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Chemical Diffusion in the Bi, Sr, Ca, Cu/O System: The Kinetics and Mechanism of the Solid-State Synthesis of a Single-Phase "2212" Material

G. Flor,[1] P. Ghigna, U. Anselmi-Tamburini, and G. Spinolo

Department of Physical Chemistry and CSTE/CNR, University of Pavia, I 27100 Pavia, Italy

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Monodimensional (chemical) diffusion measurements have been used to find a *clean* solid-state path to a pure Bi–Sr–Ca–Cu–O superconductor with two-layer structure, i.e., a suitable sequence of solid-state reactions such that each step gives a single-phase product. When starting from carbonate precursors of CaO and SrO plus Bi_2O_3 and CuO, the critical point of a reaction path of this kind is an appropriate choice of the external conditions of temperature, oxygen partial pressure, and cation molecularities, which must be different from the ideal "2212" values. The results show that a clean solid-state synthesis of a single-phase two-layer material is achieved by reacting at 750°C under $P(O_2) = 10^{-3}$ atm the $Sr_{14}Cu_{24}O_{41}$ phase and the ternary solid solution with monoclinic symmetry and cation molecularity near 0.376 : 0.082 : 0.543 (Ca : Sr : Bi).

1. INTRODUCTION

This work is part of a research program on the mechanism and kinetics of solid-state reactions in oxide superconductor systems such as Y, Ba, Cu/O (1, 2); Bi, Sr, Cu/O (3, 4); and Bi, Sr, Ca, Cu/O (5). Briefly, in these papers it has been shown that chemical diffusion experiments on binary and pseudobinary systems are a powerful tool for reaching a rational understanding of the whole set of solid-state reactions that occur at each interface between a couple of phases (starting reagents, intermediate products, and so on) when a complex powder mixture is allowed to react under various external conditions.

The results can in turn be used to outline a sequence of solid-state reactions that, when separately performed under their most appropriate external conditions, are actually able to produce the desired material as a single phase, i.e., free from the spurious phases (unreacted reagents, intermediate phases, or alternative or decomposition products) that can segregate at the grain boundaries of the main phase during a powder mixture synthesis. Such sequences have been named *clean paths*. In a candidate step of a clean path, the reacting phases define a pseudobinary cut of the phase diagram, only one product phase is formed under the given external conditions; the product also lies on the pseudobinary cut, and either corresponds to the desired final material, or is a candidate reactant for a further step of the path.

By means of chemical diffusion experiments it is possible to verify directly whether a given reacting couple fulfills the above constraints. When coupled with the knowledge of the equilibrium phase diagram, these experiments provide the basis for a systematic search for a clean path.

Our previous work on the Bi, Sr, Ca, Cu/O system (5) has been devoted to such a systematic search for a clean path toward the superconducting phase usually known as $Bi_2Sr_2CaCu_2O_8$, and referred to in the following as the two-layer phase, denoted L2. The experimental investigation was at that time restricted to one set of external conditions:

- reaction temperature, 750°C;
- environmental atmosphere, 1 atm oxygen partial pressure;
- 2 : 2 : 1 : 2 (Bi : Sr : Ca : Cu) cation molecularity; and
- carbonate precursors for Sr and Ca cations, plus copper and bismuth oxides.

According to our results (5), a clean path as defined above does not exist under these external conditions.

In the present work, the objective of the previous paper is reconsidered in light of some recent works on cation molecularity and oxygen nonstoichiometry of the L2 phase (6–12), and the effect of these external variables on the possibility of a clean path toward the L2 phase is investigated.

The paper is organized as follows. We start from a promising sequence of solid state reactions found in the previous work, and described, in a largely simplified manner, as follows:

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[1] To whom correspondence should be addressed.

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$$Bi_2O_3 + CaCO_3 \rightarrow CaBi_2O_4 + CO_2 \quad [1]$$

$$SrCO_3 + CuO \rightarrow SrCuO_2 + CO_2 \quad [2]$$

$$CaBi_2O_4 + 2\ SrCuO_2 \rightarrow Bi_2Sr_2CaCu_2O_8. \quad [3]$$

As shown previously (5), the critical point of this path is the last step, where a complex mixture of metathetic products is formed instead of the desired superconducting phase. As a first trial, therefore, we investigate the effect of cation molecularity and oxygen partial pressure on the last step of this sequence. It will be shown that, although it is unsuccessful, this approach is eventually able to provide important insights into a clean path toward L2 materials. Finally, one effective reaction sequence complying with the above requirements is described using these results.

In this work we still take into account carbonate precursors for Sr and Ca cations, plus copper and bismuth oxides. The effect of the reaction temperature can be safely discussed independently of the other external variables on the basis of known thermodynamic features of the whole system and of our previous diffusion results (5). In particular, we note here that L1 (the one-layer superconducting phase also known as "2201") is formed at lower temperature than L2, and that raising the reaction temperature surely enhances the amount of L2. However, formation of liquid phase(s) by peritectic or eutectic transformations must be carefully avoided in a sequence of reaction steps, if each step must give rise to a single-phase product. In this respect, it should be remembered that (i) $CaBi_2O_4$ incongruently melts near 800°C (13) and (ii) in the Bi, Cu/O binary there is an eutectic near 770°C (14). In conclusion, the best operating temperature can be selected on the basis of the conflicting requirements that a high temperature should be preferred for kinetic reasons, but without exceeding the upper thermodynamic limit (around 750°C).

2. EXPERIMENTAL

Chemical diffusion experiments have been done in a horizontal electrical furnace using a home-built cell (5) under isothermal (±1°C) conditions and under flux of a certified oxygen-in-argon mixture at 1 atm total pressure. Monodimensional diffusion geometry was used, the reacting couples being made of two sintered pellets of the pertinent phases. The practical rate constants (k) have been obtained by setting up a number of replicate experiments under the same external conditions, removing at selected times (t) each reacting couple from the cell, cutting along the diffusion direction, measuring under the optical microscope the thickness (x) of the product layer(s), and fitting a number of (x, t) determinations to the appropriate solution of Fick's law: $x^2 = 2\ kt$.

Differential thermal analysis (DTA) and thermogravimetry (TG) were done on a TA Thermal Analyst 2000 using alumina crucibles.

X-ray powder diffraction (XRPD) patterns were taken on a Philips 1710 instrument equipped with a copper anode operated at 45 kV and 20 mA an adjustable divergence slit (15), a vertical goniometer, and a graphite monochromator on the diffracted beam.

A Zeiss Axioplan optical microscope and a Cambridge Stereoscan SEM were used for microscopic observations. A Link attachment of the latter instrument was used for electron microprobe analyses (EMPA). Standard materials for EMPA analytical determinations were either the starting materials or the intermediate compounds described in the following.

Bi_2O_3, CuO, $CaCO_3$, and $SrCO_3$ (Aldrich, 99.99%) were used as starting materials. The intermediate products $Sr_{1-x}Ca_xCuO_2$ ($x = 0$ and $x = 0.25$) and $CaBi_2O_4$ were prepared by solid-state synthesis (5).

The intermediate product $Sr_{14}Cu_{24}O_{41}$ was prepared by reacting a 12 : 7 ($CuO : SrCO_3$) pelletized powder mixture at 800°C under pure oxygen flux for a total time of 48 hr, with one intermediate cooling step with grinding and repelletization.

The oxide ternary solid solution with monoclinic symmetry (Space group: $C2/m$) (16) and 0.376 : 0.082 : 0.543 (Ca : Sr : Bi) cation composition was prepared in a similar way from stoichiometric amounts of $CaCO_3$, $SrCO_3$, and Bi_2O_3 (reaction T = 800°C; air atmosphere; reaction time = 72 hr; cooling, grinding, and repelletization after each 24 hr). This phase will be referred to as the TM (ternary monoclinic) phase.

3. RESULTS AND DISCUSSION

The problem of cation molecularity and/or oxygen nonstoichiometry has been discussed by a number of authors (6–12, 17–19), in connection with the structure, stability, and superconducting properties of the L2 phase. There is now general agreement that the stability field of L2 does not include the rational composition corresponding to the simple chemical formula $Bi_2Sr_2CaCu_2O_8$. With respect to the "ideal" 2212 composition, Bi is always overstoichiometric, and Ca can replace Sr to a large extent; for instance, $1.04 < Bi/Cu < 1.27$ and $0.64 < Sr/Ca < 1.47$ according to our results (11).

Structural determinations by several authors (20–22) explain the cation nonstoichiometry of L2 by placing some Bi on Sr (or Ca) sites and by allowing a large degree of substitution of Sr by Ca. This structural model can be accounted for by the chemical formula $Bi_{2+y}Sr_{3-y-x}Ca_xCu_2O_{8+z}$, i.e., by *two* cation composition degrees of freedom. To the contrary, however, some of the above-quoted experimental determinations of the stability field of the phase indicate that a formula such as $Bi_{2+y+w}Sr_{3-y-x}Ca_xCu_2O_{8+z}$ (i.e., with *three* cation composition degrees of freedom) is more appropriate.

Moreover, the effects of cation molecularity and reaction atmosphere (oxygen nonstoichiometry) are expected to be strongly coupled to each other, because the stability relationships between the different phases are expected to depend jointly on oxygen partial pressure and cation molecularity. Also, these external variables are able to affect the diffusion coefficients, and therefore the reaction rates, and to provide alternative reaction mechanisms, for instance, when there is competition between oxygen transport in the gas phase and solid-state diffusion. Therefore, they can show relevant kinetic effects; in some cases, they can even kinetically hinder the formation of a particular phase with respect to another one.

For these reasons, it is more convenient to discuss step by step the effect of the various kinds of nonstoichiometry, and we start with Sr/Ca cation ratio and oxygen partial pressure.

A preliminary information on the role played by oxygen partial pressure can be gained by investigating *powder* mixtures of parent reagents. We hereafter discuss the results obtained using Sr/Ca = 1, i.e., with a starting 2 : 1.5 : 1.5 : 2 (Bi : Sr : Ca : Cu) cation ratio, but qualitatively similar results have been obtained with other Sr/Ca ratios.

We started using DTA, TG, and XRPD determinations to single out the lower and upper temperature limits (T_1 and T_2) of the $[T, P(O_2)]$ field where the solid state synthesis of L2 appears to be feasible. For T_2, two similar mixtures were allowed to react under $P(O_2)$ = 1 atm for 12 hr at temperatures slightly below and slightly above 870°C; the XRPD analysis then shows that L2 and L1 are the majority phases, respectively. T_2 is therefore related to L2 "decomposition" to form L1. Under the same oxygen partial pressure, the mixture containing L2 as majority phase shows a weight loss of about 1.3% near 870°C (see Fig. 1). It is worth noting here that the results do not show any evidence of the decomposition of the L1 phase to its well-known insulating polymorph. This decomposition has been discussed in our previous work on the Bi, Sr, Cu/O system (3); a reasonable explanation of the different result can be found in the different cation composition of the system.

The lower limit (T_1) corresponds to L2 formation from a complex powder mixture containing the one-layer superconductor, L1, and is more difficult to determine, because it does not correspond to a significant weight change (thus ruling out the use of TG) and because the DTA trace is very crowded and shows very different behaviors when different external conditions (Sr/Ca ratio and oxygen partial pressure) are considered. For this reason, a long series of XRPD determinations was needed to obtain this information. Compared to T_2, T_1 is also less clearly defined, because L2 formation from a powder mixture of suitable reagents is a kinetically complex process which depends from the rate constants of several reactions and from sizes and shapes of the parent grains. Actually, we merely considered these T_1 values as a practical guide for planning the chemical diffusion experiment described hereafter.

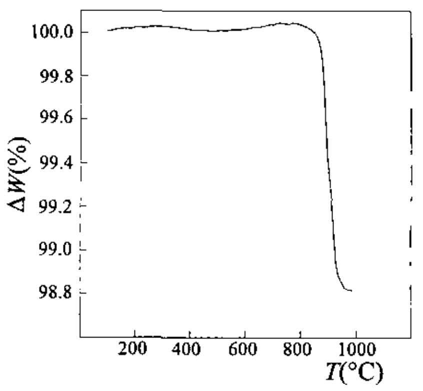

FIG. 1. TG under pure oxygen (1 atm) of a powder mixture previously heated at 850°C for 12 hr. According to XRPD, the mixture is mainly L2.

Under different oxygen partial pressures, T_1 changes from ~800°C (at $P(O_2)$ = 1 atm) to ~740°C (at $P(O_2) = 10^{-3}$ atm). Also the T_2 value decreases with decreasing $P(O_2)$. These T_1 and T_2 values are plotted as filled circles and triangles in Fig. 2. The trend of the T_2 values is not very far from that obtained by Rubin *et al.* (23) by oxygen partial pressure determinations on L2 samples with molecularity close to 2212.

When combined with the discussion of the introduction about the most suitable reaction temperature, the circles and triangles of Fig. 2 outline the $(T, P(O_2))$ we are looking for. In particular, the figure shows that, for a reaction

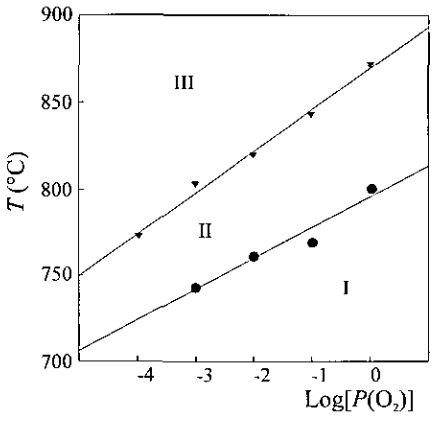

FIG. 2. Interaction of the L2 phase with gaseous oxygen; for the meaning of ranges I, II, and III, see text.

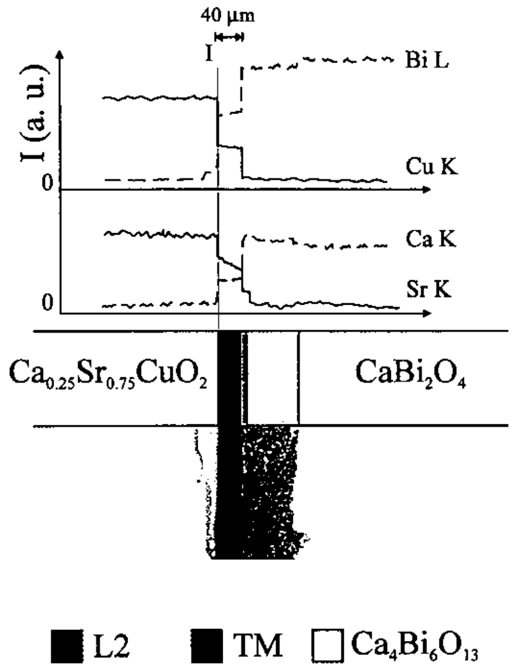

FIG. 3. Scheme of the product layers formed by the $CaBi_2O_4$ + $Sr_{0.75}Ca_{0.25}CuO_2$ couple at 750°C and $P(O_2) = 10^{-3}$ atm.

temperature around 750°C, the most appropriate oxygen partial pressure is $\leq 10^{-3}$ atm.

The effect of the Sr/Ca ratio can be investigated in a very direct way because the binary phase previously indicated as $SrCuO_2$ extends its stability field into the Sr, Ca, Cu/O system (24), and can be prepared, for instance, with composition $Ca_{0.25}Sr_{0.75}CuO_2$. Substituting this material for $SrCuO_2$ in the last step of the reaction path would hopefully produce a single-phase L2 product with 2 : 1.5 : 1.5 : 2 (Bi : Sr : Ca : Cu) cation ratios or, more precisely, with cation ratios $2 : (0.75x) : (1 + 0.25x) : x$, with x close to, but not necessarily equal to, 2.

Therefore, to clarify the coupled effect of environmental atmosphere and Sr/Ca ratio on the reaction mechanisms, the diffusion couple ($CaBi_2O_4$ + $SrCuO_2$) already discussed in our previous work (5) has been reinvestigated under the same conditions, but using both a different oxygen partial pressure (10^{-3} instead of 1 atm) and these two Sr/Ca ratios.

Under this atmosphere, these reacting couples ($CaBi_2O_4$ + $SrCuO_2$ and $CaBi_2O_4$ + $Ca_{0.25}Sr_{0.75}CuO_2$) behave very similarly and form three product layers.

Figure 3 shows the microscopic observation of the second couple ($CaBi_2O_4$ + $Ca_{0.25}Sr_{0.75}CuO_2$) after a reaction time of 100 hr. The left layer (layer I) is black and contains all four cations; by EMPA and XRPD it corresponds to the desired L2 phase. Its position on the $CaBi_2O_4$ side of the original reaction interface indicates that its formation involves O^{2-}, Cu^{2+}, and Sr^{2+} diffusion. On the basis of our knowledge of the pertinent diffusion coefficients in this material or in other cuprate superconductors (25, 26), we may argue that L2 formation is kinetically controlled by the diffusion of the cations.

The second layer (II) is yellow, much thinner than the other layers, and as determined by EMPA mainly contains Ca and Bi, with small amounts of Sr. Under the optical and electron microscope, this layer is seemingly homogeneous and has been assigned to the ternary (Ca, Sr, Bi) oxide solution found by Roth *et al.* (16) in the Ca, Sr, Bi/O system, and denoted in the experimental section as TM. According to these authors, the TM phase is a broad-range solid solution. It is probably to be identified with the $Sr_2Ca_5Bi_8O_x$ compound described by Hong *et al.* (18), when analyzed by XRPD, the four strongest peaks of layer II actually correspond to those reported by them. To emphasize the nature of broad-range solid solution, its composition can be written as $(Ca_{1-x}Sr_x)_{1-y}Bi_{1+y}O_{5+y/2}$.

The dark yellow layer close to the $CaBi_2O_4$ pellet only contains Bi and Ca, and has been assigned by EMPA and XRPD to the $Ca_4Bi_6O_{13}$ compound.

The practical rate constants are 2×10^{-11}, 1×10^{-12}, and 1×10^{-10} cm^2 s^{-1} for the formation of L2, TM, and $Ca_4Bi_6O_{13}$, respectively.

We can now compare the present result with that for reaction of the same phases at the same temperature, but at $P(O_2) = 1$ atm [Fig. 12 of Ref. (5)]. There, four product layers were found: $Sr_{14}Cu_{24}O_{41}$, the one-layer superconductor (L1), $Ca_4Bi_6O_{13}$, and a Bi-poor $CaBi_2O_4$. Here, the L2 phase is at last formed, but it is coupled with spurious phases.

The results thus far discussed can be summarized as follows: low oxygen partial pressure is necessary for producing an L2 phase, but this condition (alone or simply coupled to a change in the Sr/Ca ratio, at least within the investigated range) is not sufficient for producing *only* this phase. We are therefore obliged to infer that Bi excess of the L2 phase must also be taken into account, and that a different path must be determined.

As a matter of fact, a number of experimental results indicate that the crucial point is the full cation molecularity of the desired phase. The first argument relies on the observation that the formation of L2 requires segregation of phases ($Ca_4Bi_6O_{13}$ and TM) lying outside the investigated pseudobinary joints. As a further argument, let us note that the diffusion experiments discussed so far involve three reagents: $CaBi_2O_4$ and two compositions ($SrCuO_2$ and $Ca_{0.25}Sr_{0.75}CuO_2$) of the same phase. In the pseudoquaternary system (oxygen partial pressure being kept constant) of Bi, Sr, Ca, and Cu oxides, the compositions corresponding to these reagents define a plane. The experimental observation that the L2 layer is in contact with a phase (TM) lying outside the plane, and the assump-

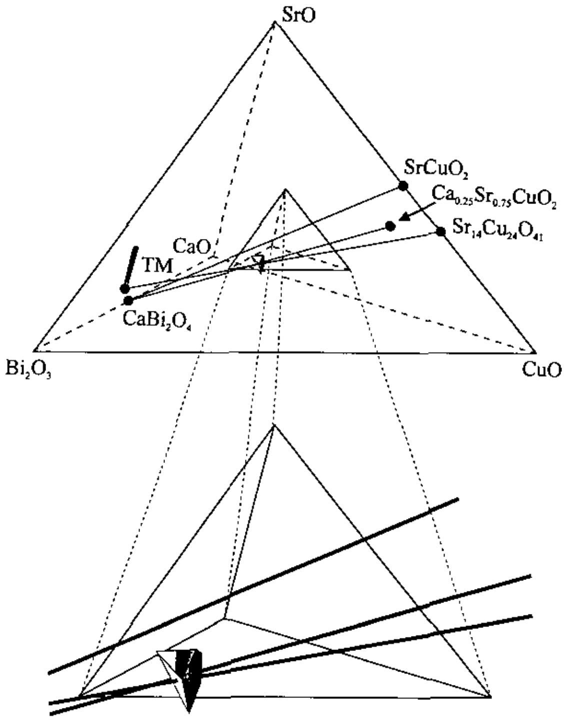

FIG. 4. Composition tetrahedron of the Bi, Sr, Ca, Cu/O system at $P(O_2) = 10^{-3}$ atm and $T = 750°C$. The irregularly shaped polyhedron schematically indicates the stability field of the L2 phase, drawn on the basis of the previous experimental results (11); the lines indicate the investigated diffusion couples.

tion of thermodynamic equilibrium at the interface mean that the stability field of L2 does not cross this plane (with respect to TM, it must be on the other side of the plane).

The above conclusion is in agreement with the most recent experimental determinations of the stability field of the L2 phase, and is graphically shown in Fig. 4. In this figure we have schematically drawn, in the form of a polyhedron, the stability composition field (at 750°C and $P(O_2) = 10^{-3}$ atm) of L2 using our previous determinations (11). The figure shows that the line corresponding to the reaction couple here discussed does not cross the stability field of L2.

Now, to search for an alternative path, a useful starting point is still given by the previous experimental results and by the conclusion inferred from them, because they clarify a number of thermodynamic and kinetic constraints which must hold for any candidate path. These experiments and conclusions also provide some clues in the search for an alternative path. Broadly speaking, we may argue (i) that the required join is not very different from the $Ca_tSr_{1-t}CuO_2$–$CaBi_2O_4$ ($0 \leq t \leq 0.25$) joins thus far investigated, because these phases do indeed form the L2 phase by reaction at 750°C and $P(O_2) = 10^{-3}$ atm and (ii) that obvious candidates for the phases defining the new join can be searched among the phases involved as reagent or product in the previous joins.

As already stated, it is an experimental fact that the 2212 cation composition does not fall into the stability range of L2, and, in particular, that Bi excess must be explicitly taken into account. We can start our search from this point. In this regard, $CaBi_2O_4$ does not seem useful, because it is a line compound.[2] The same conclusion applies to the (Ca, Sr)CuO_2 solid solutions, which do not allow varying Cu/(Ca + Sr) ratios.

Things are different for the TM phase, which is formed in the neighboring layer when reacting the $Ca_tSr_{1-t}CuO_2$–$CaBi_2O_4$ joins, so that it is not unreasonable to assume its thermodynamic compatibility with L2.

If TM is one member of the reacting couple we are looking for, the other reagent phase must be $Sr_{14}Cu_{24}O_{41}$. This phase is formed as a methatetic product of the $CaBi_2O_4$–$SrCuO_2$ couple at 750°C and $P(O_2) = 1$ atm (5), but can be produced in a clean and faster way by reacting $SrCO_3$ and CuO powders in the appropriate stoichiometric amount at $T = 800°C$ and $P(O_2) = 1$ atm. Figure 4 shows that the segment connecting these reagents does indeed cross the stability field of L2, if the TM phase is prepared with an appropriate cation molecularity. We actually selected the cation ratios 0.376 : 0.082 : 0.543 (Ca : Sr : Bi), which correspond to $x = 0.179$, $y = 0.085$ in the chemical formula $(Ca_{1-x}Sr_x)_{1-y}Bi_{1+y}O_{(5+y)/2}$, but other nearby compositions can be used.

As a test of the effectiveness of this reaction step, a diffusion couple experiment has been performed at $T = 750°C$ under $P(O_2) = 10^{-3}$ atm on the reagents $Sr_{14}Cu_{24}O_{41}$ and $(Ca_{1-x}Sr_x)_{1-y}Bi_{1+y}O_{(5+y)/2}$ (with $x = 0.179$, $y = 0.085$). This couple is a clean step toward L2. Figure 5 shows the reacting couple after 200 hr, with a single black product layer between the reagent layers. The overall reaction (not considering oxygen nonstoichiometry of the L2 phase) is

$$Sr_{14}Cu_{24}O_{41} + 23\ (Ca_{0.821}Sr_{0.179})_{0.915}Bi_{1.085}O_{2.543} \\ \rightarrow 12\ Bi_{2.08}Sr_{1.48}Ca_{1.44}Cu_2O_{8.04} + 1.505\ O_2.$$

By Fick-law analysis, the practical rate constant is 3×10^{-12} cm^2 sec^{-1}, which is about 10 times lower than the rate constant for formation of the L2 layer from the $CaBi_2O_4 + Ca_{0.25}Sr_{0.75}CuO_2$ couple under the same T, $P(O_2)$ conditions.

It is quite interesting to note that the L2 phase so formed shows a remarkable composition variation for Ca and Sr

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[2] For the sake of completeness, we can note here that from previous diffusion experiments (5) we gained some evidence that this compound can be Bi understoichiometric. However, this information is not useful, because Bi overstoichiometry, instead of Bi understoichiometry, is required.

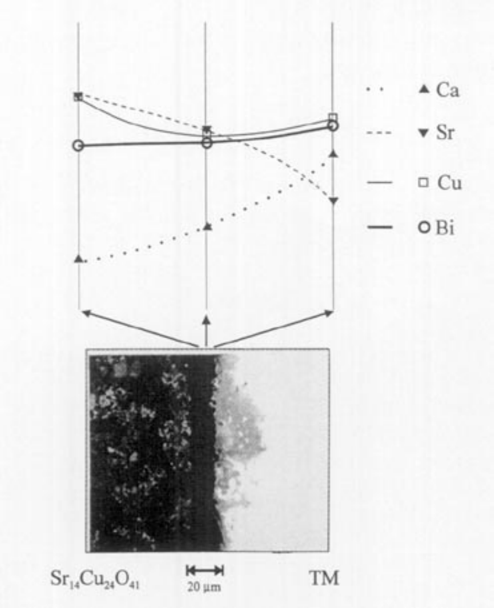

FIG. 5. Electron microprobe analysis (EMPA) and optical micrograph of the diffusion couple between $Sr_{14}Cu_{24}O_{41}$ and $(Ca_{1-x}Sr_x)_{1-y}Bi_{1+y}O_{(5+y)/2}$ (with $x = 0.179$, $y = 0.085$) at 750°C and $P(O_2) = 10^{-3}$ atm.

cations along the diffusion direction (see upper part of Fig. 5). In light of the previous discussion about cation molecularity, this experimental result is not surprising, and it indicates that the reaction path here found can hopefully be used to produce materials with L2 structure and a broad range of cation compositions.

For the sake of completeness, we must report that, in a few cases, also CuO segregation has been observed near the phase boundary with the Sr, Cu/O reagent, but the segregated phase disappears as the reaction proceeds. Clearly, all these features indicate a complex reaction mechanism, and further work is in progress to gain a better understanding of all these aspects, and to single out the best compositions of the starting reagents for a performing synthesis of a superconducting material with a preset cation molecularity.

The reaction path has been tested also on the corresponding *powder* reaction. Figure 6 reports the XRPD pattern of the material obtained by reacting at 750°C and $P(O_2) = 10^{-3}$ atm a mixture of $Sr_{14}Cu_{24}O_{41}$ and TM with the above composition. The pattern is in good agreement with the results of Idink *et al.* (27). The (*hkl*) indexes of the figure do not take into account the peaks due to the incommensurate lattice modulation and follow the indexing scheme of the latter authors. By least-squares analysis according to this indexing scheme, the lattice constants are $a = 0.54284(30)$ nm, $b = 0.54107(30)$ nm, $c = 3.0691(17)$ nm. Generally, we prefer microscopic inspection to XRPD analysis for detecting impurity phases. In diffusion couple experiments, impurity phases generally segregate at or near the well-defined boundaries between product layer and reagent layers, thus making the microscopic observation simpler and possibly more sensitive. With the exception of the above-mentioned cases of CuO segregation and redissolution, we have never been able to see impurity phases with optical microscopy at 1000 × magnification and with SEM at 20,000 × magnification.

Finally, we note that the external $[T, P(O_2)]$ conditions respectively required for a performing synthesis and for achieving the best electrical properties may conflict with each other. Actually, the L2 phase produced by this three-step path does not show outstanding superconducting performance ($T_c \sim 70$ K) and therefore requires further heating in the most appropriate oxygen atmosphere to gain its optimal hole concentration.

4. CONCLUSIONS

The results of the present work, coupled with the systematic investigation of our previous work (5), show that a *clean* solid-state synthesis of the two-layer Bi, Sr, Ca, Cu/O superconductor usually referred to as $Bi_2Sr_2Ca Cu_2O_8$ is indeed possible by selecting a suitable reaction path.

The critical point of the clean synthesis is the last step, which requires an appropriate choice of reaction temperature, reaction atmosphere, and cation molecularity. The experimental data indicate that all these external conditions are mandatory: it is impossible to produce the desired phase without reducing the environmental oxygen pressure, but it is also impossible to obtain the L2 phase alone without taking into account the appropriate cation ratios and reaction temperature.

The influence of the reaction temperature is a compromise between kinetic and thermodynamic reasons: the need for achieving high reaction rates and avoiding formation of liquid phases through peritectic or eutectic transformations.

The influence of cation molecularity is related to the

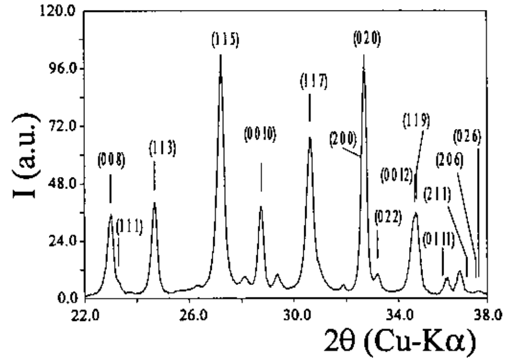

FIG. 6. X-ray powder diffraction pattern of the L2 material produced by reacting a powder mixture of $Sr_{14}Cu_{24}O_{41}$ and $(Ca_{1-x}Sr_x)_{1-y}Bi_{1+y}O_{(5+y)/2}$ (with $x = 0.179$, $y = 0.085$) at 750°C and $P(O_2) = 10^{-3}$ atm.

topology of the phase diagram. The segment indicating the pseudobinary reaction of the last step must cross the thermodynamic stability field of the L2 phase; otherwise, formation of spurious phases cannot be avoided.

The influence of $P(O_2)$ is reasonably due to a combination of thermodynamic and kinetic factors. The point to be stressed here is the competition with formation of the one-layer Bi, Sr, Cu/O superconducting phase (L1). We recall, on one hand, the thermodynamic instability of L1 under low $P(O_2)$ values (3). On the other hand, it has been already shown (4) that the solid-state synthesis of L1 requires oxygen transport through gas phase. Also, it is not unreasonable to argue that a smaller oxygen nonstoichiometry may provide easier paths for cation diffusion inside the L2 structure.

In conclusion, the clean synthesis of L2 can be achieved by a three-step process as follows:

- synthesis of the $Sr_{14}Cu_{24}O_{41}$ compound by reacting stoichiometric amounts of $SrCO_3$ and CuO powders at $T = 800°C$ and $P(O_2) = 1$ atm;
- synthesis of the ternary (Sr, Ca, Bi) solid solution with monoclinic structure and 0.376 : 0.082 : 0.543 (Ca : Sr : Bi) cation molecularity by reacting stoichiometric amounts of $CaCO_3$, $SrCO_3$, and CuO powders at $T = 800°C$ under $P(O_2) = 1$ atm;
- reaction of the above intermediate products at $T = 750°C$ under $P(O_2) = 10^{-3}$ atm.

We again stress the fact that each step of the above-described process gives a single-phase material, so that the final product is obtained free of the spurious phases that reportedly segregate at the grain boundaries when other synthetic routes are followed.

More generally, we think that the present work outlines an approach to the synthesis of large classes of chemically complex oxides. When performed by reaching powder mixtures of suitable precursors under various atmosphere and temperature conditions, these processes are difficult to rationalize. In particular, they lack the large number of guidelines, experimental tools, and, in simple words, scientific knowledge which is often available for the chemical reactions occurring in a fluid phase. For many solid-state reactions, this knowledge is provided (i) by the theoretical background of diffusion-driven solid-state reactions; (ii) by the experimental investigation of more simple and clean systems by means of chemical diffusion experiments; (iii) the thermodynamics of the pertinent system; and (iv) some general experimental tools, such as thermal, microscopic, microanalytic, and diffraction methods. In our opinion, the present work shows that this theoretical background and these experimental investigations are actually able to provide a deeper understanding of the heterogeneous reactions occurring when these complex materials are formed, and therefore are able to provide a rational way of planning and a controlled manner of completing their synthesis.

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