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Isothermal study of the formation mechanism of 2223 phase in BPSCCO and BPSCCO–10 wt% Ag precursors

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Abstract

Isothermal heat treatments were employed to investigate the transformation mechanism from 2212 phase to 2223 phase in the (Bi, Pb)–Sr–Ca–Cu–O system. Precursors prepared by a citrate route were annealed; the phase composition did not include these superconducting phases. Silver was added at 10 wt% to observe modifications in the reaction. The sintering conditions were chosen to enhance the 110 K phase formation: 840°C for undoped and 825°C for doped precursors in an atmosphere of 7% oxygen in nitrogen. With the aid of the Rietveld refinement, the fractional conversion of 2223 phase with the annealing time was calculated. Silver addition was observed to stabilize the $PbCa_2O_4$ phase and to slow down the initial formation of the 2212 phase, consequently delaying the transformation to 2223 phase. SEM analysis of the samples showed that in both cases, with and without silver, the 110 K phase grew by deposition of a viscous liquid in layers over the platelets. We assigned this mechanism to the coherent superficial nucleation of 2223 phase on 2212 plates, the rate of formation being controlled by nuclei growth at a speed related to the velocity of migration of the liquid.

Keywords: BPSCCO; Isothermal; Mechanism; Phase

1. Introduction

It is well known that the $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (2223) phase exists only in narrow ranges of stoichiometry and temperature. Its velocity of formation depends on the oxygen partial pressure present during the transformation from 2212 to 2223 phase. This process is extremely sluggish and requires several hours of heat treatment to obtain a single-phase compound, even if annealed under the most favorable atmos-

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phere. Thus, it is important to have a complete knowledge of the formation mechanisms and kinetics of reaction, in order to achieve materials with useful properties for applications.

In the literature, a great deal of research has been reported on the formation mechanisms of the superconducting phases of the (Bi, Pb)–Sr–Ca–Cu–O system, using mostly non-isothermal techniques, on precursors prepared by melting and quenching, and on silver-sheathed tapes [1–7]. In particular, to analyse the kinetics of reaction of the 2223 phase, as the process under study is so slow, a DTA run would hardly detect the onset of the transformation from 2212 to 2223 [8]. The whole range of formation-decomposition temperatures is so narrow that the different processes cannot be well resolved. In order to get a correct idea of 2223 phase evolution, an isothermal method should be employed.

The aim of our work was to establish the transformation process from 2212 phase to 2223 phase, starting from a mixture of oxides (with and without silver addition), annealed at a fixed temperature under an atmosphere of oxygen partial pressure of 1/14. After submitting the powders to isothermal anneals of different duration, we obtained the fractional conversion of 2223 phase as a function of time. We report our results after fitting these curves with different models for solid state reaction mechanisms.

2. Experimental procedure

Precursors were prepared by a citrate route, as explained in an earlier publication [9], with two nominal stoichiometries: $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$ (BPSCCO) for the undoped samples and $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$ plus 10 wt% silver (BPSCCO–Ag) for the doped samples. Both powders had the same composition, a mixture of oxides, and they differed only in the presence of silver in metallic form. Neither 2212 nor 2223 phases were detected by poweder X-ray diffraction analysis.

Initially, the precursors were characterized by DTA–TG–DTG measurements. Runs were performed on Nezscht STA equipment, heating at a rate of 5 K min^{-1} in flowing 7% oxygen in nitrogen.

For the isothermal analyses, samples of these precursors were annealed for different periods of time in a dynamic atmosphere of nitrogen with 7% oxgyen at 840°C for BPSCCO and 825°C for BPSCCO–Ag. Such temperatures were found to promote the formation of the 2223 phase in these precursors, its quantity increasing with the annealing time. Precursors annealed for 150 h at these temperatures, with intermediate grindings each of 50 h, produced almost pure 2223 phase (more than 90%) in both cases, but for the doped samples a small amount of $PbCa_2O_4$ remained as a secondary phase [9]. In order to analyse the process of formation of our samples, we continued using intermediate grindings for anneals of more than 50 h.

After each heat treatment, the composition of the samples was controlled by X-ray diffraction analyses with Cu Kα radiation in 0.05°C and 5 s steps. We selected three samples of each precursor (annealed for different periods of time) and their diffractograms were analysed using the quantitative Rietveld refinement. In this way, we were able to make a calibration curve so that the quantities of 2212 and 2223 phases formed after each anneal, could be obtained by a rapid measurement of the relative intensities of the 002 reflections of both phases.

3. Results and discussion

DTA runs showed the existence of several endothermic peaks, which shifted to lower temperatures for the silver-doped precursor (Fig. 1). The principal endotherm is located around 850–860°C and has a shoulder for BPSCCO–Ag. In both cases, the onset of this peak coincides with the optimum sintering temperatures for obtaining an almost pure 2223 phase material. We assume that this peak is related to the formation of 2212 and 2223 phases and their subsequent partial melting. It should be noted that this formation-decomposition range is quite narrow and the peak results from the overlapping of several processes. This is clear evidence that non-isothermal methods are not a good approach for the study of 2223 phase formation. Prior to this endotherm, several small endothermic peaks are detected, with a wide exotherm at around 800°C which is more evident for BPSCCO–Ag. DTA profiles of Bi_2O_3 in air showed the existence of two principal peaks: an endotherm around 740°C and an exotherm around 820°C. However, $CaCO_3$ was observed to decompose to CaO forming a broad endotherm in the range 680–860°C in air. Although these phases were not detected by X-ray diffraction, they can be present in our precursors as their peaks overlap with the Bragg reflections of other detected phases and, consequently, can be responsible for some of the observed peaks in this temperature range. Peaks observed after the principal endotherm are assigned to the melting of the phases that develop after the partial melting of 2212 and 2223 phases, among them the 2201 phase which

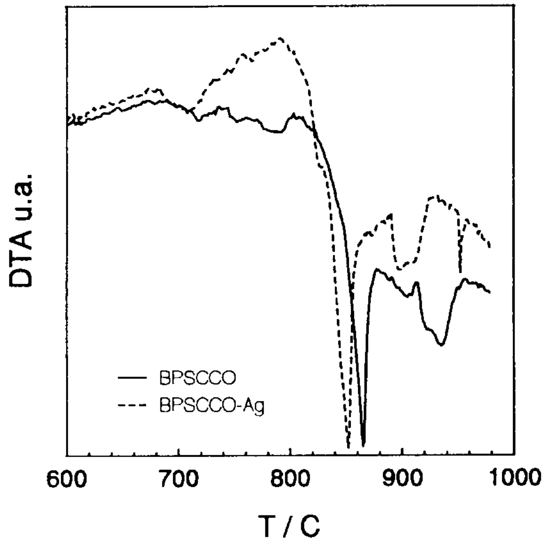

Fig. 1. DTA curves in flowing 7% oxygen in nitrogen at 5 K min^{-1} for both precursors.

was observed to melt around 919°C in air and around 879°C in helium [10]. The endotherm at around 950°C in BPSCCO–Ag corresponds to silver melting.

The weight loss as a function of temperature (TG) and its derivative (DTG) showed a similar behaviour for both precursors (Fig. 2). As expected, the presence of silver shifted the peaks to lower temperatures. After the heating cycle is completed, the weight loss of the silver-free precursor is 2% larger than that of the doped precursor. Comparing the DTG peaks of both compounds, a larger weight loss can be observed on the undoped one at around 780°C. Idemoto et al. [11] determined a curve for PbO evaporation as a function of temperature and oxygen partial pressure. According to their results, for our working atmosphere, PbO evaporation begins at around 760°C. However, $PbCa_2O_4$ decomposes in air in the range 822–830°C into CaO and a liquid phase [12]. In our case, the decomposition temperatures should be lower because of the lower oxygen content of the atmosphere. We can consider that $PbCa_2O_4$ phase decomposes allowing the evaporation of PbO, which gives rise to the observed weight loss around 780°C. Furthermore, if we assume that silver impedes the total decomposition of $PbCa_2O_4$, as it remains as a secondary phase in the silver-doped samples, the weight loss for BPSCCO–Ag at this temperature should be smaller.

In a multiphase compound, if the X-ray diffraction peaks of its components do not interfere, a linear relation can be obtained between the intensity ratio of the peaks of any two compounds in the mixture and their weight fraction ratio [13]. Choosing two peaks that are well defined, one for each phase in the compound, the relation can be mathematically expressed as

$$\frac{x_1}{x_2} = A\frac{I_1}{I_2}$$

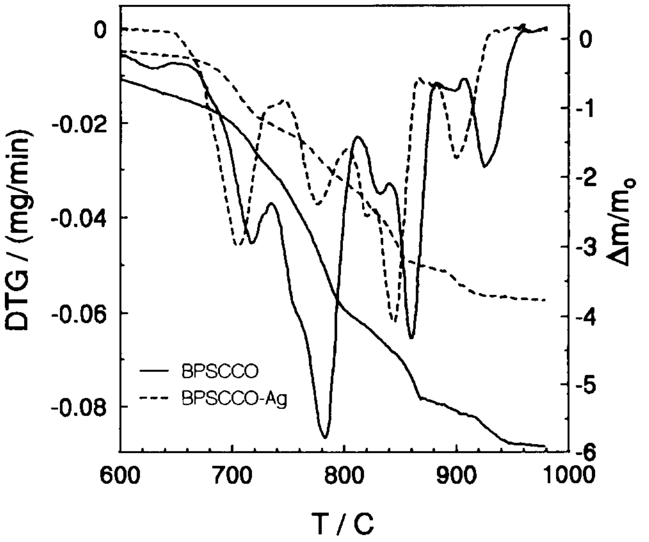

Fig. 2. TG–DTG curves in flowing 7% oxygen in nitrogen at 5 K min^{-1} for both precursors.

or

$$\ln\left(\frac{x_1}{x_2}\right) = \ln A + \ln\left(\frac{I_1}{I_2}\right) \tag{1}$$

where x_i is the weight fraction of compound i, A is a constant and I_i is the intensity of the Bragg reflection of the chosen peak for compound i.

For our study, we picked the (002) peaks of the 2212 and 2223 phases as their corresponding Bragg reflections are well-differentiated in a mixture of both; $2\theta \cong 5.65°$ for the former and $2\theta \cong 4.75°$ for the latter. The weight fractions of each phase were obtained from a quantitative analysis performed using the Rietveld refinement [14] on selected samples, sintered for 43, 50 and 100 h for BPSCCO and sintered for 50, 100 and 150 h for BPSCCO–Ag. For the refinement performed on the silver-doped samples, the zones of the diffractograms that contained Bragg reflections corresponding to silver and $PbCa_2O_4$ were excluded ($17 \leq 2\theta \leq 18.5$, $37 \leq 2\theta \leq 39$ and $43 \leq 2\theta \leq 45.5$). The results showed that the quantity of 2223 phase increases as the quantity of 2212 phase decreases. This is a clear indication that 2212 phase is the precursor for the formation of 2223. Applying Eq. (1) to our data, a straight line with a good correlation factor was fitted.

Once the proportionality constant A is obtained for each precursor, the law followed by the fractional conversion α in each case can be easily derived. In this way, α can be rapidly obtained from the relative intensity of the (002) peaks measured on a diffractogram of each sample. The expression obtained for α is

$$\alpha = \frac{A(I_{2223}/I_{2223} + I_{2212})}{[1 - (A-1)(I_{2223}/I_{2223} + I_{2212})]} \tag{2}$$

With the aid of Eq. (2), we calculated the fractional conversion of the 2223 phase as a function of annealing time for BPSCCO and BPSCCO–Ag precursors. Danusantoso and Chaki [5] observed in silver-free compounds, that after only 4 h of heat treatment in air the quantity of 2212 phase formed is about 80%. Evidently, the kinetics of formation of this phase is faster. The shorter annealing time employed for our study is 10 h, more than enough for the 2212 to achieve complete reaction. In this way, we assure that the 2212 phase formation process is not reflected in our analysis of the BPSCCO precursor.

After taking the corresponding X-ray diffractograms with 2θ varying between 3° and 10°, the fractional conversion α of the 2223 phase was calculated from the relative intensity of the (002) peaks as explained above. In Fig. 3, the fractional conversion vs. annealing time curves are presented. It can be observed that the evolution of the transformation from 2212 phase to 2223 phase is initially retarded in the presence of silver. Furthermore, no 2223 phase is observed after treatments for 10 and 20 h on BPSCCO–Ag, while the quantity of 2212 phase for these two samples increased with the annealing time. This indicates that the presence of silver slows down the initial formation of the 2212 phase, thus retarding the appearance of the 2223 phase. The experimental data were fitted to an exponential law, this approximation being good for the undoped samples but not for the silver-doped ones. The latter suffer a rather abrupt

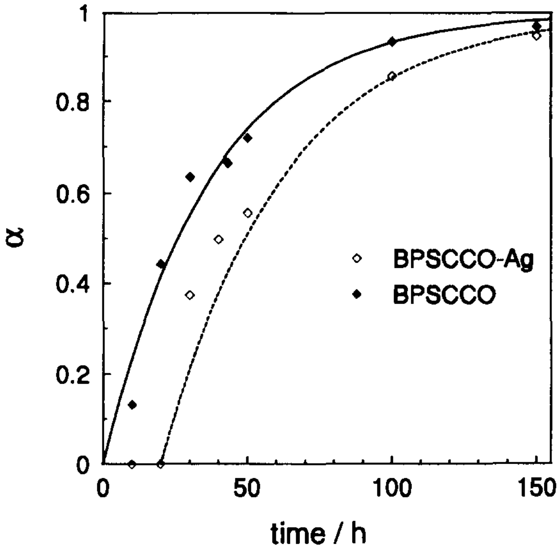

Fig. 3. Evolution of the fractional conversion of the 2223 phase with the annealing time. The curves result from fitting the experimental data with an exponential law.

transformation after an incubation time of 20 h, but achieve a degree of transformation similar to that of the silver-free precursor after a total anneal of 150 h.

The rate of the process can be described by two functions, $k(T)$ and $f(\alpha)$ [15], as

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{3}$$

where $k(T)$ is only dependent on temperature and $f(\alpha)$ describes the phase composition of the system under study, based on the fractional conversion α. Once the dependence of α with time at a fixed temperature is obtained, upon integration of Eq. (3) a new function can be derived for the description of the process

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = k(T)t \tag{4}$$

This linear dependence makes possible to find by trial and error the function that best fits the experimental data $\alpha(t)$. The analytical form of $g(\alpha)$ has been established for several models of solid state reaction mechanisms. The most suitable model would be the one whose $g(\alpha)$ best fists a straight line when plotted as a function of the annealing time.

Four mechanisms were found to satisfy these requirements for both precursors, excluding the 20 h incubation time for the silver-doped sample, as is presented in Figs. 4(a) and (b). Using Sharp's symbols [16], they are F1, D2, D3 and D4. The F1 model considers the random formation of one nucleus in each particle and its subsequent growth. Avrami, Yerofeev and Koglomorov [15] modified Eq. (4), by

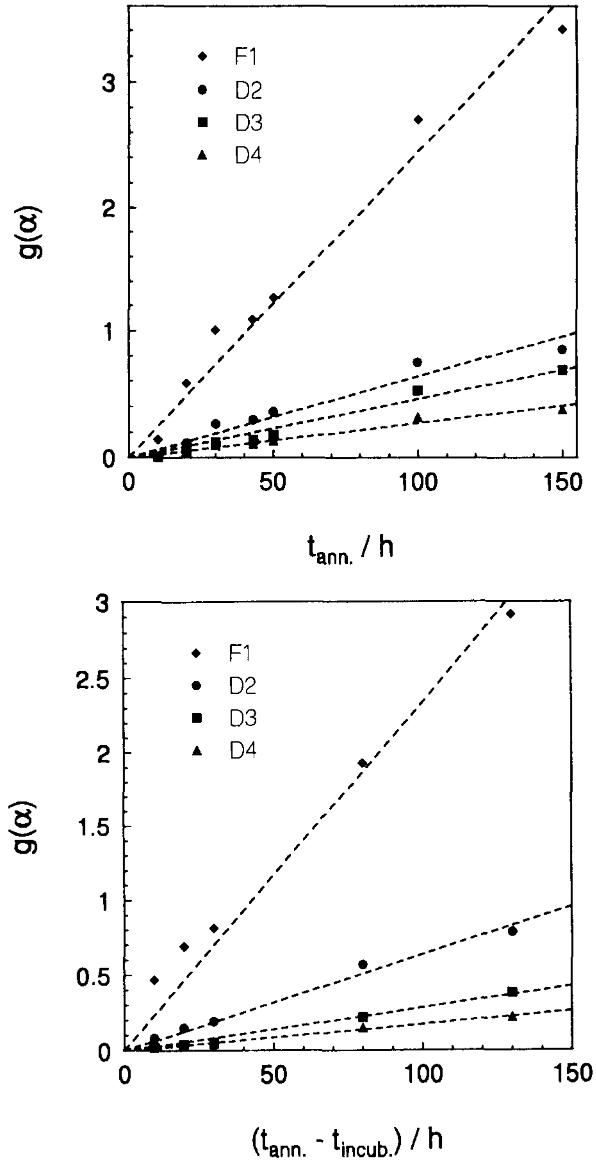

Fig. 4. Plots of $g(\alpha)$ vs. annealing time for the four best fitting models for (a) BPSCCO and (b) BPSCCO–Ag. For the latter, the incubation time before the formation of the 2223 phase is taken into account by reducing the effective annealing time by 20 h.

introducing the Avrami factor r whose value depends on the shape of the product domains, the rate of nucleation and the type of subsequent growth of the nuclei. The modified Eq. (4) is

$$g(\alpha) = -\ln(1-\alpha) = kt^r$$

Using this relation, the mechanism F1 has an Avrami factor equal to 1. For plate-like particles, this model indicates a diffusion-controlled growth, starting with instantaneous nucleation. Many authors had observed using TEM that there are always some 2223 cells inside the 2212 platelets. We can assume that these act as embryos and that the further growth of them is limited by the diffusion of Ca and Cu toward the 2223 nuclei on the surface of the 2212 platelets.

The D2, D3 and D4 mechanisms correspond to a shrinking core model in two (D2) and three (D3 and D4) dimensions. This model assumes that when diffusion starts, a thin layer of product is already distributed coherently and propagates to the centre of the particle. In our case, for the D2 model, we have to assume that 2212 platelets have cylindrical symmetry, and are rapidly covered by a layer of 2223 which grows leaving the 2212 phase in the interior. Both D3 and D4 models assume spherical shape for the 2212 phase with isotropic diffusion, which does not fit the real shape of the grains of these materials.

In order to establish which model fits the real process better, samples were examined with an SEM. It was observed that, at equal annealing times, the grains of the undoped material grew larger. Aggregates were observed on the surface of the plates for the doped material, presumably of $PbCa_2O_4$, as EDX analysis indicated, the quantity of which diminished but did not disappear with the annealing time (Fig. 5). As previously observed, silver stabilizes the $PbCa_2O_4$ phase. Silver was found at the boundaries of

Fig. 5. SEM photograph of the broken surface of a BPSCCO–AG sample annealed for 40 h. The composition of the aggregates on the plates is $PbCa_2O_4$,

some plates. On some grains, a layered growth can be observed as if a viscous liquid had been deposited on the plates (Figs. 5 and 6). With increasing annealing time, the quantity of these grains increases. For the silver-doped samples annealed for 10 h, no grains with these characteristics were found and very few can be observed for 20-h annealed samples. These two specimens have no 2223 phase as detected by X-ray diffraction. After complete transformation is achieved (150 h annealing), all grains present this layered morphology. We can conclude that this is the way in which the 2223 phase grows.

The samples sintered for 150 h, with two intermediate grindings, have smaller grain sizes than those annealed for 30 h, indicating that grinding has a grain-reducing effect. For comparison, a sample was sintered for 150 h without intermediate grinding. The resulting grains are much larger but grew very unhomogeneously, leaving holes inside the plates as the layer grew, as observed before (Fig. 7). The fractional conversion for this sample was 84%, less than that obtained with intermediate grindings of 50 h each. Thus, we can conclude that grinding speeds up the reaction, for example by favoring the diffusion of Ca and Cu by a redistribution of these elements.

It is evident from these observations that the mechanism of formation of the 2223 phase is better represented by the F1 model, because growth does not take place in the interior of the plates. According to this mechanism, the 2223 phase nucleates coherently on each 2212 plate and grows by deposition of a viscous liquid in layers over the

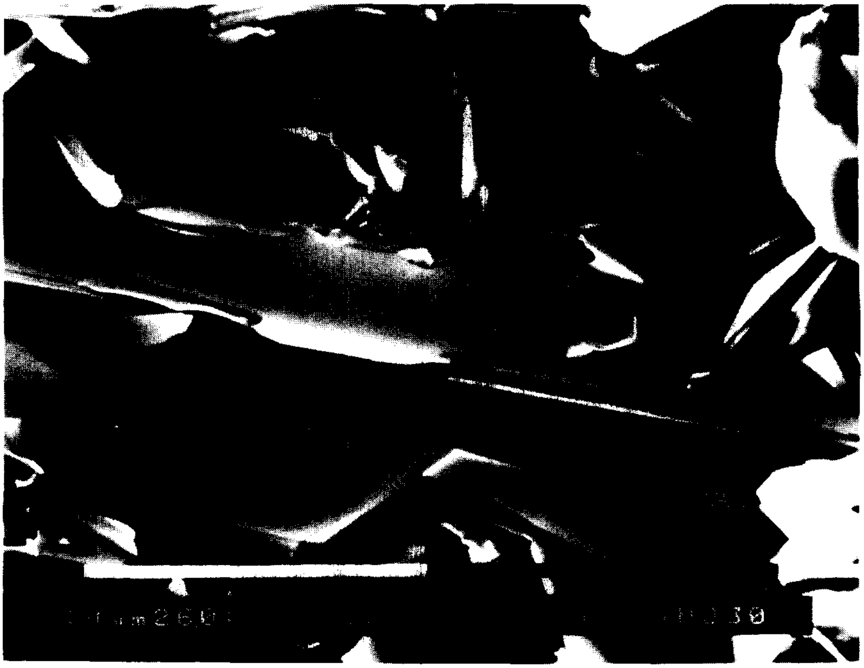

Fig. 6. SEM photograph of the broken surface of a BPSCCO sample annealed for 30 h.

Fig. 7. SEM photograph of the broken surface of a BPSCCO sample annealed for 150 h without intermediate grindings.

platelets. The growth rate is limited by the migration of this liquid phase. The velocity of migration must be connected with the velocities of diffusion of Ca and Cu toward the liquid, as this phase must be rich in these elements in order to transform the 2212 phase to 2223 phase.

4. Conclusions

Using isothermal methods, we analysed the mechanism of transformation from 2212 to 2223 phase under the conditions that were previously found to promote this reaction. With the aid of the quantitative Rietveld refinement, we established the evolution of the fractional conversion of the 2223 phase with the annealing time. We observed that silver addition to the system slowed down the initial formation of the 2212 phase, thus retarding the subsequent transformation to 2223. The fractional conversion vs. time curve follows an exponential law for the undoped precursor while evolution in the presence of silver is more abrupt after an incubation time of 20 h.

Comparison of the experimental data with different models of solid state reaction processes gave four models as the most probable. SEM observations of the specimens revealed that the 2223 phase grew in layers by deposition of a liquid phase on the 2212 platelets. The F1 mechanism was then assigned to the transformation process from 2212 phase to 2223 phase. The growth rate is probably ruled by the velocity of diffusion of Ca and Cu atoms toward this liquid phase.

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