

An Investigation of the Transformation from $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ to $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$

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The phase stabilization of the $(\text{Bi}_{1.6+y}\text{Pb}_{0.4})\text{Sr}_{2-x}\text{Ca}_{2+x}\text{Cu}_3\text{O}_z$ system has been studied in the composition ranges $0 \leq x \leq 0.25$ and $0 \leq y \leq 0.4$ by X-ray powder diffraction, magnetic susceptibility, and electrical resistivity measurements. The transformation from $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ to $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ is a slow process and the $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ phase can be stabilized by a small excess of Bi and partial substitution of Sr by Ca. A final, nearly pure $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ phase ($T_c = 107$ K, $\Delta T_c = 6$ – 8 K) was obtained after 200 h annealing. Both X-ray analysis and magnetic susceptibility measurements appear to be excellent methods for monitoring such superconducting phases. © 1998 Academic Press

Key Words: Oxide superconductors; (Bi,Pb)–Sr–Ca–Cu–O system; X-ray diffraction; superconductivity.

1. INTRODUCTION

It is well known that, in the Bi–Sr–Ca–Cu–O system, a series of superconducting phases $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ ($n = 1, 2, 3$) with differing numbers of Cu–O layers and hence different T_c can be formed. The pure monophasic $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (2223) material with the highest T_c (~ 110 K) is very difficult to obtain. Previous research has shown that a partial Pb substitution for Bi stabilizes the (2223) phase (1–4).

Recent publications showed that variations in the Sr–Ca ratio further facilitate the formation of the (2223)-type superconductors (5–8). A few other investigations reported that an excess of Ca and Cu seems to favor the formation of the high- T_c phase (9, 10). There are great discrepancies in the literature about optimum composition and heat treatment conditions for the preparation of the (2223) phase. These discrepancies mainly due to: (a) the narrow stability range (11) of the (2223) phase and its limited formation temperature (situated just below the incongruent melting line); (b) its very slow growth rate; (c) the possible formation of a large number of impurity phases such as $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (2212), $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (2201), $(\text{Sr,Ca})_2\text{CuO}_3$, and Ca_2PbO_4 ,

whose relative amounts depend on the starting composition and heat treatment conditions; and (d) possible cationic substitution between Sr and Ca sites.

In order to complete the knowledge of the composition range of the (2223) phase, it was desirable to extend the study to nominal compositions lying beyond the pseudo-binary line $(\text{Bi}_{1.6}\text{Pb}_{0.4})\text{Sr}_2\text{CuO}_6$ – CaCuO_2 investigated in Ref (11). In this issue we report the results obtained by varying Sr–Ca ratios with a Bi excess, and also the influence of annealing time on the relative amounts of the (2223) phase. We also report also a nearly complete isolation of the 110 K phase.

2. EXPERIMENTAL CONDITIONS

2.1. Sample Preparation

Starting compounds, with a purity higher than 99% (Aldrich Company), were CaCO_3 , SrCO_3 , Bi_2O_3 , PbO , and CuO . They were mixed according to the desired composition. All products liable to become hydrated were submitted to an appropriate thermal treatment before use (long stov-ing at 160°C).

The ceramic synthesis of $(\text{Bi}_{1.6+y}\text{Pb}_{0.4})\text{Sr}_{2-x}\text{Ca}_{2+x}\text{Cu}_3\text{O}_z$ with nominal composition was performed in two steps to avoid the formation of a liquid phase due to an eutectic reaction including Bi_2O_3 and CuO near 770°C . In the first step, a precursor sample “ $\text{Sr}_{2-x}\text{Ca}_{2+x}\text{Cu}_3\text{O}_7$ ” was prepared by decarbonation at 940°C for 48 h. During the second step, the corresponding amounts of Bi_2O_3 and PbO were incorporated into the precursor. The mixture was then progressively heated (10°C/h) from 750 to 850°C , then maintained at this latter temperature for 24 h, with several intermediate grindings for accelerating the cationic diffusion. All syntheses were carried out in ambient air using alumina crucibles. The powder was then formed into 13 mm diameter pellets under 8 kbar pressure and sintered at 855°C in air.

In order to study the influence of initial composition and annealing duration, two different series of samples were prepared:

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(1) For given overstoichiometric $(\text{Bi}_{1.6+y}\text{Pb}_{0.4})\text{Sr}_{2-x}\text{Ca}_{2+x}\text{Cu}_3\text{O}_z$ with $0 \leq y \leq 0.4$, we varied the Sr/Ca content in the range $0 \leq x \leq 0.25$; and

(2) We annealed the sample at 855°C for varying durations (24, 72, and 144 h).

2.2. Characterization

The phase analysis was investigated by X-ray analysis, magnetic susceptibility, and electrical resistivity measurements. The XRD analysis employed $\text{CuK}\alpha_1$ radiation with a quartz crystal as a monochromator.

The main problem in the quantitative analysis comes from the preferred orientation that is exhibited by the plate-like crystallites of the (2212) and (2223) phases.

From previous studies it appears that the Rietveld analysis method can be an efficient method of quantitative X-ray analysis (12). A semiquantitative estimation of the volume fraction of the (2223) phase present in the sample was made by using the Q intensity factor given by the relation

$$Q = \frac{I_{002} + I_{115}}{I_{115} + I_{002} + I'_{115} + I'_{002}}, \quad [1]$$

where I_{hkl} and I'_{hkl} are respectively the hkl diffraction peak intensities of the (2223) and (2212) phases (13–15).

The magnetic susceptibility was measured by cooling a specimen in a field of 20 Oe with a SQUID magnetometer. We should mention here that the densities of the (2212) and (2223) phases are approximately equal and we suppose the powder particles to be spherical, so we can consider that the volume fractions are the same as the weight fractions.

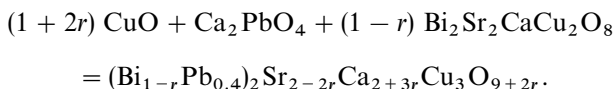
Plates of approximate dimensions $1 \times 2 \times 4 \text{ mm}^3$ were cut from the annealed samples for measurement of the temperature dependence of the electrical resistivity by a standard four probe method.

3. RESULTS AND DISCUSSION

3.1. Influence of Starting Composition

A. X-ray Diffraction Analysis

The phase analysis carried out after annealing at 855°C for 24 h revealed the (2212) and (2223) phases with a small amount of Ca_2PbO_4 phase. The latter plays both positive and negative parts in the (2223) formation (16–18). The CaO and PbO released from Ca_2PbO_4 react with (2212) and CuO to form (2223), which is rather a positive role:



However, Ca can also react with CuO to form Ca_2CuO_3 phase, which is a negative one:

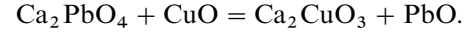


Figure 1 shows the phase analysis by comparison of (002) and (115) peaks in (2212) and (2223) phases, using Eq. [1]. Relative intensities of the (2223) phase change with the initial composition of $(\text{Bi}_{1.6+y}\text{Pb}_{0.4})\text{Sr}_{2-x}\text{Ca}_{2+x}\text{Cu}_3\text{O}_z$. For the compositions corresponding to $y = 0$ and $y = 0.4$, every peak can be assigned to that of the (2212) phase, but for $y = 0.2$ – 0.3 compositions, an additional peak ($2\theta = 4.7^\circ$) corresponds to the (2223) phase. The (2223) phase is formed most easily in samples with $(\text{Bi}_{1.8}\text{Pb}_{0.4})\text{Sr}_{2-x}\text{Ca}_{2+x}\text{Cu}_3\text{O}_z$ nominal composition, where x equals 0.1 and 0.25. This result shows that the (2223) phase is stabilized by partial substitution of Sr by Ca according to the previous studies (8). After this first study, in order to find appropriate conditions for increasing the amount of the (2223) phase, the composition in which both (2212) and (2223) phases coexisted, for example $x = 0$ – 0.1 and $y = 0.2$ – 0.3 were selected.

B. Magnetic Susceptibility

As a typical example, the temperature dependence of the magnetic susceptibility measured for ZFC (zero field cooling) and FC (field cooling) of the sample $(\text{Bi}_{1.6+y}\text{Pb}_{0.4})\text{Sr}_{2-x}\text{Ca}_{2+x}\text{Cu}_3\text{O}_z$ after annealing at 855°C for 24 h is given in Fig. 2. Clearly two transitions due to (2212) and (2223) were observed for a series of (A), (B), (C), and (D) samples corresponding respectively to $(x; y) = (0; 0.2)$, $(0; 0.3)$, $(0.1; 0.2)$ and $(0.1; 0.3)$.

We can estimate the relative volume fractions of each superconducting phase from the susceptibility signal. The ratio of the (2212) and (2223) phases estimated from the steps in the magnetic transition is found to be close to that determined from the X-ray analysis using Eq. [1].

In order to compare the magnetic susceptibility results with the results of X-ray analysis, we show XRD analysis and magnetic susceptibility data for a series of (A), (B), (C), and (D) samples (see Fig. 2). As the Sr concentration decreases, the 110 K phase becomes more dominant. These data suggest that the fraction of the present high- T_c phase is very sensitive to the Sr–Ca ratio (19). We have found that both X-ray analysis and magnetic susceptibility measurements are excellent methods for monitoring such superconducting phases.

C. Resistivity Measurements

In order to study the effect of partial substitution of Sr by Ca, the bismuth concentration was fixed at $y = 0.2$, whereas x increased from 0 to 0.25.

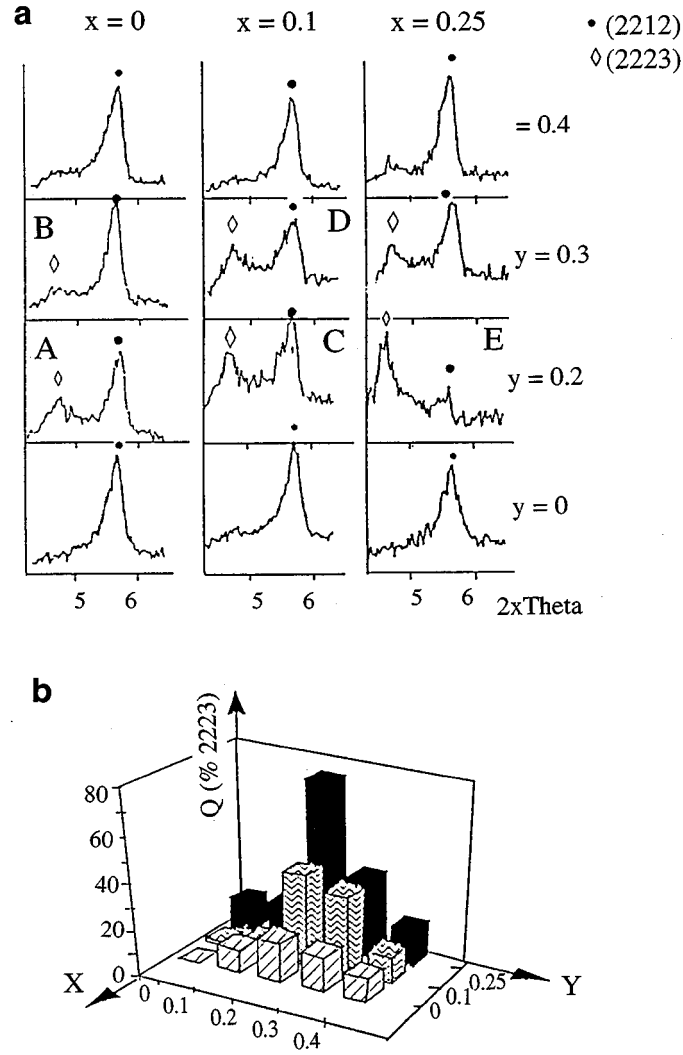


FIG. 1. (a) XRD measurements for the $(\text{Bi}_{1.6+y}\text{Pb}_{0.4})\text{Sr}_{2-x}\text{Ca}_{2+x}\text{Cu}_3\text{O}_z$ composition after annealing at 855°C for 24 h; (b) amount of the (2223) phase vs x and y .

Resistivity was measured for the annealed samples at 855°C for 24 h. In Fig. 3 some typical $R/R_m = f(T)$ curves are given for samples (A), (C), and (E), corresponding respectively to $x = 0$, 0.1, and 0.25 (resistances have been normalized by R_m , measured at 300 K). The $R-T$ plots of (A), (C), and (E) samples showed two-step superconducting transitions due to the presence of separated large grains of the (2223) phase surrounded by the (2212) phase: one with a T_c near 110 K corresponding to the (2223) phase, the other near 90 K corresponding to the (2212) phase in agreement with the X-ray analysis.

D. Structure Evolution

The observed XRD pattern of (2223) has been indexed with a tetragonal system, and cell parameters have been

calculated, as shown in Fig. 4. The a parameter is essentially constant ($a \approx 0.54$ nm), while the c/a ratio decreases monotonically with increasing x in $(\text{Bi}_{1.6+y}\text{Pb}_{0.4})\text{Sr}_{2-x}\text{Ca}_{2+x}\text{Cu}_3\text{O}_z$ for a fixed y . The decrease in c with x can be related to the decrease in the mean ionic sizes of Sr^{2+} (112 pm) and Ca^{2+} (99 pm).

The (2223) structure may be considered a sandwich sequence: a pack of three CuO_2 layers, which are separated by sheets of Ca atoms, is inserted between two $(\text{BiSrO}_2)_2$ layers, and $[\text{SrO}-\text{CuO}_2-\text{CaO}]$ constitutes a perovskite block.

The tolerance factor t , which has been used for discussing the structural stability of the cubic perovskite, is adopted here (20):

$$t = \frac{d_{A-O}}{\sqrt{2}(d_{B-O})}, \quad [2]$$

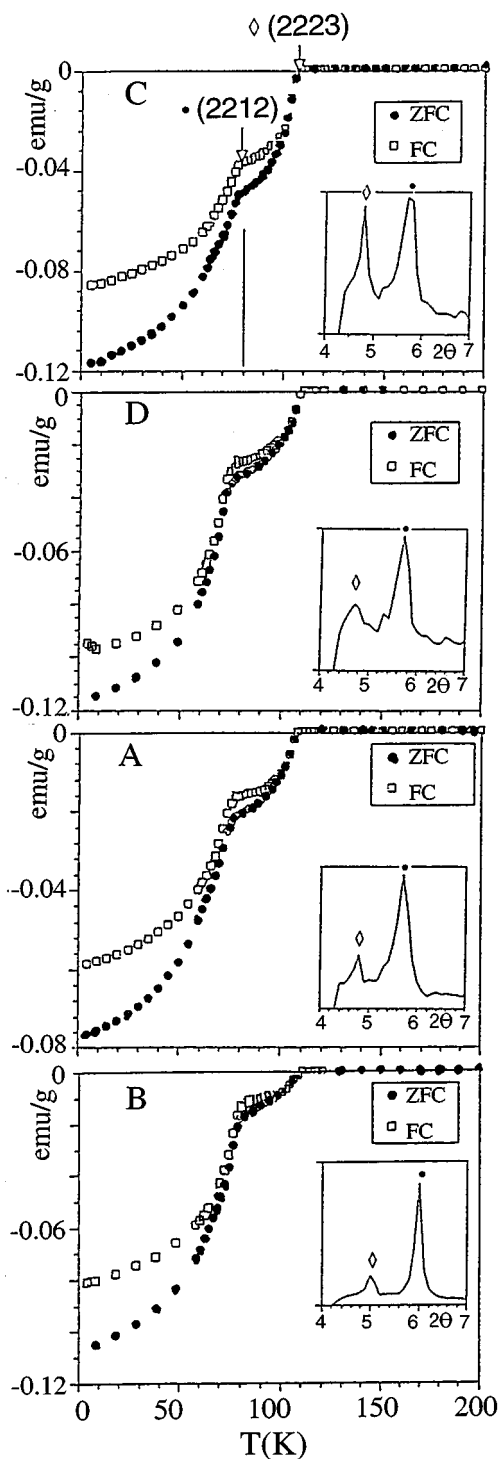


FIG. 2. Comparative XRD analysis with magnetic susceptibility for (A), (B), (C), and (D) samples.

where the bond lengths A–O and B–O are taken to be the sum of the ionic radii of cation and oxygen for the rock salt, and that of Cu and oxygen in the perovskite block, respectively, e.g., $A-O = R_{Bi}^{3+} + R_O^{2-}$ and $B-O = R_{Cu}^{2+} + R_O^{2-}$ for

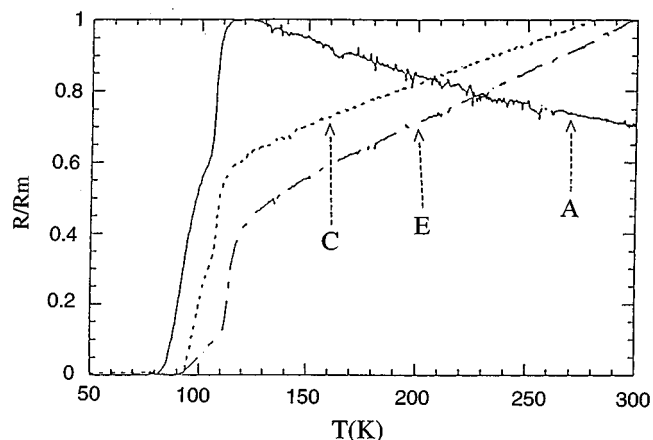


FIG. 3. Resistivity vs temperature of (A), (B), and (E) samples after annealing at 855°C for 24 h (Resistance has been normalized by R_m , measured at 300 K).

the Bi compounds. For a cubic perovskite the structure is stable only if $0.8 < t < 0.9$.

From Eq. [2] it can be seen that, in order to raise the tolerance factor for stabilizing the structure of a perovskite cuprate, two factors can be considered. One is the increase of the effective A–O bond length. The other factor is the decrease in the Cu–O bond length. In this study a partial substitution of Sr by Ca induces a c parameter and Cu–O bond length decrease. As a consequence, the tolerance factor t increases and enhances the thermodynamic stability of the (2223) phase.

Toledano *et al.* (8) supposed that the structure (2223) is stabilized by the mutual mechanical coupling of $CaCuO_2$, which is in a “compressed” state, and $BiO-SrO$, which is in a “stretched” state.

3.2. Influence of Annealing Duration

A. X-ray Investigation

The (2223) phase preparation requires a long annealing time. Here, the influence of the annealing time is investigated

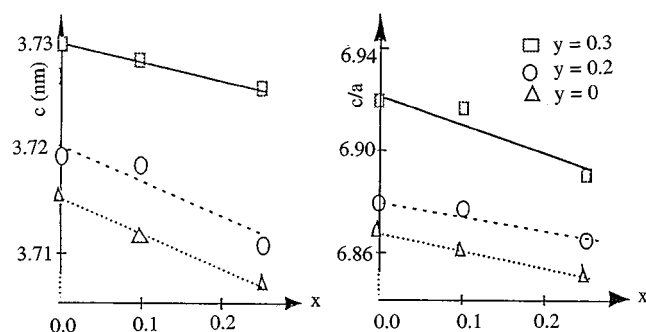


FIG. 4. Variation of c parameter and c/a ratio with x and y for the $(Bi_{1.6+y}Pb_{0.4})Sr_{2-x}Ca_{2+x}Cu_3O_z$ nominal composition.

by X-ray diffraction. Figure 5a shows the (002) peaks in the (2212) and (2223) phases ($4^\circ \leq 2\theta \leq 6^\circ$) for (A), (C), and (E) samples. The peak at $2\theta = 4.7^\circ$ corresponding to the (2223) phase was found to grow in intensity only after a long period of sintering. With long sintering periods the high- T_c phase may be formed from the low- T_c one by atomic rearrangement:

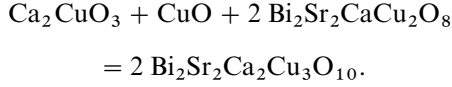


Figure 5b presents the variation of the amount of the (2223) phase (Q) as a function of the reaction time. The

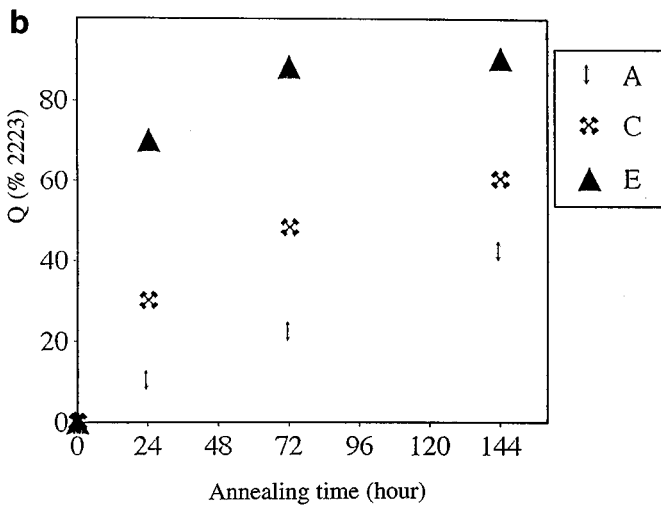
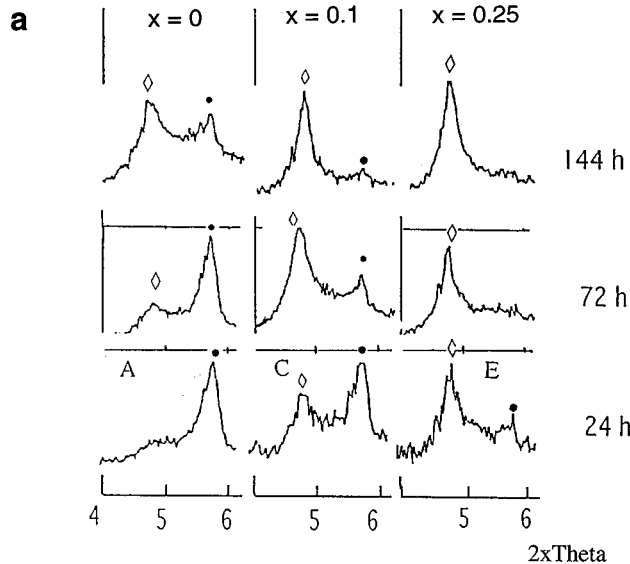


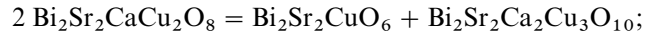
FIG. 5. (a) X-ray diffraction of the $(\text{Bi}_{1.8}\text{Pb}_{0.4})\text{Sr}_{2-x}\text{Ca}_{2+x}\text{Cu}_3\text{O}_z$ sample; (b) dependence of the amount of the $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_z$ phase on the annealing time (A, C, and E samples).

fraction of the (2223) phase increases with sintering time. The influence of the starting composition on the growth of the (2223) phase seems obvious from the comparison of the time dependence for the series (A), (C), and (E), respectively.

Figure 5b shows that the transformation of (2212) into (2223) is almost a slow, monotonous process for (A) and (C) compositions. But for the (E) sample, the Q percentage of (2223) follows the relation $Q_{(t)} = Q_{\infty}(1 - e^{-Kt})$ (12), where t represents the annealing duration in hours, $Q_{\infty} = 0.9$ is the percentage of (2223) after infinite time, and K is a coefficient, in this case 0.06 h^{-1} . This relation is characteristic of a first order reaction. It soon becomes obvious that the percentage of the (2223) phase increases with the annealing time and reaches an upper limit of 90% in the (E) sample. This result proves that the partial substitution of Sr by Ca makes (2223) phase growth easier (5, 6, 8).

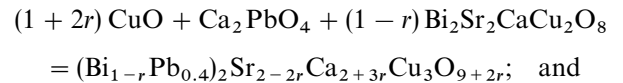
The synthesis of a pure (2223) phase requires a long annealing time ($> 144 \text{ h}$) and great difficulty to keep the $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_z$ starting composition. The (2223) formation could consequently be explained, not by a unique mechanism, but more probably by several mechanisms, which would coexist and be in competition with each other:

(a) the decomposition reaction of the (2212) phase to form the (2223) and (2201) phases (21):

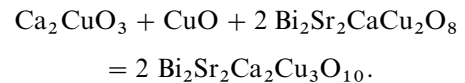


(b) the intergrowth process starting on the surface of the original (2212) phase grains accompanied by the migration of the respective high angle grain boundaries (13);

(c) the interaction between (2212), CuO, and CaO produced during the decomposition of Ca_2PbO_4 (22):



(d) the insertion of the CuO_2/Ca bilayers into the $\text{CuO}_2/\text{Ca}/\text{CuO}_2$ blocks of (2212) (23, 24):



The X-ray diffraction intensity for the Ca_2PbO_4 phase decreases with increasing sintering time and the simultaneous growth of the (2223) phase. This result suggests that the high- T_c phase may be formed by reaction of the low- T_c phase with calcium oxide produced during the decomposition of Ca_2PbO_4 (25).

B. Resistivity Measurements

Typical resistance vs temperature is shown in Fig. 6 for the (A), (C), and (E) samples after annealing at 855°C

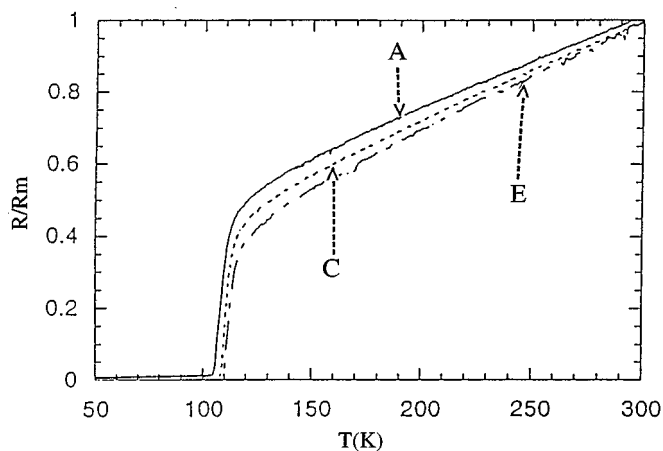


FIG. 6. Resistivity vs temperature of (A), (B), and (E) samples after annealing at 855°C for 144 h (Resistance has been normalized by R_m , measured at 300 K).

for 144 h. The resistivity begins to decrease slowly at about 120 K and shows a sharp drop corresponding to the (2223) phase. A zero resistivity was observed at 104–108 K with ΔT_c equal to 4–8 K.

Quantitative analysis from resistance vs temperature modeling for the (2223) superconducting phase based on percolation calculations shows that the (2223) amount is lower than 30% (26).

In our case, a single-step superconducting transition is observed, and two cases are possible:

(1) mutual contact among relatively fine grains of the (2223) phase is preserved and percolation is achieved at higher temperatures (26); and

(2) the core of the (2212) phase grains is screened by a “shell” formed by the (2223) phase (27). The real ratio of the coexisting (2223) phase can be observed by X-ray analysis and magnetic measurements, but is undetectable by resistivity measurements when the amount of (2223) is higher than percolation threshold.

3.3. Isolation of the (2223) Phase

For all samples, long annealing treatment at 855°C in air is necessary to recover good superconducting properties. Figure 7a illustrates the magnetization measurements for the (2223) phase corresponding to (E) composition after annealing at 855°C for 200 h. The measurement was made in a field of 20 Oe, ZFC and FC. The critical temperature is determined at the temperature below which Meissner signal appears. The $M-T$ plot shows a one-step superconducting transition corresponding to the (2223) phase. The critical temperature is close to 107 K with $\Delta T_c = 6-8$ K, consistent with the X-ray analysis (see Fig. 7b), confirming the quality and the purity of the high critical temperature supercon-

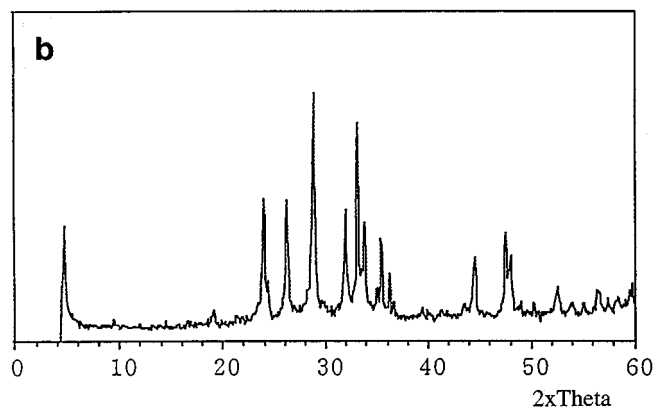
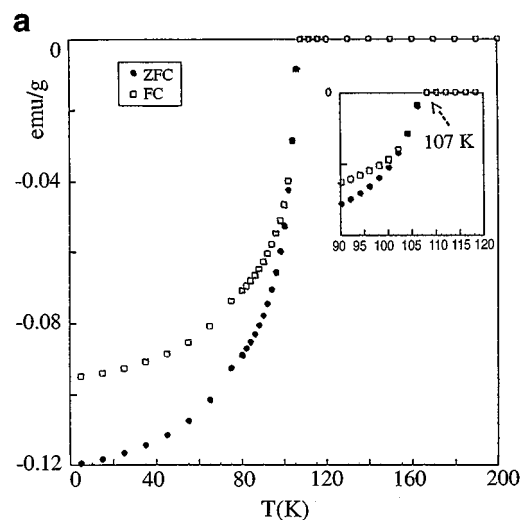


FIG. 7. (a) Susceptibility measurements with a SQUID, zero field cooled (circle symbols) and field cooled (square symbols); (b) XRD measurements for $(\text{Bi}_{1.8}\text{Pb}_{0.4})\text{Sr}_{1.75}\text{Ca}_{2.25}\text{Cu}_3\text{O}_z$ after annealing at 855°C for 200 h.

ducting phase. As can be seen, the (2223) single phase ceramic was obtained for the (E) sample. However, long annealing is necessary to obtain the pure single phase.

4. CONCLUSION

We have studied the influence of initial composition and annealing duration on the stability of the (2223) phase by X-ray analysis, magnetic susceptibility, and resistivity measurements. We found that the transformation from (2212) to (2223) is a slow process and is accelerated by a partial substitution of Sr^{2+} by Ca^{2+} and a small excess of Bi^{3+} . Pure $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ phase ($T_c = 107$ K, $\Delta T_c = 6-8$ K) can be obtained after 200 h annealing for a sample with composition $(\text{Bi}_{1.8}\text{Pb}_{0.4})\text{Sr}_{1.75}\text{Ca}_{2.25}\text{Cu}_3\text{O}_z$. We have found that both X-ray analysis and magnetic susceptibility measurement are excellent methods for monitoring such superconducting phases.

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