JOURNAL OF MATERIALS SCIENCE 29 (1994) 2678–2682

Effects of sintering temperature on the superconducting and microstructural properties of $Bi_{1.7}Pb_{0.4}Sr_{1.6}Ca_{2.4}Cu_{3.6}O_Y/Ag_2O$ composites

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The effects of sintering temperature on the superconducting and microstructure properties of $Bi_{1.7}Pb_{0.4}Sr_{1.6}Ca_{2.4}Cu_{3.6}O_y$ (BPSCCO)/Ag_2O (0–50 wt%) superconductors were investigated. Based on the differential thermal analysis data, it was found that the addition of Ag_2O to the BPSCCO system lowered the partial melting temperature (peritectic point), thereby promoting extra liquid formation in this system and affecting the stability of 2223 high-T_c phase of these composites. For example, the T_c (zero) of the BPSCCO/Ag_2O (10 wt%) composite which was sintered at 843 °C in air was depressed by as much as 52 K. However, the addition of Ag_2O (10–50 wt%) in the BPSCCO samples resulted in no significant effect on T_c when samples were treated under a lower sintering temperature (827 °C) in air. The correlations of superconducting properties with microstructures of these materials are discussed.

1. Introduction

The discovery of high-temperature superconductors has generated the exciting possibility of practical applications of superconductivity at liquid nitrogen temperature [1]. However, the bulk superconductor has the characteristics of low critical transport current density, low strength and toughness which limit its application [2–5]. During the last few years, the addition of silver or Ag_2O to the superconductor has been extensively used to improve both the superconducting and mechanical properties [6–12]. Nishio *et al.* [9] reported that composite superconductors prepared by sintering a mixture of YBCO and silver powders in various proportions were able to enhance the mechanical strength against fracture to about four to five times as large as that in the sintered YBCO sample, without seriously lowering the superconducting transition temperature. On the other hand, Peters *et al.* [13] first demonstrated that the addition of Ag_2O to the YBCO did not change the superconductivity of YBCO. In addition, the reported results suggested a strong flux pinning effect in these Ag_2O addition composites.

However, there are conflicting reports in the literature regarding the poisoning character of silver in the Bi(Pb)–Sr–Ca–Cu–O system. Song *et al.* [14] reported that the detrimental effect of silver in the lead-doped Bi–Sr–Ca–Cu–O system can be prevented only by treating the composite specimens in low oxygen partial pressures (0.030–0.067 atm). On the other hand, for silver contents between 0 and ~ 15 vol %, the bulk critical temperature was depressed by as much as 40 K, and the relative proportion of the 2223 phase with respect to the 2212 phase was decreased, compared to the pure BPSCCO specimen, as reported by Sarkar *et al.* [15]. Jin *et al.* [16] found silver to be innocuous even when specimens containing 20 wt % silver were sintered and cooled in pure oxygen. However, an enhancement of superconductive properties due to the addition of silver to the BPSCCO system has been reported by Savvides *et al.* [17]. It was found that silver enhances flux pinning in the intergranular regions with optimum critical current densities occurring at 20–30 vol % Ag. The transport critical current density (at 77 K) was found to be increased by more than ten times its value at 0 vol % Ag.

For most practical applications, superconducting and mechanical properties are desirable. Our recent work [18], which indicated some interesting results on the mechanical properties of BPSCCO/Ag_2O composites, concluded that the Vickers hardness decreased with increasing porosity for all specimens sintered at 830 °C for 6, 24, and 72 h, respectively. Thus, in order to gain a better understanding of the superconducting properties of this BPSCCO/Ag_2O system, the present work was initiated to study the

0022-2461

effect of sintering temperature on the superconducting properties of BPSCCO/Ag_2O composite superconductors. Correlations of the superconducting properties and microstructures of these materials were also investigated.

2. Experimental procedure

The $Bi_{1.7}Pb_{0.4}Sr_{1.6}Ca_{2.4}Cu_{3.6}O_y$ (BPSCCO) powders for this investigation were prepared by oxalate coprecipitation. The starting powders were heated at 800 °C for 10 h for decomposition of oxalate and then heated at 850 °C for 48 h. Details of the powder synthesis were reported previously [19]. The sintering powders were prepared by thoroughly mixing BPSCCO powder with Ag_2O (0–50 wt %), and subsequently pressing the mixture into pellets with a diameter of 10 mm at 400 MPa. The pellets were sintered at 825–845 °C for 48 h in air, and then cooled to room temperature in the furnace. The structure of the sintered specimens was identified using X-ray diffraction with a copper target, a nickel filter and a graphite single-crystal monochromator. The microstructure was examined by optical and scanning electron microscopy (SEM) in combination with energy dispersive X-ray analysis (EDX). The melting behaviour of the samples was analysed by the conventional differential thermal analysis (DTA) technique. The DTA curves were obtained in air at a heating rate of 10 °C min^{-1}. The electrical resistivity was measured using a standard four-probe technique.

3. Results and discussion

Fig. 1 shows the temperature dependence of resistivity for BPSCCO/Ag_2O (0–50 wt %) specimens which were carried out at 827 °C for 48 h sintering in air. The values of T_c (zero) for those specimens (0–50 wt %) were 103.2, 101.7, 101.6, 101.2, 100.1 and 100.9. These results are supported further by the XRD patterns as shown in Fig. 2. The X-ray peaks obtained from these pellets, appeared to contain mainly the high-T_c (2223) phase and the silver XRD peak increased with increasing Ag_2O content in the composites.

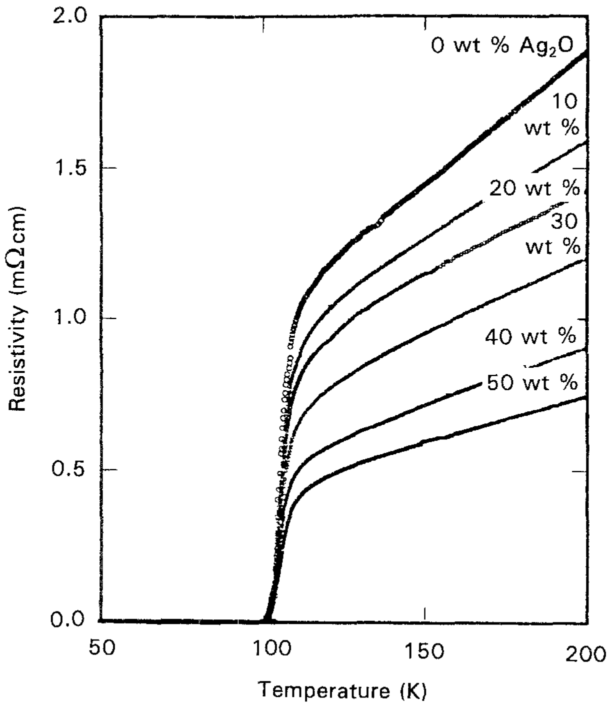

Figure 1 The temperature dependence of resistivity for the BPSCCO/Ag_2O (0–50 wt %) specimens after sintering at 827 °C for 48 h in air.

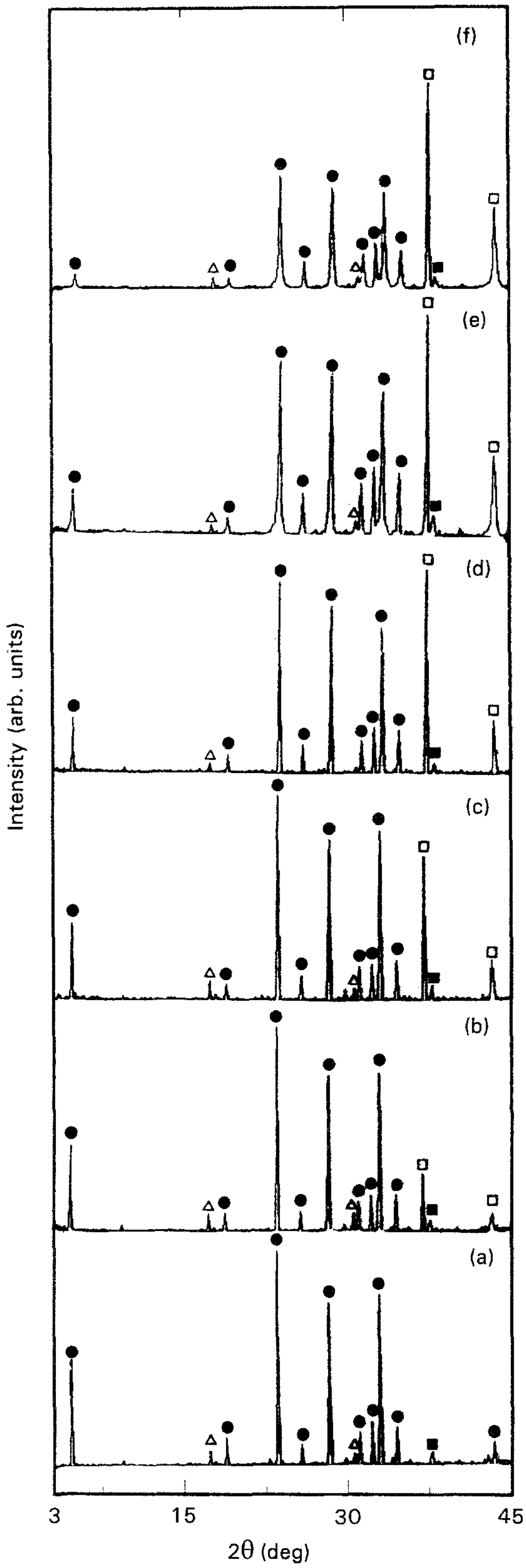

Figure 2 XRD patterns of the BPSCCO/Ag_2O (0–50 wt %) specimens sintered at 827 °C for 48 h in air. Ag_2O (wt %): (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, (f) 50. (●) 2223, (△) Ca_2PbO_4, (■) CuO, (□) Ag.

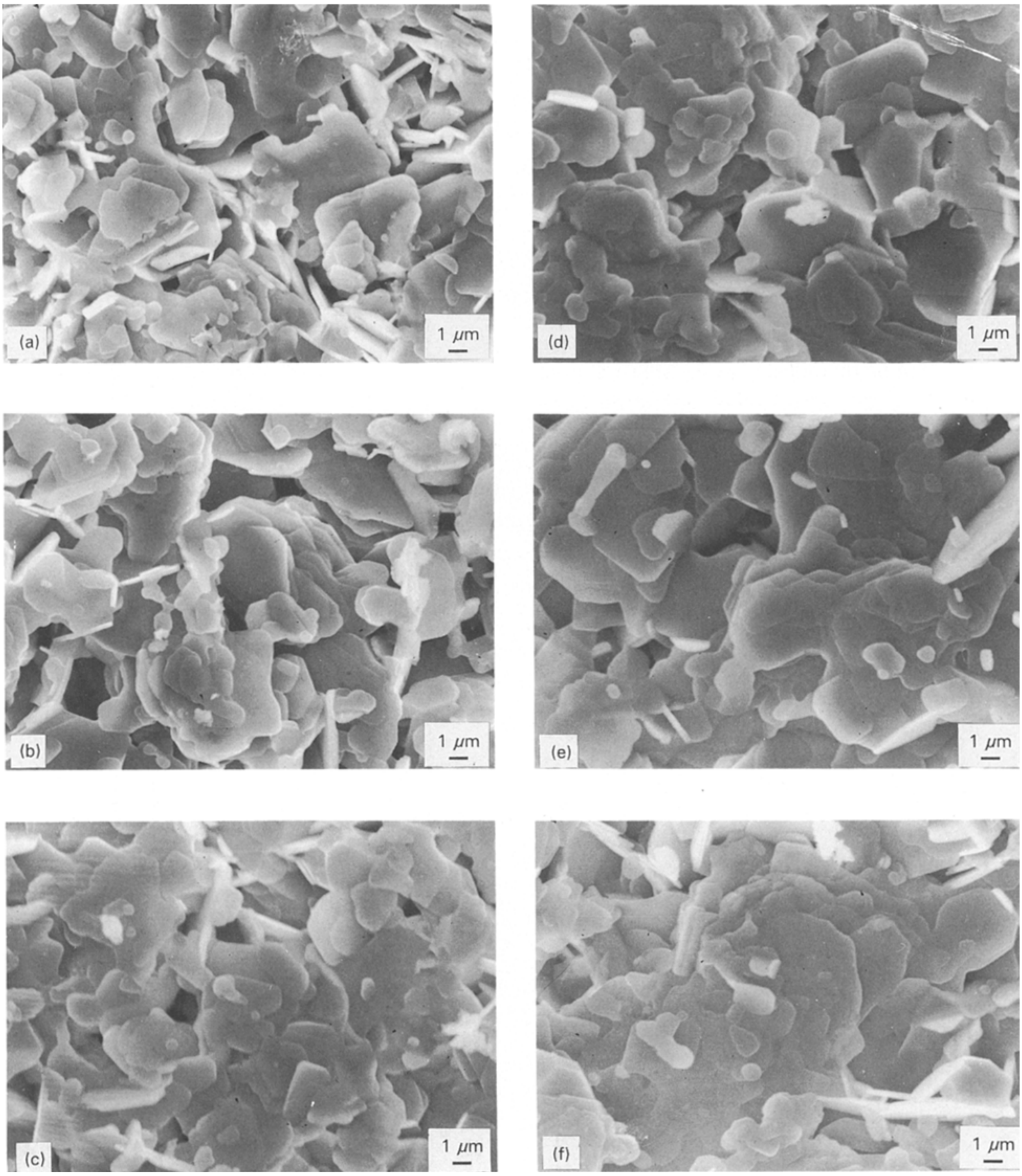

Figure 3 Scanning electron micrographs of the surface of BPSCCO/Ag_2O (0–50 wt %) specimens sintered at 827 °C for 48 h in air. Ag_2O (wt %): (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, (f) 50.

Fig. 3a–f show scanning electron micrographs of the surface of BPSCCO compound and BPSCCO/Ag_2O (10–50 wt %) composites which were sintered at 827 °C for 48 h in air. Plate-like structures are clearly visible in these specimens both of which show a similar microstructure which contains a high-T_c (2223) phase. However, the addition of Ag_2O to the BPSCCO system should lead to a slight increase of the plate-like grain size of BPSCCO/Ag_2O composites with increasing Ag_2O content. From EDX analysis, all specimens contained high-T_c (2223) phase and no silver was detected in association with the superconducting phase.

It is interesting to note that the addition of Ag_2O (10–50 wt %) in the BPSCCO specimens resulted in no significant effect on T_c when specimens were sintered at 827 °C in air. Our results are inconsistent with those of Song *et al.* [14], who reported that the formation of the high-T_c 2223 phase was suppressed when the silver-doped specimen was treated in air, and proposed that the major obstacle for the formation of the 2223 phase was the introduction of the Ag_2O–PbO–CuO solid solution. In order to clarify the relationship between the BPSCCO and Ag_2O, detailed differential thermal analysis (DTA) studies were made. The DTA curves were taken, on heating at

10 °C min^{-1}, of these specimens which were prepared by mixing the BPSCCO starting powder and Ag_2O (0–50 wt %). Based on our DTA data, we believe that the addition of Ag_2O to this system lowers the melting temperature (peritectic point), thereby promoting extra liquid formation in the system and affecting the stability of the 2223 high-T_c phase of these composites. For example, as shown in Fig. 4, a mixture containing the starting powder and 10 wt % Ag_2O shows the onset of partial melting at ~ 849 °C with an endothermic peak at 860 °C, whereas the pure powder shows these events at 869 °C and at 884 °C, respectively.

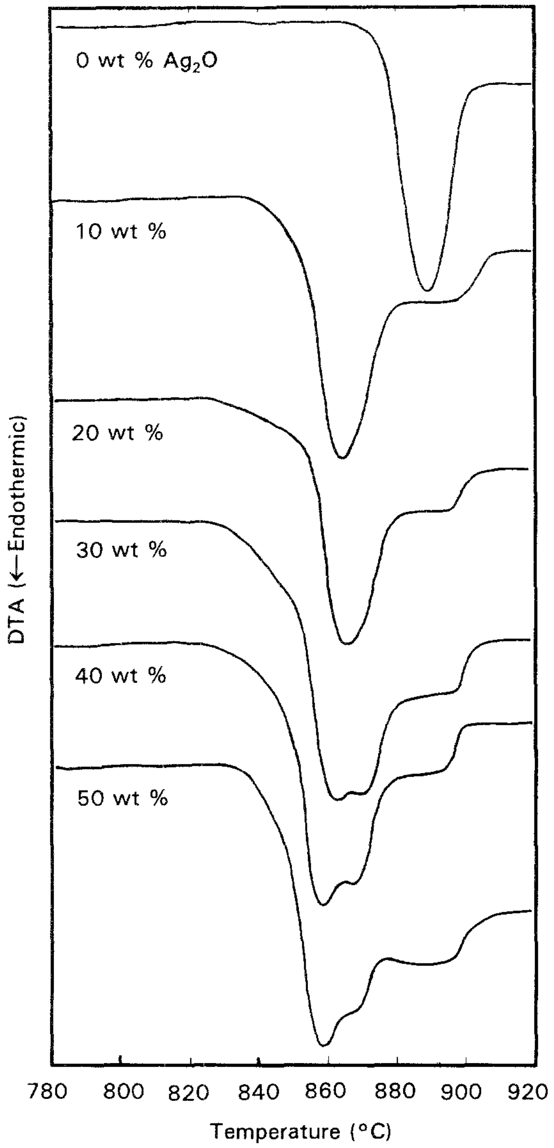

Figure 4 DTA curves for $BPSCCO/Ag_2O$ (0–50 wt %).

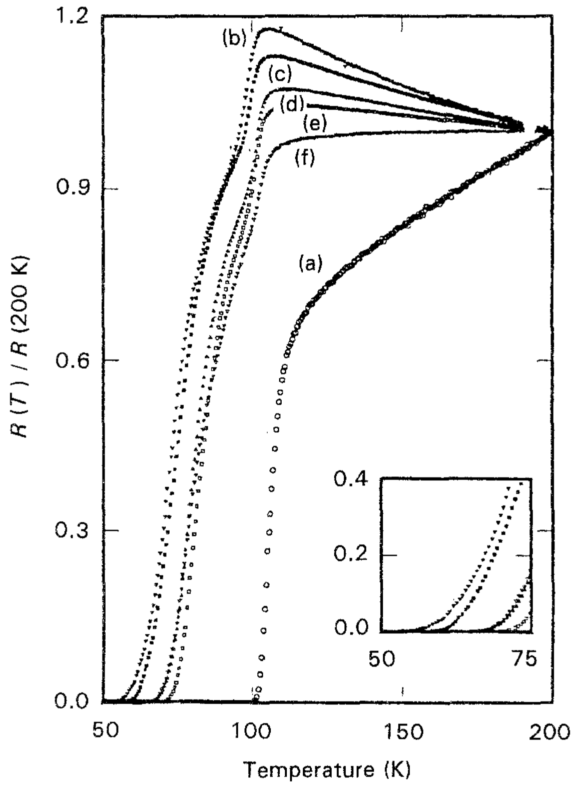

Figure 5 The temperature dependence of the normalized resistance for the $BPSCCO/Ag_2O$ (0–50 wt %) specimens sintered for 48 h at 843 °C in air. Ag_2O (wt %): (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, (f) 50.

More detailed information about this $BPSCCO/Ag_2O$ composite was obtained by sintering it for 48 h in air at 825–845 °C. It was observed that the partial and total melts of these pellets were sintered at 843 and 845 °C, respectively. The results for the undoped specimens are also included for comparison. Fig. 5 shows the temperature dependence of normalized resistance for BPSCCO compound and $BPSCCO/Ag_2O$ (10–50 wt %) composites which were sintered for 48 h at 843 °C in air, respectively. From Fig. 5, the T_c onset and T_c (zero) of the BPSCCO specimen are seen to be about 110 and 102 K, respectively. The T_c onset of the $BPSCCO/Ag_2O$ (10–50 wt %) specimen after sintering at 843 °C in air was about 100 K and then T_c (zero) was depressed by as much as 52–70 K. These results were further supported by the XRD patterns which showed the 2223, 2201 phases and some non-superconducting phases. A typical XRD pattern of the $BPSCCO/Ag_2O$ (10 wt %) specimen is shown in Fig. 6. This result is quite different from the BPSCCO superconductor which was sintered at 843 °C in air, strongly indicating that the addition of Ag_2O to the BPSCCO system lowers the eutectic temperature, thereby promoting extra liquid formation and affecting the stability of the 2223 high-T_c phase of these composites. This result is consistent with our DTA data and further supported by scanning electron micrographs.

Fig. 7 shows the scanning electron micrograph for the surface of $BPSCCO/Ag_2O$ (10 wt %) specimen which was sintered for 48 h at 843 °C in air. The partial melt morphology is shown in the Fig. 7. From EDX analysis, some non-superconducting phases, such as Ca_2PbO_4, CuO and (Sr, Ca)–Cu–O solid solution were found in the $BPSCCO/Ag_2O$ (10 wt %) composite and these results were consistent with the XRD pattern (Fig. 7). The major phase, however, for the $BPSCCO/Ag_2O$ (10 wt %) specimen treated at a lower temperature (827 °C) when sintered in air, was the 2223 high-T_c phase as mentioned above. This indicates that Ag_2O additions promote the decomposition of the 2223 high-T_c phase under the higher sintering temperature (843 °C).

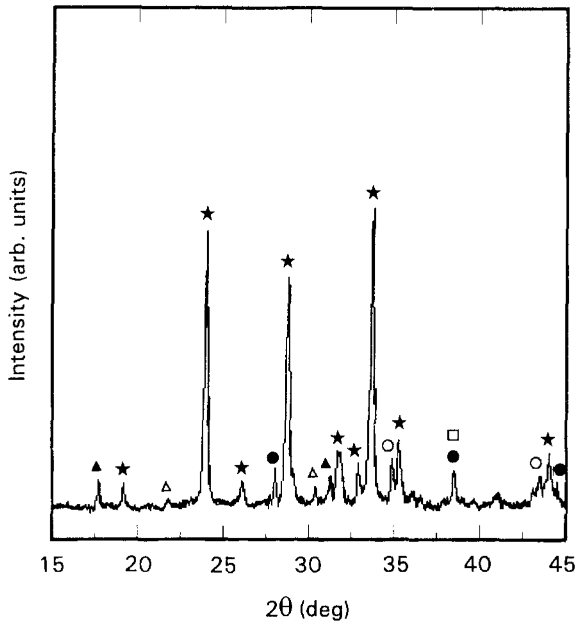

Figure 6 XRD pattern of the BPSCCO/Ag_2O (10 wt %) specimen sintered at 843 °C for 48 h in air. (*) 2223, (△) 2201, (▲) Ca_2PbO_4, (○) Ca_2CuO_3, (●) Sr_2CuO_3, (□) CuO.

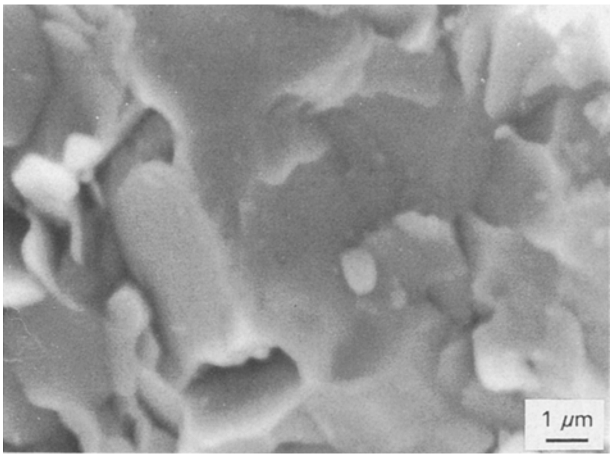

Figure 7 Scanning electron micrograph of the surface of the BPSCCO/Ag_2O (10 wt %) specimen sintered at 843 °C for 48 h in air.

From the results of resistivity, SEM morphology, XRD and DTA investigations, we believe that the addition of Ag_2O to the BPSCCO system does not necessarily lead to decomposition of the 2223 phase, but that the decomposition is dependent on temperature when sintering in air. The addition of Ag_2O to the BPSCCO pellets had no significant effect on T_c when specimens were sintered at 827 °C in air. However, the T_c onset of the BPSCCO/Ag_2O (10–50 wt %) specimens after sintering at 843 °C in air was about 100 K and then T_c (zero) was depressed by as much as 52–70 K. Therefore, this indicates that the addition of Ag_2O to the BPSCCO system lowers the eutectic temperature and promotes the decomposition of the high-T_c 2223 phase when the sintering temperature is above 843 °C in air.

4. Conclusions

The $Bi_{1.7}Pb_{0.4}Sr_{1.6}Ca_{2.4}Cu_{3.6}O_y$ powders for this investigation were prepared by oxalate coprecipitation. Based on the DTA data, it was found that the addition of Ag_2O to the BPSCCO system lowered the peritectic temperature, thereby promoting extra liquid formation in this system and affecting the stability of the 2223 phase of these composites. The addition of Ag_2O to the BPSCCO system does not necessarily lead to decomposition of the 2223 phase, decomposition being dependent on the temperature when sintering in air.

Acknowledgements

This work is supported by the NSC Grant NSC82-0511-M-007-140. The authors thank Dr S. H. Sheen for supplying the starting powder and for support, and Dr M. K. Wu for his advice and support.

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Received 5 April
and accepted 30 November 1993