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Optimization of the composition for synthesizing the high-T_c phase in Bi(Pb)SrCaCuO system

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The optimal composition for synthesizing the high-T_c phase 2223 in the Pb-doped bismuth oxide system has been presented. It was shown by using DTA, SEM (EDAX) and XRD that a single 2223 phase could be fabricated when the sample of a $Bi_{2.1-x}Pb_xSr_{1.9}Ca_{2.05}Cu_{3.0}O_z$, where x is between 0.2 and 0.3 (not including the loss of Pb), was sintered at 850–860 °C. It was also indicated that excessive Pb is more effective than excessive Cu in promoting the formation of 2223. © *1999 Kluwer Academic Publishers*

1. Introduction

Among the three superconducting phases, $Bi_2Sr_2Ca_{n-1}Cu_nO_z$ ($n = 1, 2, 3$) named 2201, 2212 and 2223 respectively, 2223 has the highest zero-resistance transition temperature (T_c), which makes it the most attractive. Many investigations have directed to the formation mechanism [1–5], the optimal composition [6–10] as well as the synthesis process including heat-treatment schedule [11, 12] and atmosphere [8, 13–15].

The properties such as T_c and J_c (the critical electric density) of the superconducting materials are closely related to the volume fraction of 2223. Generally, the higher the content of 2223 is, the better. Although the content of 2223 up to more than 90% can be obtained according to the researches mentioned above, the process are much complicated because several times of intermediate grinding have to be employed and a long time sintering is also essential. In addition, although it is reported that 2223 can also be formed via melting [12, 16, 17], a single 2223 phase is not easily obtained. When the amorphous sample is annealed at the formation temperature (T_f) of 2223, the impurity phases with higher negative free energy will crystallize prior to 2223. Again, additional regrinding and a longer duration are therefore necessary. Hence, temperature and duration are the most important. The optimal process have been proved to be sensitive to the starting composition. This paper aims at optimizing the composition for synthesis of 2223 by solid state reaction.

2. Experimental

2.1. Sample preparation

Table I lists the compositions of the samples, among which no. 1, 2 and 5 are cited from previous reports, the others are proposed by the present paper. The loss of Pb is ignored in Table I.

Since CaO is more reactive than SrO [18], and excessive Ca helps the formation of 2223 [19], all the compositions except sample 1 are located in the Ca-enriched region. Bi_2O_3, $Pb(NO_3)_2$, $SrCO_3$, $CaCO_3$ and CuO (purities higher than 99.9%) were used as raw materials. The mixtures were calcined at 760–780 °C for 12 h, then ground, pelletized (∅20 mm) and calcined at 820 °C for 44 h, subsequently reground and compacted (∅9 mm). After finally sintered with an intermediate grinding, the samples were cooled in air.

2.2. Measurement techniques

In order to choose a suitable temperatures for sintering, differential thermal analysis (DTA) was performed to the precursors calcined at 820 °C, which closes to the formation temperature of Pb-doped 2223, with heating rate of 5 °C/min and Al_2O_3 as reference material.

X-ray diffraction (CuK_α) was used to indentify phases in the finally treated samples. The microstructure was observed by a scanning electron microscopy (SEM) with EDAX.

3. Results

3.1. DTA

The formation temperature (T_f) of 2223 measured by DTA of the calcined samples are listed in Table I. It is well known that partial melting of all these specimens occurs in the range of T_f, which promotes the formation of 2223 [21, 22]. Based on the DTA results, all these samples were sintered at 850 and 860 °C for different durations.

3.2. XRD

Table II lists the phases in the sintered specimens. Fig. 1a, b, c are the XRD patterns of sample 2, 5 and 8 sintered at 850 and 860 °C respectively. At 850 °C, there are impurity phases coexisting with 2223 in most samples (except sample 7), even treated for 140 h. The volume fraction of 2223 in sample 2, 5, 7 and 8 can be up to 90% or more. It is shown that a little amount of CuO or Ca_2PbO_4 still exists in sample 5 and 8 while no

TABLE I The starting compositions and formation temperature of 2223

No.	Cation mole ratio Bi	 Pb	 Sr	 Ca	 Cu	T_f (°C)	Ref.
1	1.7	0.4	2.0	2.0	3.0	852–862	[5]
2	1.8	0.4	2.0	2.2	3.0	851–862	[7]
3	1.9	0.3	2.0	2.2	3.0	852–864	
4	2.0	0.2	2.0	2.2	3.0	852–865	
5	1.84	0.34	1.91	2.05	3.06	850–862	[8]
6	2.0	0.1	1.9	2.05	3.0	853–861	
7	1.9	0.2	1.9	2.05	3.0	849–861	
8	1.8	0.3	1.9	2.05	3.0	847–860	
9	1.7	0.4	1.9	2.05	3.0	846–860	

TABLE II XRD identified phases in the samples sintered at 850 and 860 °C

No.	Annealing	Major phase[a]	Minor phase
1	850 °C × 140 h	2223 (80%)	Ca_2PbO_4, Ca_2CuO_3, 2212
	860 °C × 90 h	2223 (50%), 2212	2201, Ca_2CuO_3
2	850 °C × 140 h	2223 (90%)	Ca_2PbO_4, $77\underline{24}$, Ca_2CuO_3
	860 °C × 90 h	2223 (85%)	CuO, 2201, 2212
3	850 °C × 140 h	2223 (80%)	Ca_2CuO_3, 2212, CuO
	860 °C × 90 h	2223 (90%)	Ca_2CuO_3, 2201, 2212
4.	850 °C × 140 h	2223 (80%), 2212	Ca_2CuO_3, $77\underline{24}$
	860 °C × 90 h	2223 (85%)	$77\underline{24}$, 2201, 2212
5.	850 °C × 140 h	2223 (95%)	CuO
	860 °C × 40 h	2223 (90%)	2201, CuO
6	850 °C × 140 h	2223 (30%), 2212	Ca_2CuO_3
	860 °C × 90 h	2223 (80%)	2212, Ca_2CuO_3, $77\underline{24}$
7	850 °C × 140 h	2223 (>95%)	
	860 °C × 40 h	2223 (>95%)	
8	850 °C × 140 h	2223 (90%),	Ca_2PbO_4
	860 °C × 40 h	2223 (>95%)	
9	850 °C × 140 h	2223 (70%), Ca_2PbO_4	
	860 °C × 40 h	2223 (90%)	2201, Ca_2PbO_4

[a] Numbers in parentheses are the volume fraction of 2223 estimated by XRD $77\underline{24}$: $(Sr, Ca)_{14}Cu_{24}O_{41}$.

observable impurity phase in sample 7. However, after annealed at 860 °C, part of 2223 in sample 1, 2 and 5 decomposes into 2212 and/or 2201, whereas the content of 2223 increases significantly in sample 6, 8 and 9. Obviously, single 2223 phase can not be synthesized in the samples with the previously reported starting compositions such as sample 1 and 2. Although the volume fraction of 2223 in sample 2 and 5 can be up to 90%, there are a relatively large amount of impurity phases remaining in sample 2 and 5 even sintered for a long time. However sample 8 contains almost a single 2223 phase after annealed at 860 °C for 40 h, as well as sample 7 at 850 °C for 140 h and 860 °C for 40 h. This is also confirmed by the microstructures (Fig. 2) under SEM.

4. Discussion

It is almost impossible to fabricate a single 2223 phase in non-leaded bismuth oxide system even though a long period and high temperature annealing together with several times of intermediate grinding were employed. However addition of Pb does help to the formation and stabilization of the high-T_c phase 2223. It has been reported that T_f of 2223 decreases with increasing Pb [5]. The higher T_f is, the less amount of partial liquid appears and the slower 2223 is formed when the sample were sintered at 850 °C. This is the reason why sample 6 contains less 2223 than other samples after sintered at 850 °C.

Hong [23] has stated that 2223 is deficient in $(Sr + Ca)$ compared with its stoichiometric composition, and Wada [24] also suggested that when the sample was deficient in $(Sr + Ca)$ and rich in Bi and/or Cu, 2223 could be formed much easily, which is readily confirmed by the present results. In fact, almost single 2223 phase can be formed in sample 5, 7 and 8 if appropriate heat-treatment is adopted, however, the sample with stoichiometric composition such as sample 1 has much lower content of 2223 though the substitution amount of Pb for Bi is up to 20 at %. This agrees well with the report of Zaharescu [18], who has pointed out that SrO is much less reactive than CaO, and higher SrO concentration may retard the formation of 2223. Although Ueyama [7] reported that the high J_c might be realized by using the same composition as sample 2, but as shown in Fig. 1a, a large amount of impurities is retained in the sample sintered either at 850 or 860 °C.

Koyama [8] considered that a low partial pressure of oxygen was necessary to get a high volume fraction of 2223 with the starting composition of sample 5. The present results indicated that a high volume fraction (>90%) of 2223 can also be reached in air, but an impurity phase CuO can not be excluded when sintered in air at 850 °C even for 140 h as shown in Fig. 1b, which undoubtly affects the quality and consequently the physical properties of the material.

As to the starting compositions of the present work such as sample 7–9, a very high volume fraction of 2223 can be got, even treated at a low temperature such as 850 °C for no more than 140 h (except sample 9). As indicated by sample 8 and 9, excess of Pb leads to the formation of Ca_2PbO_4, which, however, is easily avoided by elevating temperature. This is because: (1) Pb is volatilizable at above 850 °C [6, 26], and (2) excessive Pb and Ca produced by the decomposition of Ca_2PbO_4 can easily enter into the lattice site of Bi [27] and Sr [28, 29] respectively. Thus an almost pure 2223 could form without detectable impurity phase, which is confirmed by XRD patterns of sample 8 shown in Fig. 1c. Even for sample 9, it is possible to exclude Ca_2PbO_4 by annealing for a longer period. In fact, compared with the reported compositions of sample 5 by Koyama [8], the concentration of CuO and SrO in sample 7–9 are little lower, but Pb content changed remarkably. Tripathi [25] has suggested that excessive Cu can help formation of liquid too, which can accelerate the diffusion of cations and prompts the formation of 2223. Nevertheless, as indicated by Fig. 1b, the excess of CuO may remain as impurity phase after reaction. Chen [5] concluded that the effect of Cu on the formation of 2223 is limited when Pb is present. Furthermore, as clearly illustrated by Fig. 2, sample 8 is more densified than sample 7

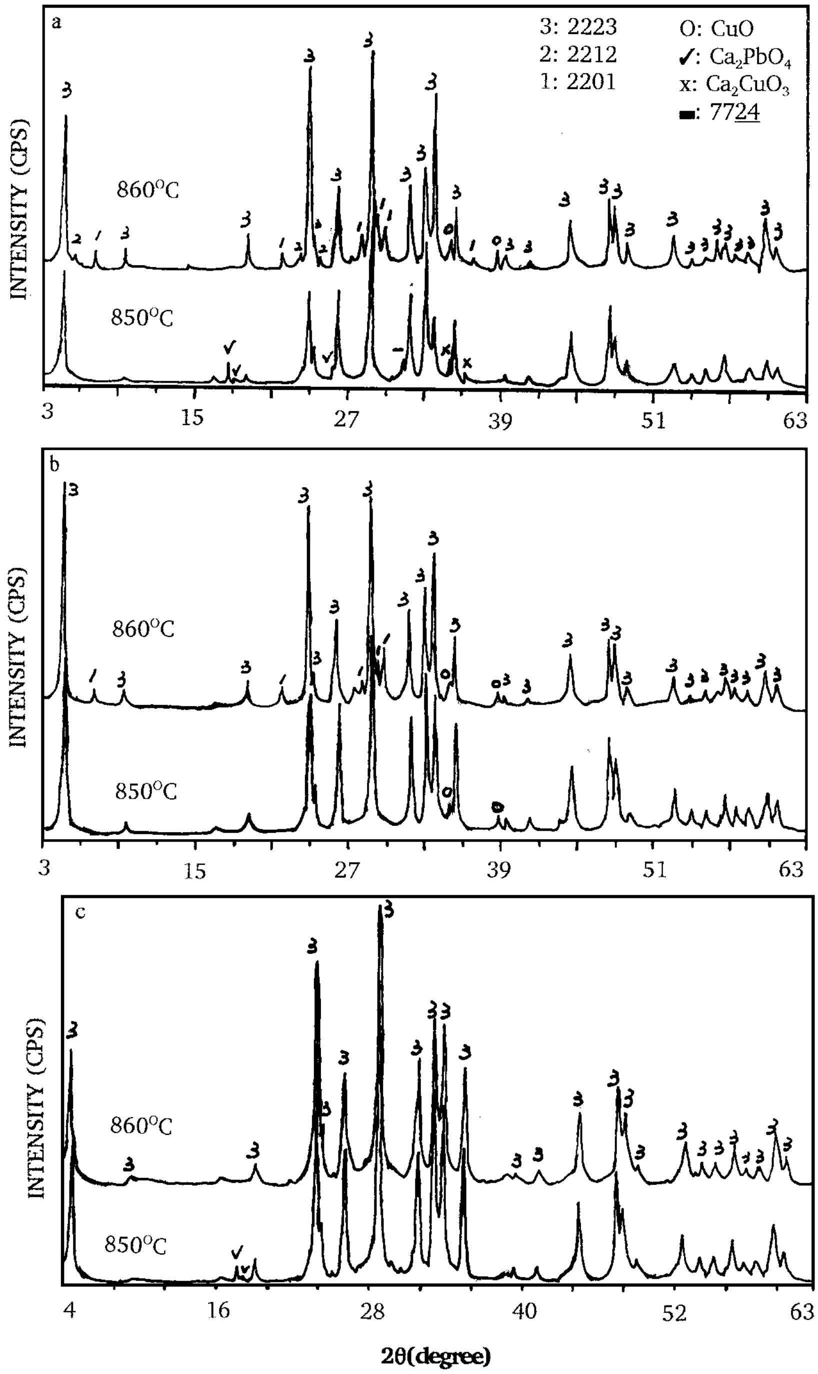

Figure 1 XRD patterns of sample 2, 5 and 8 annealed at 850 and 860 °C respectively: (a) sample 2; (b) sample 5; and (c) sample 8.

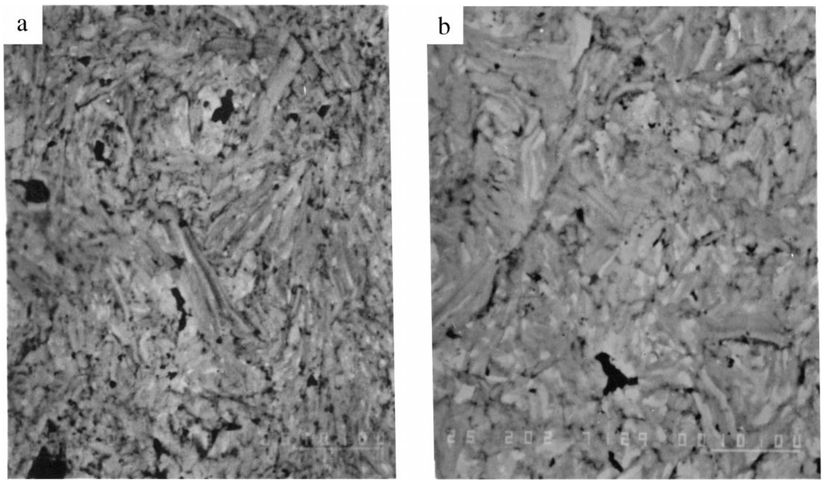

Figure 2 The back-scattered electron images of sample 7 and sample 8 sintered at 860 °C: (a) sample 7 and (b) sample 8.

although both of them contain only 2223. Therefore it may be more effective to adopt excessive Pb for fabricating a pure densified 2223 phase.

Finally, in order to obtain a homogeneous 2223, intermediate grinding is necessary during final annealing in order to eliminate the heterogeneity caused by the partial liquid as well. Additionally, the intermediate grinding may be very helpful in shortening heat-treatment time.

5. Conclusion

The optimal composition for synthesizing pure 2223 has been obtained by using DTA, SEM and XRD techniques. With starting compositions of $Bi_{2.1-x}Pb_xSr_{1.9}Ca_{2.05}Cu_{3.0}O_z$ where $x = 0.2$ and 0.3 (not including loss of Pb during sintering), single 2223 phase can be formed without detectable impurity after the sample was sintered at 850–860 °C. Although excessive Pb may also leads to the formation of Ca_2PbO_4 as an impurity phase, it is more effective than Cu in fabricating pure densified 2223.

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