Optimization of a new modified wet-chemistry process for the synthesis of BPSCCO superconductor precursor powders with specific stoichiometry

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A modified coprecipitation process has been developed based on a stoichiometry study of the oxalate coprecipitation process in water for the synthesis of Bi–Pb–Sr–Ca–Cu–O multi-component powders. The coprecipitation reaction is carried out in a mixed solution composed of water, ethanol (90 vol%) and poly(ethylene glycol), thus overcoming the serious shortcoming of water-medium coprecipitation, namely the inability to maintain stoichiometry in Bi-system superconductor powders. The modified process is optimized by the study of the effects of the pH value, oxalic acid concentration and ageing time on stoichiometry maintenance in the precipitate. The precipitation parameters have dramatic effects on the stoichiometry and homogeneity, which in turn affect the superconductivity of a silver-sheathed $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (2223) superconducting tape prepared by the powder-in-tube process. Our results highlight the importance of controlling powder synthesis conditions for obtaining high critical current density (J_c) tape.

Bismuth-based superconductors (BiPbSrCaCuO) belong to a multi-component system, so it can be expected that compositional homogeneity will have a dramatic effect on the phase composition, microstructure and superconducting properties. This is why much emphasis has been laid on chemical processes to synthesize precursor powders. Silver-sheathed Bi-system (Bi–Pb–Sr–Ca–Cu–O) $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (2223 phase) tapes, *i.e.*, Ag/Bi(2223) tape, prepared by the powder-in-tube (PIT) process, have made practical applications of Bi-system superconductors possible. The first stage of the powder-in-tube process is the preparation of a high-quality precursor powder. The coprecipitation process has become more and more important in the preparation of precursor powders because of its practicality, simplicity and ability to synthesize large quantities of powder.[1,2] Since the solubilities of the oxalates of each metal component in Bi–Pb–Sr–Ca–Cu–O are very low, when a mixed cation solution and oxalic acid ($H_2C_2O_4$) solution are mixed by titration (the former into the latter), the same oxalic acid concentration is supplied to each metal ion for the metal oxalate to be nearly saturated, nucleate and grow at the same time, which makes it possible for the coprecipitation process to synthesize homogeneous Bi-system superconductor precursor powders. However, the thermodynamic properties of the precipitation reaction of each metal ion are different, and there are many factors affecting the precipitation reaction. $H_2C_2O_4$ can be both precipitant and chelating agent. In practice, in the oxalate coprecipitation process, because of the presence of common ion effects, acid effects and complex effects, cations will be left in the filtrate in many forms,[3] which will affect the solubility of each precipitate. Therefore, stoichiometry maintenance is a major problem for coprecipitation.

The initial composition is a key factor in Bi(2223) phase formation.[4,5] If there is a large deviation between the composition of the precipitate and that of the original solution which is suitable for 2223 phase formation, the 2223 phase volume fraction in the bulk made from such a powder will be lowered, as will the critical current density of a Bi(2223)/Ag tape.[6] So it is important practically to study the stoichiometry of the coprecipitation process by which the powder is prepared. In fact, the best maintenance of stoichiometry and homogeneity from solution are realized at the same time because both result from the lowest solubility of each oxalate and thereby from the easy simultaneous nucleation and growth of each oxalate. In this paper, a new modified coprecipitation process is presented, based on a stoichiometry study of water-medium coprecipitation, where the precipitation medium is composed of water, ethanol (>90% vol. fraction) and poly(ethylene glycol) (PEG). In addition, the effects of the process parameters on both stoichiometry maintenance and the superconductivity of Bi(2223)/Ag tapes are systematically studied.

Experimental

A mixed solution with a total cation concentration of 0.5 mol l^{-1} and a Bi : Pb : Sr : Ca : Cu ratio of 1.8 : 0.4 : 2.0 : 2.2 : 3.06 was prepared. Oxalic acid was dissolved in ethanol and PEG was added (10 g per mol of cations). The coprecipitation process was carried out by adding the mixed cation solution into oxalic acid solution dropwise under constant electromagnetic stirring. The pH was adjusted by the addition of A.R. pure aqueous ammonia and measured by precise pH indicator paper and an acidity meter. After the above solutions were mixed, the total concentration of oxalic acid was 0.115 mol l^{-1} and the volume percentage of ethanol >90%. The precipitate was vacuum-filtered off. The residual contents of Bi, Pb, Sr, Ca and Cu were analysed by atomic absorption spectrometry (AAS). For comparison, the procedure was repeated using water instead of alcohol (in the same amount) for water medium coprecipitation.

The filtered precipitate was calcined in air at 800 °C for 20 h. After grinding, the as-calcined powder was pressed into bulk under a pressure of 25 tonnes cm^{-2}. Further sintering of the compressed pellet was performed in air at 850 °C for 80 h. The ac susceptibility curve of the as-sintered bulk was determined by an ac inductive method.

The powders were used to fabricate Ag/Bi(2223) composite tapes by the standard PIT process with all thermomechanical parameters fixed. The powder was packed into a silver tube (o.d. = 10 mm, i.d. = 8 mm). The ends of the tube were sealed with copper columns and swaged into a bar ($3 \times 3\ mm^2$ cross-section). The bar was drawn through a series of dies into a wire with a diameter of 1.4 mm, then cold-rolled into a tape

(0.15 mm in thickness and 4 mm in width) with 50% reduction per pass. Thirty short samples (*ca.* 1.5 cm) were cut from one as-rolled tape and subjected to heat treatment with a ramping rate of 1.5 °C min^{-1} and a dwelling temperature of 830 °C. Every 50 h, the tapes were cooled to room temperature at 1.5 °C min^{-1} and pressed uniaxially at a pressure of 2 GPa, then subjected to the same heat-treatment cycle. The critical current (I_c) at 77 K and 0 T was measured by the standard four-probe method using a 1 μV cm^{-1} criterion. The microstructure of the tape was examined using a S-2700 scanning electron microscope. The phase composition was determined by X-ray diffraction (XRD) on a D-S X-ray diffractometer (Cu target) after the silver layer on one surface was peeled off. The morphology of the precipitate was observed on a JEM 200cx transmission electron microscope.

Results and Discussion

Effect of pH on the stoichiometry of modified coprecipitation and water-medium coprecipitation

Fig. 1 and 2 show the experimental curves of individual residual cation concentrations at different pH values in the water-medium and modified coprecipitation processes. Tables 1 and 2 list the stoichiometries (normalized to Bi) of the precipitates of experimental points in Fig. 2 and 1, respectively, calculated from the filtrate. The amount of a metal element in the precipitate is equal to the difference between that in the original solution and that in the filtrate. From Fig. 1 and Table 2, we can see that a pH higher than 2 does not favour the complete precipitation of Cu^{2+}, because the stability constants of the soluble complexes formed by the reaction of $C_2O_4^{2-}$ or $HC_2O_4^-$ and Cu^{2+} are much higher than those of $C_2O_4^{2-}$ or $HC_2O_4^-$ and Bi^{3+}, Pb^{2+}, Sr^{2+} and Ca^{2+},[3] and a pH lower than 2 does not favour the complete precipitation of Bi^{3+}, Pb^{2+}, Sr^{2+} and Ca^{2+}, because too high a H^+ concentration $[H^+]$ leads to the reduction of the $C_2O_4^{2-}$ concentration $[C_2O_4^{2-}]$. This results in the absence of a pH range for Bi–Pb–Sr–Ca–Cu–O powder to maintain stoichiometry. However, comparison of Fig. 2 with Fig. 1 shows the individual cation residual concentrations were lowered dramatically in our modified coprecipitation process. As shown in Table 1 the precipitate could maintain the original stoichiometry excellently at $3 \leqslant pH \leqslant 7.4$. These results show that the stoichiometry of Bi-system superconductor powders synthesized by coprecipitation is greatly improved, because the solubilities of the individual cation oxalates and stability constants of the soluble complexes of each cation (especially Cu^{2+}) in the mixed medium are lower than those in water, which results in the reduction of each cation residual concentration (especially Cu^{2+}).

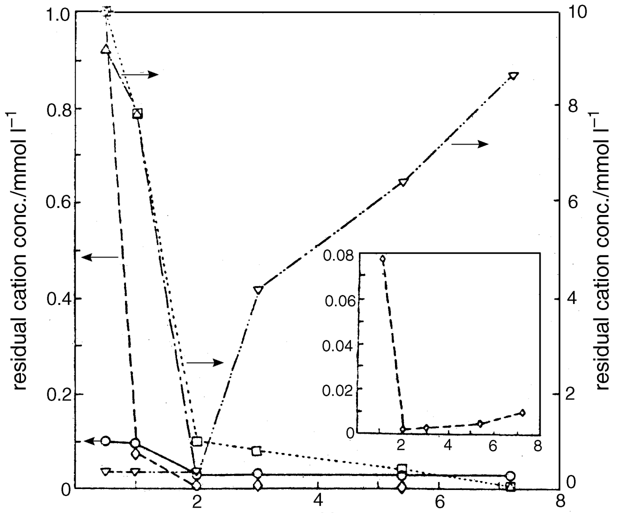

Fig. 1 Experimental curve of individual residual cation concentrations at different pH values in the water medium coprecipitation process (ageing time 48 h) (inset is the magnification of Pb^{2+}). ○, Bi^{3+}; ◇, Pb^{2+}; □, Sr^{2+}; △, Ca^{2+}; ▽, Cu^{2+}.

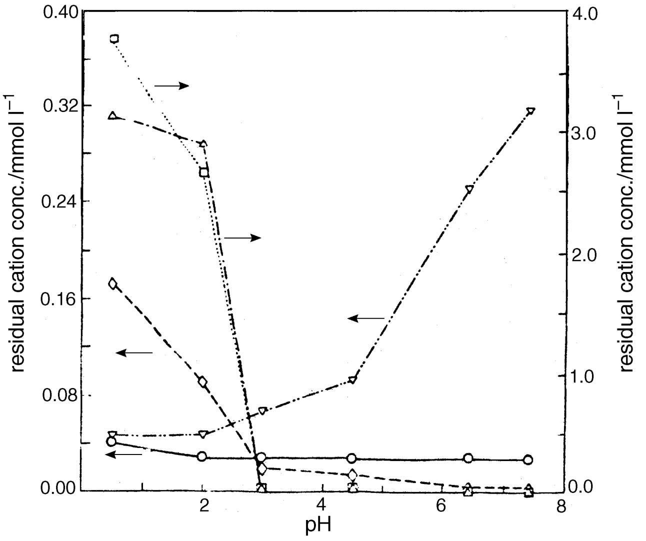

Fig. 2 Experimental curve of the individual residual cation concentrations at different pH values in the modified coprecipitation process (ageing time 48 h). Symbols as in Fig. 1.

Table 1 Stoichiometry normalized to Bi in the precipitate of the modified coprecipitation process

pH	Bi	Pb	Sr	Ca	Cu
0.5	1.8	0.3880	1.6468	1.9091	3.0619
2.0	1.8	0.3921	1.7541	1.9320	3.0603
3.0	1.8	0.3998	2.0004	2.2024	3.0884
4.5	1.8	0.3994	2.0004	2.2024	3.0558
6.4	1.8	0.4003	2.0022	2.2024	3.0409
7.4	1.8	0.4003	2.0022	2.2024	3.0349
original	1.8	0.4	2.0	2.2	3.06

Table 2 Stoichiometry normalized to Bi in the precipitate of the water-medium coprecipitation process

pH	Bi	Pb	Sr	Ca	Cu
1.0	1.8	0.3947	1.2609	1.4640	3.0423
2.0	1.8	0.3998	1.9080	2.1979	2.1979
3.0	1.8	0.4005	1.9269	2.1972	2.6668
5.4	1.8	0.3998	1.9970	2.2015	2.4538
7.2	1.8	0.3998	1.9970	2.2015	2.2448
original	1.8	0.4	2.0	2.2	3.06

Effect of oxalic acid concentration on the stoichiometry of the modified coprecipitation process

Fig. 3 shows the residual cation concentrations under different excess percentages of oxalic acid. It is found that an excess percentage of oxalic acid of 15–20% favours stoichiometry maintenance. When the excess percentage is lower than 15–20%, lowering the excess percentage of oxalic acid results in a reduction of $[C_2O_4^{2-}]$; this moves the precipitation reaction to the direction of precipitate dissolution, and so increases the individual remnant cation concentrations, *i.e.*, the common ion effect is strong. When the excess percentage is higher than 15–20%, there is a greater excess of $[H_2C_2O_4]$, $[C_2O_4^{2-}]$ and $[HC_2O_4^-]$; this moves the common ion complex reaction equilibrium to the direction of soluble complex formation, and so increases the individual residual cation

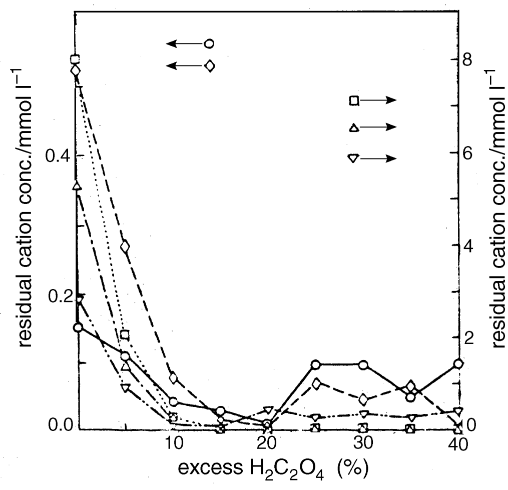

Fig. 3 Dependence of the individual residual cation concentrations on the percentage of excess oxalic acid in the modified coprecipitation process (pH = 4.5, ageing time 48 h). Symbols as in Fig. 1.

concentrations, *i.e.*, the common ion complex effect is strong. Furthermore, because the stability constants of soluble complexes formed between $C_2O_4{}^{2-}$ or $HC_2O_4{}^{-}$ and Bi^{3+}, Pb^{2+} or Cu^{2+} are several orders of magnitude higher than those formed between $C_2O_4{}^{2-}$ or $HC_2O_4{}^{-}$ and Sr^{2+} or Ca^{2+},[3] it is more difficult for Bi^{3+}, Pb^{2+} and Cu^{2+} to achieve complete precipitation when the excess percentage of $H_2C_2O_4$ is higher than 20%.

Effect of ageing time on stoichiometry

Fig. 4 shows the dependence of the individual residual cation concentrations on ageing time after precipitation in the modified coprecipitation process. It is found that ageing times higher than 8 h help to further improve the stoichiometry of the precipitate, which may be explained based on the surface physicochemistry principle.

The relation of solubility between small crystals and common crystals can be expressed as follows:[7]

$$\ln(C/C_0) = 2\sigma M/(r\rho RT) \qquad (1)$$

where C is the solubility of small crystals; C_0 is the solubility of common crystals; M is the molecular mass of common crystals; ρ is the mass density of the crystals; R is the gas constant; T is the absolute temperature; and r is the radius of the crystal.

When r is very small, the left side of the above formula is much greater than zero, so the solubility of the fine crystal is much higher than that of the common crystal ($C > C_0$). For an insoluble material, the precipitation process reaches the limit of oversaturation, which leads to the formation of a new active state composed of ultrafine crystals.[8] Fig. 5 shows a TE micrograph of precipitate particles of the modified process. The fresh precipitate is composed of ultrafine crystals (50–100 nm). During ageing, the active state transforms to an inactive state slowly, resulting in a precipitate with a large and complete crystal structure.[8] So, at the end of the coprecipitation, the solution is oversaturated with respect to the solubilities of common crystals of the individual cation oxalates.[7] During ageing, the crystals of the individual cation oxalates become larger.[8] According to eqn. (1), solubility is reduced slowly, which results in the precipitation of individual cations in the form of oxalates. So individual residual cation concentrations are reduced slowly. When the precipitation system is aged for 8 h, the solubility of the fine precipitate of each cation reaches that of its common crystal, and the solution becomes a truly saturated solution which is an equilibrium state. Therefore, the individual residual cation concentrations do not change with further ageing.

Properties of superconductors made from the coprecipitated powders

Bulk. Fig. 6 shows ac susceptibility curves of the sintered powders synthesized by the water-medium and modified

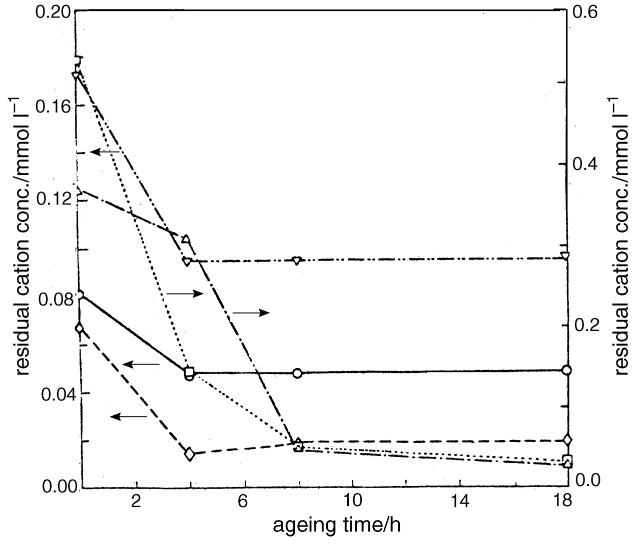

Fig. 4 Dependence of the individual residual cation concentrations on the ageing time in the modified coprecipitation process (pH = 4.5, 15% excess oxalic acid). Symbols as in Fig. 1.

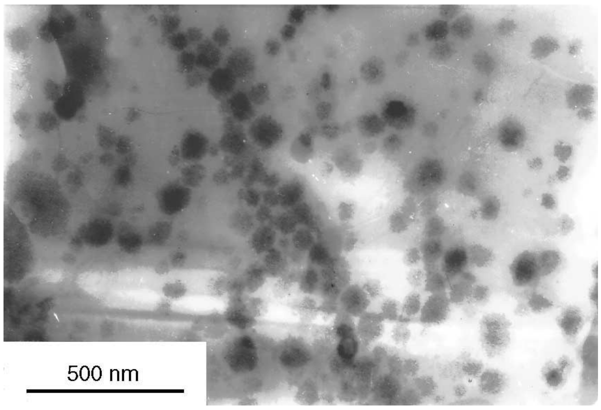

Fig. 5 TE micrograph of the fresh precipitate of the modified coprecipitation process

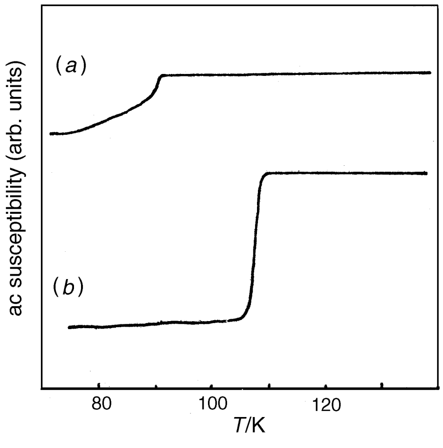

Fig. 6 Ac susceptibility curves of the bulk samples sintered from the powders synthesized by (*a*) water medium coprecipitation, and (*b*) modified coprecipitation

coprecipitation processes under the same precipitation condition (pH = 4.5), with a Bi : Pb : Sr : Ca : Cu ratio of 1.85 : 0.35 : 1.95 : 2.0 : 3.06. A diamagnetization transition near 110 K of the bulk material prepared by modified coprecipitation is seen, while that prepared by water-medium coprecipitation shows only a transition near 90 K of the 2212 phase, *i.e.*, a low T_c phase. The powder XRD patterns of these two bulk samples are shown in Fig. 7. It is found that the bulk synthesized by the modified process is nearly single-phase 2223, because of the maintenance of stoichiometry in the precipitate. However, it is difficult for the 2223 phase to form in the sample prepared by the water-medium process; this still includes the 2212 phase as the main phase and Ca_2CuO_3 as the impurity phase. This is because the formation of the 2223 phase results from the reaction between the 2212 phase and the Ca and/or Cu containing phase.[9–12] Because the precipitate of the water-medium coprecipitation process cannot maintain the original stoichiometry (especially the serious loss of Cu), it is difficult to form the 2223 phase.[9–12] These results show that the presented modified coprecipitation process can synthesize high-quality 2223 phase superconductors because of the maintenance of the original stoichiometry.

Ag/Bi(2223) tape. From Table 1 we find that the stoichiometry of the powders prepared at pH 3–7.4 does not vary greatly with pH. However, from Fig. 2 we find that the solubility still differs with pH. The homogeneity comes from the simultaneous nucleation of each oxalate. Thus, where the solubilities of all the oxalates reach their minima, *i.e.*, pH 3–4.5, the homogeneity will be at a maximum.

Fig. 8 shows the heat-treatment time dependence of J_c (77 K, 0 T) of Ag/Bi(2223) tapes derived from the BPSCCO powders prepared at pH 4.5 and 6.7. None of the Ag/Bi(2223) tapes formed at pH 2 were superconducting. This is due to serious loss of Cu and also to poor homogeneity in the BPSCCO powder. The XRD pattern of such an Ag/Bi(2223) tape heat-treated for 150 h shows that there is no 2223 phase besides the phases in the precursor powder. It is shown in Fig. 8 that the higher the degree of homogeneity of the precursor powder, the higher are the value and the reproducibility of J_c. This shows that J_c is related to the homogeneity of the BPSCCO powder. The phenomenon that J_c of the tape differs with the degree of homogeneity of the BPSCCO powder results mainly from the different phase compositions and microstructures of the tapes which are caused by the different homogeneities of the precursor powders, although instability towards mechanical deformation may also affect J_c. This point can be explained as follows. Only if care were taken to ensure that all the tapes were deformed under identical parameters, such as original size and reduction per pass, would it be possible to neglect in this study the effects of instability towards mechanical deformation (low J_c, poor reproducibility). It should also be noted that the stoichiometry in the powder synthesized by our new modified coprecipitation process is well maintained at pH 3–7.4; therefore we cannot attribute the above result to stoichiometry variations at pH 3–7.4.

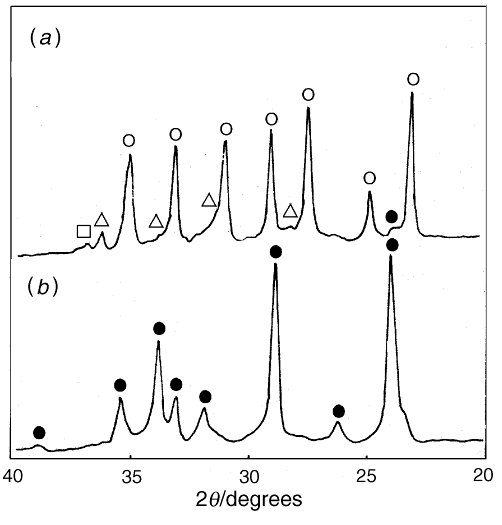

Fig. 7 Powder XRD patterns corresponding to the two bulk samples in Fig. 6 [●, 2223; ○, 2212; □, 2201; △, $(Ca,Sr)_2CuO_3$]

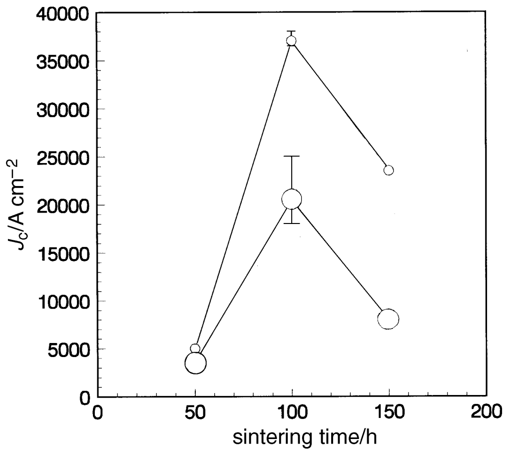

Fig. 8 Heat-treatment time dependence of J_c (77 K, 0 T) of Ag/Bi(2223) tapes derived from the BPSCCO powders prepared at pH = 4.5 (○) and 6.7 (◯)

For a short tape sample (1.5–2 cm in length), the volume of the powder and the thickness of the superconducting layer are of the order of magnitude of 10^{-3} cm^3 and 10 μm, respectively, In addition, the powder is multi-component and multi-phase and the formation of a high T_c phase is a very complex chemical reaction. So it can be expected that the compositional homogeneity of the powder is very important and will influence the homogeneity of the microstructure and the superconducting property (J_c) of Ag/Bi(2223) tapes.

The formation mechanism of the 2223 phase has been widely studied and is not well understood.[9–12] But it is clear that the 2223 phase is formed by reaction of the 2212 phase and Ca or Cu containing oxide, and the formation process is a liquid-assisted solid-state reaction controlled by diffusion of reactants.[13–16] From the viewpoint of solid-state chemistry, nucleation of the product phase originates from the phase interface and the growth of the product phase continues by diffusion of reacting species into the product layer. In addition, the single-phase field of the 2223 phase has shown to be very narrow although it has not been established completely.[13] When the powder is inhomogeneous in composition, the localized composition in the microzone where the 2223 phase nucleates and grows will deviate from the average composition which may be favourable for 2223 phase formation, thus leading to the inability to obtain highly pure 2223 phase. From the chemical viewpoint, inhomogeneity of the BPSCCO powder will result in divergence of both the average composition and the compositional homogeneity along the longitudinal direction of a long tape. So as-sintered short samples (*ca.* 1.5 cm in length) cut from one such long tape will have different phase compositions and preferable orientations of the high T_c phase.

Fig. 9 shows the XRD patterns of superconducting layers of tapes sintered for 100 h derived from powders with different homogeneities. Two patterns of each kind of tape derived from one powder are shown, corresponding to the maximum and minimum of the error bar in Fig. 8. Phases in tapes derived from pH 4.5 are only single 2223 phase within the detection limits of XRD. In the patterns only (001) diffraction peaks are seen, which shows the highly preferential orientation with *ab*

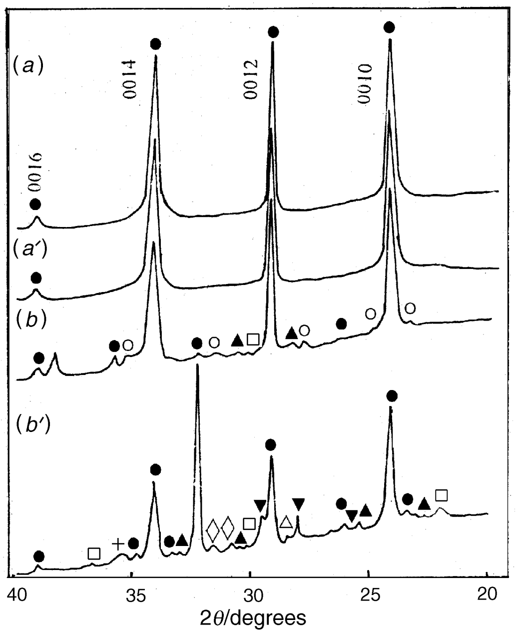

Fig. 9 XRD patterns of superconducting layers of tapes sintered for 100 h (shown in Fig. 8) derived from BPSCCO powders prepared at pH = 4.5 (*a*, *a′*) and 6.7 (*b*, *b′*). (*a*, *b*) maxima, (*a′*, *b′*) minima of the error bars in Fig. 8. ●, 2223; ○, 2212; □, 2201; ◇ $(Ca,Sr)_2PbO_4 + CuO$; △, $(Ca,Sr)_2CuO_3$; ▽, $(Sr,Ca)_2Bi_2O_5$; ▲, $(Ca,Sr)CuO_2$.

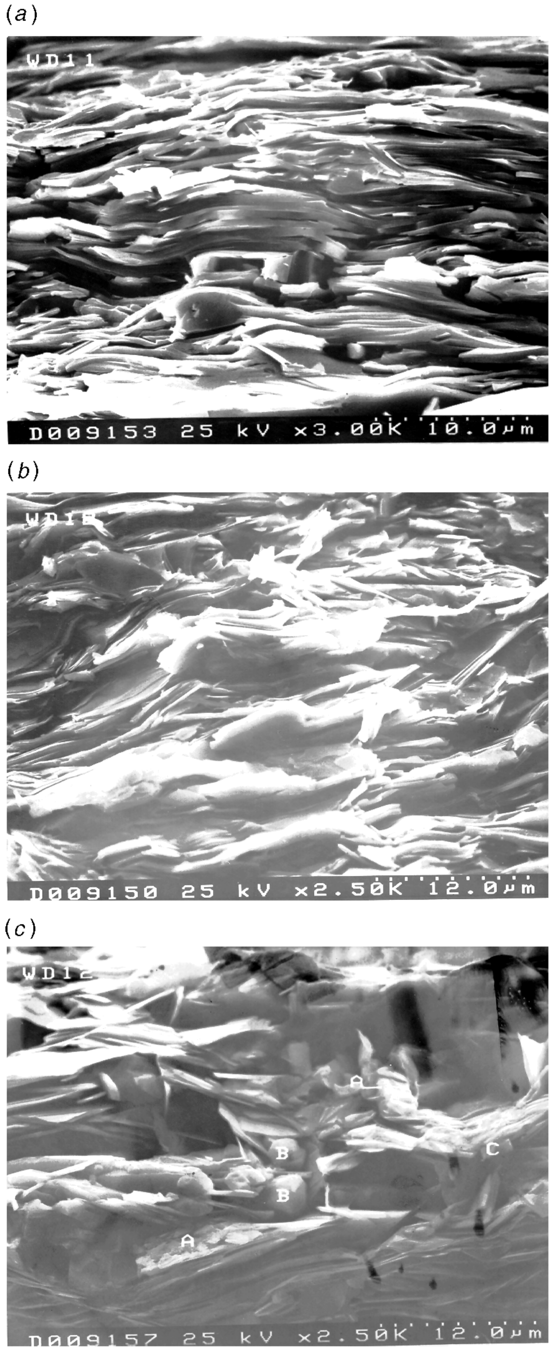

Fig. 10 SE micrographs of the central parts of transverse sections of the tapes shown in Fig. 9. (*a*, *b*, *c*) are sections of the tapes shown in Fig. 9 (*a*, *b*, *b′*) respectively.

planes parallel to the tape surface. Moreover, the patterns of different samples cut from one single tape are nearly the same by comparison of patterns (*a*) and (*a′*). The patterns of short samples cut from one long tape derived from the powder synthesized at higher pH (6.7) show obvious differences both between each other and from those of tapes derived from pH 4.5. All the tapes derived from pH 6.7 contain small amounts of non-superconducting phases and a low T_c phase as well as the high T_c phase. The sample corresponding to the maximum of the error bar (*i.e.*, higher J_c) contains less non-superconducting phases than that corresponding to the minimum of the error bar (*i.e.*, lower J_c). The former contains $(Ca,Sr)CuO_2$ and $(Ca,Sr)_2CuO_3$, while the latter contains $(Ca,Sr)CuO_2$, $(Ca,Sr)_2CuO_3$, $(Sr,Ca)Bi_2O_5$, Ca_2PbO_4 and CuO. So it seems that the lower the J_c, the more impurity phases are present. Moreover, the existence of the (11*l*) peak of the high T_c phase in these samples shows poor preferable orientation with the (001) plane parallel to the tape surface, *i.e.*, poor degree of texture. To our surprise, the (119) peak of the 2223 phase, which is much stronger than the (001) peak of the 2223 phase, shows a much poorer degree of texture in the tape corresponding to the minimum of the error bar (*i.e.*, lower J_c). Therefore, it is conceivable that the lower value and poorer reproducibility of J_c for short samples cut from one long tape derived from the more inhomogeneous powder result from the increased amount of non-superconducting phases and poorer degree of texture, both of which are due to the inhomogeneity of the BPSCCO powder.

Since XRD can only provide information about the phase composition and degree of texture on a surface layer of thickness 3–5 µm, SEM–EDAX studies should be used to investigate the phase composition and texture degree of the central part of the superconducting layer. Fig. 10 shows the typical SEM microstructures of the central parts of the fractured transverse sections of the tapes corresponding to the samples (*a*), (*b*), (*b′*) in Fig. 9. We could find no obvious difference of SEM microstructures between samples (*a*) and (*a′*) in Fig. 9. So Fig. 10 (*a*) is also the typical microstructure of the tapes derived from pH 4.5, which is consistent with the XRD results. EDAX did not provide evidence for the existence of secondary phases in either samples.

As seen in the XRD patterns, short samples cut from one long tape derived from pH 7 exhibit very different microstructures, *i.e.*, inhomogeneous case. As shown in Fig. 10 (*b*) and (*c*), a short sample with higher J_c shows better grain alignment and grain contact together with no obvious existence of secondary phase particles, while that with lower J_c shows much poorer grain alignment and grain contact with the existence of coarse secondary phase particles, which are SrO (B) and CuO (C) as determined by EDAX. The poorer grain alignment and grain contact result from the impedance of texture growth of the high T_c phase by secondary phase particles. So the above results further confirm that the higher value and better reproducibility of the J_c values of short samples cut from one long tape derived from a more homogeneous powder result from the higher phase purity and better grain alignment and contact, both of which are due to the higher homogeneity of the BPSCCO powder.

Mechanism of the effect of compositional homogeneity on the microstructure. The above results show that compositional homogeneity dramatically affects J_c through its effect on both phase purity and grain alignment and contact of high T_c phases. It thus confirms the idea that the phase purity, grain alignment and grain contact are the important factors which control high J_c in high T_c superconductors.[14] To understand the mechanism of the effect of compositional homogeneity on the phase purity, grain alignment and grain contact, a model is described based on solid-state chemistry. It should be stated first that the phase compositions of BPSCCO powders derived from different pH values (3–7.4) are almost identical, with the 2212 phase as the main phase. This is because the powder is a multi-phase mixture rather than a mono-phase state as in a sintered tape. It has been found that the inhomogeneity only results in slight differences in the relative contents of each phase. However, in the process of 2223 phase formation, homogeneity plays an important role in the formation of a single phase.

The model contains several main points, as follows. (1) The 2223 phase is formed by insertion of a Ca/CuO_2 layer into the 2212 phase while Ca or Cu containing secondary phases, such as Ca_2PbO_4 and Ca_2CuO_3, just act as a source of the Ca/CuO_2 layer. (2) Formation of the 2223 phase occurs in each domain which contains the 2212 phase and a source of the Ca/CuO_2 layer, as illustrated in Fig. 11; the 2223 phase nucleates at the interface between the 2212 phase and the Ca/CuO_2 source, and then grows in some mechanism which needs to be further studied. (3) When the powder is homogeneous in composition and has suitable stoichiometry, the 2212 phase in one domain will all transform into the 2223 phase with the consumption of all the Ca/CuO_2 source. (4) When the powder is inhomogeneous in composition, there will be another two cases as well as case (3): (I) the Ca/CuO_2 source is insufficient to make all the 2212 phase in one domain transform into the 2223 phase, so there will be residual 2212 phase as shown in Fig. 11(*a*); (II) Ca/CuO_2 source is in excess after the transformation of all the 2212 phase in one domain into the 2223 phase, so there will be residual Ca/CuO_2 source as shown in Fig. 11(*b*). (5) When there is residual 2212 phase after high-temperature reaction, the residual 2212 phase may decompose into a non-superconducting phase at 200–650 °C during cooling.[15,16] The decomposition reaction may be

$$Bi_2Sr_2CaCu_2O_5 \rightarrow SrBi_2O_5 + SrO + CaCuO_2 \tag{2}$$

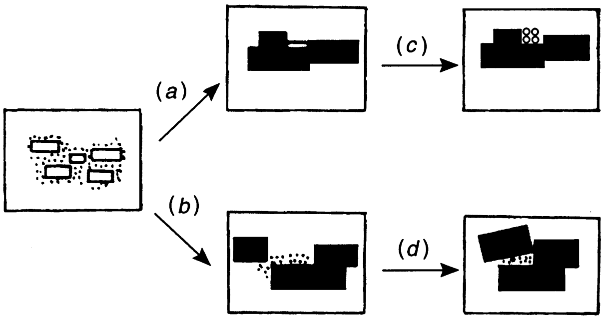

Fig. 11 Schematic illustration of the model of the effect of homogeneity on phase purity, grain connectivity and grain alignment, showing: (*a*) inhomogeneity resulting in the remains of the 2212 phase; (*b*) inhomogeneity resulting in the remains of the Ca/CuO_2 source; (*c*) inhomogeneity resulting in poor grain connectivity; (*d*) inhomogeneity resulting in poor grain alignment and connectivity. □, 2212; ■, 2223; ·, CaCuO phase; ○ $(Sr,Ca)_2Bi_2O_5 + (Sr,Ca)O + (Ca,Sr)CuO$

Thus the non-superconducting phase will result in grain decoupling as illustrated in Fig. 11(*c*). This point was confirmed by the lack of $SrBi_2O_5$, SrO and $CaCuO_2$ in a quenched sample. (6) When the Ca/CuO_2 source is residual, the residual secondary phase particles will impede the texture growth of the 2223 phase as shown in Fig. 11(*d*).

Therefore, based on the presented model, the inhomogeneity of the powder leads not only to the formation of a non-superconducting phase such as $SrBi_2O_5$ $CaCuO_2$ or SrO, and the remnants of the non-superconducting phase in the precuror powder, such as Ca_2PbO_4, Ca_2CuO_3 and CuO, and the remains of lower T_c phases, such as 2201 and 2212 phases, but also to poorer grain alignment and contact of 2223 phase. This results in lower values and poorer reproducibility of J_c in Ag/Bi(2223) tapes.

Conclusion

Our modified coprecipitation process, with the precipitation in a mixed medium (organic solvent >90% by volume), overcomes the inability to maintain the original stoichiometry in precipitates of the water-medium coprecipitation process. This new process, with the control of pH at 3–7.5, a $H_2C_2O_4$ excess percentage of 15–20% and an ageing time >8 h, results in the best maintenance of stoichiometry and homogeneity which lead to the formation of high-quality 2223 phase superconductors.

Fabrication of high J_c Ag/Bi(2223) tapes with lengths of the order of km, is the prerequisite of preparations of practical magnets with bismuth-based superconductors. Our results show that the first key problem is the synthesis of homogeneous BPSCCO powder in large quantities to fabricate high J_c long tapes. If the precursor powder is not homogeneous, the phase purity and microstructure of the superconducting layer will be different from section to section along the longitudinal direction and thereby J_c of the whole long tape will be dramatically reduced. To obtain Ag/Bi(2223) tapes with higher J_c, the optimization of the thermomechanical parameters during the PIT process is now under way.

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