due to evaporation of bismuth and lead.

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