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The melting behaviour of the lead-doped 2223 phase in Bi(Pb) SrCaCuO system

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The melting behaviour of the lead-doped 2223 phase in the bismuth oxide system has been investigated by using DTA, XRD and EPMA techniques. The results indicated that 2223 phase began to decompose into liquid, (Ca, Sr)$_2$CuO$_3$ and (Sr, Ca)$_{14}$Cu$_{24}$O$_{41}$ phases when fired at $T \geqslant 860\,^{\circ}$C in air. The liquid composition is located on the line between 2212 and 2201 phases. When the liquid was cooled in air, 2212 and 2201 phases crystallized from it.
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1. Introduction

The 2223 phase, which has the highest critical transition temperature, T_c, among the reported three superconducting phases, 2201, 2212 and 2223, corresponding to (Bi, Pb)$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_x$ with $n = 1, 2, 3$, respectively, has attracted much attention. So far, many attempts have been made to fabricate this high-T_c phase, including optimization of composition [1–4] and heat treatment [5, 6], and the formation mechanism [1,6–8]. However, there are few reports about the phase equilibria of the leaded BiSrCaCuO system except for the studies by Strobel and Fournier [9] and Liu and Jin [10]. The experimental data are insufficient to optimize thermodynamically and calculate this multicomponent system, although many suggestions concerning the decomposition of 2223 phase have been reported which are different from or even in contradiction with each other, due to impurities coexisting with 2223 in the sample employed. Hence, it is necessary to study the melting behaviour of 2223 phase again, in order to obtain correct phase relations in this system.

2. Experimental procedure

The key step to investigate the melting behaviour of 2223 phase is to synthesize a pure 2223 phase. Koyama *et al.* [4] suggested that a high volume fraction of 2223 could be obtained by using the starting composition of Bi$_{1.84}$Pb$_{0.34}$Sr$_{1.91}$Ca$_{2.05}$Cu$_{3.00}$O$_z$ when the partial pressure of oxygen is 1/13 atm. However, according to our former experiment, impurity-phase CuO unavoidably remains in the sample when annealed in air, even for a long time. In the present work, a nominal composition Bi$_{1.7}$Pb$_{0.4}$Sr$_{1.9}$Ca$_{2.05}$Cu$_{3.0}$O$_x$ (not including loss of lead during heat treatment) was adopted. Bi$_2$O$_3$, Pb(NO$_3$)$_2$, SrCO$_3$, CaCO$_3$ and CuO, with purities higher than 99.95 at %, were used as starting materials. The materials were carefully weighed using an analytical balance, then well blended in an agate motar. The mixture thus obtained was calcined at 640 °C for 4 h, then 720 °C for 6 h, and subsequently calcined at 780 °C for 20 h, with intermediate grindings. After that, the resultant precursor was reground and pressed into pellets of diameter 20 mm, and again calcined at 820 °C for 45 h, then ground again and compacted into pellets of diameter 10 mm. All calcinations were carried out in a box furnace. After final heat treatment in a diffusion furnace with a temperature error of ± 1 °C, the sample was quenched in air.

In order to select suitable temperatures for final heat treatment, differential thermal analysis (DTA) was performed onto the sample calcined at 820 °C, with a heating rate of 5 °C min^{-1} and Al$_2$O$_3$ as the reference material. Phase identification was carried out by X-ray diffraction (XRD) on a Japan 3014 diffractor with CuK_α radiation. CAMEBAX SX-50 was employed to perform electron probe microanalysis (EPMA).

3. Results and discussion

Because 2223 may form at temperatures lower than 830–840 °C [9–13], calcining at 820 °C of the sample for DTA is necessary to avoid the effect of other non-equilibrium phases. Fig. 1 illustrates the DTA result. It can be seen that there are two endothermal reactions in the range 800–900 °C, which are related to the endothermic peaks at 848–860 °C and 860–875 °C, respectively. This agrees well with the previous reports [14, 15] although the starting compositions used are different. In view of the DTA data, 850, 860 and 870 °C were chosen as the temperatures for final treatments.

Fig. 2a, b and c illustrate the XRD patterns of samples treated at 850, 860 870 °C for 140, 90 and 1 h, respectively. At 850 °C, 2223 predominates, which coexists with a small amount of Ca$_2$PbO$_4$, while the

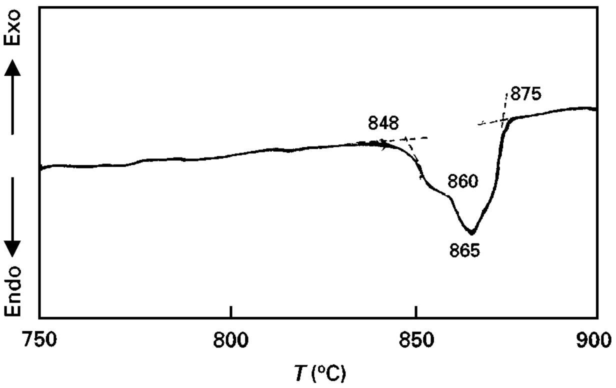

Figure 1 DTA curve of the sample calcined at 820 °C.

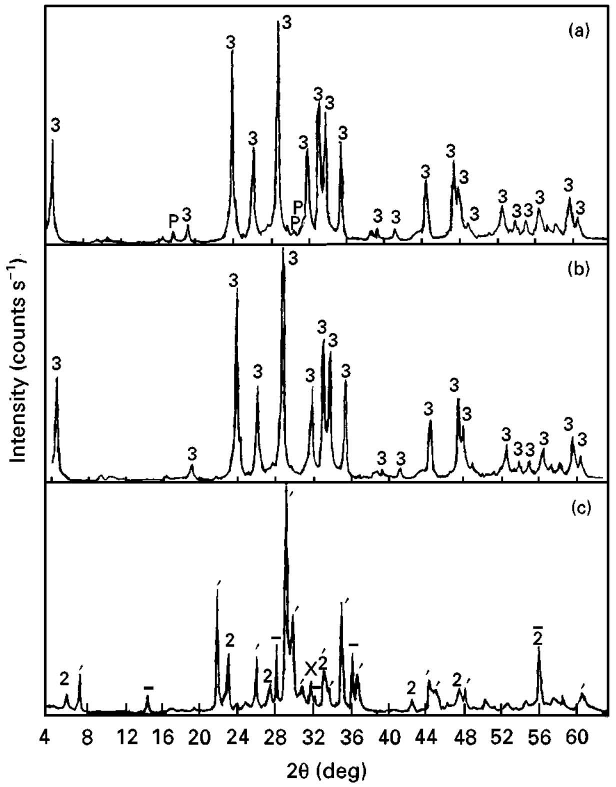

Figure 2 XRD patterns of the sample treated at (a) 850, (b) 860 and (c) 870 °C. 1, 2201; 2, 2212; 3, 2223; (×) $(Sr, Ca)_{14}Cu_{24}O_{41}$, ρ, Ca_2PbO_4, (■) Ca_2CuO_3.

sample treated at 860 °C contains only 2223. However, after holding at 870 °C for an hour, 2223 decomposed completely, 2212, 2201, $(Ca, Sr)_2CuO_3$ and $(Sr, Ca)_{14}Cu_{24}O_{41}$ occurring instead. Grievel and Flukiger [15] pointed out that partial melting might occur in the sample at about 850 °C, which coincides with the formation of 2223 [16–18]. In fact, during sintering at 850 °C, a small amount of liquid did form in the first several hours. But after the sample underwent an intermediate grinding and continued to sinter, the liquid was no longer observed. Furthermore, 2223 became predominant after the sample was sintered at 850 °C for 10 h. Thus, the liquid formed at 850 °C is thought to be a non-equilibrium liquid which facilitates the formation of 2223. This is different from the case at 870 °C where a large amount of liquid may form. In addition, when the sample was fired at 870 °C subsequent to sintering at 860 °C, the XRD results demonstrated no difference from the above. Therefore, the first endothermic peak (848–860 °C) on the DTA curve (Fig. 1) may correspond to a non-equilibrium reaction in the sample, called partial melting, which prompts the formation of 2223 [18–20], and the second peak (860–875 °C) to the melting of 2223.

Although the proposal that 2223 melts incongruently and 2201 crystallizes from the melt when cooled in air is widely accepted, the views about the decomposition products are different, or even contradict each other. Chen and Stevens [5] considered that lead doped 2223 began to melt at 856 °C; this is obviously consistent with the results reported by Wong *et al.* [3], but the temperature is a little lower than that of the present work. This may be due to the heat-treatments employed being different. However, the suggestion by Chen and Stevens [5] that 2223 decomposed into liquid and 2212, is worth doubting. It should be noted that the sample used by Chen and Stevens was not pure, and contained 2212 before the sample was melted. Apparently, 2212 was considered by Chen and Stevens to be an equilibrium phase and $(Ca, Sr)_2CuO_3$ to be a solidified phase of the liquid. This is obviously contrary to the reports by Hatano *et al.* [6] and Oh and Osamura [21], both of whom found that 2223 decomposed into a liquid and a high melting point phase which was guessed to be a cuprate of Sr/Ca. It was also found [6, 21] that 2212 and 2201 might crystallize from the liquid during quenching in air. Additionally, by using high-temperature XRD, Oka *et al.* [22, 23] studied the melting behaviour of the lead-free sample with the composition of "4336" which was reported to be able to form 2223, and concluded that the sample melted into a liquid and a crsytalline phase that could not be indexed to either 2212 or 2201. In addition, if 2212 is an equilibrium product of 2223 during decomposition, another endothermic peak may exist on the DTA curve. Unfortunately, this is not the case. Thus, 2212 and 2201 are thought to be solidified phases of the cooled liquid.

Although the XRD pattern (Fig. 2) shows the existence of $(Sr, Ca)_{14}Cu_{24}O_{41}$ and $(Ca, Sr)_2CuO_3$ phases in the melted sample, it is not clear whether they are equilibrium products or only crystallines of the liquid. Owing to the small amount of these phases in the melting sample and the overlap of XRD peaks of $(Sr, Ca)_{14}Cu_{24}O_{41}$ and $(Ca, Sr)_2CuO_3$ caused by substitution between Strontium and Calcium, it is very difficult to distinguish the above-mentioned cuprates, and Oka *et al.* [22, 23] could not have identified them. As in formerly reported investigations, there is no direct argument in the present work to confirm that the high melting point phases (cuprates) are equilibrium phases. However, it can be seen from the back-scattered electron image (Fig. 3) that an almost pure 2223 phase existed in the sample sintered at 850 °C or 860 °C, but after treatment at higher temperature, such as 870 °C, 2223 disappeared and 2212, 2201, $(Sr, Ca)_{14}Cu_{24}O_{41}$ and $(Ca, Sr)_2CuO_3$ formed instead. In the molten sample, 2212 intergrew with 2201; these must be formed eutectically during quenching of the

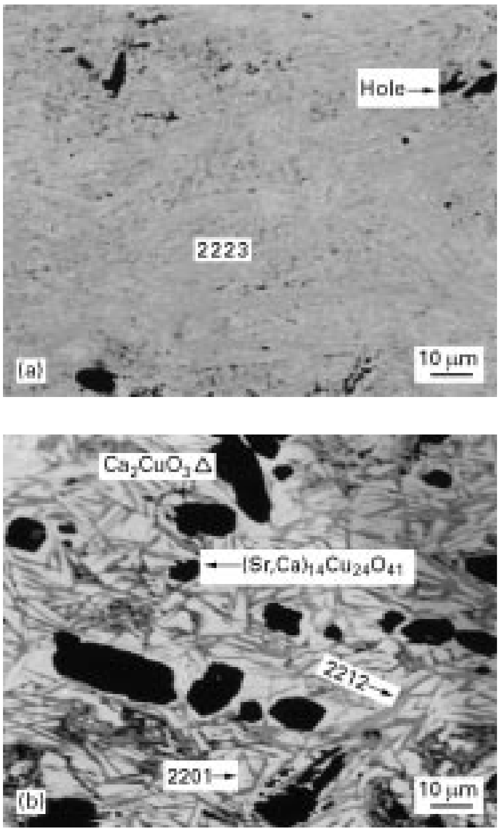

Figure 3 Back-scattered electron images of the sample at (a) 860 and (b) 870 °C.

TABLE I The EPMA results of all phases occurring in the sample molten at 870 °C

Phase	cation mole ratio (at %)				
	Bi	Pb	Sr	Ca	Cu
2212	23.75	5.25	21.84	19.24	30.92
2201	40.43	3.46	28.80	6.05	21.27
Ca_2CuO_3	0.00	0.00	7.38	58.72	33.90
$(Sr, Ca)_{14}Cu_{24}O_{41}$	0.36	0.00	20.09	17.31	62.24
2223(860 °C)	20.33	3.69	19.50	23.07	33.41

liquid, while $(Sr, Ca)_{14}Cu_{24}O_{41}$ and $(Ca, Sr)_2CuO_3$ are equilibrium products which remain at room temperature, because they appear to exist alone in the form of large-sized bulk. The EPMA results of all phases in the molten sample are listed in Table I.

MacManus-Dricsoll and Bravman [24] proposed that lead-doped 2223 decomposed into a liquid and $(Ca, Sr)_2CuO_3$. This may be partially due to that the samples containing elemental Silver, or due to $(Sr, Ca)_{14}Cu_{24}O_{41}$ being confused with $(Ca, Sr)_2CuO_3$ [24]. Oka *et al.* [22, 23] found (Sr, Ca) CuO_2 in the solidified sample with the composition of $(Bi, Pb)_4Sr_3Ca_3Cu_6O_z$; nevertheless, they admitted that 2223 coexisted with 2212 before the sample melted. It should be noticed that 2212 melts into a liquid and (Sr, Ca) CuO_2 [22, 23, 25–27]. Wang *et al.* [28] stated that the leaded 2223 phase decomposed into 2212 and $(Sr, Ca)_{14}Cu_{24}O_{41}$ after the sample was sintered at 855 °C for 450 h; this must be caused by volatilization of lead and bismuth during annealing at high temperature [29].

Finally, it was concluded that lead-doped 2223 decomposed into a liquid and two high melting point phases which are $(Sr, Ca)_{14}Cu_{24}O_{41}$ and $(Ca, Sr)_2CuO_3$. When the liquid was quenched in air, 2212 and 2201 may coprecipitate from it.

4. Conclusion

The melting behaviour of the lead-doped 2223 phase has been investigated. The statement that lead-doped 2223 begins to melt incongruently in air into a liquid, $(Sr, Ca)_{14}Cu_{24}O_{41}$ and $(Ca, Sr)_2CuO_3$ at $T \geqslant 860\,^{\circ}C$, has been established.

Acknowledgements

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References

1. Y. L. CHEN and R. STEVENS, *J. Am. Ceram. Soc.* **75** (1992) 1142.
2. B. -S. HONG and T. O. MASON, *ibid.* **74** (1991) 1045.
3. W. WONG-NG, C. K. CHIANG, S. W. FREIMAN, L. P. COOK and M. D. HILL, *Am. Ceram. Soc. Bull.* **71** (1992) 1261.
4. S. KOYAMA, U. ENDO and T. KAWAI, *Jpn J. Appl. Phys.* **27** (1988) L1861.
5. Y. L. CHEN and R. STEVENS, *J. Am. Ceram. Soc.* **75** (1992) 1150.
6. T. HATANO, K. AOTA, S. IKEDA, K. NAKAMURA and K. OGAWA, *Jpn J. Appl. Phys.* **27** (1988) L2055.
7. H. NOBUMASE, K. SJIMIZU, Y. KITANO and T. KAWAI, *ibid.* **27** (1988) L846.
8. N. KIJIMA, H. ENDO, J. TSUCHIGA, A. SUNIYAMA and K. OGAWA, *ibid.* **27** (1988) L1852.
9. P. STROBEL and T. FOURNIER, *J. Less-Common Metals* **164/165** (1990) 519.
10. L. LIU and Z. JIN, *J. Mater. Res.* **11** (1996) 2142.
11. H. JIN, Z. HU, Y. GE, Q. LIU, C. LIU and C. SHI, *Physica C* **211** (1993) 49.
12. N. MERCHANT, J. S. LUO, V. A. MARONI, G. N. RILEY Jr and W. L. CARTER, *Appl. Phys. Lett.* **65** (1994) 1039.
13. V. V. PANKOV and P. STROBEL, *Physcia C* **235–240** (1994) 333.
14. W. LO, Y. L. CHEN, T. B. TANG and R. STEVENS, *Br. Ceram. Trans. J.* **89** (1990) 218.
15. J. -C. GRIEVEL and R. FLUKIGER, *J. Alloys and Compounds* **235** (1996) 253.
16. I. MATSUBARA, R. FUNAHASHI, T. OGURA and H. YAMASHITA, *Physica C* **218** (1993) 181.
17. J. TSUCHIYA, H. ENDO, N. KIJIMA, A. SUMIYAMA, M. MIZUNO and Y. OGURI, *Jpn J. Appl. Phys.* **28** (1989) L1918.
18. A. OOTA, K. OHBA, A. ISHDA, A. KIRIHIGASHI, K. IWASAKI and H. KUWAJIMA, *ibid.* **28** (1989) L1171.
19. Y. S. SUNG and E. E. HELLSTROM, *J. Am. Ceram. Soc.* **78** (1995) 2003.
20. *Idem, Physica C* **253** (1995) 79.
21. S. S. OH and K. OSAMURA, *Supercond. Sci. Technol.* **4** (1991) 239.
22. Y. OKA, N. YAMAMOTO, H. KITAGUCHI, K. ODA and J. TAKADA, *Jpn J. Appl. Phys.* **28** (1989) L213.
23. Y. OKA, N. YAMAMOTO, Y. TOMII, H. KITAGUCHI, K. ODA and J. TAKADA, *J. Jpn Soc. Powder Powder Metall.* **35** (1988) 930.

24. J. L. MACMANUS-DRISCOLL and J. C. BRAVMAN, *J. Am. Ceram. Soc.* **77** (1994) 2305.
25. H. LIU, L. LIU, H. YU, and Z. JIN, *J. Central South Univ. Technol.* (Chinese Edn) **28** (1997) 146.
26. D. GAZIT, P. N. PESZKIN, L. V. MOUTON and R. S. FEIGELSON, *J. Crystal Growth* **98** (1989) 545.
27. D. P. MATHEIS, S. T. MISTWE and R. L. SNYDER, *Physica C* **217** (1993) 319.
28. Z. WANG, B. W. STATT, M. J. G. JEE, S. BAGHERI and J. RUTTER, *J. Mater. Res.* **6** (1991) 1160.
29. C. J. KIM, C. K. RHEE, H. G. LEE, C. T. LEE, S. J. -L. KANG and D. Y. WON, *Jpn J. Appl. Phys.* **28** (1989) L45.

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