

High-Density Superconducting Ceramics in the Bi-Sr-Ca-Cu-O System, II

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In our earlier work, we successfully prepared a high-density, single phase of 85 K superconductor in the Bi-Sr-Ca-Cu-O system by properly annealing an amorphous precursor obtained by quenching from melts. Utilizing the same technique here, we try to prepare a high-density, single phase 110 K superconductor in similar systems. We have succeeded in preparing materials with the zero resistance temperature ($T_{c,0}$) as high as 99 K in the system $(\text{Bi}_{0.8}\text{Pb}_{0.2})\text{-Sr-Ca-Cu-O}$ with the molar ratios 1:1:1:2 and 2:2:2:3. Measurements of the Meissner effect indicate, however, that the materials obtained consist of two phases, 85 K and 110 K phases, and the volume of the 85 K phase amounts to 50 to 80%. Transmission electron microscopy indicated the possibility, however, that the high-temperature phase was structurally indistinguishable from that of the low-temperature phase. © 1989 Academic Press, Inc.

In a previous paper, we reported that quenching of Bi-Sr-Ca-Cu oxides from melts was found to produce a more or less amorphous material with high density (1). If such quenched material is then annealed at a temperature below the melting point, a specific structure characteristic of that annealing temperature is expected to nucleate, and, hence, the production of high-density, single-phase materials would be possible at certain specific compositions (1). In the Bi-Sr-Ca-Cu-O system, several superconducting phases with T_c up to 120 K are reported in sintered materials (2-6). However, it is also known that materials obtained by sintering inevitably include several phases and also that it is difficult to obtain high densification by sintering. The work is motivated thus to prepare high-den-

sity, single-phase superconducting materials without going through sintering processes.

In our previous paper (1), we reported the preparation of a high-density Bi-Sr-Ca-Cu-O ceramic with a single superconducting phase with T_c approximately 85 K. By using lower annealing temperatures with the same precursors, in addition to the 85 K phase, a second phase with $T_c \sim 55$ K appears. This 55 K phase has a cubic symmetry and has a distinctly different structure from the 85 K phase but its structure has not been identified yet. Previous workers have reported efforts to obtain a single superconducting phase with T_c around 110 K in sintered ceramics. Here we report our efforts to do the same but by using the high-density materials obtained by quenching

TABLE I
SUMMARIES OF DATA ON THE 2212 COMPOUNDS
($\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$)

Sample	Heat treatment ^a	$T_{c,\text{onset}}$ (K)	$T_{c,0}$ (K)
1	820°C in O ₂ , 8 hr, fc	86	72
2	820°C in O ₂ , 16 hr, fc	86	73
3	850°C in O ₂ , 8 hr, fc	86	76
4	850°C in O ₂ , 19 hr, fc	86	53
5	875°C in O ₂ , 8 hr, fc	87	67
6	500°C in O ₂ , 72 hr, fc	66	39

^a fc, furnace cooling.

from the melt. Since our previous paper was published (1), several papers have appeared which also deal with melt-quenching of the Bi-Sr-Ca-Cu-O system for similar purposes to ours (8-11).

The 85 K phase was prepared from a material with a nominal composition Ba : Sr : Ca : Cu equal to 2 : 2 : 1 : 2. Let us call such

a material 2212 compound for brevity. The structure of the 85 K phase has been identified and is known to have the chemical formula $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$. In this case, it was found that only the 85 K phase nucleated by heat treatment at relatively high temperatures in O₂ (1), while a superconducting phase with $T_c \sim 55$ K was found to form by heat treatment at low temperatures in O₂ ($\sim 500^\circ\text{C}$ for 3 days) (see Table I and Fig. 1) (7). Zandbergen *et al.* (6) identified the structure of a third phase with $T_c \sim 110$ K in a sintered material by means of high-resolution electron microscopy to be isomorphous with $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ (12). This compound belongs to the same group of modulated structures as the 2212 compound, but with one more Cu-O layer in a structural unit than the 2212 compound and with the composition 2223. On the other

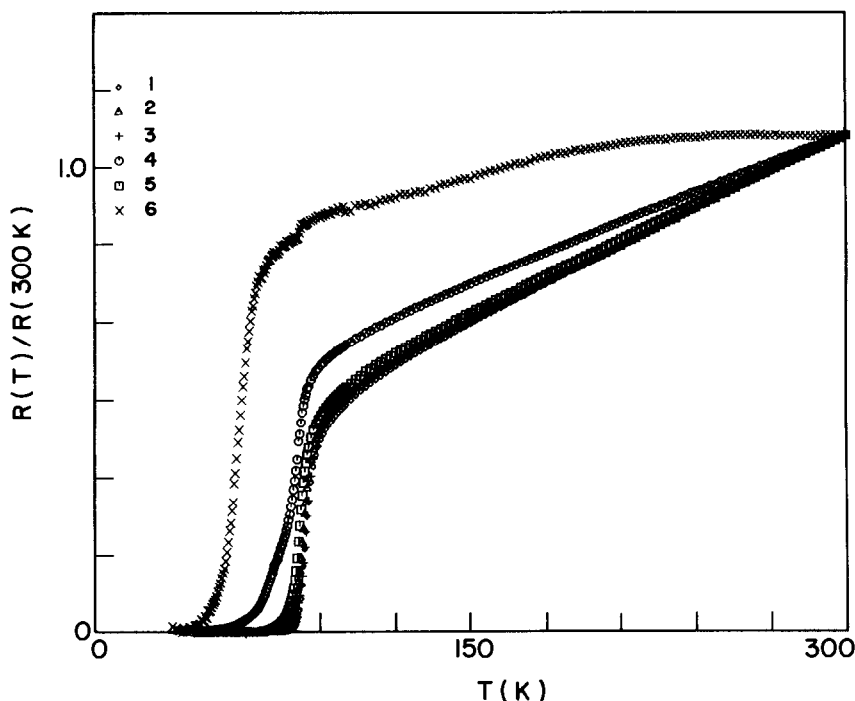


FIG. 1. Resistivity vs temperature for some of the differently treated specimens of 2212 compound ($\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$) (see Table I).

hand, in sintered materials, the 110 K phase was most commonly found in materials with composition 1112. In this connection, we investigated materials with the compositions of 2223 and 1112 in the search for the 110 K phase from the amorphous precursors in the Bi–Sr–Ca–Cu–O system.

The method of preparation of specimens is the same as that reported earlier (1). Mixtures of Bi_2O_3 (99.9%), SrCO_3 (99.999%), CaCO_3 (99.999%), and CuO (99.9%) with molar ratios of 2:2:1:2, 1:1:1:2, and 2:2:2:3, respectively, are used as starting materials. In order to ensure the proper composition and homogeneity of the melt, prereacted and well heat-treated powders of right compositions were prepared for melting as described earlier (1). These powders were molten in a platinum crucible at 1000°C for $\frac{1}{2}$ hr and were then poured onto a heavy copper sheet and pressed by another copper sheet. This process produces high-density, somewhat ductile, homogeneous materials which are primarily amorphous but also partially crystalline (1). The fraction of amorphous material depends on the composition and the 2223 compound seems to be most ductile upon quenching.

The melt-quenched specimens were then heat treated at various temperatures for various lengths of time, mostly in O_2 atmosphere, with the hope of nucleating single superconducting phases of desired structures. Resistivity–temperature curves and X-ray powder patterns of these specimens were then taken for characterization. Mea-

TABLE II
SUMMARIES OF DATA ON THE 1112 COMPOUNDS
($\text{BiSrCaCu}_2\text{O}_y$)

Sample	Heat treatment	$T_{c,\text{onset}}$ (K)	$T_{c,0}$ (K)
1	860°C in O_2 , 6 hr, aq ^a	85	67
2	875°C in O_2 , 4 hr, aq	85	43
3	880°C in O_2 , 12 hr, aq	85	35

^a aq, quenching in air.

TABLE III
SUMMARIES OF DATA ON THE 2223 COMPOUNDS
($\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_z$)

Sample	Heat treatment	$T_{c,\text{onset}}$ (K)	$T_{c,0}$ (K)
1	860°C in O_2 , 6 hr, aq ^a	92	76
2	875°C in O_2 , 4 hr, aq	91	71
3	880°C in O_2 , 12 hr, aq	92	75

^a aq, quenching in air.

surements of the temperature dependence of the Meissner effect (cooled in an applied field of 50 Oe) and the critical current density based on magnetic measurements (Bean's Method) were also made on some of the specimens. Each heat treatment represents a separate specimen. Because the search for 110 K phase is the major objective of this paper, approximate results, mainly based on the resistivity–temperature curves, depending on types of heat treatment, are tabulated in Tables I, II, and III.

Tables I, II, and III concern the 2212, 1112, and 2223 compounds, respectively. Here, $T_{c,\text{onset}}$ indicates the temperature at which the resistivity curve shows a downward trend as commonly utilized but without any other physical basis. The agreement with those determined by the Meissner effect, where applicable, is generally good. On the other hand, the temperature where the resistivity of the specimen reaches zero is indicated by $T_{c,0}$. The value of $T_{c,0}$ is found to depend, to a large extent, on the degree of structural development. The value of $T_{c,0}$ is found to depend far more sensitively on the annealing treatment than $T_{c,\text{onset}}$ and it is rather difficult to relate the degree of structural development and the location of $T_{c,0}$. This variation is also due to the fact that each specimen is prepared from different precursors. Due to a slight variation of quenching condition, properties such as the crystallinity of precursors can be somewhat different.

In Table I, properties of the 2212 compound are summarized and some of the resistivity-temperature curves are shown in Fig. 1. Samples 1 and 2 in Table I result from annealing the precursor at 820°C in O₂ atmosphere for 8 and 16 hr, respectively, and the results have been presented in our previous paper (1). The value of $T_{c,onset}$ in these cases was determined by the measurement of the Meissner effect to be ~85 K. The powder patterns indicate that the structure is typical of that of the 2212 compound (1). On the other hand, annealing at 850°C in O₂ atmosphere for 19 hr produces a $T_{c,0}$ of 53 K (Sample 4) which is far lower than 76 K (Sample 3) obtained by annealing for a shorter time (8 hr) although $T_{c,onset}$ is practically the same. No appreciable difference between the X-ray powder patterns of these two specimens is observed. By an-

nealing at 500°C in O₂, the structure observed in the as-quenched specimen (7) was found to be enhanced based on X-ray powder patterns. This sample was superconducting with $T_{c,onset} = 66$ K and $T_{c,0} = 39$ K. The structure of this phase has not been analyzed yet, but seems to have a cubic symmetry with $a \approx 0.840$ nm (7).

In Tables II and III, characteristics of specimens with compositions 1112 and 2223 obtained from amorphous precursors are shown. Resistivity-temperature curves of corresponding specimens are shown in Figs. 2 and 3. Based on information in Refs. (3-6) which report the existence of 110 K phase in sintered specimens, annealing temperatures of 860 to 880°C were selected to obtain the 110 K phase and annealing at lower temperatures was not tried. Although $T_{c,onset}$ was found to be somewhat higher es-

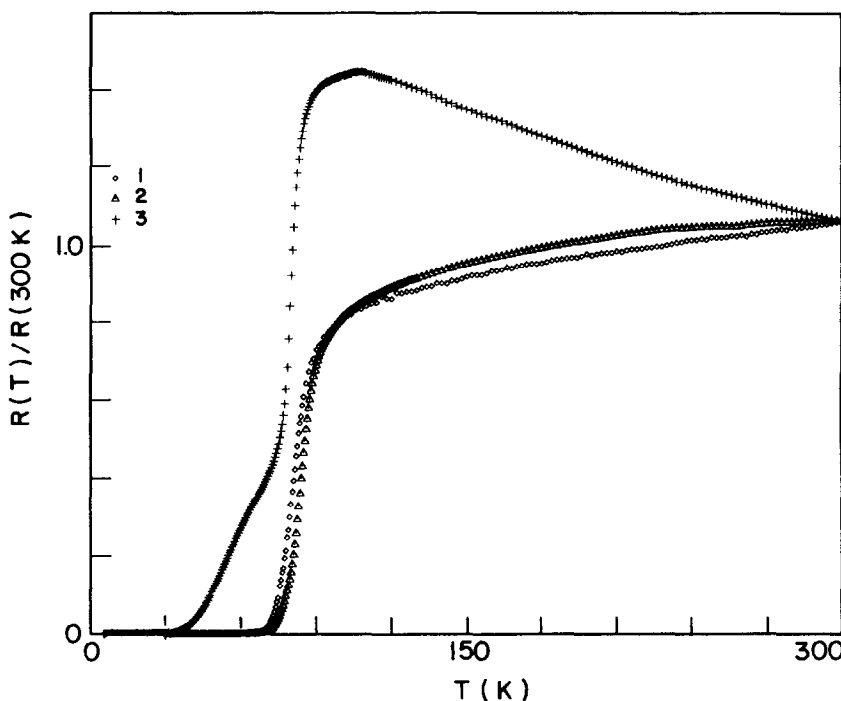


FIG. 2. Resistivity vs temperature for some of the differently treated specimens of 1112 compound (BiSrCaCu₂O₇) (see Table II).

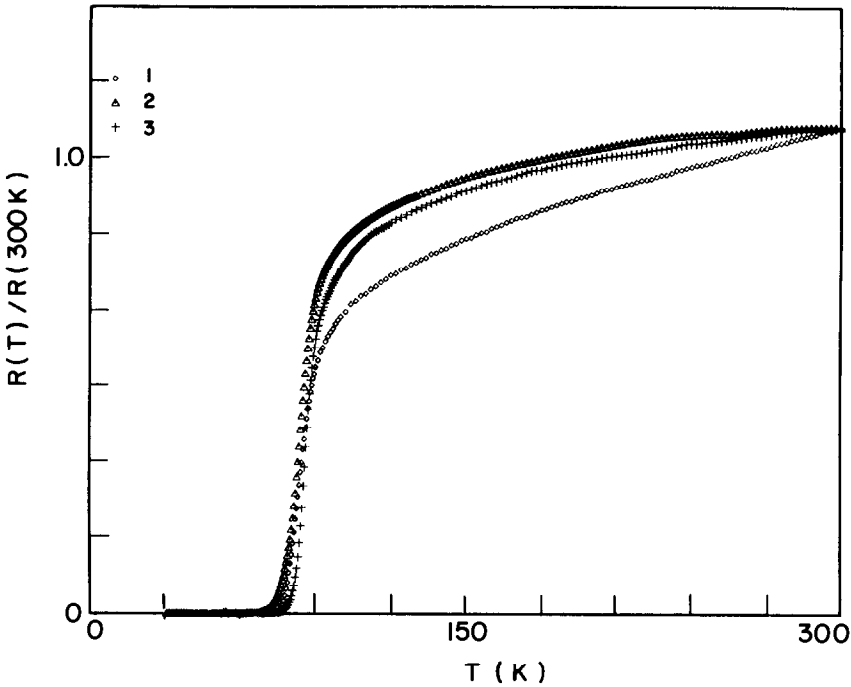


FIG. 3. Resistivity vs temperature for some of the differently treated specimens of 2223 compound ($\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_z$) (see Table III).

pecially in the 2223 compound than in the 2212 compound which might indicate the existence of a small amount of the 110 K phase, $T_{c,0}$ was found to be below 80 K for all of these treatments. In addition, annealing temperatures of 880°C for these specimens were found to be definitely too high. In these cases, the temperature coefficient of the resistivity above $T_{c,\text{onset}}$ for these specimens becomes negative (Sample 3 in Table II), as in the case of as-quenched specimens, and this may indicate a partial melting of specimens during annealing. In addition, the values of $T_{c,0}$ for these specimens are relatively low, indicating a low degree of structural development. In any case, in 2212, 1112, and 2223 specimens obtained from amorphous precursors, the existence of a substantial amount of the 110 K phase was not detected by the use of high annealing temperatures.

More recently, the existence of a substantial proportion of the 110 K phase in a specimen of partially lead-substituted 2223 compound was reported (13). Therefore, we also turned our attention to this system. Melt-quenched specimens of $(\text{Bi}_{0.8}\text{Pb}_{0.2})\text{SrCaCu}_2\text{O}_y$ and $(\text{Bi}_{0.8}\text{Pb}_{0.2})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_z$, were prepared exactly the same way as that for specimens with no Pb. Amorphous precursors including lead were found to be more brittle. In Fig. 4, X-ray ($\text{CuK}\alpha$) powder diffraction pattern of a melt-quenched specimen of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ is shown. While this shows a typical amorphous pattern as expected, electron micrographs indicated that a small fraction of crystalline substance is present, and also shows a marked contrast to that of a melt-quenched specimen of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (refer to Fig. 1 in Ref. (1)). However, a detailed characterization of the crystallinity

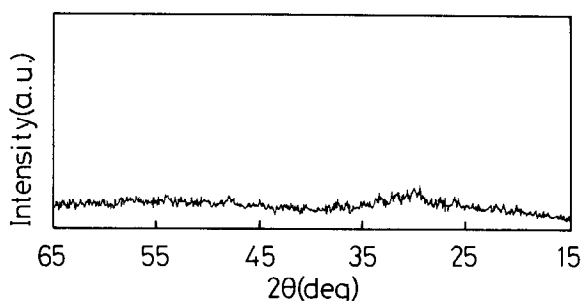


FIG. 4. X-ray ($\text{CuK}\alpha$) powder pattern for an as-quenched specimen of Pb-substituted 2223 compound ($\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$).

was not attempted. A resistivity-temperature curve of this melt-quenched specimen showed, just as in the case of unannealed $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$, the resistivity has a negative temperature coefficient (refer to Fig. 3, in Ref. (1)) as is common in amorphous materials. Superconducting behavior of these materials which depends on heat treatment is summarized in Table IV and V, respectively. Corresponding resistivity-temperature curves are summarized in Figs. 5 and 6, respectively. Again, temperatures near the melting point were selected as annealing temperatures and annealing at lower

temperatures was not yet tried. In these cases, annealing at or above 850°C produces specimens with negative temperature coefficient of resistivity above $T_{c,\text{onset}}$ (Sample 7 in Table IV and in Fig. 5).

Lead-substituted materials definitely yield a larger amount of the 110 K phase than their nonsubstituted counterparts (14). High-density materials which show $T_{c,0}$ very close to 100 K were found in both the 1112- and the 2223-type compounds. In Fig. 7, the resistivity-temperature curve and the Meissner effect of a 1112-type material heat treated in O_2 at 830°C for 15 hr and

TABLE IV
SUMMARIES OF DATA ON THE Pb-SUBSTITUTED 1112
COMPOUND ($\text{Bi}_{0.8}\text{Pb}_{0.2}\text{SrCaCu}_2\text{O}_y$)

Sample	Heat treatment	$T_{c,\text{onset}}$ (K)	$T_{c,0}$ (K)
1	830°C in O_2 , 6 hr, aq ^a	85	42
2	830°C in O_2 , 6 hr, 830°C in air, 38 hr, aq	109	72
3	830°C in O_2 , 15 hr, 840°C in air, 96 hr, aq	105	96
4	840°C in air, 48 hr, aq	105	75
5	840°C in air, 72 hr, 850°C in air, 24 hr, aq	105	72
6	830°C in O_2 , $15\frac{1}{2}$ hr, 840°C in air, 156 hr, aq	105	88
7	840°C in air, 72 hr, 850°C in air, 72 hr, aq	85	72
8	830°C in O_2 , 48 hr, aq	87	57
9	830°C in O_2 , 96 hr, aq	86	64
10	840°C in O_2 , 96 hr, aq	87	68

^a aq, quenching in air.

TABLE V
SUMMARIES OF DATA ON THE Pb-SUBSTITUTED 2223
COMPOUND ($\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_z$)

Sample	Heat treatment	$T_{c,\text{onset}}$ (K)	$T_{c,0}$ (K)
1	830°C in O_2 , 6 hr, 830°C in air, 38 hr, aq ^a	85	72
2	830°C in O_2 , 15 hr, 840°C in air, 96 hr, aq	105	80
3	830°C in O_2 , $15\frac{1}{2}$ hr, 840°C in air, 156 hr, aq	109	99
4	840°C in air, 144 hr, aq	105	87
5	840°C in air, 144 hr, fc ^b	108	70
6	860°C in O_2 , 6 hr, aq	85	68
7	840°C in air, 48 hr, aq	104	78
8	840°C in air, 48 hr, fc	74	68
9	840°C in air, 96 hr, aq	106	82
10	840°C in O_2 , 96 hr, aq	84	73
11	830°C in O_2 , 48 hr, aq	92	70
12	830°C in O_2 , 96 hr, aq	93	77

^a aq, quenching in air.

^b fc, furnace cooling.

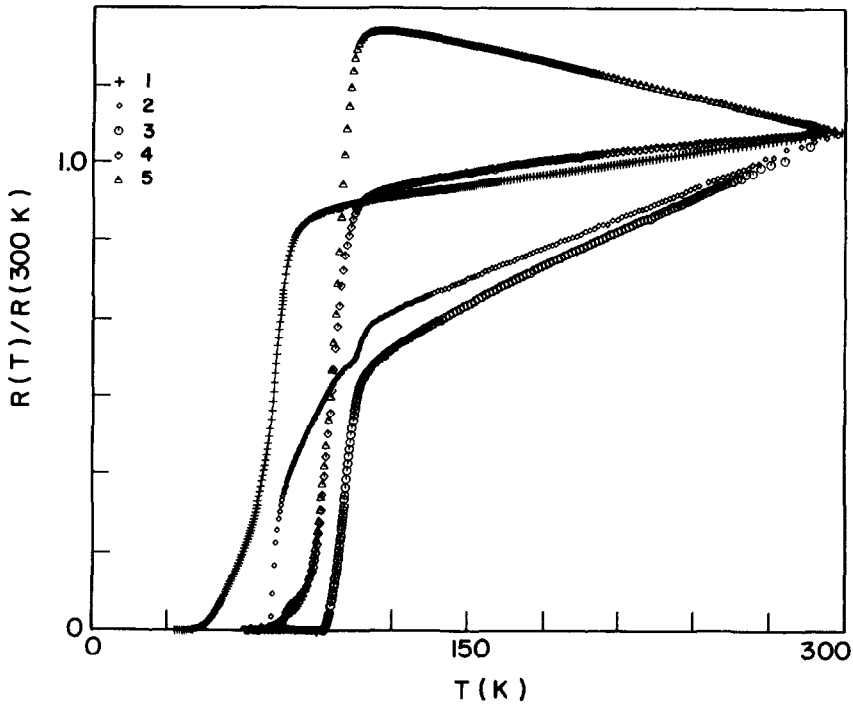


FIG. 5. Resistivity vs temperature for some of the differently treated specimens of Pb-substituted 1112 compound ($\text{Bi}_{0.8}\text{Pb}_{0.2}\text{SrCaCu}_2\text{O}_y$) (see Table IV).

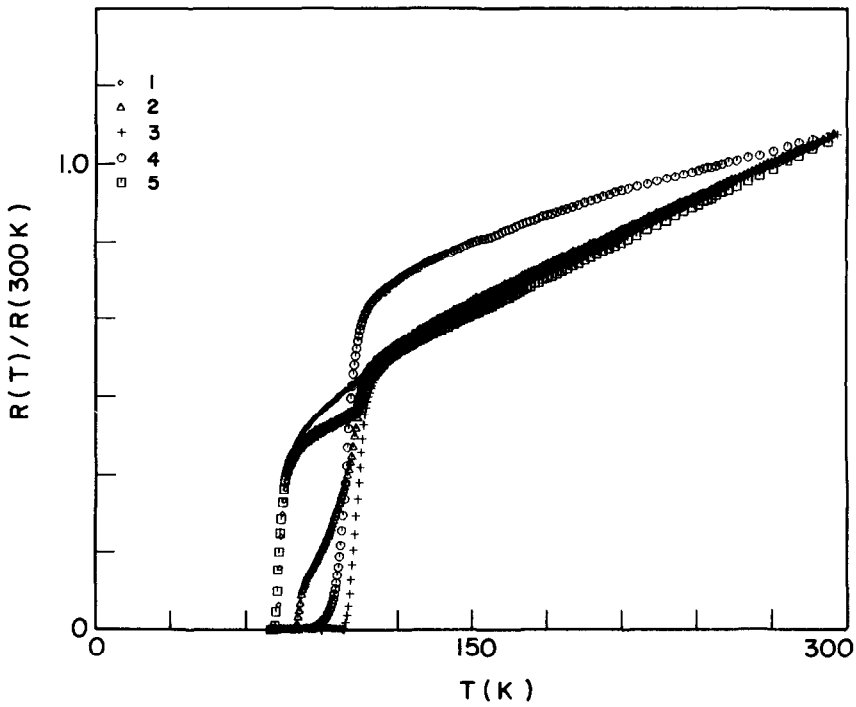


FIG. 6. Resistivity vs temperature for some of the differently treated specimens of Pb-substituted 2223 compound ($\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_z$) (see Table V).

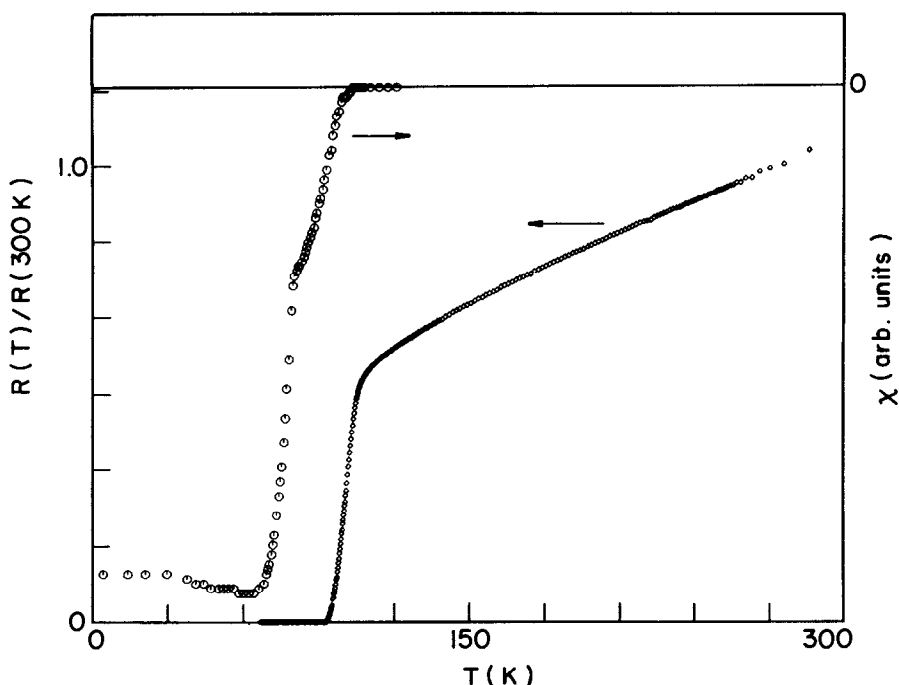


FIG. 7. Temperature dependence of the resistivity and the Meissner effect of specimen No. 3 of Pb-substituted 1112 compound (see Table IV).

then in air at 840°C for 96 hr and quenched in air are shown (specimen No. 3 in Table IV). In Fig. 8, those properties of a 2223-type material similarly treated (Sample 3 in Table V) are shown. The $R-T$ curves of these two specimens are practically identical; $T_{c, \text{onset}}$ is around 105 K for both specimens while the values of $T_{c,0}$ are 96 K and 99 K, respectively. Similar to materials with no lead, sample characteristics, especially the values of $T_{c,0}$, are sensitive to heat treatment. For example, heat treatment in air for a certain amount of time rather than in O_2 was found to give better results (see Table V, Samples 9 and 10). This is consistent with the report that greatly improved yields of the 110 K phase have been obtained in bulk samples under a reduced partial pressure of oxygen (15). Also, quenching from the heat treatment temperature to room temperature in air was

found to give higher values of $T_{c,0}$ than furnace cooling. The measurement of the Meissner effect of the above two specimens shown in Figs. 7 and 8, however, reveals that the lead-containing samples are not single-phase materials as expected, but consist of both the 110 K phase and the 85 K phase similar to those differently treated specimens reported by other groups (13, 14). Based on the measurement of the Meissner effect, the amount of the 110 K phase is $\sim 40\%$ in the 1112 compound and $\sim 20\%$ in the 2223-type compound, respectively. In other words, the percolation effect is complete at the amount as low as 20% in the 2223-type compound. The measurement of the critical current density of the specimen shown in Fig. 8 at 4.2 K yields a value of $\sim 6000 \text{ A/cm}^2$. On the other hand, the measurement of the density of Sample 3 in Table V gives the value of 6.42 g/cm^3 ,

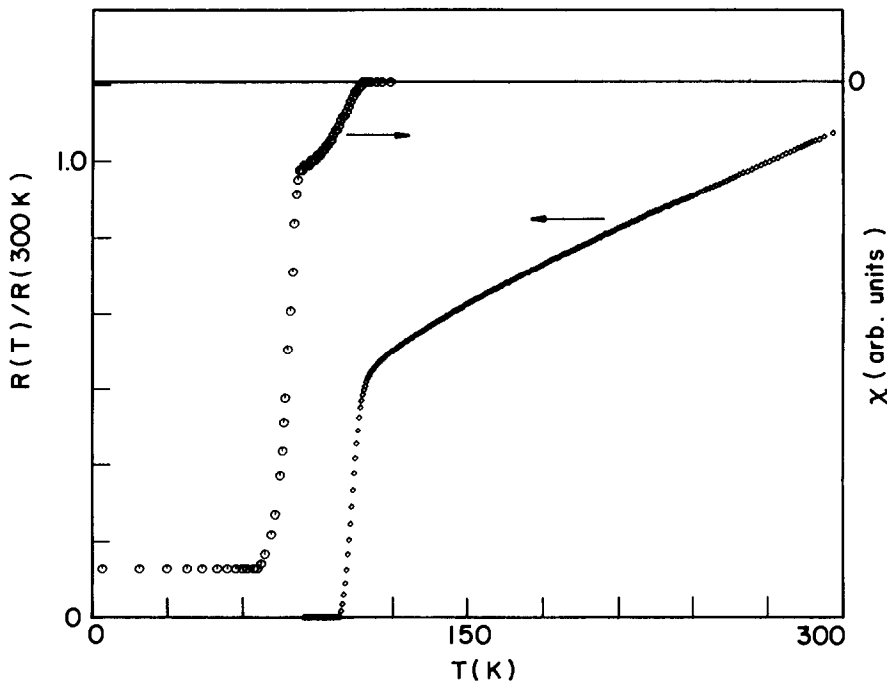


FIG. 8. Temperature dependence of the resistivity and the Meissner effect of specimen No. 3 of Pb-substituted 2223 compound (see Table V).

indicating that the specimen is practically of 100% theoretical density. The theoretical densities of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$ and $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ are estimated to be 6.25 and 6.51 g/cm³, respectively, based on the lattice constants $a = 0.5418$ nm, $b = 0.5414$ nm, and $c = 3.06$ nm and 3.71 nm, respectively (16).

Among various phases found in sintered materials, the existence of a series of homologous compounds $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$ with $n = 1, 2,$ and 3 has been proposed and associated with $T_c = 20, 85,$ and 110 K, respectively (16). A series of these structure shows common characteristics with respect to their intergrowth behavior (microsyntactic intergrowth) (17–19) to other series of long period compounds such as β -alumina (17), SiC (18), and $\text{V}_n\text{O}_{2n-1}$ (19, 20) which have been extensively investigated. This feature of intergrowth would thus play

a significant role in interpreting various properties of these superconducting compounds.

In Fig. 9, a high-resolution electron micrograph taken perpendicular to the c -axis (along the [110] direction) of a Pb-substituted 2223 compound cited in Fig. 7 is shown. According to the measurement of the Meissner effect, the amount of the 110 K phase should be around 20%, embedded in the 85 K phase. This picture, however, shows mostly a regular array of stripes of ~ 1.53 nm which are supposed to correspond to the structure of the 85 K ($n = 2$) phase (the length of the c -axis is 30.6 Å) with the nominal composition corresponding to 2212. Only occasionally, we observe stripes of the width of 1.88 nm which is half of the unit cell of that attributed to the 110 K phase (the length of the c -axis is 3.76 nm) with the nominal composition correspond-

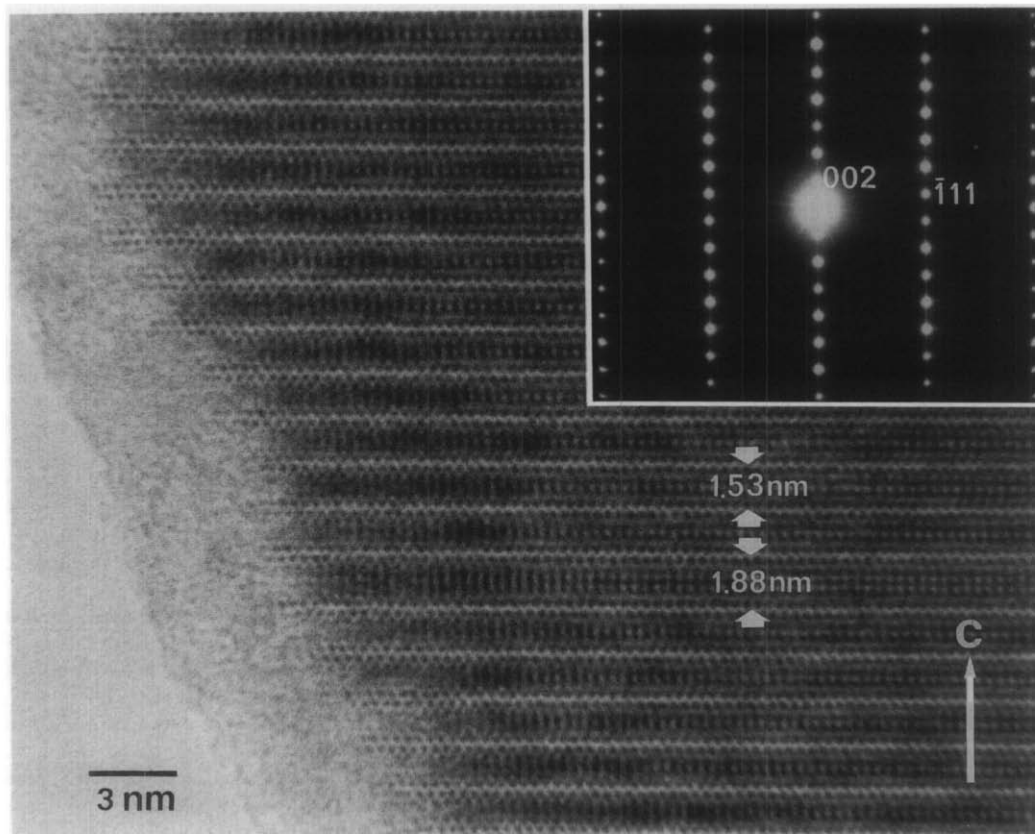


FIG. 9. Electron micrograph of specimen No. 3 with the incident beam perpendicular to the c -axis of the crystal. This shows the formation of the 2212 phase (the 85 K phase) with the stripe width 3.18 nm.

ing to 2223 ($n = 3$) (15). Observation of other parts of the specimen gives more or less the same pattern. In other words, the proportion of the 110 K ($n = 3$) phase judged by the stripe widths is far less than that expected from the measurement of the Meissner effect or the resistivity. It is naturally hard to assess the proportion of the $n = 3$ phase as a whole from these types of micrographs which only represent local situations. However, it is also certain that in observed portions, at least, the formation of the $n = 2$ phase is predominant. Because it is difficult to visualize the formation of the $n = 2$ phase of such a large amount as being due to the local concentration fluctuation toward $(\text{Bi}_{0.8}\text{Pb}_{0.2})_2\text{Sr}_2\text{CaCu}_2\text{O}_y$, it is

plausible that the $n = 2$ structure can accommodate off stoichiometric composition with a higher Cu content. If so, the change of T_c with composition of Cu can be expected for the same apparent structure. This possibility is now being investigated (21). These structures are also found to be modulated in the b -direction with modulation period close to $5b$ (incommensurate modulation). The details of this type of modulation will be reported elsewhere.

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