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Increased percolation threshold for 100-K superconductivity in lead-substituted Bi-Sr-Ca-Cu-O thin films

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In lead-substituted Bi-Sr-Ca-Cu-O thin films (<1 μm thickness), containing the (2:2:1:2) and the (2:2:2:3) phases in variable proportions, we observe that zero resistance above 100 K is obtained only if the proportion of the (2:2:2:3) phase exceeds ~50%. This result contrasts with the situation found in the lead-free thin films, for which zero resistance above 100 K can be achieved with the (2:2:2:3) phase constituting less than 10% of the sample. This difference is explained on the basis of modifications induced by lead substitution in the structures and in the intergrowth of the considered phases, which determine a two-dimensional type of percolation for the conductivity of the Pb-substituted thin films, while the other system can be associated with a three-dimensional type of percolation, having a much lower threshold.

The family of superconducting compounds with the generic formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ has two prominent members labeled (2:2:1:2) ($n=2$) and (2:2:2:3) ($n=3$) which have critical temperatures equal to ~80, and ~110 K, respectively, and often coexist in the prepared samples. Extensive research has been motivated by the aim of obtaining samples containing a large enough proportion of the (2:2:2:3) phase to yield zero resistivity up to temperatures exceeding 100 K.[1] In bulk ceramics, this result could only be achieved through the substitution of a certain amount of lead to the bismuth constituent. In thin films, although this objective has also mainly been realized with the help of lead substitution, several successful attempts have been performed in the standard lead-free compound.[2]

In the course of the elaboration of bulk ceramics and of thin films of the lead-substituted compounds, we have been struck by the fact that the proportion of the (2:2:2:3) phase needed to yield zero resistivity above 100 K was much higher in the thin films than in the bulk ceramics. Namely, more than 50% seemed to be required in the former system while less than 15% was sufficient in the latter system. On the other hand, published data relative to the lead-free thin films (of comparable thickness) seemed to indicate that, in these films, zero resistivity could be achieved with less than 10% of the (2:2:2:3) phase present in the films, in contrast with the situation of lead-substituted films.

In this paper, we specify, through a systematic investigation of lead-substituted films containing the (2:2:1:2) and (2:2:2:3) phases in variable proportions (between 5% and 85% of the latter), the relationship between the onset of zero resistance above 100 K and the phase content of the films. We then discuss the chemical and physical origin of the aforementioned different behaviors for the lead-substituted and the lead-free films, and we show that the observed differences can be related to the modification of the microstructure of these compounds which is induced by the lead substitution.

Lead-substituted films were deposited on MgO(100) substrates by a laser-ablation method, with post-deposition annealing, the details of which are described elsewhere.[3] Let us specify here the characteristics of the films which are relevant to the results discussed.

The thickness of the films was in the range of 0.2–1 μm. Their composition in the as-deposited amorphous state, determined by means of an electron microprobe, was found close to $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{3.5}O_x$. The preceding amount of lead substitution is known to correspond to the maximum proportion of lead which can effectively substitute the bismuth within the structure.[1] An essential feature of the annealing procedure was to preserve the lead content of the films by capping the films with a ceramic of similar composition.

The phase contents and the crystallographic orientation of the films was studied by means of their x-ray diffractometry diagrams. In bulk ceramics, the validity of this method for evaluating the phase contents has been established by comparing its results to those provided by ac magnetic-susceptibility measurements.[1] It has been shown, that in order to sort the proportions of the various superconducting phases of the considered family of compounds, one can rely on the relative intensities of the (002) Bragg reflections which, for the (2:2:1:2) and (2:2:2:3) phases, correspond to the angles $2\theta=5.8°$ and 4.8°, respectively.

We selected 13 films, the spectra of which displayed only the lines relative to these two phases, the proportion of the (2:2:2:3) phase being comprised between 5% and 85%. Figure 1 shows examples of the spectra at low angle for the 33% and 85% samples.

As pointed out previously by many authors, Bi-Sr-Ca-Cu-O films grown on MgO show a high degree of orientation, the *c* axes of the various crystalline grains of the film being perpendicular to the substrate: the spectra essentially contain lines with (00l) indices. Figure 2 shows,

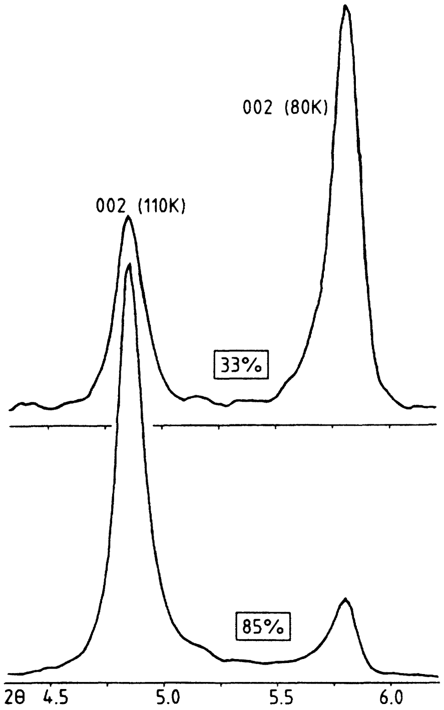

FIG. 1. Low-angle range of the Cu $K\alpha$ spectrum of two thin films showing the (002) lines on which the determination of the proportion p of the 110-K phase is based.

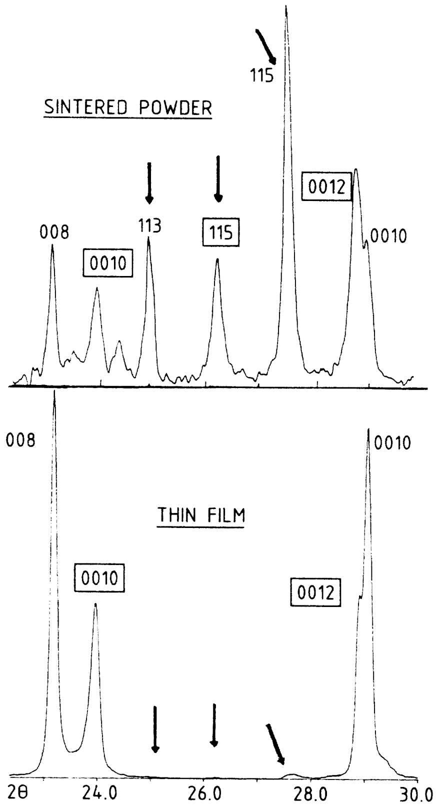

FIG. 2. Portion of the x-ray spectrum of a powdered sample and of a thin film (containing 33% of the 110-K phase) showing the high degree of orientation of the film (c axis normal to the substrate). The captioned lines are relative to the 110-K phase. The arrows point to prominent lines of the powder spectrum which are absent from the spectrum of the film.

more precisely, the spectra of a powder sample and that of a typical film. The (115) reflections, which are the most intense lines of the powder spectrum, are absent or very small in the spectrum of the film. Figure 2 reveals that this preferential c orientation of the films occurs for both the (2:2:1:2) and the (2:2:2:3) phase.

The dc resistance of the films between room temperature and 20 K was measured by a four-terminal method, the contacts, distant from each other by 1–2 mm, being realized with silver paste on the surface of the films. In order to avoid current densities in excess of the critical density, in the cases where the conduction paths are very narrow, we have generally performed the measurements with current densities of the order of 50 mA/cm^2, and in some cases smaller than 5 mA/cm^2. These values have to be compared to the value of the critical current density of the elaborated films with the highest proportion of the (2:2:2:3) phase. We find these densities in the range of 10–10^2 A/cm^2 at 100 K.

Figure 3 shows the behavior of the resistance of the films for four samples corresponding to proportions of ~33%, 47%, 58%, and 85% for the (2:2:2:3) phase. Most of our films displayed the same type of variations with relatively narrow (~5–10 K) transitions at ~110 and ~80 K corresponding to the critical temperatures of the (2:2:2:3) and the (2:2:1:2) phase, respectively. Above and between these transitions the films show a linear decrease of the resistance on cooling.

Figure 4 displays, as a function of the proportion p of the (2:2:2:3) phase, the variations of the ratio $Y=[B/(A+B)]$, where A and B are the respective amplitudes of the resistance jumps at ~110 and at ~80 K (Fig. 3). This ratio vanishes when zero resistivity is reached above 100 K, the 80-K transition being absent from the resistance plot in this case.

We have also reproduced on this plot the values of p relative to lead-substituted films with zero resistance above 100 K, drawn from results of other groups.[4,5] We have not retained, instead, the results of the latter works corresponding to films which become superconducting at lower temperatures and display two resistance jumps at 110 and 80 K. Indeed, these films have often been elaborated with an excess of lead with respect to the optimum value indicated here. Additional nonsuperconducting phases (e.g., Ca_2PbO_4) can then be present in the films,[1] and as a consequence, a poor correlation has generally been noted between p and Y in these works[4] while an excellent correlation exists in our data.

The variations plotted in Fig. 4 show that, in lead-substituted films, the critical proportion p_c above which zero resistance is obtained, at the transition of the

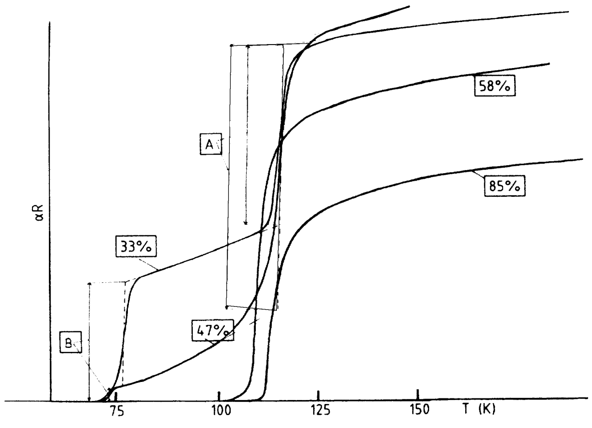

FIG. 3. Variation of the resistivity of four films. The vertical scale differs for the different films, although for all films the room-temperature value of the resistivity is of the order of 1 mΩ cm.

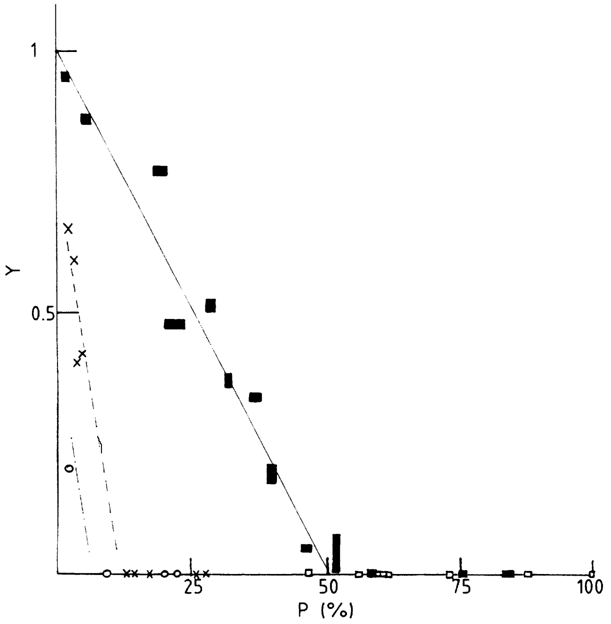

FIG. 4. Variations of the relative magnitude of the 80-K resistivity jump with respect to the 110-K one $Y=[B/(A+B)]$ (cf. Fig. 3), as a function of the proportion p of the 110-K phase in the film. $Y=0$ corresponds to samples having zero resistivity above 100 K. Solid squares: present work for lead-substituted samples. Open squares: data for lead-substituted samples deduced from Refs. 4 and 5. Open circles: data for lead-free samples deduced from Ref. 2. Crosses: data for lead-substituted bulk ceramics. The lines are a guide for the eye.

(2:2:2:3) phase, is (50±2)%. Below p_c, the configuration of experimental points seems consistent with a linear dependence of $Y(p)$. Two additional sets of data are plotted on Fig. 4.

On the one hand, we have represented the results relative to lead-free films, which we have deduced from published data[2] by using the same procedure as for the lead-substituted films, i.e., calculating p on the basis of the x-ray spectra displayed in Ref. 2, and evaluating Y from the resistivity plots available in the same references.

Though these data are scarce as compared to those for lead-substituted films, they show very clearly that zero resistance can be obtained for much smaller p values. For instance, it has been stressed by Kuroda *et al.*[2] that p values smaller than 10% were sufficient in this view. Our analysis of existing data shows that for these films the value of p_c lies in the range of 5–9 %.

On the other hand, in order to specify the behavior of bulk samples, as compared to films, we have extracted from a recent systematic investigation of lead-substituted ceramics,[1] values of Y and p. In the former study, it was found that samples with p in the range of 12–15 % keep a zero resistance up to 100–103 K as indicated on Fig. 4. By contrast, samples with $p \sim 5-7$ % have a residual resistance down to 70 K. Moreover, it was observed that, for the samples with $p \sim 12-15$ %, one has to use a very small measuring current density (~ 1 mA/cm^2) in order to avoid surpassing the critical current density at ~ 100 K, and keep the offset of superconductivity above 100 K. This denotes that such values of p are close to p_c.

In summary, the described experimental data show that for lead-substituted films, lead-free films, and lead-substituted ceramics there are different thresholds p_c for the onset of zero resistivity of the samples at ~ 100 K in the ranges of 48–52 %, 5–9 %, and 10–15 %, respectively.

Previous observations of the films by scanning electron microscopy show that both the lead-free films,[2] and the lead-substituted ones[4,5] are formed by oriented grains of the two phases with similar shapes and dimensions, in agreement with our own observations. Viewed along c, the grains appear as plates with the shape of irregular ellipses or discs. The diameter of these plates is in the range of 1–10 μm, i.e., larger than the thickness of the films (0.2–1 μm).

The occurrence of a large difference between the values of p_c for lead-free and lead-substituted films, suggests that lead modifies, in an essential manner, the electrical connectivity between the superconducting grains. The aforementioned microscopic observations show that the modification concerns more subtle aspects than the size, morphology, and orientation of the grains.

In order to explain the observed differences, the relevant theoretical framework is that of percolation.[6,7] In this framework, the quantity p_c can be interpreted as a percolation threshold. For $p > p_c$, the grains of the (2:2:2:3) phase will form a continuous path across the sample, while for $p < p_c$ no such path will exist, due to the presence of grains of the (2:2:1:2) phase. The choice of plotting the quantity Y in Fig. 4, which does not take into account the temperature dependence of the resistivity between the two critical temperatures, corresponds to a standard model[7] in which one deals with two types of grains having zero resistance and a given nonzero resistance, independent of temperature.

In theories of percolation, many characteristics of the system will influence the value of p_c.[6] However, the main ones are the effective dimensionality of the system (more paths can be formed in higher-dimensional spaces), and the number of connections which a given unit can form with its neighbors. Let us examine the application of these principles to the properties of the considered superconducting compounds in the light of our present understanding of the microstructural role of the lead substitution.[1,8]

The crystal structure of the considered family of superconducting compounds can be conveniently schematized as consisting in slabs stacked upon each other along the *c* direction, each slab comprising a pair of BiO planes enclosing an atomic configuration resembling the perovskite structure [Fig. 5(a)]. The thickness of a slab depends on the superconducting phase considered, e.g., ~12 Å for the (2:2:1:2) phase, and 15 Å for the (2:2:2:3) phase. The separation between slabs is ~3 Å.

It has recently been suggested,[1,8] on the basis of a number of experimental observations, that the main structural modification induced by the substitution of bismuth by lead, is to change the strength of the bonding between consecutive slabs. Namely, while this bonding is very weak in the lead-free compound, it is strong in the lead-substituted compounds.

With regard to the percolation problem examined, an essential practical consequence of this structural difference is to suppress from the lead-substituted samples the intergrowth of different phases that exists, at microscopic level, in the lead-free samples. In the latter samples, such an intergrowth consists, as attested by numerous high-resolution electron-microscopy[9] observations, in the fact that different slabs are "occupied" by different superconducting phases of the considered structural family. Hence, the different phases are stacked randomly upon each other at a scale which can be smaller than 100 Å [Fig. 5(b)]. Clearly, the weak bonding between slabs is responsible for this situation since each slab is almost independent from the neighboring ones, and the nucleation and growth of a given phase in a slab cannot extend easily to the other slabs.

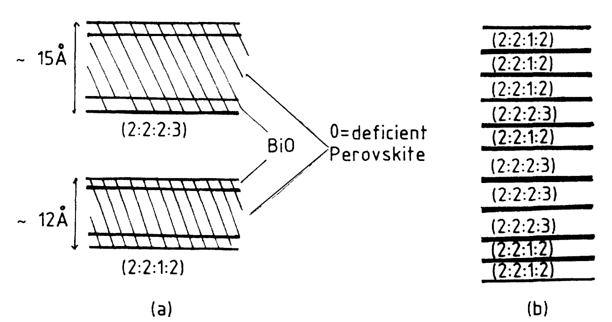

FIG. 5. (a) Schematic representation of the slabs which are the building blocks of the structures of the 80- and 110-K phases. (b) Schematic representation of the stacking of slabs in samples where the 80- and 110-K phases are intergrown.

On the other hand, it has also been often checked,[10] by means of high-resolution electron microscopy, that no intergrowth is present in the lead-substituted compounds, consistently with the stronger bonding between slabs. Accordingly, each grain of a thin film or of a ceramic sample can be assumed to be constituted of a single phase, either the (2:2:1:2) phase or the (2:2:2:3) phase. By contrast, in a lead-free sample, a grain will generally be a composite unit whose homogeneous components have the thickness of a few slabs.

An additional difference, also consistent with the aforementioned description, is that, based on observations[11] of their respective single-crystal habits, one can expect that for a given diameter of the grains perpendicular to the *c* axis, lead-free grains are likely to be much thinner than their lead-substituted counterparts. For the level of lead substitution considered here, single crystals show[11] thicknesses, along *c*, a few times smaller than their lateral dimensions, while lead-free crystals are generally very thin plates whose thickness is 10^2-10^3 smaller than their lateral size. On the basis of the preceding considerations, we can elaborate a simple model of the conducting properties of the films.

Consider first a lead-substituted film of thickness 0.2–1 μm. The diameters of the grains being in the range of 1–10 μm, and their thickness in the range 0.1–1 μm, a film will contain one grain or a few grains within its thickness, and will consist in the juxtaposition of such grains all oriented with their *c* axis perpendicular to the substrate [Fig. 6(a)]. Each grain is entirely occupied either by the 80-K phase or by the 110-K phase.

Owing to the fact that the thickness of the film is comparable to that of the homogeneous units, the percolation through the 110-K superconducting grains is expected to be of the two-dimensional type. In order to evaluate the number of connections a given grain can establish with its neighbors, we can note that the crystalline grains of a film, develop during the annealing, out of a uniform

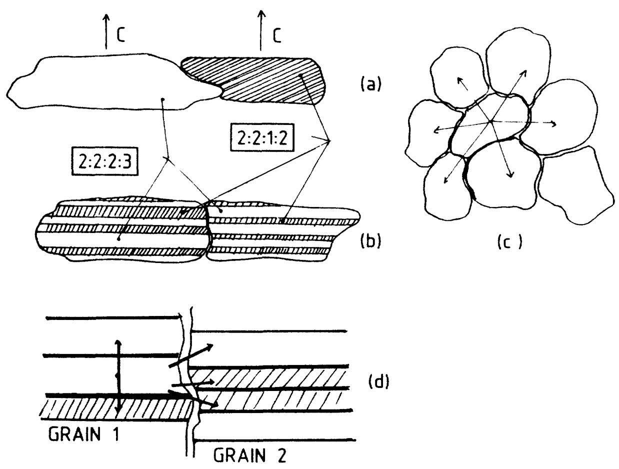

FIG. 6. Model-representation of the microstructure of a film. (a) Pb-substituted film viewed across its thickness. (b) Same view for a Pb-free film for which the grains display extensive intergrowth of phases. (c) View along the normal to the substrate. (d) Illustration of the possible connections between slabs, within a grain, or between neighboring grains.

amorphous film, and that, as a consequence, the grains must be considered as paving the film, with no voids between them. Considering their plate shapes with no filamentary characteristics, we can infer that in this compact (and random) arrangement each grain has, on the average, six neighbors [Fig. 6(c)].

For such a configuration, we could refer to the theoretical situation of the percolation on a two-dimensional triangular lattice for which, similarly, there are six links around each site.[6] It is preferable, however, to refer to a general symmetry argument[12] valid in the case of two-dimensional "continuous" percolation[13] (as opposed to the type constrained by the topology of a lattice) whenever the two types of juxtaposed objects *A* and *B* have similar morphologies. In this situation, there will necessarily exist a percolating path across the sample for one of the two phases in presence. Indeed, in two dimensions, the impossibility to form such a path for *A* implies that a percolating path exists for *B* interrupting all possible paths for *A* across the sample. Therefore, *A* and *B* being symmetric, the theoretical value for p_c is 50%.[12] This symmetry argument is certainly relevant to the thin films considered here, since the grain percolation does not involve a lattice, and since the grains of the 80- and 110-K phases have similar morphologies and sizes ($p_c = 50\%$ also arises for the site percolation on the triangular lattice invoked above).

In summary, the experimental value found for p_c ($\sim 50\%$) in the lead-substituted films appears consistent with the microstructural characteristics known for these superconducting materials (and, in particular, with their absence of intergrowth of phases at microscopic level).

Let us now consider the lead-free films. The occurrence in these films of an extensive intergrowth, along the *c* axis between the 80- and 110-K phases at a scale much smaller than the thickness of the film, has the consequence that the micron-size grains are not the relevant elementary units to consider in a percolation model. The proper units are thin discs having the diameter of the grains and the thickness of a few slabs. In a given grain, the discs are stacked upon each other [Fig. 6(b)]. We can assume, in a simplified picture, that a given slab can consist, randomly, either at the 80-K phase, or at the 110-K phase with probabilities equal to the respective proportions of the two phases.

In this picture, the thickness of the film corresponds to several hundred homogeneous units of either phases. The film must therefore be considered as a three-dimensional array of these units. Percolation through the film can be achieved through various paths. It can proceed along the *c* axis by means of the interaction between consecutive slabs in a given grain. Sidewards, between neighboring grains, a slab can connect to two or three slabs situated at the same elevation in the film [Fig. 6(d)]. Considering, as in the case of lead-substituted films, that there is a close packing of grains [Fig. 6(c)], each grain being the neighbor of six grains, we can estimate on the basis of the preceding discussion, that a given slab is linked to 14–20 other slabs [i.e., $6(2)+2$ or $6(3)+2$]. Taking into account the fact that the grains themselves may be much thinner than the film for the lead-free situation, would not modify our qualitative conclusion that the considered microstructure has a high connectivity.

For the three-dimensional percolation, we cannot use the symmetry argument stated above. We then refer to the theoretical results for the fcc lattice which yield $p_c = 11-19\ \%$ when 12 bonds (to nearest neighbors) are taken into account, and $p_c = 6-14\ \%$ when 18 bonds (including further neighbors) are considered.[6] Again, the experimental value of $p_c = 5-9\ \%$ appears consistent with the current description of the microstructure of the lead-free materials which includes 14–20 bonds.

The case of lead-substituted ceramics is less well defined since it is associated to a configuration of homogeneous flat grains of micron size with random orientation in space, and that, in addition, ceramics generally have a substantial porosity ($\sim 20-25\ \%$ in our samples) which will increase the percolation threshold. Nevertheless, it seems reasonable to relate them to a three-dimensional type of percolation. Our experimental results ($p_c = 10-15\ \%$) agree qualitatively with the theoretical results indicated above for a close-packed three-dimensional configuration.

In conclusion, the striking differences found for the onset of zero resistance above 100 K, are satisfactorily accounted for, by considering that this onset results from a percolation through the homogeneous units of the (2:2:2:3) phase which are of a different nature in the lead-free and in the lead-substituted Bi-Sr-Ca-Cu-O superconducting thin films. The main element of this explanation relies on the different habit of intergrowth in the two cases.

It would be desirable to compare in detail the behavior of the *Y* quantity below p_c to the results of percolation theory. In principle, this behavior should be described, in the vicinity of p_c, by a power law with exponent *s* as defined by Straley.[7] However, our experimental data appear insufficiently accurate, at present, for such a comparison.

Finally, note that, from a practical point of view, the influence of lead on the onset of zero resistivity above 100 K is of a complex nature. Lead substantially increases the proportion of the (2:2:2:3) phase in the films, but, conversely, it raises the percolation threshold for the superconductivity of the films from 10% to 50%. Existing data[2,4,5] clearly show that the former effect is predominant, since it seems easier to obtain zero resistivity above 100 K in the lead-substituted films. Considering the different mode of percolation in the films, one also expects different values of the critical current density at 100 K in the two types of films, for a given proportion of the 110-K phase.

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