Lawrence Berkeley National Laboratory
Recent Work

**Title**
Microstructure Property Relationships in the Bi(Pb)-Sr-Ca-Cu-O Ceramic Superconductors

**Permalink**
https://escholarship.org/uc/item/1mr5058d

**Journal**
Studies of High Temperature Superconductors, 4

**Authors**
Ramesh, R.
Green, S.M.
Thomas, G.

**Publication Date**
1989
Microstructure Property Relationships in the Bi(Pb)-Sr-Ca-Cu-O Ceramic Superconductors

R. Ramesh, S.M. Green, and G. Thomas

July 1989

For Reference
Not to be taken from this room

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
An overview of the inter-relationships between microstructure and electrical transport properties in the Bi(Pb)-Sr-Ca-Cu-O system is given. The crystal structure and defect structure of the polytypoidic superconducting phases in this system have been investigated using advanced electron microscopy techniques. The defects in this system are typical of those found in layered structures. The changes in the transport properties, mainly the resistive transition and the diamagnetic susceptibility, are shown to be sensitive to the grain boundary microstructure.
INTRODUCTION: The discovery of high temperature superconductivity in Bi-Sr-Ca-Cu-O (BSCCO) and Tl-Ba-Ca-Cu-O(TBCCO) compounds has provided further impetus to the exciting area of research on oxide superconductors, opened up through the work of Bednorz and Muller. Considerable effort is being focussed on understanding the structure, properties, processing and the mechanisms responsible for the properties involved. The Bi and Tl based compounds belong to a family of layered structures termed as polymorphs. Fig. 1 schematically illustrates the crystal structure of the three commonly observed polymorphs in the BSCCO system. It consists of Cu-O perovskite layers stacked between NaCl-like, double layers of BiO, that bear similarity to the Aurivillius phase. The bonding between the BiO layers is relatively weak, thus imparting graphite-like mechanical properties to this system. The change in the Cu-O coordination from the n=1 to n=3 is to be noted. The Tc increases with the number of Cu-O layers, n,(upto n=3) in both the types of compounds. For example, in the case of the Bi compounds, the n=1 (2201) polymorph has a transition temperature in the range of 7-22K, the n=2 (2212) of about 75-85K and the n=3 (2223) a transition temperature of 110K. Several interesting structural features and electrical transport properties have been experimentally observed in the Bi based system. For example, a strong incommensurate structural modulation has been observed in all the Bi based compounds whereas a weaker modulation is observed in the Tl based compounds. The origin of this modulation is still being debated, although the most probable reason is likely to be an almost periodic (incommensurate) structural deformation of the BiO double layers due to the intercalation of oxygen in these layers. Another interesting observation is that in nominally n=3 solid state processed BSCCO samples, zero resistance is not obtained above 100K. Although there is a large resistive drop at about 110K, with zero resistance obtained in the neighbourhood of 70K, in general, a step is observed in the plot, the location and height of which is very sensitive to processing conditions and to the composition of the sample.

A fundamental understanding of the structure of these layered materials and the possible inter-growths and defects that can occur between the different polymorphs is required in order to design microstructures suitable for specific applications. Recently there has been considerable attention paid to the understanding of the effect of magnetic fields and the current carrying capability of these materials. This is important if
these oxides are to be used in applications involving high magnetic fields, e.g., transmission lines, superconducting magnets, NMR etc. It has been observed that the resistive transition is considerably broadened under magnetic fields. The exact origin(s) of this is still not completely transparent, but is possibly related to the relatively easy mobility of the flux lattice in a magnetic field, at temperatures much lower than the transition temperature in zero field.

One of the main interests is in the understanding of the inter-relationship between microstructure and electrical transport properties of the BSCCO system with and without Pb substitutions. Subsequent to the initial discovery of the BSCCO system, it was found that additions of small quantities of Pb were helpful in obtaining a step free resistive transition above 100K\(^{28,29}\). The effects of composition, processing conditions, oxygen ambient, etc. are being systematically studied to optimize the transport properties of this system\(^{30-41}\). The structure of the different polytypoidic phases has been characterized using several advanced transmission electron microscopy techniques now available\(^{29-33, 42-47}\). Consequent to a detailed examination of the microstructure, especially the grain boundary structure, it has been possible to correlate the transport properties to specific features of the microstructure. In this paper, we present the salient features of our research effort, which is aimed at understanding the role of microstructure in the evolution of the transport properties on solid state processed BSCCO superconductors.

The results are presented in three sections. In the first section the structural details, analysed by high resolution imaging and diffraction, are presented. This is followed by a section in which the microstructure of the leaded and the unleaded samples are discussed. In the third section, our current understanding of the inter-relationships between microstructural features and transport properties are presented. This will be followed by an overall summary of the microstructure-property inter-relationships and the potential for applying the inferences obtained from the electron microscopy studies to improve the transport properties of this system.

**GENERAL EXPERIMENTAL DETAILS** : The specific experimental conditions used to carry out the different experiments have been presented in various publications\(^{28,29,31-33,35,70}\). However, for the sake of completeness of the arguments presented, the general details of the processing steps are outlined.

(1) **Sample Preparation** : Appropriate amounts of Bi\(_2\)O\(_3\)(99.9%),
PbO(99.999%), SrCO₃(99.9%), or SrO₂(99.5%, dried overnight at 120°C), CaCO₃(99.5%) or CaO(99.5%, dried at 200°C) and CuO(99.5%) were ground together until no visual evidence of inhomogeneities was observed. After calcining overnight at 800°C, the samples were thoroughly ground, pressed into pellets and sintered at 850°C for 60 hours in air (with one intermediate grinding), followed by furnace cooling to room temperature. Two different types of samples, leaded and unleaded, have been characterized.

2) Resistivity-temperature plots: Resistivity-temperature plots were measured on bars approximately 10x2x1 mm³ from room temperature down to 77K in a liquid nitrogen thermos. Contacts consisted of spring loaded Rh-plated steel pogos (Augat-pylon) pressed onto silver paint pads in the standard four-point configuration. About 1mA rms current was supplied at 40Hz with the sample's voltage drop being detected by a lock-in amplifier. The zero resistance temperature was defined as the temperature below which the amplifier could not detect a signal. The detection limit was typically 0.5μΩcm.

3) Magnetic measurements: dc magnetic measurements were carried out using a SQUID magnetometer at 20 Oe in the temperature range of 10-150K. Both the shielding and the Meissner plots were obtained.

4) Transmission electron microscopy (TEM): Samples for TEM were prepared by slicing a piece of about 250μm thickness, mechanically polishing it to about 50μm and finally Argon ion milling it to electron transparency in a liquid nitrogen stage at 6kV. High resolution electron microscopy (HREM) was performed in the Atomic Resolution Microscope (ARM) at 800kV located at the National Center for Electron Microscopy (NCEM) or a JEOL 200CX at 200kV. Image simulations and processing facilities available at the NCEM have been used to verify the structural determinations and to improve the quality of the images. Image simulations were carried out using the NCEMSS software while image processing is carried out using the SEMPER program 48. Analytical electron microscopy (AEM) was carried out in a JEOL 200CX at 200kV, using a Be window energy dispersive X-ray (EDX) detector. In all cases, a minimum of 10⁵ counts was acquired to ensure proper statistics. Quantification was carried out using the KEVEX 8000 system software. Electron diffraction experiments were carried out using a 100kV Philips 400T microscope that also has the capability for examining samples at temperatures as low as 25K. The ARM is a key part of the facilities that are available at the NCEM, which is a U.S. Department of Energy facility.
I. STRUCTURE OF POLYTYPOIDS IN THE BSCCO SYSTEM

The primitive structure of the different polytypoids is pseudo-tetragonal, and is illustrated in Fig. 1. Convergent beam electron diffraction (CBED) was employed to study the point group symmetry of the n=2 and n=3 phases. Fig. 2 shows a typical CBED pattern obtained in the [001] zone. Clearly, the intensity distribution in this pattern does not have the four fold rotation required for a crystal with tetragonal symmetry. Detailed analyses using established methods reveal the point group to be 2mm. Determination of the space group symmetry requires the observation of the Gjonnes-Moodie lines of extinction in the spots that are prohibited by the crystal symmetry but appear due to double diffraction. This is however complicated by the heavily faulted structure and the structural modulation.

The structure of the BSCCO compounds consists of double layers of NaCl type BiO and SrO between which are corner shared perovskite units of Cu-O. In the n=1 polytypoid, Cu is in a distorted octahedral environment. In the n=2 polytypoid, Cu has a four fold oxygen coordination in the plane with a fifth oxygen atom in the apical position, farther away. In this compound, there is one Ca position between the two Cu-O layers. The n≥3 compounds are unique since the Cu atoms in the central Cu-O layers are coordinated to only four oxygen atoms. Hence, for example, in the n=3 compound, the central Cu-O layer is likely to have properties different from that of the other two Cu-O layers. The primitive unit cell of the different polytypoids has been determined by several techniques, although the full structure, including the structural modulation, is still not fully understood.

Atomic resolution imaging has been employed to determine the stacking sequence of the different cationic layers in these polytypoids. In general, it is essential to verify the structure determinations by carrying out detailed image simulations. We have concentrated our efforts on the n=2 and n=3 polytypoids, since they are observed commonly in the samples being studied and are also of practical relevance. The [110] zone axis projected potentials for the n=2 and n=3 polytypoids are shown in Figs. 3(a&b) respectively.
orientation, the different cations project as columns. Therefore contrast in
HREM images obtained from crystals in this orientation can be interpreted
in terms of the projection of atomic potentials. Low atomic number
elements such as oxygen cannot be imaged with a large degree of certainty,
although attempts are being made to interpret the image contrast in terms
of oxygen vacancies by detailed comparisons with simulated images. At
this juncture, it may be pointed out that the structure of the n=2 and n=3
polytypoids in the unleaded and leaded samples are not different and are
treated identically.

Fig.4(a) shows a [110] HREM image of the n=2 polytypoid, in which
the different atomic layers, schematically illustrated in Fig.1, can be
observed. In this image, the contrast consists of bright spots on a dark
background. The two rows of large spots correspond to the Bi (Z=83)
atom positions. In between the Bi rows, the cationic stacking sequence
consists of Sr-Cu-Ca-Cu-Sr. The doubling of the unit cell along the
c-direction due to the presence of a glide plane between the two BiO layers
is also clear from this image. In Fig.5(a), a [110] zone axis HREM image
of the n=3 polytypoid is presented. This structure has the cationic sequence
of Bi-Sr-Cu-Ca-Cu-Ca-Cu-Sr-Bi-.... The simulated images shown in
Fig.4(b) and Fig.5(b) confirm the interpretation of the image contrast in
terms of the different atomic species. It may be pointed out that since the
image is a projection of the atomic potential along the column of atoms, it
may be possible, if thin enough crystals are examined, to identify cationic
substitutions. For example, Bi+3 (0.99Å) and Ca+2 (0.96Å) are of almost
the same radius, but very different in atomic numbers. Thus, the presence
of Bi in Ca sites may be recognized directly from the image contrast. In
Fig.4(a), the arrows indicate one such possible location where the intensity
in the Ca site is much brighter than the adjacent sites. Quantitative X-ray
microanalysis results do indicate that Bi replaces Ca while the converse is
not observed.

The high voltage used in examining the samples (200-800kV) produces
considerable displacement damage in these alkali earth based oxides. Thus,
the experiments have to be carried out in a very short time. On the other
hand, it is also possible to process the images such that the periodic part of
the information in the image is enhanced. One typical example of the
advantage of image processing is illustrated in Fig.6(a&b). In Fig.6(a), the
actual image is shown. While the different atomic positions can be
discerned in this image, there is a significant amount of non-periodic
"noise" in the image. By carrying out the image processing, which consists
of Fourier transforming the negative, filtering the image and inverse Fourier transforming, the non-periodic part of the information is considerably reduced. This is illustrated in the filtered image in Fig.6(b).

One interesting feature in the image in Fig.5(a) is illustrated better in the processed image shown in Fig.7(a). In this [110] zone axis image of the n=3 polytypoid, the intensity distribution in the central CuO layer can be noticed (indicated by arrows). Specifically, examination of the oxygen position indicates that the oxygen atom along the Cu-O chain in the plane of the figure, may not exist. This possibility was examined by simulating the image without the oxygen atom along one of the Cu-O chains in the central Cu layer. The simulated image, Fig.7(b), shows an asymmetry in the intensity distribution for the central CuO layer, compared to the other two. This suggests that there is a possibility that the n=3 polytypoid is oxygen deficient in the central Cu-O layer. An oxygen depleted Cu-O layer is likely to have significant implications in the doping mechanism of these superconductors.

The Bi-based superconductors are characterized by an incommensurate structural modulation\(^3,9,15-23,41,51-54\). This modulation is identified by the presence of satellite reflections in the [001] and [100] zone axis diffraction patterns. In the [100] zone axis HREM image of the n=3 polytypoid in Fig.8(a), this structural modulation is clearly illustrated. The corresponding selected area diffraction pattern is shown in the inset. This modulation has displacement components along the c-direction and the b-direction. It is commensurate along the c-direction and incommensurate (4.76xb) along the b-direction and is characterized by the modulation vector [0,1/4.76,1]. There have been several studies aimed at explaining the origin of this modulation, but it is still not fully understood\(^3,9,15-23,41,51-54\). However, one current postulate of this modulation is that it is caused by the intercalation of oxygen in between the BiO layers. It has also been suggested that the modulation is due to the ordering of vacancies in the Sr sites or Bi sites\(^51,52\). It may be pointed out that the spacing between the two BiO layers is quite large (3.0Å) compared to, for example, the spacing of the BiO layers (2.5-2.6Å) in the Aurivillius phase\(^14\) and hence can accommodate excess oxygen. In the Aurivillius phase, the inter layer spacing is smaller due to the presence of a fully occupied layer of oxygen between the two BiO layers. This suggests that the excess oxygen being intercalated in the BiO layers in the BSCCO compounds is due to an attempt by the system to increase the oxygen coordination around the Bi ions. Bi, which can take variable coordinations
(6-9) has a lower oxygen coordination in the BSCCO compounds compared to the Aurivillius phase. This difference in the oxygen coordination around the Bi ion has been used to explain the origin of doping in this system. The question arises as to why oxygen is intercalated in the BiO layers, since this would destroy the charge neutrality of the compound. But results of detailed X-ray microanalysis as well as other characterization studies aimed at understanding the cationic stoichiometry, reveal that the compounds are deficient in Ca and Sr, with the deficiency being made up by the presence of excess Bi in the Ca (and Sr) sites. Considering only the formal valences of the different cations, the presence of trivalent Bi in the divalent Ca (and Sr) site, will necessitate the incorporation of excess oxygen for charge compensation. This excess oxygen is most likely to be located in the BiO layers, for steric reasons.

The oxygen intercalation mechanism for explaining the structural modulation is supported by the effect of Pb substitution on the modulation. It has been observed that Pb goes primarily into the Bi sites, although a small amount appears to replace Sr. Substitution of increasing amounts of Pb for Bi causes a systematic change in the modulation vector and in the nature of the modulation. For example, in the case of the sample with the nominal formula of Bi\(_{1.4}\)Pb\(_{0.6}\)Sr\(_2\)CaCu\(_2\)O\(_{8+y}\), the modulation vector is 9.5\(\times\)b and is in the direction \([0, 1/9.5, 0]\). Fig.8(b) is a SAD pattern in the [100] zone from the above sample and clearly shows the difference in the modulation. Note that there is no component along the c-direction. This change in the modulated structure can be explained by a change in the oxygen concentration due to the replacement of Bi by Pb. If the formal oxidation states are valid then for every two Pb atoms replacing Bi, one oxygen is lost. The reduction in the excess oxygen content in the BiO layers is reflected as an increase in the modulation vector. The reason for the absence of the c-component of the modulation is not clear, but it is hypothesised that this may be due to the difference in the ionic radii of Bi(0.99Å) and Pb(1.2Å). The modulation can also be systematically altered by cationic substitutions on the Ca or Sr sites. For example, replacement of divalent Ca by a trivalent rare earth species such as Tm, leads to a decrease in the modulation vector, although the direction of the modulation vector remains the same. Such a cationic substitution is accompanied by an increase in the oxygen content, suggesting that the change in the modulation is indeed related to excess oxygen in the BiO layers.

The large amount of data acquired on the structural modulation...
indicates the interest in understanding the origin of the modulation. It must be emphasised that further studies are required to completely unravel the mechanism of the modulation and also to clarify if the structural modulation is in any way related to the superconducting properties. For example, it would be interesting to study the effect of composition and processing conditions on the cationic stoichiometry of the \( n=2 \) and \( n=3 \) polytypoids and whether stoichiometric phases can be individually prepared.

## II MICROSTRUCTURE AND DEFECTS

The microstructure and defects observed in this oxide system are reflective of two main physical properties of this system. The first is the fact that the bonds between the Bi-O layers are very weak and hence can be broken very easily. This attributes graphite-like mechanical properties to these polytypoids. Hence, shear in the a-b plane i.e., between the BiO layers, is very easy. The second property is that these are layered structures and hence the defects that form in these materials are reminiscent of those observed in other ceramic systems, such as the SiAlONs. Indeed, the class of structural oxides based upon the SiAlONs and derivatives thereof, are good precursors for the understanding of the structural properties and defect structure in the BSCCO system. In this paper, defects have been classified into three classes, based upon their dimensionality. Thus, point defects are considered first, then line defects and finally coherent and incoherent interfaces.

(i) **Point defects**: The formation of point defects in the BSCCO system is found to be governed by the size and coordination constraints of the layered structure. One of the main types of point defects observed indirectly, by X-ray microanalysis, is Bi and Sr in Ca sites. The fraction of Ca sites occupied by Bi and Sr is dependent upon the processing history of the sample. However, based upon examination of microanalysis data from several samples, it is concluded that there is a definite fraction of the Ca site that is occupied by Bi and in some cases, Sr. This has also been found by several researchers, who have used other microanalytical techniques to probe the cationic stoichiometry of these phases\(^4,7,22,61-64\). Such a cationic substitution of Ca by Bi can be a reason for the excess oxygen and the consequent structural modulation in these compounds, as explained earlier.
It may be noted that the converse, i.e., Ca (and Sr) in Bi sites, has not been observed in all these experiments. This observation is significant, since the ionic radii, and hence coordination, of Bi and Ca are very similar. It can, however, be rationalized based upon the notion that the bonding in the BiO layers and the Ca-O layer is quite different. Conversely, this observation may be taken as additional evidence to justify a claim that the bonding in the BiO double layers is significantly covalent (or metallic). Ca being strongly ionic, cannot occupy the BiO sites, but Bi can occupy the Ca site. It is currently thought that the covalency of the BiO layers is due to the lower oxygen coordination around the Bi ion, compared to, for example, the Aurivillius phase. In the Aurivillius phase, Bi is bonded strongly to 8 oxygen atoms and weakly to another, giving a total of 9. In the BSCCO phase however, the coordination is only 6 (in the primitive unit cell, without taking into account the excess oxygen). This means that electron transfer from Bi to oxygen is not complete to yield the +3 oxidation state of Bi. Consequently, the valency of Bi is lower than +3 and is thought to be responsible for the p-type doping in this system53.

Sr in Ca sites has been observed in several of the samples examined. This observation has been made by other researchers4, 7, 61. Vacancies in Sr sites and in Bi sites have also been cited as possible reasons for the structural modulation51, 52. The presence of vacancies in the Bi site is not validated by the X-ray microanalysis results, which always indicate a Bi excess. Sr in Ca sites is not likely to affect the doping mechanism since both of them are divalent.

(ii) Line defects: The nature of dislocations in the BSCCO system is dictated by the bonding characteristics in the different layers and by the need for the accommodation of local composition fluctuations. Since the BiO double layers are spaced far apart (about 3.0Å) the bonding between these two layers is weaker than that in the other parts of the crystal. This is evidenced by the easy cleavage between the BiO layers and by the fact that in general the grain boundary planes are BiO planes. This weak bonding is responsible for the formation of dislocations in the basal (001) plane whose Burger's vectors are also in the plane. The analysis of dislocations in such layered structures has been treated in detail by Amelinckx65. In the BSCCO system, two main types of translations in the a-b plane are likely to exist. The first is of the type 1/2[110] while the other is of the [100] type. The pseudo-tetragonal symmetry of the primitive unit cell means that the two orthogonal Burger's vectors, i.e.,
and [010] or [110] and [110] should both be observed. Since the energy of the dislocation is related to the magnitude of the Burger's vector, in some cases, the [100] type dislocation will split into partials, with the formation of a stacking fault.

Dislocations in the a-b plane are discussed first. Fig. 9 is a multi-beam image showing a network of dislocations. The fringes with a large spacing are rotational Moire fringes due to the growth of sheets of the BSCCO polytypoid with small mutual misorientations. This dislocation network consists of two types of dislocations. The first is a set of orthogonal dislocations indicated as A and B with an indication of strong interaction between the two sets at the points of intersection, while the second, C, is at 45° to both A and B. The orthogonal nature of A and B suggests that they are [100]/[010] or [110]/[110] dislocations, while dislocation C is likely to be of a [100] type. Since the energy of the dislocation is proportional to the square of the magnitude of the Burger's vector, it is likely that dislocation C split into two partials of the [110] type to reduce the energy of the defect.

In the HREM image in Fig. 10(a), a dislocation with Burger's vector along the c-direction is shown. Such a dislocation is characteristic of those in layered structures and is termed a structural dislocation. They have Burger's vector that are larger than a single lattice plane spacing. This "structural" dislocation transforms 5 units of the n=2 polytypoid into 4 units of the n=3, thus creating an extra half unit of the n=2 phase. The four n=3 units and the five n=2 units are marked on the figure and this is shown schematically in Fig. 10(b). In this diagram, it can be seen that the maximum relative displacement is at the center of the two stacking sequences. It can also be seen that the third and fourth BiO double layers in the n=2 structure are almost level with the second and third Ca double layers in the n=3 stacking. The Burger's vector of this structural dislocation is equal to n[001], where n need not be an integer. Such a dislocation forms to accommodate a local change in the composition of the crystal and hence is non-conservative. The mobility of this dislocation may be sensitive to changes in point defect concentration.

Another type of stacking defect observed very often in the BSCCO system is illustrated in the lattice image in Fig. 11(a). The defect is located within the circle in the figure and is schematically illustrated in Fig. 11(b). This defect is a step in the stacking sequence of the different planes in the structure. Measurement of the spacing of the blocks involved in this type of defect indicates that the ratio of the inter-block spacing is equal to that
of the different polytypoids, i.e., n=2, n=3, n=4 or n=5. Hence, the formation of the step changes the polytypoid from "n" to "n-1" or "n+1". This means that a CuO+Ca unit has been either lost or introduced to create the stacking fault. Examination of the n=2 and n=3 stacking sequences in Fig.11(b) reveals that in order for the defect such as in Fig.11(a) to form, cationic disorder has to occur. Up to the second Cu layer from one end of the stacks, there is perfect registry of the layers in the two stacking sequences. In the next layer, a Sr layer is aligned with a Ca layer, which is explicable since Sr and Ca are known to form solid solutions in the BSCCO system. However, in the next four planes, there is an inversion of the stacking sequence, indicated by the boxed region in Fig.11(b). Beyond this boxed region, the stacking is in perfect atomic registry. It is interesting to note that this defect always occurs in pairs, i.e., there is another such step very close to each of the steps.

Two-dimensional rotational boundaries: The layered nature of the BSCCO system can be associated with the formation of several types of coherent intra-granular interfaces. These interfaces are always found to occur on the BiO planes, which again correlates to the weak bonding between the two BiO layers. 90° boundaries that have been observed, Fig.12(a), are allowed by the pseudo-tetragonal symmetry (ignoring the structural modulation) of the primitive unit cell. Across the boundary, the two parts of the crystal are in the [100] and [010] orientations. But more detailed investigation has led to the conclusion that such a 90° twist boundary is but one special case of a general class of coherent rotational boundaries. Fig.12(b) shows a typical example of one such non-90° boundary. In this grain, one part has been imaged in the [110] zone axis. If the other part of the grain were to be rotated 90° from this [110] zone, it should be imaged in the [110] zone. For the pseudo-tetragonal unit cell, these two orientations are almost identical and hence the structure should have been resolved if it were in the [110] zone. Since this is not the case, the conclusion is that the boundary separating these two regions is a coherent non-90° boundary. In many grains, several such planar defects were observed. In general, their width varied from between 10nm to the extent of the grain itself. It is interesting to note that in all the cases, such coherent interfaces are observed at a n=2 layer.

Knowledge of the mechanism of formation of these interfaces may help in the understanding of the growth mechanism of these polytypoids. In the case of polytypic structures, such as Si-Al-O-N or SiC, several mechanisms
of growth have been proposed and are still in debate. One among them is based upon a spiral growth about a screw dislocation, while another mechanism proposes the periodic or non-periodic insertion of stacking faults. In the BSCCO system, long period superstructures have not been observed, although in the homologous Tl based system, such long range periodicities have been reported. Currently, attention is being focused on understanding the relationship between these growth defects and the mechanism of growth.

Another type of coherent defect is stacking faults. In general, the faults consist of n=3 regions in a matrix of the n=2 polytypoid. The density of stacking faults is dependent upon the composition of the sample and the processing steps. In general, the unleaded samples exhibit heavier faulting compared to the leaded samples that have the optimized composition. This is well exemplified by the lattice images shown in Fig.13(a&b). Fig.13(a) was obtained from an unleaded sample, and shows n=3 regions intermixed with n=2 regions. Very rarely has the n=1 polytypoid been observed as faults inside the grain, although near the boundaries, it has been observed quite frequently. In the leaded samples, Fig.13(b), the structure inside a n=3 grain is much more homogeneous. It may be noted that the heavy faulting in the unleaded sample is reflected as a smearing of the Meissner signal, an aspect that is discussed in the next section. The difference in fault density can be attributed to two causes. The first is the fact that in the unleaded sample, the slow growth kinetics may cause local compositional fluctuations, that may lead to the formation of the n=3 phase in a n=2 matrix. It is equally possible that the free energies of formation of the two polytypoids are very similar and hence a very intimate intergrowth occurs. Both these mechanisms are supported by the decrease in the fault density in the leaded samples.

Pb substitution leads to the formation of a liquid phase during sintering, that presumably enhances the reaction kinetics. In the leaded samples, an amorphous phase is generally observed at the triple grain junctions, Fig.14(a), and frequently at the two grain boundaries, Fig.14(b). The amorphous phase is likely to be the solidification product of a liquid that existed at the sintering temperature. X-ray microanalysis reveals that it is considerably richer in Pb compared to the nominal starting composition. In general, transport rates are enhanced in the presence of a liquid phase. Thus, one of the causes for the better homogeneity of the BSCCO phases may be the easier availability of the different species, especially Cu and Ca, that are required for the formation of the n=3 polytypoid. However, the
difference in ionic radii and charge of Pb compared to Bi may also influence the free energy of the system, so that the n=3 phase is favored.

**Grain boundaries**: The other important internal interface is grain boundaries. Characterization of the nature of grain boundaries and the phases that form at these interfaces is important in understanding the transport properties. A detailed correlation of the grain boundary structure and the phases that form at these interfaces, is deferred to the next section.

### III. MICROSTRUCTURE - TRANSPORT PROPERTY INTER-RELATIONS

As observed in most technologically relevant materials, some or all of the properties of interest are sensitive to the microstructure. The term microstructure here includes the crystal structure and aberrations of the same, coherent or incoherent second phase particles, point, line and surface defects, etc. In the above two sections, the characteristics of the defects present in the BSCCO system have been discussed. In this section, the definite role of grain boundary phases on the transport properties is illustrated using two examples. In the first example, the leaded and unleaded samples are used to illustrate the effect of lead additions. The second example illustrates the effect of Bi/Ca ratio on the microstructure and transport properties. The results in this section also highlight the prominent influence of grain boundary microstructure on the transport properties.

(i) **Effect of lead substitutions**: In one of the earliest reports on the BSCCO system, Sunshine et al. had reported that substitution of a small amount of the Bi by Pb leads to an increase in the transition temperature (determined magnetically) to above 100K, due to the formation of the n=3 polytypoid. This report was subsequently improved upon and zero resistance was obtained around 107K in samples in which the lead content was varied from 0-50% of the total Bi content. The leaded samples showed a marked difference in the shape of the resistive transition, as the temperature was decreased. By careful optimization of the processing conditions, it is now possible to obtain samples without any steps, within a resistivity resolution of 0.5μΩ.cm. In Fig.15, typical resistivity-temperature and Meissner susceptibility-temperature data for the leaded and unleaded samples are shown. The step in the resistivity plot
of the unleaded sample, following the large drop in resistivity at about 110K, leads to a zero resistance at 70K. The resistive transition for the leaded sample is in general, although not always, free of steps. The Meissner signal of the unleaded sample shows an onset of diamagnetism at 110K, but there is a considerable smearing of the signal compared to the signal from the leaded sample, which shows a sharp drop at 110K and another step at about 70K. The magnetic data for both the samples indicate the presence of almost equal amounts of the lower transition temperature \( n=2 \) phase. However, from the resistivity data it is clear that the connectivity of the 110K regions is somehow influenced by the presence of lead.

Detailed examination of the microstructure of both the leaded and the unleaded samples revealed two main differences between them. The first difference is the higher density of stacking faults in the unleaded sample compared to the leaded sample, as shown in Fig.13(a&b). This higher density of stacking defects in the unleaded sample is likely to be the cause for the smearing out of the Meissner signal. Examination of the grain boundaries revealed specific microstructural features that are most likely to be the cause for the steps in the resistive transition of the unleaded sample. Fig.16(a&b) show typical lattice images of the grain boundary regions in the unleaded and leaded samples respectively. In the case of the grain from the unleaded sample, Fig.16(a), the structure inside the grain consists mainly of the \( n=3 \) polytypoid. However, upon approaching the grain boundary the structure changes to the \( n=2 \) polytypoid and finally adjacent to the boundary the \( n=1 \) polytypoid is observed. In general, the \( n=2 \) polytypoid is observed at the grain boundary. Since the grains in the sample are not aligned, the c-axis and the a-b planes in each grain are not aligned with those in the neighbouring grains. Thus for current to flow from one grain to the next, there has to be some transport along the c-direction. At a temperature below 110K but higher than the transition temperature of the grain boundary polytypoid, a percolative path does not exist since the grain boundary polytypoid is still normal. This explains the step observed in the resistive transition.

In the leaded sample, the grain boundary microstructure is very different. In the samples with the optimum composition, the \( n=3 \) polytypoid is continuous up to the grain boundary interface, as shown in Fig.16(b). The difference in the grain boundary microstructure is reflected in the resistive transition, Fig.15, and no steps are observed. The mere presence of a disordered region, such as the grain boundary, does not
appear to be any serious impediment to the flow of current of 1mA, although a broadening of the transition is observed at a higher current and also in magnetic fields. One of the reasons for the change in the grain boundary microstructure is the presence of a liquid phase, Fig.14(a&b), that is thought to assist in material transport. However, the fact that the structure near grain boundaries is different in the leaded sample compared to the unleaded sample, irrespective of the presence of the liquid phase at that boundary, suggests that there may be a more fundamental effect of lead substitution on the thermodynamics of the formation of the n=3 phase. From experiments on the effect of Bi:Ca ratio and Sr:Ca ratio, it is clear that the mere addition of Pb to the BSCCO system is not sufficient for obtaining a step free resistive transition. Indeed, the optimum cationic stoichiometry appears to be very close to the 2223 composition. The effect of the nominal composition is illustrated by the studies on the effect of Bi:Ca ratio on the microstructure and transport properties. This is detailed below.

(ii) Effect of Bi:Ca ratio: The studies on the effect of Bi:Ca ratio clearly illustrate the systematic changes in the transport properties with composition and the corresponding changes in the microstructure. To carry out this set of experiments samples with the general composition of Bi$_{1.85-x}$Pb$_{0.25}$Sr$_2$Ca$_2-x$Cu$_3$O$_{10+y}$ where x=-0.2, -0.1, 0.0, 0.1 and 0.2, were prepared. The ρ vs. T plots, Fig.17, for three of these samples with x=-0.2, 0.0 and 0.2, are normalized to their room temperature values for clarity (all the samples had ρ(295 K)=2.5 mΩcm). The height of the resistive step systematically increases with "x" while the temperature coefficient of the normal-state resistivity, ρ(T>T$_c$)/dT, and the zero resistance temperature, T$_c$0, decrease. The resistivity plots for samples with x=0.1 and 0.2 were identical. The small step (with zero resistance at 100K) in the case of the x=0.0 sample is to be noticed and is discussed later. The samples with x=-0.2 and 0.2 exhibit distinctly different resistive behaviour, while the x=0.0 sample shows an intermediate behaviour. So these three samples were chosen for detailed microstructural investigation.

The magnetic susceptibility versus temperature curves (χ vs. T) for samples with x=-0.2, 0.0 and 0.2 are displayed in Figs. 18(a-c) respectively. In the case of the Ca-deficient sample (Fig.18a), the discontinuity in the Meissner plot at T=70 K indicates the coexistence of regions in the sample which are 2212 and 2223. The abrupt nature of the step and the flatness of the curve on either side of the step, suggest that the two polytypoids exist predominantly as independent grains. The magnitude
of the Meissner signal above 70 K is more than 50% of the total signal at 10 K and is far above the fraction of superconducting material which should be necessary to create a percolation path.

The Meissner data for the x=0.0 and x=0.2 samples (Figs. 18b and 18c, respectively) are qualitatively similar to each other, but distinct with respect to the x=-0.2 sample. The curves clearly show the presence of the n=3 polytypoid (bulk T_c ≈ 108 K) with 50-60% of the total signal obtained above 105 K. In contrast to the x=-0.2 sample, no discontinuity is observed below this temperature. This structure, resulting from a gradual increase (rather than a sharp step) in the magnitude of the Meissner signal over the interval 100 ≥ T ≥ 60 K, is interpreted as the signature of n=2 stacking faults within grains which are predominantly n=3 and/or the existence of a small number of n=2 grains in the sample.

In a shielding experiment, superconducting surface currents are established at low temperatures which "shield" the enclosed volume from an applied (dc) magnetic field. The data represents the temperature dependence of flux penetration into this volume, as opposed to a Meissner experiment where the data indicates the temperature dependence of flux expulsion. In granular high-T_c (Bi,Pb)SSCO ceramics (as in Y-Ba-Cu-O ceramics), two likely sites for flux penetration at temperatures significantly below the bulk T_c are grain boundaries, internal surfaces which are known to be diamagnetically weak and reduced T_c stacking faults, within individual grains or as grain boundary layers. So also, the effect of intergranular misorientation has been shown to be an important factor in determining the intergranular critical current. For the case of stacking faults inside the grains, the geometry must be such that the adjacent, higher T_c material does not itself act as a flux shield (as in the case of a thin, perfectly conducting sphere having the same shielding signal as a solid sphere, per unit volume). All three samples demonstrate continuously increasing flux penetration with rising temperature, with a maximum observed at 65-70 K, Fig.18(a-c). Below this maximum, the x=-0.2 sample admits significantly more flux than either the x=0.0 or x=0.2 samples.

From the p vs. T, Meissner and shielding data, the following microstructures can be abstracted:

(a) For the x= -0.2 sample, grains of predominantly the 2212 or 2223 polytypoid exist independently, with the n=3 regions separated from each other by rather thick (in comparison with the superconducting coherence length) regions of a lower T_c or non-superconducting material. This sample behaves similarly to the unleaded sample.
For the $x=0.0$ and $x=0.2$ samples, the majority of grains are $n=3$, contain $n=2$ stacking faults, and the $n=3$ regions are likely to be continuous up to the grain boundary in a significant fraction of the grains in the sample. Thus, there is good electrical connectivity of the $n=3$ phase in these samples. However, the manner in which the magnetic flux penetrates the bulk samples in the shielding experiments indicates that some prevalent internal feature, such as the grain boundaries; is particularly weak, with a "shielding $T_c$" significantly lower than the bulk $T_c$. This is also supported by the fact that the resistive transition is very sensitive to magnetic fields. The small step in the $\rho$ vs $T$ plot of the $x=0.0$ sample suggests some barrier to intergranular connectivity that is overcome at 100K. It may be noted that the exact location of the knee in the shielding plot, which signifies flux penetration into the crystal, is very dependent upon the processing conditions, post-anneal in oxygen, etc.

Fig. 19 is a lattice image of a $n=3$ grain from the $x=-0.2$ sample in which stacking faults are apparent. Some of the grains encountered were so heavily faulted that they can not be uniquely described as either $n=2$ or $n=3$. The $n=2$ grains also exhibit frequent faulting in the stacking sequence, similar to the the image in Fig.19.

Fig. 20 displays a $n=3$ grain from the $x=-0.2$ sample in which adjacent to the grain boundary, the $n=2$ polytypoid has formed and is several unit cells thick. The presence of this lower $T_c$ material adjacent to the grain boundary was confirmed by analytical electron microscopy elemental line profiles across the grain boundary. An increase in the Bi signal and a decrease in the Ca and Cu signals was observed near the grain boundary which is consistent with the fact that the $n=2$ polytypoid is richer in Bi compared to the $n=3$ polytypoid. It may be noted that the smallest electron probe used for xray microanalysis (about 100Å) is still larger than the polytypoid spacing. Hence high resolution structural imaging is a better method of mapping out the local composition, than is possible by current spectroscopic methods, especially near grain boundaries and interfaces in these oxide superconductors whose superconducting coherence lengths are only a few nanometers.

In the case of the $x=0.0$ sample, a majority of the grains encountered were $n=3$. Structural imaging revealed that the $n=3$ polytypoid was continuous up to the grain boundary, with the last half unit cell adjacent to the boundary identified as $n=2$ in most cases. It was also found that the grain boundary plane was, in all cases examined, a Bi-O plane. Fig. 21 is a HREM structural image in the [110] zone axis orientation of the grain.
boundary region in a typical $n=3$ grain from the $x=0.0$ sample. In this image, the two rows of large bright spots represent the Bi atoms. Inside the grain, the stacking sequence of the cations is clearly discernible as Bi-Bi-Sr-Cu-Ca-Cu-Ca-Cu-Sr-Bi-... In the half unit cell adjacent to the grain boundary, only two Cu (and 1 Ca) atomic positions are observed. The $n=1$ polytypoid was not observed adjacent to grain boundaries in samples with this nominal composition.

The intragranular microstructural features of the $x=0.2$ sample were almost identical to those of the $x=0.0$ sample. However, one significant difference between these two samples was that in the $x=0.2$ sample the 2223 polytypoid is continuous right up to the grain boundary, as exemplified by the lattice image in Fig.22. It may be noted that the magnetic properties of these two samples are almost the same, while the resistivity plot for the $x=0.0$ sample shows a small step. This may be related to the slight Bi-rich composition of this alloy, and also to the observation of the one half unit cell of the $n=2$ polytypoid adjacent to the grain boundaries. Thus, there appears to be a clear dependence of the transport properties on the grain boundary microstructure. Experiments aimed at understanding the role of the grain boundary phases on the flux nucleation and penetration are presently underway.

IV. GENERAL DISCUSSION AND CONCLUSIONS:

(i) Cationic stoichiometry and the incommensurate modulation:
Considerable cationic solid solution formation has been observed in the $n=2$ and $n=3$ polytypoids. This is mainly due to the similarity in the ionic radii and coordination. The presence of the nominally trivalent Bi in Ca site is one of the reasons for the intercalation of excess oxygen in the BiO layers. This excess oxygen ($y=0.21$) is thought to be responsible for the structural modulation in these BSCCO compounds.

(ii) Defect structure: A variety of defects have been observed and characterized in this system. Many of them are typical of layered structures, such as graphite, that exhibit weak bonding between the layers (as in between the Bi-O layers in the BSCCO system). As is true in the case of other properties, the defect structure is likely to have some influence on the transport properties, although the exact dependence is still not clear. For example, at a temperature below the $T_c$ of the $n=3$ phase but above that of the $n=2$ phase, locally normal regions will co-exist with superconducting regions. These normal regions can be potentially good
pinning sites for the fluxoids. It is however realized that in order to obtain effective pinning of the fluxoids on a large scale, a uniform and dense distribution of such pinning sites, which should also have a large pinning energy, is required. Examination of the stacking sequence in the neighbourhood of the structural dislocation also reveals another potential source of dissipation of the current flowing through the grain. The large anisotropy coupled with the fact that the primary conduction planes are the Cu-O planes, suggests that structural continuity of the Cu-O planes is a requirement for uninterrupted current flow. In the middle of the n=2 and n=3 stacks, the Cu-O planes align with Bi-O planes. Thus, the core of the structural dislocation is likely to be a source of dissipation of the current passing through the crystal. On the other hand, the large localized structural distortions in the vicinity of the dislocation core can also be potential sites for pinning of fluxoids. In n=2 single crystals it has been observed that there is very low resistance to flux motion above 35K, although \( T_c \) is about 82K\(^2\). In essence, the flux lattice that develops in the two phase regime, is not stable in the presence of the driving current and melts, leading to dissipation. In order that the flux lattice is pinned strongly, such pinning sites have to be introduced. It may be possible that the introduction of structural defects on the scale of a few nanometers, is one of the solutions to overcome this problem. Indeed, in thin films of the Y-Ba-Cu-O superconductor, the resistance to flux flow is much better and is attributed to the presence of a uniform distribution of structural defects, such as structural dislocations, that pin the flux lattice\(^7\).  

(iii) Microstructure-transport property relationship: It is clear that the structure and composition near grain boundaries determines the nature of the transport properties. Grain boundaries have been thought to be the main type of weak links in granular superconductors. It has been shown that the nature of this weak link is very sensitive to the composition, sintering additives such as PbO, the post-annealing treatments, etc. In recent studies the beneficial effects of crystallographic alignment by deformation has also been demonstrated.

ACKNOWLEDGEMENTS: The work at Lawrence Berkeley Laboratory is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under contract No. DE-AC-03-76SF00098. The work at UC, San Diego is supported by the California MICRO program and the Hughes Aircraft Co. The authors wish to extend their
gratitude to C.J.D.Hetherington, C.Nelson, M.A.O'Keefe, R.Kilaas, M.Moore of the National Center for Electron Microscopy and Professors H.L.Luo and M.L.Rudee at University of California, San Diego for their continued scientific support of this program. One of the authors (R.R) gratefully acknowledges the enthusiastic support and encouragement of P.L.Key, J.H.Wernick, M.J.Bowden and J.M.Rowell and P.L.Liao at Bellcore. Stimulating discussions with J.M.Tarascon, M.S.Hegde, T.Sands, B.G.Bagley, L.H.Greene, C.C.Chang, P.England at Bellcore are gratefully acknowledged. The assistance of R.Sudha is greatly appreciated.
REFERENCES


[73] See for example, articles in Jl. of Metals, Jan., (1989).


FIGURE CAPTIONS

Figure 1: Schematic illustration of the structure of the n=1,2 and 3 polytypoids in the BSCCO system.

Figure 2: [001] CBED pattern from the n=3 polytypoid, showing the 2mm point group symmetry. Note the absence of the four fold rotation axis of symmetry.

Figure 3: (a&b) Projected potentials in the [110] zone axis for the n=2 and n=3 polytypoids respectively.

Figure 4: (a) HREM image in the [110] zone from the n=2 polytypoid. The image contrast consists of bright spots on a dark background (reversed contrast); (b) simulated image of the n=2 polytypoid in the [110] orientation, for a foil thickness of 30Å and objective defocus of -250Å.

Figure 5: (a) [110] HREM image of the n=3 polytypoid, consisting of black spots on a bright background; (b) simulated image of the n=3 polytypoid in the [110] zone, verifying the cationic positions. Foil thickness is 30Å and objective defocus is -500Å.

Figure 6: (a) HREM image in the [110] zone without any image processing. Note the fuzziness in the image due to the non-periodic background; (b) same image as in (a), after SEMPER image processing, with the background noise considerably reduced.

Figure 7: SEMPER processed image of the n=3 polytypoid in the [110] zone, showing intensity difference between the central Cu-O layer and the other two layers; (b) simulated image in which the oxygen atoms in the central Cu-O chain have been removed, showing a close resemblance to the image in (a).

Figure 8: [100] HREM image of the unleaded n=3 polytypoid showing the structural modulation. The inset shows the SAD pattern from this zone; (b) [100] SAD pattern from a leaded sample showing a different modulation.
Figure 9: Bright field image of the a-b plane showing a network of dislocations, identified as A, B and C.

Figure 10: (a) [100] Lattice image of a structural dislocation with the Burger's vector along the c-direction; (b) schematic illustration of the formation of the structural dislocation in (a), through the conversion of five \( n=2 \) layers into four \( n=3 \) layers.

Figure 11: (a) [100] Lattice image of a defect characterized as a step in the layered structure, that changes the stacking sequence from "n" to "n-1" or "n+1"; (b) schematic illustration of the mechanism of formation of the above defect, also showing the cationic disorder that is likely to take place near the defect.

Figure 12: (a) 90° rotational boundary across [100] and [010] "domains" in a leaded sample; (b) a non-90° rotational boundary in the leaded sample. These coherent intra-granular boundaries are commonly observed in both the leaded and the unleaded samples.

Figure 13: (a) lattice image of the unleaded sample, illustrating the extensive faulting in these samples; (b) [110] zone axis HREM image of the leaded sample, showing an almost fault free \( n=3 \) phase.

Figure 14: (a) Amorphous phase observed at the triple grain junctions in the leaded sample and (b) in the grain boundaries of the leaded sample. This phase is generally found to be rich in Pb.

Figure 15: Resistivity and Meissner diamagnetic susceptibility versus temperature for the leaded and unleaded samples. The unleaded sample is plotted as (+, Meissner) and broken line (resistivity) while the leaded sample is plotted as (o, Meissner) and full line (resistivity).

Figure 16: (a) Lattice image of the unleaded sample showing the formation of the lower \( T_c \) \( n=2 \) and \( n=1 \) polytypoids adjacent to the grain boundaries; (b) HREM image from the leaded sample, showing the \( n=3 \) polytypoid continuous up to the grain boundary.
Figure 17: Resistivity-temperature plots for samples in the series Bi$_{1.85-x}$Pb$_{0.25}$Sr$_2$Ca$_{2-x}$Cu$_3$O$_{10+y}$ where $x = -0.2, 0.0, 0.2$.

Figure 18: (a-c) Meissner (full circles) and shielding susceptibility (open circles) - temperature plots for the samples in the series Bi$_{1.85-x}$Pb$_{0.25}$Sr$_2$Ca$_{2-x}$Cu$_3$O$_{10+y}$ where $x = -0.2, 0.0, 0.2$.

Figure 19: Lattice image from a grain in the sample with $x = -0.2$, exhibiting intragranular stacking faults.

Figure 20: [100] HREM image of a grain in the $x = -0.2$ sample showing the formation of the lower $T_c$ polytypoid near the grain boundary.

Figure 21: [110] zone axis HREM image of the $n=3$ polytypoid in the $x=0.0$ sample. Note the fault free $n=3$ phase in this sample, although the half unit cell next to the grain boundary is the $n=2$ polytypoid. This correlates to the small step in the resistivity-temperature plot of this sample, Fig.17.

Figure 22: [110] HREM image of a grain in the $x=0.2$ sample showing the $n=3$ polytypoid to be continuous up to the grain boundary interface.
Fig. 1

\[ \text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{\delta} \]

- Bi
- Sr
- Ca
- Cu
- O

24.6 Å  
30.6 Å  
37.1 Å  

n = 1  
n = 2  
n = 3

XBL 897-2619
Fig. 3
Fig. 4
Fig. 6
Fig. 7

XBB 887-6875A
Fig. 11b
Fig. 17

Resistivity Ratio \([R(T)/R(295 \text{ K})]\)

Temperature (K)
Fig. 18a
Fig. 18b
Fig. 18c