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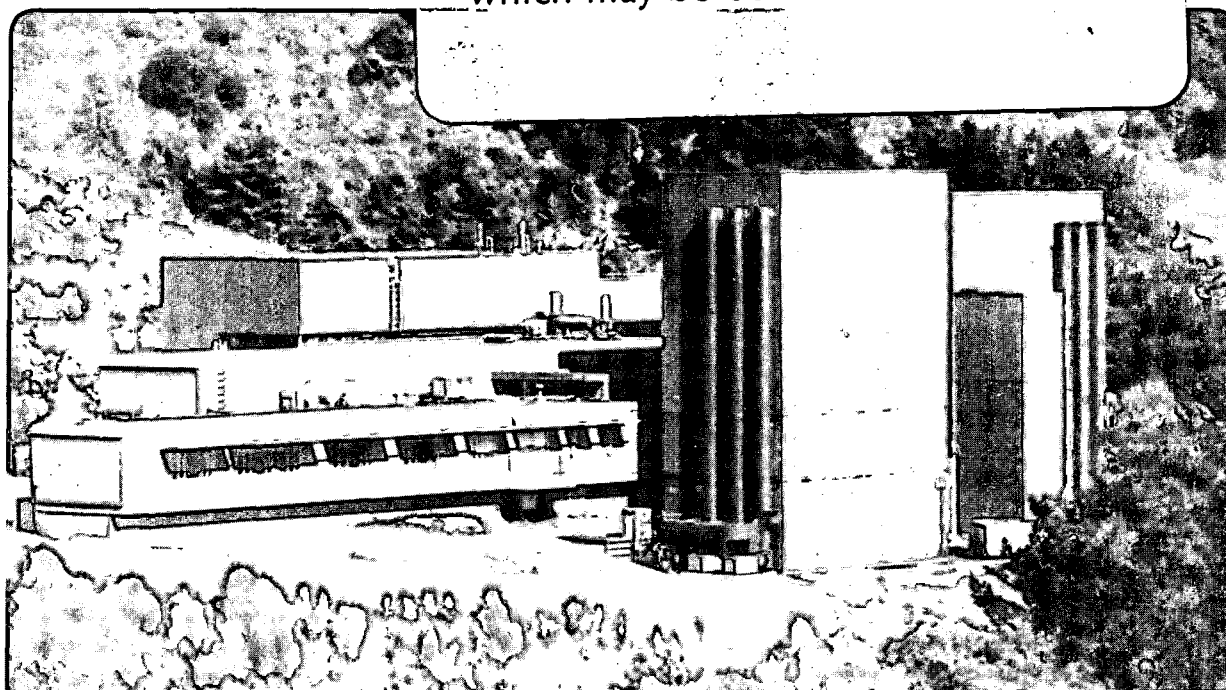
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MICROSTRUCTURE OF Pb MODIFIED Bi-Ca-Sr-Cu-O SUPERCONDUCTOR

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ABSTRACT : The microstructure of samples with and without Pb addition has been characterized by transmission electron microscopy (TEM). An amorphous Pb-rich grain boundary phase has been found in Pb doped samples. It is suggested that a Pb-rich liquid phase assists sintering and homogenization of the composition of the superconducting phase to attain the higher zero T_C . In both samples, Ca replacement by Bi has been found. The implications of such a replacement are briefly discussed.

INTRODUCTION: Recently it has been reported that the addition of small quantities of PbO to an alloy of Bi-Ca-Sr-Cu-O aids in the attainment of zero resistance at 105K following the onset of the drop in the resistivity at 112K^{1,2}. The first report of the beneficial effect of Pb addition was by Sunshine et. al.³ who noted that the T_C was raised from 84K by the addition of Pb. No steps were observed in the resistivity plot. Prior to this it has been observed by us and by several others⁴⁻⁷ that it is not possible to obtain zero resistance above 100K in this class of compounds although the onset of a resistive drop was observed at even 110K. A step is generally observed in the resistivity plot. It was suggested that this step in the resistivity could be due to a connectivity problem³, i.e., the individual superconducting grains may be isolated from each other by a region which is non-superconducting at temperatures above 75K and below 110K. Subsequently, it has been shown⁸ that in the un-doped samples, close to the grain boundaries the c-parameter is reduced to 24Å, (corresponding to the composition of $\text{Bi}_2\text{Sr}_2\text{Cu}_1\text{O}_y$), which has a T_C of about 25K. In several grains, the c-spacing close to the grain boundary was lower than that inside the grain due to a change in the composition of the superconducting phase. In the case of the Pb-doped sample preliminary experiments showed that the c-spacing was uniform inside the grains, suggesting that there was "good" connectivity of the grains. In this paper we report results of further microstructural investigations on the Pb-doped samples, showing that the Pb-doped samples have undergone liquid phase sintering. It is suggested that the liquid phase enhances transport and hence homogenization of the composition of the superconducting phase, especially near the grain boundaries.

The samples were prepared by the standard method described in ref. (1). The un-doped sample had the nominal composition of $\text{BiCaSrCu}_2\text{O}_y$, and the doped sample $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ and were processed similarly. Samples for electron microscopy were prepared by mechanically polishing a slice of the sample to about 50 μm thickness followed by Argon ion milling to electron transparency at 6kV using a liquid nitrogen stage. Transmission electron microscopy (TEM) experiments were carried out using a JEOL 200CX top entry high resolution and JEOL 200CX side entry analytical microscope. Xray microanalysis was carried out using a Kevex 8000 Analyser. All standard precautions for xray microanalysis were taken.

Fig.1 is a typical high resolution image of the grain boundary region in

the un-doped sample and clearly illustrates the absence of any second phase at these boundaries. Note that the c-spacing is smaller near the grain boundary and increases to 38.2Å inside the grain. This was a very common observation in the case of the un-lead samples. In the case of the Pb-doped samples, the c-spacing was found to be uniformly 38.2Å near the grain boundary also. In addition, an amorphous phase was observed frequently at the grain boundaries, both at the triple junctions and at the two grain boundaries. Typical examples of this grain boundary phase are shown in the bright field images in Fig.2(a&b), the microdiffraction patterns in the inset indicating that the phase is amorphous in both regions. In general the width of this amorphous region at the two grain boundaries varied from a few nanometers to a maximum of about 200Å. Xray microanalysis showed that this phase is, in general, of variable composition but rich in Pb. One typical EDX spectrum from the triple grain junction amorphous phase is shown in Fig.3, with the quantified data in the inset. Although it is still unexplored, the presence of this grain boundary phase suggests the existence of a low melting eutectic phase. This inference is supported by the experimental observation of the lowering of the melting point of the ceramic during sintering. It is also interesting to note that in the case of Tl-Ba-Ca-Cu-O superconductors, Tl₂O₃ decomposes to Tl₂O, which melts between 300-400°C and enables liquid phase sintering to occur⁹. In the Tl-compounds, steps in the resistivity plot are not observed, further suggesting that the absence of steps in the resistivity is related to the formation of a liquid phase during sintering.

In the case of the un-doped sample the microanalysis data indicated another interesting feature. Fig.4 is a microanalytical line profile across a typical grain boundary and shows the segregation of Bi to the interfaces. This behaviour was observed in the case of several grain boundaries. Note that this result is consistent with the spacing of the lattice fringes in the c-direction, near the grain boundary in the un-doped sample as shown in Fig.1. Near the grain boundaries the c-spacing decreases from 38.2Å to 30.5Å. The 30.5Å phase corresponds to the nominal composition of Bi₂Sr₂Ca₁Cu₂O_y, and its Bi content is higher than in the 38.2Å phase which has the nominal composition of Bi₂Sr₂Ca₂Cu₃O_y. Consequently, the Bi content near the grain boundary is higher, while the Cu and Ca content is lower. Since the 30.5Å polytypoid has a lower T_c than the 38.2Å polytypoid, this means that the grain boundary regions in the un-doped

sample are not superconducting until the corresponding T_C (i.e., about 75K) is reached. Consequently, a step in the resistivity plot is observed, suggesting poor connectivity between the superconducting grains. In the case of the Pb-doped sample, the enhanced transport due to the presence of the liquid phase assists in the attainment of a homogeneous composition (and c-parameter of 38.2Å) with respect to the Cu-O layers.

One striking feature, common to both the un-doped and the Pb-doped samples is the replacement of Ca by Bi and/or Sr. This is evidenced by the presence of twin-like features in off-zone axis images, as illustrated in the bright field image in Fig.5 for the Pb-doped sample. The microanalysis data from the alternating regions of dark and bright contrast are given in Table I. Note that except for Ca and Bi, all the other elemental concentrations are the same in both regions, within the statistical limits of the quantification procedure. For the chemical formula of $\text{Bi}_2\text{Sr}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_y$ ($n=2$ for the 110K polytypoid), the relative atomic fractions (without oxygen) of Bi, Sr, and Ca are 22.22% respectively, and of Cu is 33.33%. The microanalysis data in Table I show that : (i) Pb replaces Bi in the unit cell ; (ii) the region being examined is slightly higher in Sr compared to the stoichiometric composition ; (iii) more importantly, The Bi+Pb content of 24.36% in region(2) is much higher than the 22.22% expected and the 22.7% that is found in region (1). This difference is not due to the error bars (shown in Table I) in the quantification, which are much lower than the difference observed from the two regions. It is also interesting to note that this increase in Bi+Pb content has come at the expense of Ca which goes down from 18.18% to 16.6%. Since the Pb concentration itself is constant in both regions, the increase corresponds to an increase in the Bi content. This replacement of Ca by Bi has also been observed directly in high resolution structure images, as reported earlier¹⁰ and is understandable since the ionic sizes of the two ions are very similar ($\text{Bi}^{+3} = 0.96\text{\AA}$; $\text{Ca}^{+2} = 0.99\text{\AA}$). Based upon ionic radii alone, it appears less likely that Sr^{+2} (1.12Å) will participate in such a replacement.

The replacement of the Ca^{+2} ions by the Bi ions (which in all probability exists in the +3 oxidation state) can be expected to produce significant changes in the electronic configuration of the Cu-O layers. Assuming that Bi is indeed in the +3 oxidation state, it is not impossible that it loses the pair of electrons to reduce the Cu(+3) that may exist. If the Cu(+3) correlates to the T_C then such a process may affect the

transition temperature of the compound. It is clear that more experiments have to be carried out to understand the effect of such a replacement of Ca by Bi.

In conclusion, the steps in the resistivity plot, attributed to the lack of connectivity between the superconducting grains, can be avoided by the addition of small amounts of PbO, which forms a low melting liquid phase and assists sintering and compositional homogenization. Consequently, the composition of the Bi-Ca-Sr-Cu-O phase is also uniform with respect to the Cu-O layers, especially near the grain boundaries, thus ensuring good connectivity. However, the effect of the Pb-rich, amorphous phase at the grain boundaries (to the extent of a few nanometers) on the conductivity is still unknown and needs further examination. So also, the effect of Ca replacement by Bi needs more experimental analysis.

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TABLE I
MICROANALYSIS DATA FOR THE TWO REGIONS

	REGION 1	REGION 2
At.% Ca	18.18(0.36)	16.60(0.34)
At.% Cu	35.86(0.48)	35.12(0.48)
At.% Sr	23.24(0.44)	23.91(0.44)
At.% Pb	4.44(0.16)	4.52(0.16)
At.%Bi	18.26(0.26)	19.84(0.28)

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FIGURE CAPTIONS

- Figure 1: High resolution image of un-lead sample showing the decrease in the c-spacing from 38.2Å to 30.5Å near a grain boundary.
- Figure 2: (a) Bright field image of the Pb-rich amorphous phase at the triple grain junctions ; (b) bright field image of the same phase at the two-grain boundaries. The insets in both the figures identify the amorphous nature of the Pb-rich phase.
- Figure 3: A typical EDX spectrum from the triple grain junction amorphous phase.
- Figure 4: Microanalytical line profile across a grain boundary in the un-lead sample, showing the segregation of Bi to the grain boundaries.
- Figure 5: Bright field image of the leaded sample showing the presence of planar defects which differ in the Bi and Ca concentrations only (see Table I).

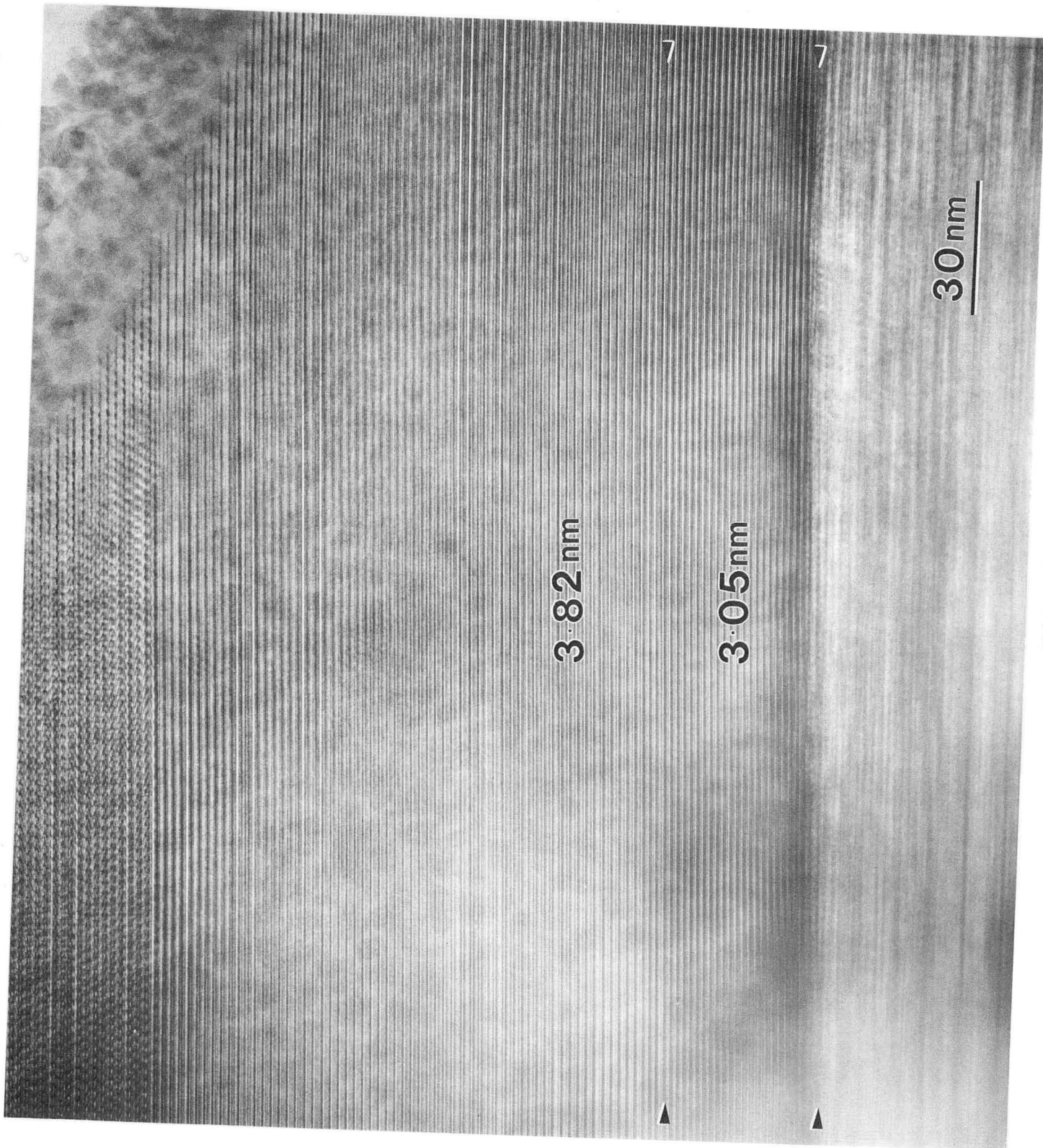
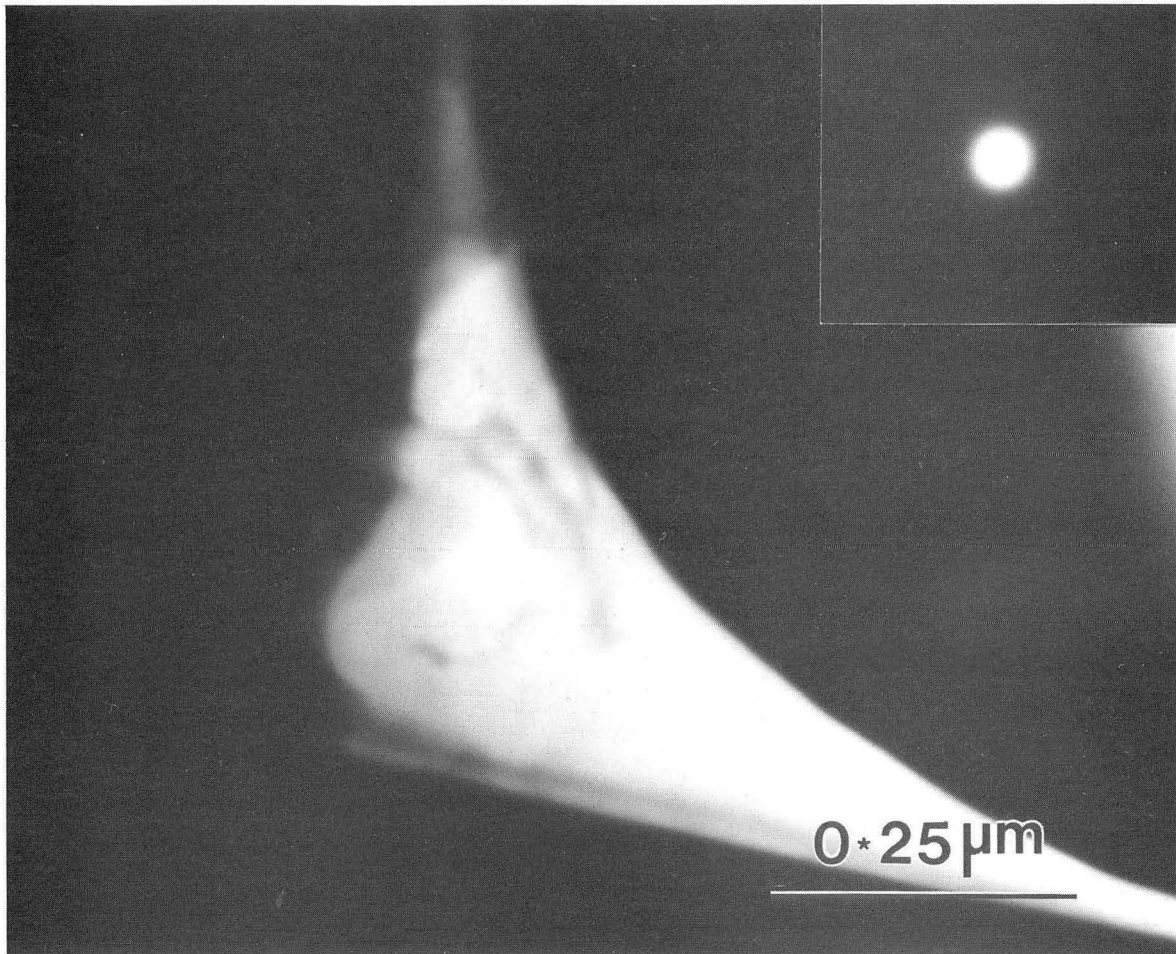


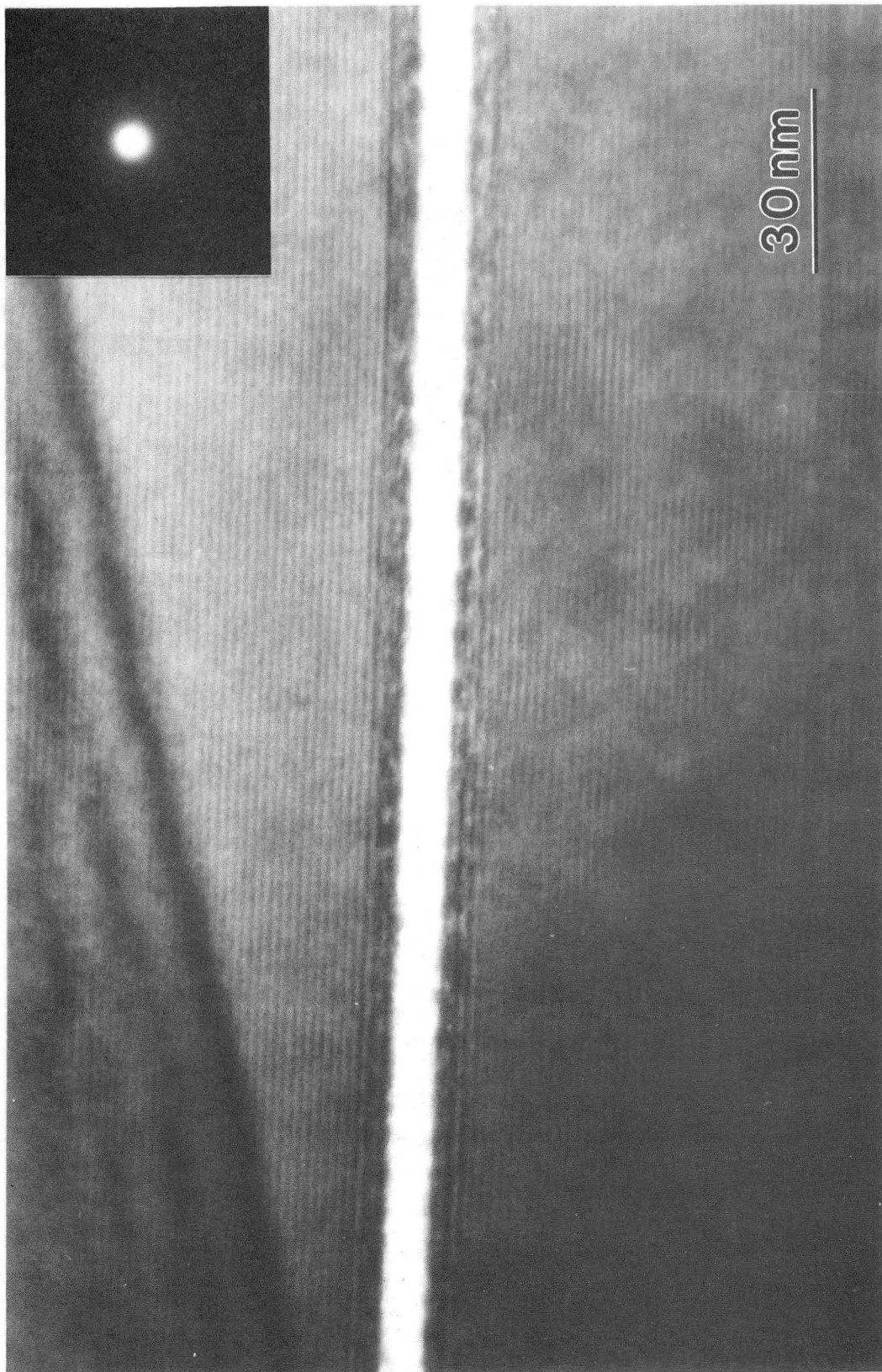
Fig. 1

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Figure 2(a)



XBB 886-5584

Figure 2 (b)

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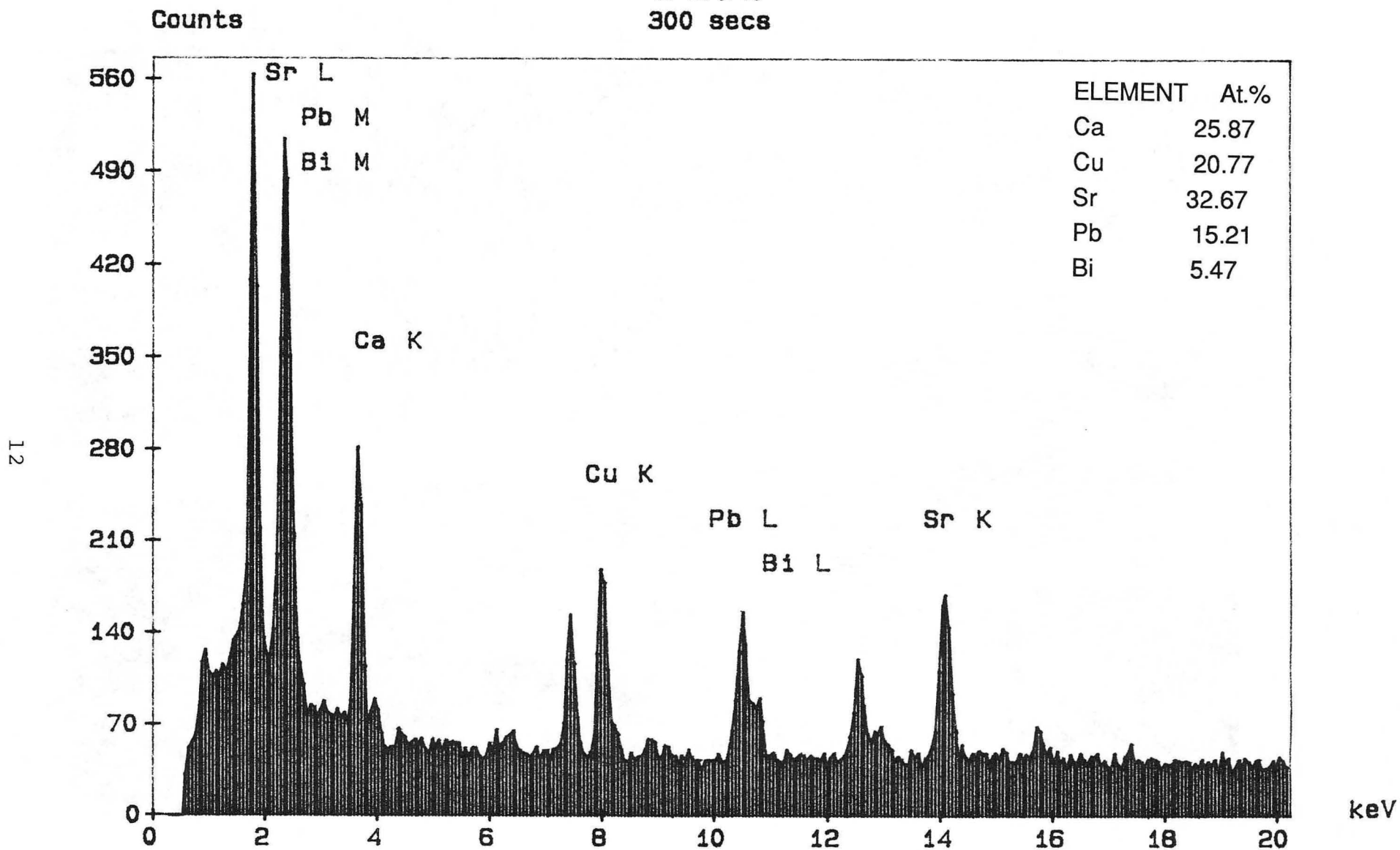


Figure 3

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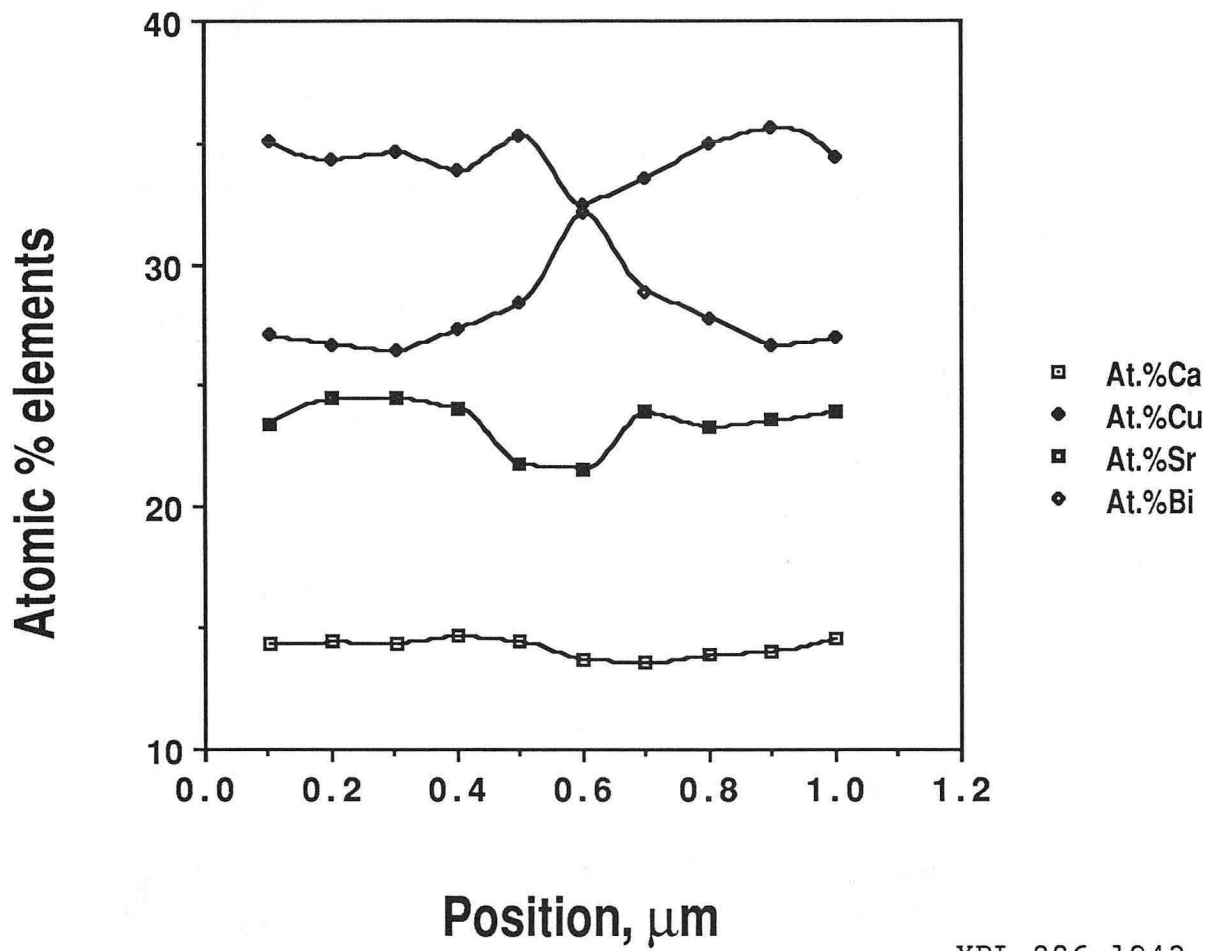


Figure 4

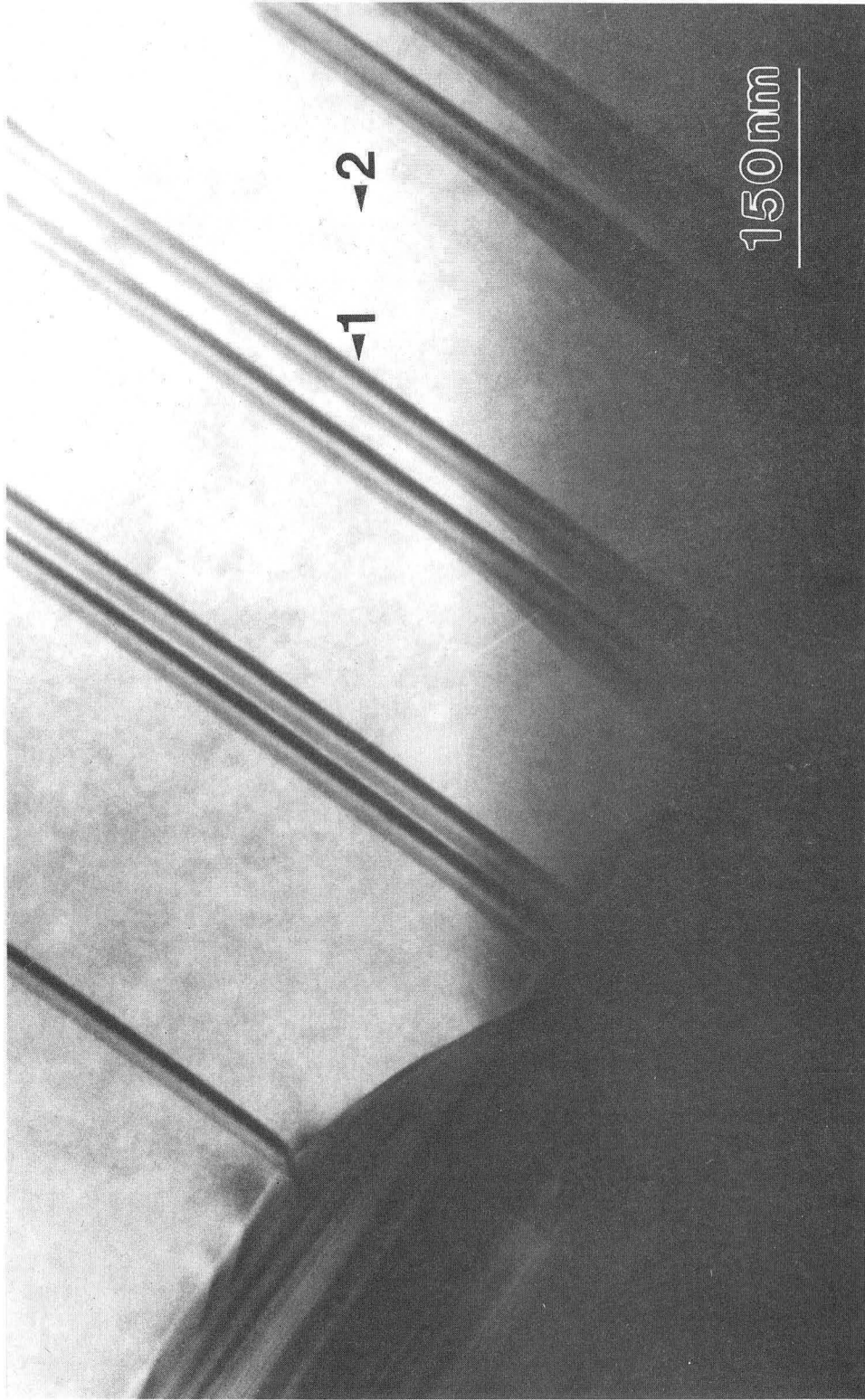


Figure 5

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