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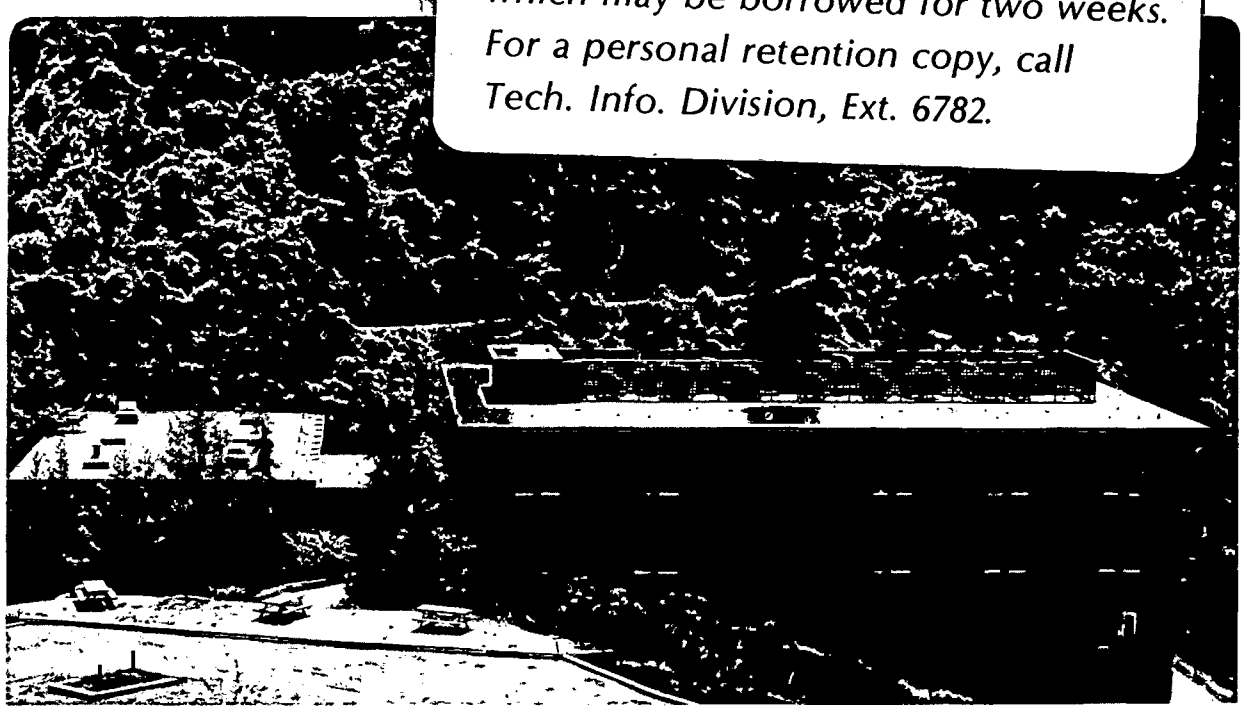

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MICROSTRUCTURE AND GRAIN BOUNDARY COMPOSITION OF HOT PRESSED SILICON NITRIDE WITH YTTRIA AND ALUMINA

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ABSTRACT

The microstructure of two hot pressed silicon nitrides containing Y_2O_3 and Al_2O has been examined by electron microscopy, electron diffraction, and quantitative, energy-dispersive X-ray microanalysis. A crystalline second phase has been identified in the material with additives of 5 w/o Y_2O_3 + 2 w/o Al_2O_3, as a solid solution of nitrogen mellilite and alumina. An amorphous third phase as narrow as 2 nm is discerned at all grain boundaries of this material by high resolution dark field, and lattice imaging.

The second phase in a material with additives of 5 w/o Y_2O_3 + 5 w/o Al_2O_3 has been found to be amorphous. Some of the additional alumina additive appears in solid solution with silicon nitride.

In situ hot stage experiments in a high voltage electron microscope show that the amorphous phase volatilizes above 1200°C leaving a skeleton of Si_3N_4 grains linked by the mellilite crystals at triple points.

The results show that intergranular glassy phases, cannot be eliminated by the Y_2O_3/Al_2O_3 fluxing.

INTRODUCTION

It is now widely recognized that silicon nitride is limited in its high temperature refractoriness due to amorphous phases formed at the grain boundaries as a result of processing with sintering aids (various oxides, e.g., Al_2O_3, MgO, Y_2O_3, etc.).[1] The use of electron microscopy and microanalysis has been significant in verifying directly the morphology and composition in certain cases, especially MgO and Al_2O_3 fluxed silicon nitride (see References 2-9). Clearly, the amorphous phase must be eliminated or made more refractory if the potential of these ceramics is to be fully realized. This is one reason that Y_2O_3 is an attractive sintering aid, but even in this case, amorphous phases have been found[5] although very little electron microscopy and microanalysis has been done on Y_2O_3 fluxed material.

The research of Tsuge, et al.[10,11] on hot pressed silicon nitride fluxed with yttria and alumina, suggested that crystallization of the amorphous phase had occurred resulting in the retention of a high fraction of the room temperature flexural strength at temperatures above 800°C. Since it is of interest to characterize these materials more closely in an attempt to establish whether they were amorphous phase-free, the present investigation was undertaken utilizing electron microscopy and microanalysis following procedures reported for characterizing other silicon nitrides.[2-9]

EXPERIMENTAL

The samples of hot pressed silicon nitride contained 5 w/o Y_2O_3 + 2 w/o Al_2O_3 (A) and 5 w/o Y_2O_3 + 5 w/o Al_2O_3 (B) were those previously studied by Tsuge, et al.[10,11] and were kindly provided by these authors.

Electron microscopy specimens were prepared in the usual way with final thinning being accomplished by ion milling in 6 kV argon ions at an incidence angle of 25°. Specimens were examined in a Phillips EM 400 electron microscope fitted with EDX (Kevex system) and an energy loss spectrometer. High resolution imaging was done in a Siemens 102 Microscope. In situ hot stage experiments were done on the 3 MeV electron microscope at Osaka University, Japan.

The Cliff-Lorimer method (e.g., Reference 12) was used to obtain quantitative spectroscopic analyses from the X-ray data. Yttrium aluminum garnet (YAG) and anorthite glass were used for standards and calibration. All data for quantitative analysis were obtained with the specimen tilted 30° towards the detector. Data were acquired in the multichannel analyser set at the 20 kV range. In order to separate the peaks due to Si_K (1.74 kV) and Y_L (1.92-2.07 kV), it was assumed that that Y_K/Y_L peak intensity ratio is constant. This ratio was measured using the YAG crystal, and from which the Y_L peak could be subtracted from the Si_K-Y_L peak (obtained from the Si_3N_4 samples) so as to deconvolute the peaks.

EXPERIMENTAL RESULTS

(A) Morphology

As already found by Tsuge, et al., sample A was found to consist of small grains of $\beta'Si_3N_4$ solid solution. These grains in the basal plane were on the order of 0.1 to 0.3μ dia. The c-direction size varied substantially from 0.1 to > 1.0μ. All displayed characteristic, highly prismatic shapes (Figure 1).

Yttrium rich phases are readily identifiable in conventional bright field images because of their greater electron absorption[5] and as a consequence, these phases appear darker on the imaging screen. Unlike the β' grains, the yttrium rich phases had no strong morphological characteristics, but did appear to wet the grains at the multigrain junctions where they were found. Some of these regions appeared to be as large as 0.5μ (Figure 2).

Once an yttrium rich phase could be identified in bright field imaging, selected area diffraction was used to obtain interplanar "d" spacings. The specimen was tilted to a condition in which prism plane reflections $(10\bar{1}0)$ of β' and the yttrium rich phases could be discerned so that the β' reflections could be used as a reference to determine the d-spacings of the yttrium phase. The yttrium rich phase was found to contain d-spacings which are consistent with those reported for the (110), (011), (111), (001), and (120) planes of the mellilite phase.[13,14]

X-ray diffraction of sample B showed that the only crystalline phase present was $\beta'Si_3N_4$. Many grains imaged in bright field did not have the highly prismatic shapes seen in sample A, although grain sizes

were in the same range (Figure 3).

The second phase in this material could also be easily identified because of the lack of electron transparency of this phase at multigrain junctions. While the distribution of the β' grains appeared to minimize the size of multigrain junctions, those junctions large enough for analysis were examined by both microdiffraction and dark field imaging using the diffuse scattered electrons to confirm that these junctions contained an amorphous phase.[6-8]

(B) Amorphous Phases

Sample A. While the 5 w/o Y_2O_3 + 2 w/o Al_2O_3 material was reported to have its grain boundary phase crystallized[10], high resolution dark field imaging revealed the presence of an amorphous phase at virtually all β'-β' β'-mellilite boundaries (Figure 2) even those β-mellilite boundaries at which the mellilite appeared to wet the β' phase.

The dark field imaging results were checked by lattice imaging[2] as shown in Figure 4. The data from many such procedures showed that the amorphous phase was as thin as 2 nm. In previous work[5] on Y_2O_3 fluxed silicon nitride, but without Al_2O_3, it was also shown that an amorphous phase was present at the silicon nitride and oxynitride grains. As is seen below with sample B, it is clear that a completely crystalline silicon nitride is not obtained by the Y_2O_3 or Y_2O_3/Al_2O_3 additions.

Sample B. The amorphous phase in this material could be seen at all multigrain junctions as well as at all β'-β' grain boundaries. Although there appears to be a higher density of smaller multigrain junctions containing the amorphous phase, severe overlap of the amorphous

and crystalline phases makes volume measurement practically impossible, so no quantitative work could be done.

(C) Qualitative Analyses

Grain boundaries between Si_3N_4 grains were imaged in STEM and a 100 Å probe was placed first on the β' grain. The spectrum showed a major $Si_{K\alpha}$ peak with a small contribution from $Al_{K\alpha}$. No yttrium could be detected in the grain although background contributions of Cr and Cu from the microscope apparatus were also detected.

The STEM probe was then placed along the boundaries where distinct changes in composition could be seen (Figure 5). A small increase in $Al_{K\alpha}$ peak height was detected and an $Y_{K\alpha}$ peak was observed. Because of the limited resolution of the instrument, quantification of the amorphous phase at the actual grain boundary was not possible.

(D) Quantitative Analyses

Thin, nonoverlapping and electron transparent regions of mellilite were selected for quantitative analysis. Areas for analysis were chosen so that the electron probe formed in TEM would exclude β' contributions. The microscope was operated in the diffraction mode and the pattern observed during acquisition of the spectrum. In this way, it was possible to assure that no drifting of the beam or specimen occurred as indicated by the appearance of β' reflections in the pattern.

The data indicate that there is some solubility of Al_2O_3 in mellilite (Figure 6). This result confirms previously reported results on the solubility of Al in nitrogen mellilite.[15] Molar stoichiometries show the mellilite to consist of 54% Si, 40% Y, and 6% Al or 44% Si_3N_4, 49% Y_2O_3, and 7% Al_2O_3.

Analysis of the amorphous multigrain regions in sample B was difficult, because these regions were somewhat smaller than the mellilite regions in sample A.

Regions greater than 50 nm in size were selected for analysis and microdiffraction was again used during acquisition to assure that the only pattern image was the diffuse scattering from the amorphous region.

The data for this amorphous phase indicated molar stoichiometries in the range of 53% Si, 27% Y, and 20% Al. Assuming Si to be present as the nitride, the molar stoichiometries are 43% Si_3N_4, 33% Y_2O_3, and 24% Al_2O_3 (Figure 7). Table 1 summarizes these results. It can be seen that the data are very consistent (10 different measurements). Many other impurities including Cr, Ca, Fe were also detected in the glass phase, the results being similar to those obtained on a similar material.[5]

In Situ Results. In an attempt to study the behavior of the intergranular phase upon heating, a specimen of sample A was heated in the Osaka University HVEM operated at 2 MeV using a special biaxial tilt hot stage[16] capable of attaining 2000°C. In the vacuum of 1.3×10^{-4} Pa, Si_3N_4 begins to vaporize at 1500°C and the grain boundary amorphous phase was observed to volatilize at about 1200°C. Figure 8 shows electron micrographs before and after heating.* Continued thermal cycling results in complete elimination of the glassy phase presumably due to vaporization of components such as SiO, leaving a skeleton of Si_3N_4 grains linked by mellilite triple points. However, it was not possible to analyze the

*Video recording allowed these changes to be followed dynamically. A video tape is available.

foil after these experiments, as the specimen literally falls apart after removal from the hot stage, and the lack of tilting facilities did not allow in situ analyses to be performed.

Qualitatively, however, these in situ experiments confirm the well known idea that the weakness at high temperatures of Si_3N_4 is due to the presence of the intergranular amorphous phase.

SUMMARY

The present investigation has resulted in the characterization of the Toshiba hot pressed silicon nitride fluxed with yttria and alumina.[10,11] It has been demonstrated that amorphous phases exist at all planar grain boundaries and multigrain junctions in material designed to eliminate such phases. Specifically, the microstructure of sample A fluxed with 5 w/o Y_2O_3 + 2 w/o Al_2O_3 consists of prismatic grains of $\beta'Si_3N_4$, a solid solution of nitrogen mellilite and alumina, and an amorphous third phase at all grain boundaries. Molar stoichiometries show the mellilite phase to consist of about 44% Si_3N_4, 49% Y_2O_3, and 7% Al_2O_3. Success in crystallizing the second phase[10] is conjectured to occur because of volatilization of surface and structural oxides of the starting silicon nitride powder.

Sample B, with additives of 5 w/o Y_2O_3 + 5 w/o Al_2O_3, has a microstructure of less prismatic grains than are seen in sample A and an amorphous second phase at all grain junctions and boundaries. The second

phase containing 43% Si_3N_4, 33% Y_2O_3 and 24% Al_2O_3 appears to result in a lower interfacial energy than in sample A. The glassy phase indicates that liquid phase sintering had occurred during processing as had been conjectured by Tsuge, et al.[17]

These results indicate the difficulties of eliminating amorphous phases in hot pressed Si_3N_4 containing oxide additives. Clearly, attempts are needed to improve the refractoriness of the finely distributed glassy phases if this type of processing is to lead to more refractory Si_3N_4.

ACKNOWLEDGEMENTS

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TABLE I. Summary of Chemical Analyses of Second Phases

Starting Composition of Additives		Composition of Major Second Phase (1)
Weight Percent	Atomic Percent	Atomic Percent
A) 5 Y_2O_3 + 2 Al_2O_3	3.1 Y_2O_3 + 2.8 Al_2O_3	7.4 (± 1.3) Al_2O_3 + 48.6 (± 1.0) Y_2O_3 + 44.0 (± 0.9) Si_3N_4
B) 5 Y_2O_3 + 5 Al_2O_3	3.1 Y_2O_3 + 6.9 Al_2O_3	24.2 (± 2.1) Al_2O_3 + 33.3 (± 4.1) Y_2O_3 + 42.5 (± 1.3) Si_3N_4

(1) These results are the average of 10 different microanalyses from different (thin) regions of foils

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FIGURE CAPTIONS

Figure 1. Bright field electron optical image of sample A.

Figure 2. Electron optical dark field image of sample A showing β'-β' boundary. The diffuse image indicates amorphous phases at all boundaries.

Figure 3. Bright field electron optical image of sample B.

Figure 4. Lattice image and high resolution dark field image of sample A indicating amorphous grain boundary thickness to be ~ 2 nm.

Figure 5. Composite illustrating the use of X-ray microanalysis for characterizing the microstructure of sample A. The dark field image is of the diffuse scattering.

Figure 6. Unsmoothed spectrum from a grain of mellilite of sample A.

Figure 7. Unsmoothed spectrum from an amorphous region of sample B.

Figure 8. a) Before heating specimen from sample A and b) after heating to 1200°C in situ at 2 MeV in vacuo 1.3×10^{-4} Pa. Bright field images. Notice elimination of intergranular amorphous phase in b) by volatilization.

TABLES

Table I. Summary of Chemical Analysis of Second Phases.

Fig. 1

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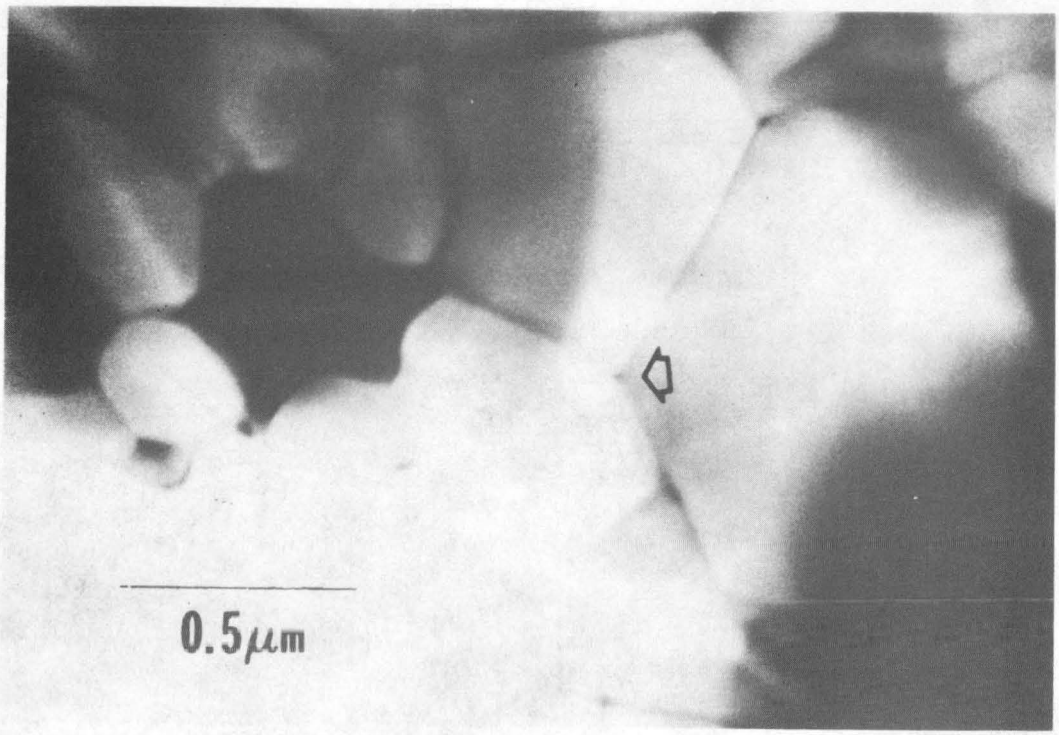

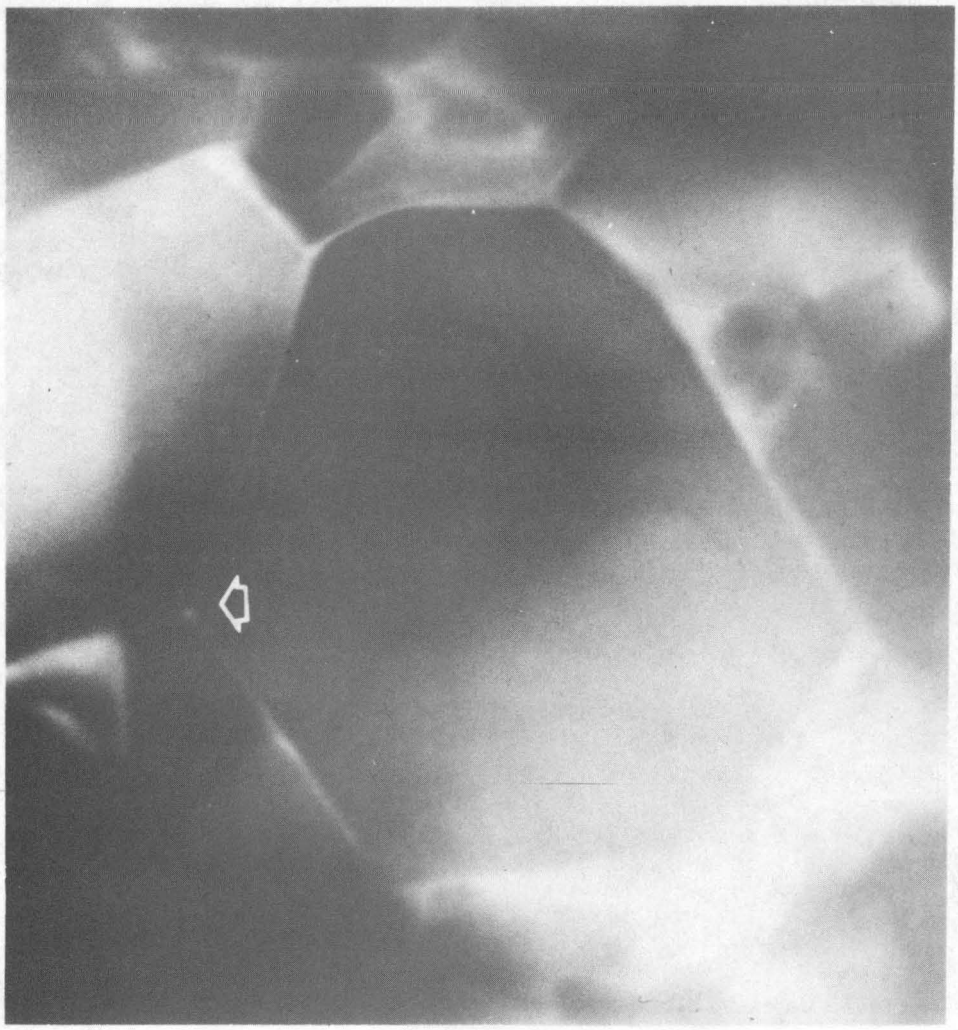

Fig. 2

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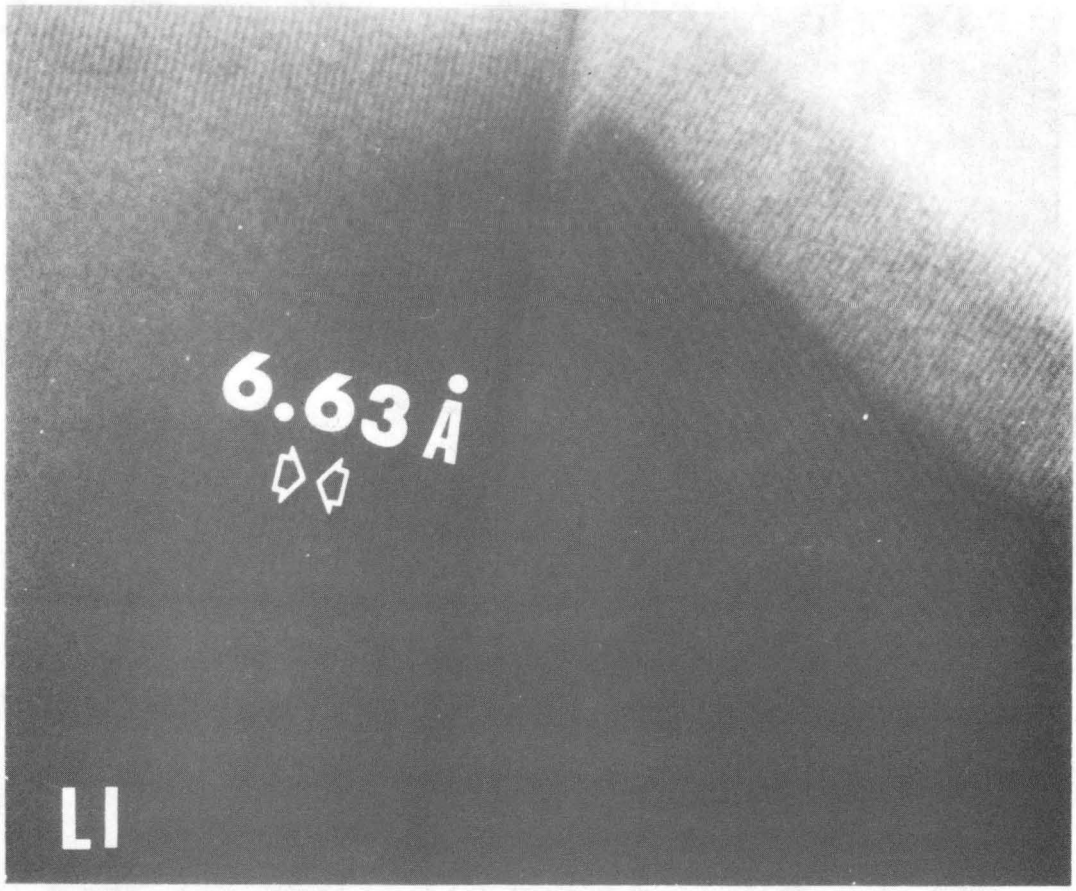

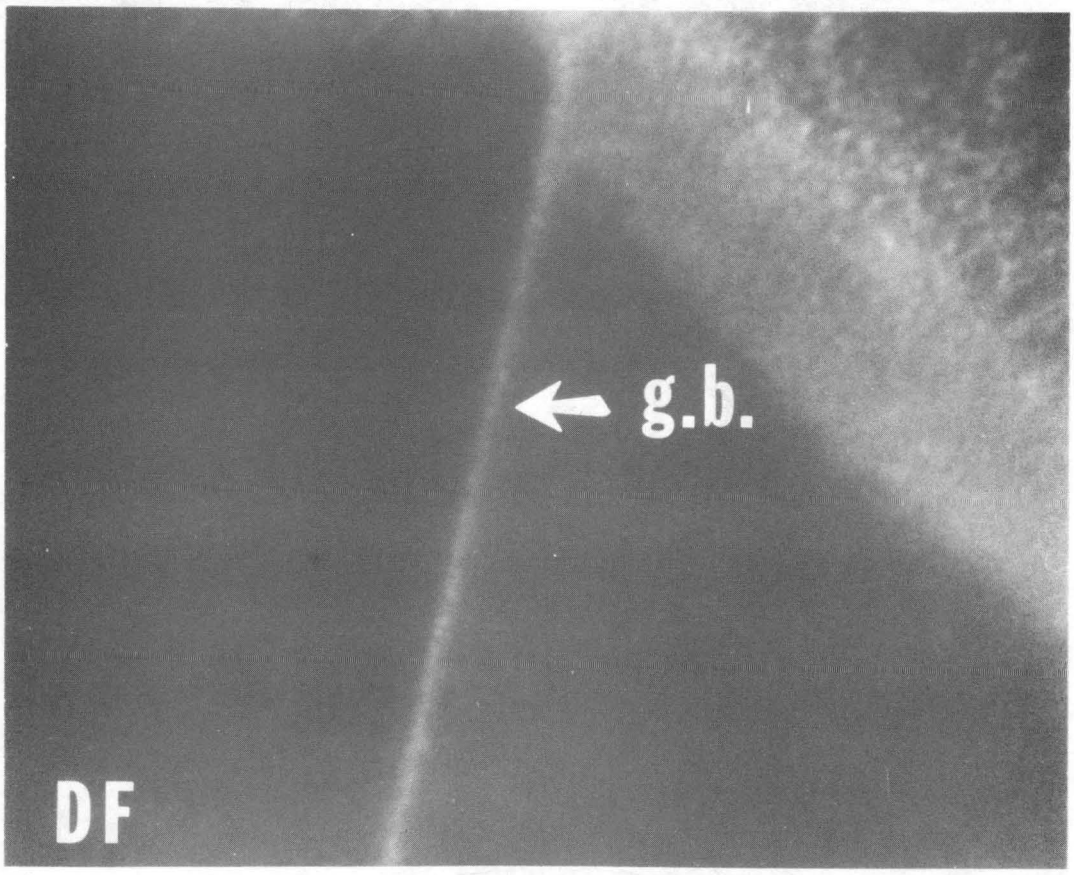

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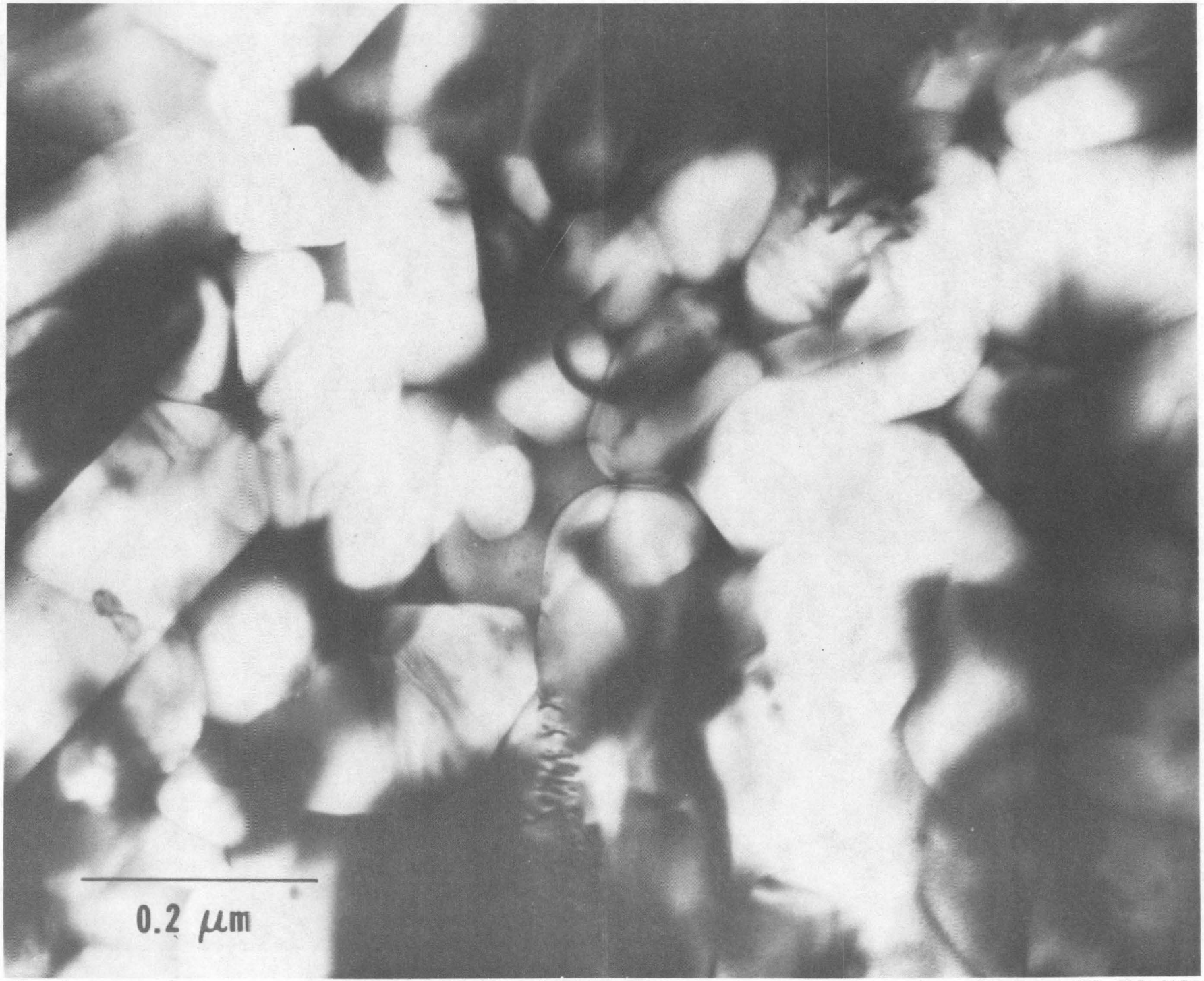

Fig. 4

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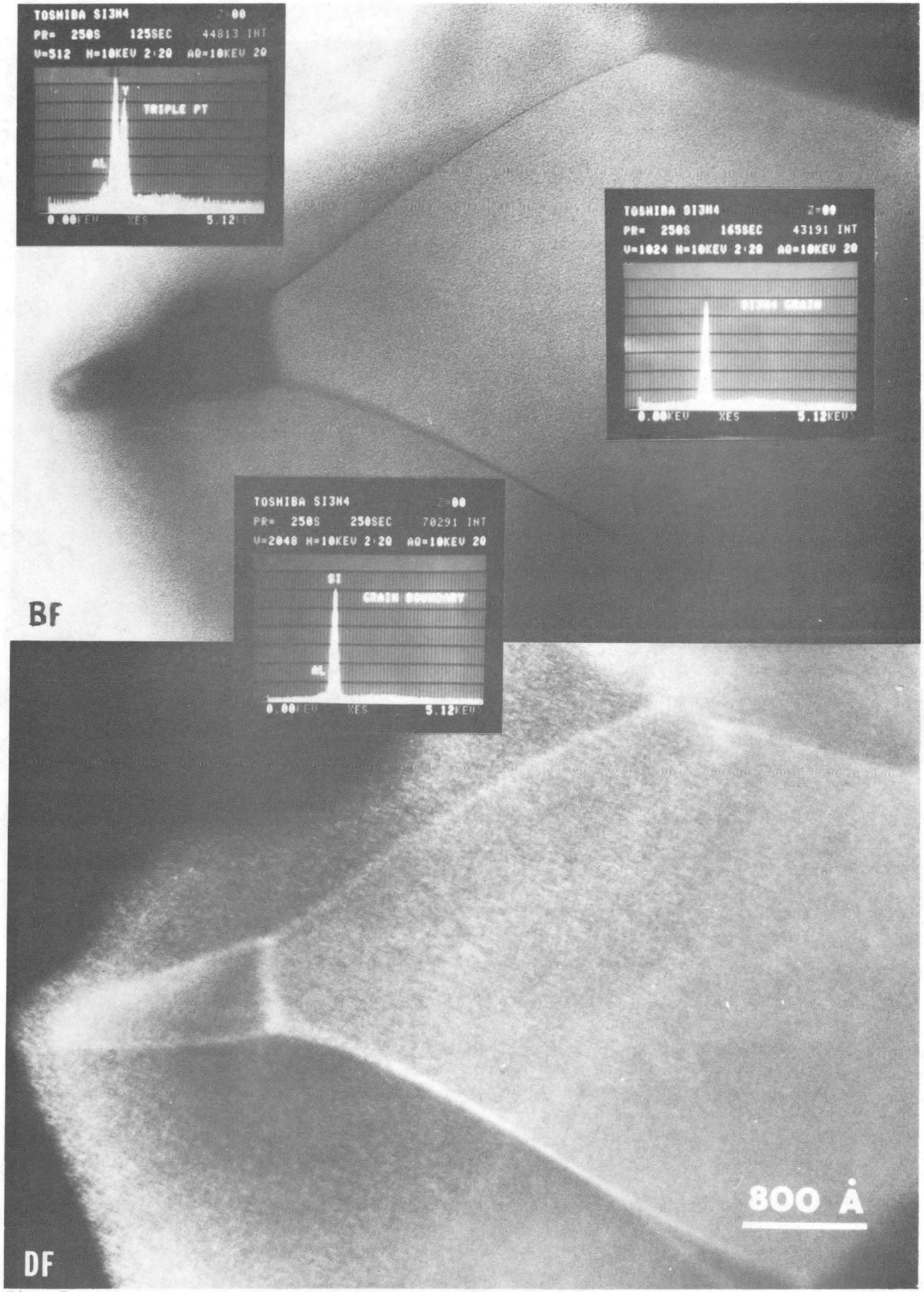

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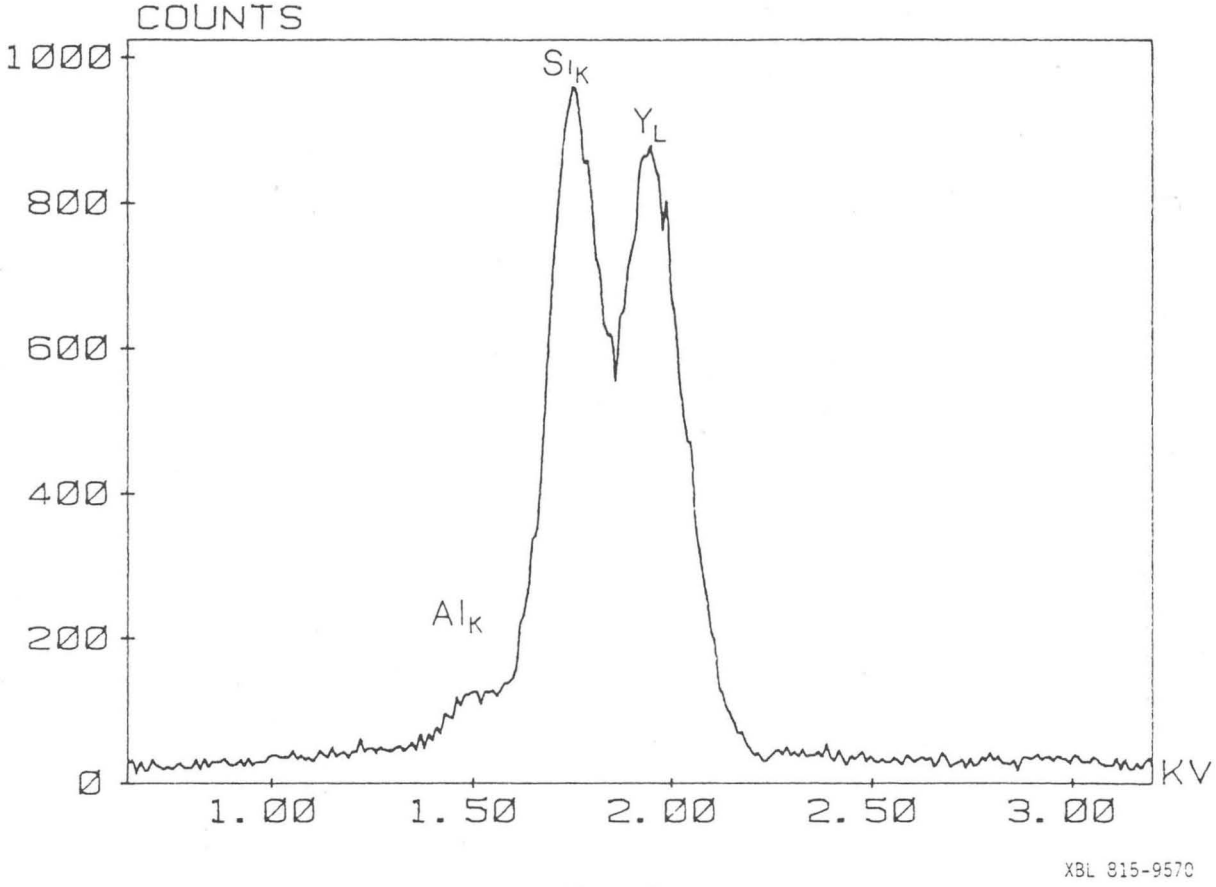
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XBL 815-9570

Fig. 6

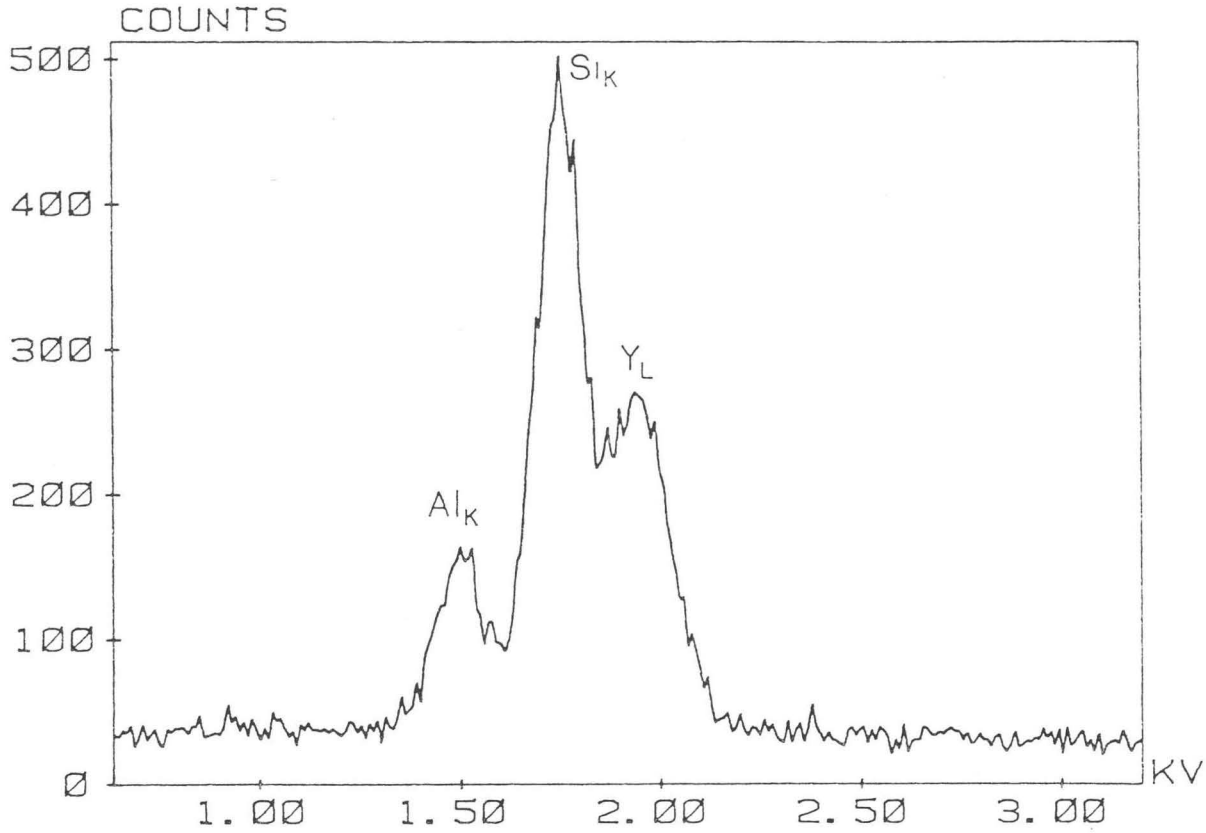

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Fig. 7

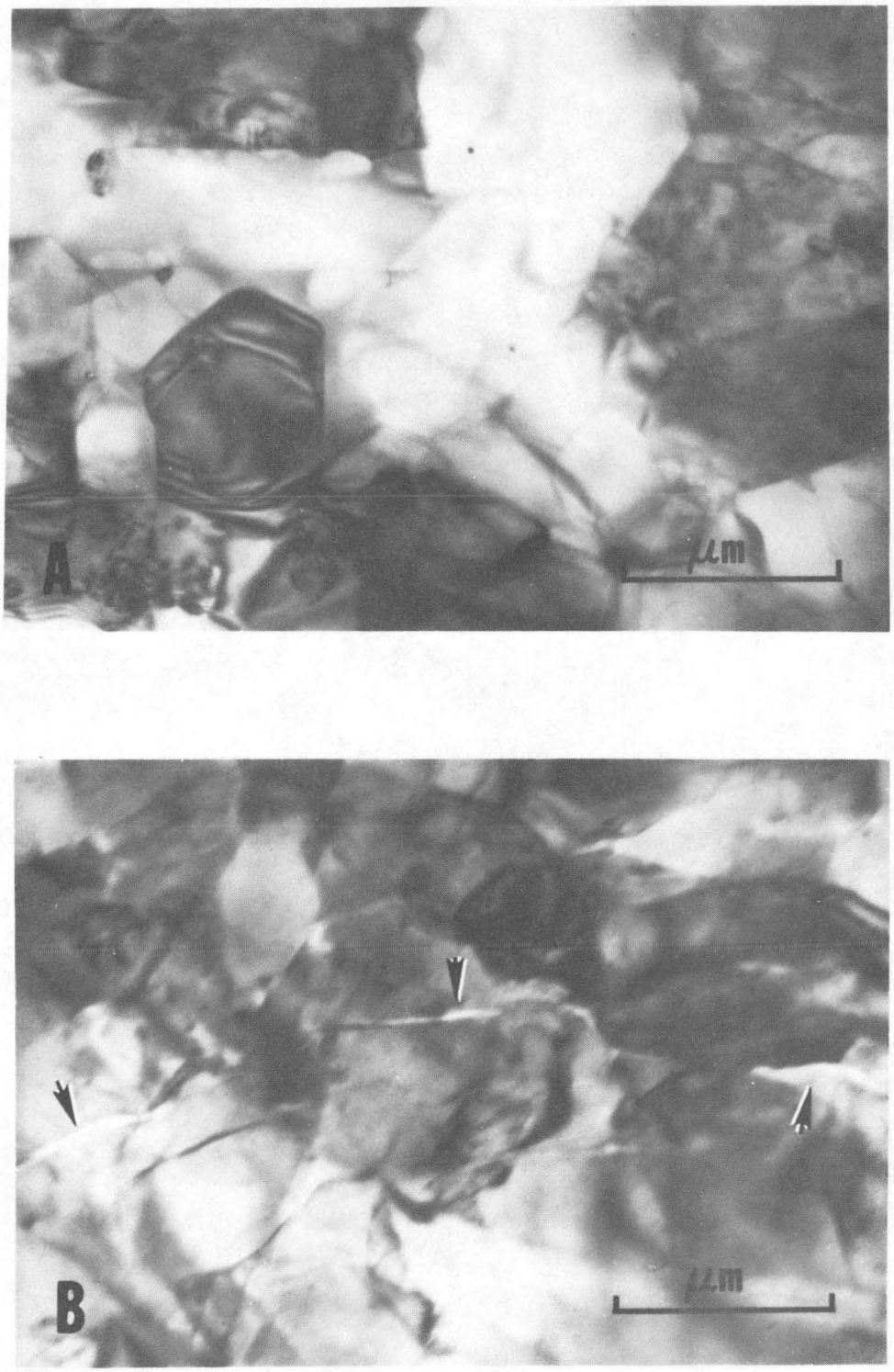

Fig. 8 XBB 810-9410

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