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CHARACTERIZATION OF Y-Si-Al-O-N GLASS



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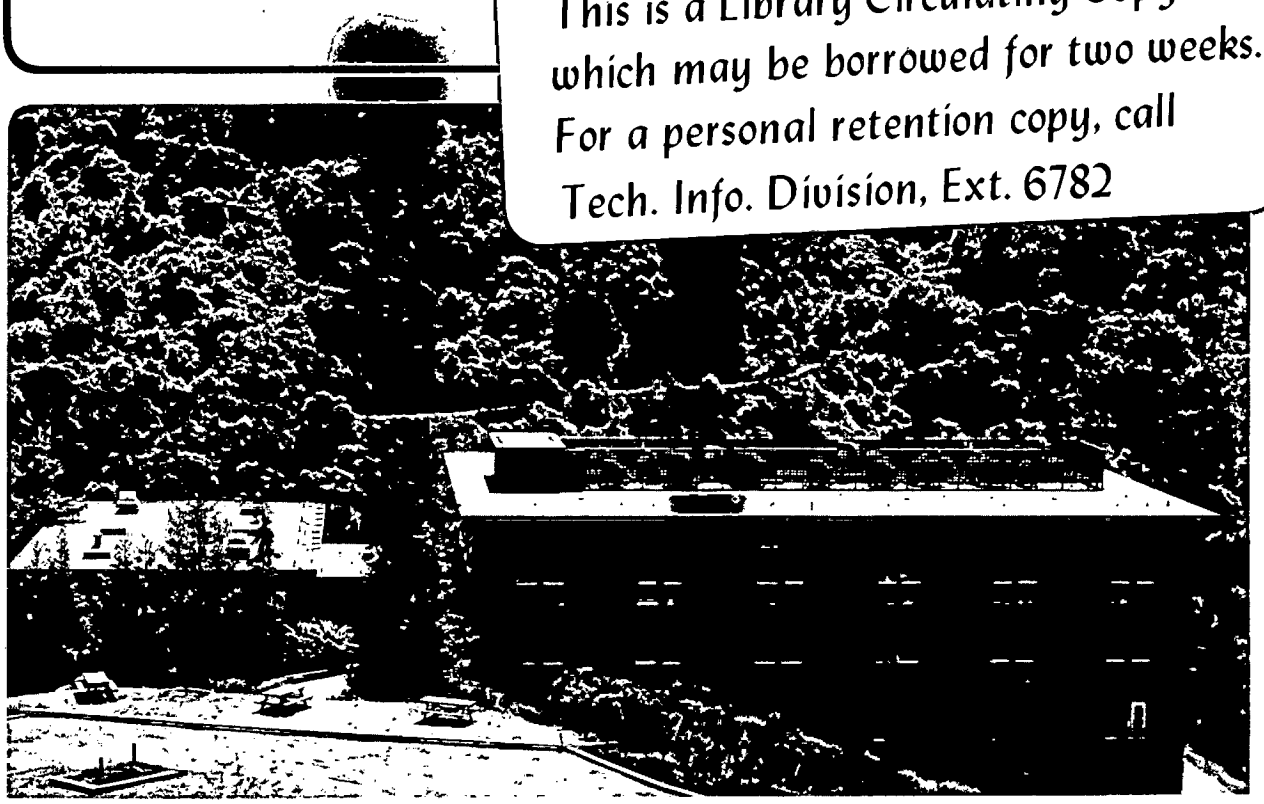

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## DISCLAIMER

# CHARACTERIZATION OF Y-Si-Al-O-N GLASS AND CRYSTALLIZATION

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## Abstract

Glasses have been prepared from sintered powders of $Si_3N_4$, $Al_2O_3$, $Y_2O_3$, AlN and $SiO_2$ in order to study the crystallization behavior on subsequent heat treatment. Appreciable crystallization was only affected after doping with up to 5 wt.% $ZrO_2$. Electron microscopy and microanalysis showed that the crystalline phase was $Y_2O_3 \cdot 2SiO_2$ without detectable Zr present in the crystalline phase. The softening temperature occurs in the range of 850-1020°C. In situ heating in a high voltage electron microscope at ~ 1200°C produced some growth of the crystalline phase; at higher temperatures, however, the glass phase volatilized.


## I. Introduction

The potential of ceramics such as silicon nitride for high temperature applications is well-recognized. However, due to its covalent nature $Si_3N_4$ can only be sintered or hotpressed to full density by use of oxide sintering additives. These additives allow the densification to proceed via a liquid phase (1-3) which yields by a solution reprecipitation mechanism, a crystalline phase. Careful TEM microanalysis, however, reveals that most grain boundaries are wetted by an amorphous grain boundary layer (4-7). This grain boundary layer has a controlling influence on high temperature strength and oxidation behavior.

It is the aim of the present study to investigate this amorphous phase in the shape of single phase glassy material with respect to its crystallization behavior. The same was done in an earlier investigation for a glass consisting of $SiO_2$, MgO and $Si_3N_4$ where crystallization was found to proceed by melt demixing (8,9). In the present study the composition for the glass was chosen from mixtures of $SiO_2$, $Al_2O_3$, $Y_2O_3$, $Si_3N_4$ and AlN, since bulk materials composed from these compounds show several features that make them more

promising:. Here the amorphous phase shows an improved tendency to crystallize upon secondary heat treatment procedures resulting in better high temperature properties (10-13).

A further aim in this research was to study the basic aspects of crystallization with respect to nucleation, nucleation sites, growth direction and local changes in chemical composition. In order to investigate this, two compositions that had been found to be low melting and completely amorphous after cooling (14,15), were chosen. One composition designated B consists of oxides only, while the other designated A includes $Si_3N_4$ that gets dissolved in the melt during fabrication. This should allow an estimate to be made of the influence of the chemically bonded nitrogen on the properties of the glass.

In a further step the influence of different amounts of $ZrO_2$ added as a nucleation aid was investigated by varying the amount of the $ZrO_2$ powder. It was found subsequently that all the $ZrO_2$ dissolved in the glass.

## II. Experimental

### II.1. Sample Preparation and Phase Analysis

The powders were weighed, mixed and milled for 2 hr in agate jars under water free alcohol, then dried and after being cold compacted to pellets, embedded in BN and sintered under flowing nitrogen. The weight loss during firing was measured and phase analysis was done by x-ray analysis of the pulverized samples. The chemical composition and the results of the phase analysis are listed together with the fabrication parameters in Table 1. Due to the weight loss, the nitrogen content of several samples had to be analyzed by the LiOH method.

### II.2. Secondary Heat Treatments, DTA and Dilatometer Runs

The as-sintered samples were sawn apart and pieces exposed to secondary heat treatments at 1100°C under $N_2$ atmosphere for different times and then

these pieces were crushed to powder and phase analysis was done by x-rays. These results are listed in Table 2. In order to determine the transition temperature for both glass compositions, DTA and dilatometer runs were carried out under nitrogen atmosphere.

II.3. Electron Microscopy and Microanalysis

Thin slices were cut from the glass billets and mechanically polished down to foils of 50μm thickness. These foils were then mounted on copper grids and ion beam thinned by 6kV argon ions at a 25° angle of incidence. A thin layer of carbon was evaporated onto the specimens to avoid charging in the electron microscopes. Specimens were normally examined at 650kV. Hot stage experiments were done in a 3meV electron microscope (16).

A Philips EM400 equipped with a Kevex Si(Li) detector and multichannel analyzer was used in the TEM mode for quantitative x-ray analysis of the materials.

To properly calibrate the EM400 for quantitative analysis, an yttrium aluminum garnet (YAG) and anorthite ($CaO.Al_2O_3 2(SiO_2)$) glass were used.

k values (17) were experimentally determined. In this way, it was possible to use the Cliff-Lorimer method which relates energy dispersive x-ray peak intensities to molar compositions. All data for quantitative analysis were collected in TEM with the specimen tilted 30°C toward the detector. Data were acquired in the multichannel analyzer set at a 20kV range.

Analysis of materials containing both yttrium and silicon requires deconvolution of the $Si_K$ peak (1.74kV) and $Y_L$ peaks (1.92 - 2.07kV). Because these peaks have Gaussian shapes, overlap occurs. In order to separate the sum, the contribution from at least one peak intensity must be determined. This was done by assuming that the $Y_K/Y_L$ peak intensity ratio is constant. After this ratio was determined using the YAG foil, further analysis of $Si_K$ containing

spectra was done by determining the $Y_K$ peak intensity. A $Y_L$ peak intensity was thereby assumed and subtracted from the net $Si_K$-$Y_L$ intensity to determine the $Si_K$ peak intensity.

Electron energy loss spectroscopy, using a spectrometer developed at Berkeley (17) was also attempted but some difficulties were encountered due to vaporization of the glass when the beam intensity was high enough to record a signal. Thus only qualitative information could be obtained by this method.

## III. Results

### III.1. Phase Analysis and Chemical Composition

Table 1 shows that the weight loss is not limited to the nitrogen containing glass but also appears in the pure oxide glass. This can be explained by the loss of SiO as has been shown by both experiments (18,19) and thermodynamic calculations (15,20). Both compositions reveal comparable weight losses and the nitrogen analysis shows that even in the nitrogen containing glass, SiO must constitute the major vaporization product, since the difference between the measured (3.7 wt%) and the theoretical value (4.4 wt%) is much too small to explain the weight loss. The phase analysis reveals that both compositions can be prepared as glass with only traces of crystal left; this is supported by the TEM analysis. It is interesting to note that if the oxide glass is prepared in air under the same conditions, it shows no weight loss and is strongly crystallized even after rapid cooling. The question of whether the weight loss shifts the composition towards stronger glass formation, remains open, although under $N_2$ atmosphere, the loss of SiO does shift the composition towards the line $Y_2O_3$-$Al_2O_3$ (the composition of which is of more refractory character), crystalline phases have only been found in glasses containing $ZrO_2$ relative to its amount.

III.2. Secondary Heat Treatments, DTA and Dilatometry

The secondary heat treatments of the pure glasses caused only very sluggish crystallization in case of the nitrogen containing glass where even after 24 hrs only traces of crystalline phases occurred. The pure oxide glass crystallizes somewhat faster. The best results of crystallization could be obtained in glasses containing $ZrO_2$. These results are listed in Table 2. This phenomenon will be discussed in more detail in the next section.

The transition temperatures of both glasses were studied by DTA and dilatometry. In the DTA composition, A shows a transition temperature of 925°C versus 850°C for B. A exhibits two further small endothermal peaks at 1170°C and 1290°C, B shows a large exothermal peak at 1070°C resulting from the start of crystallization. The dilatometer shows a similar behavior. For A the transition lies between 850 and 895°C, for B at 860°C, where the curve bends at 1000°C and 1070°C by the start of crystallization.

III.3. Electron Microscopy and Microanalysis

All as-prepared glasses (Table 1) were amorphous as evidenced by the images and their diffuse electron diffraction patterns. Some small crystalline particles were observed in all samples with or without nitrogen (Figs. 1, 2). Although the glasses showed a wavy appearance probably due to preferential ion etching suggesting composition variations or phase separation, no such variations were detectable by microanalysis at ~ 100Å resolution. Extensive crystallization was only affected when $ZrO_2$ was added. The amount of crystalline phase was higher in the 5 wt.% $ZrO_2$ than in the 1 wt.% $ZrO_2$ glasses. Crystals were in the form of thin plates, sometimes dendritic in shape (Fig. 3).

The diffraction patterns from the crystalline phase were very complex. However, careful x-ray microanalysis identified the main crystalline phase as $2SiO_2.Y_2O_3$. No Zr could be detected in the crystals, but only in the glass

phase (Fig . 4). Most of the aluminum seems to be in the glass phase compared to the crystal phase (about 4:1) with the silicon contents about equal and yttrium about 1.5 times higher in the crystals than in the glass. Some particles of undissolved $Si_3N_4$ were also identified by EELS as shown in Figs. 5 and 6. In attempts to measure the nitrogen contents, the glass phase volatilized in the beam (the mottled area in the micrograph of Fig. 6) and the $N_k$ signal decreased with exposure time. Thus, it was not possible to measure O/N ratios in these samples.

III.4. In-situ Experiments

Specimens similar to those in Fig. 3 were examined in the Osaka University electron microscope at 2meV. At these energies no ionization damage occurred although some displacement radiation damage may occur. However, it is possible to heat samples up to 2000°C in the hot stage. Heating below the volatilization temperature (~ 1300°C), e.g. at 1200°C, resulted in crystal growth suggesting that continued crystallization of these Y-Si-Al-O-N glasses may be affected by aging at 1200°C. Figs. 8a,b show examples of this result.

## IV. Discussion

The results show that nitrogen in small amounts promotes the glass formation when added to an oxide glass. This means that nitrogen lowers the tendency to crystallize. This is supported by the higher transition point. The nitrogen strengthens the glass network and thus requires a higher activation energy. Another important feature that needs to be discussed is the tendency of the glass to show phase separation, i.e. decomposition into two glasses of different composition, since phase separation is known to promote crystallization (8,9). In this work the nitrogen lowers the tendency of phase separation while the $ZrO_2$ additions that are completely dissolved in the glass,

enhance it. Both effects may be explained by phenomena found in known phase equilibria (the liquid phase equilibria of the Y-Si-Al-O-N system in this region are not known in such detail). Nitrogen lowers the eutectic temperatures. Thus the two eutectic channels that cause phase separation in the pure oxide subsystem that run into the oxy-nitride system can combine so that the tendency for phase separation is removed. On the other hand, $ZrO_2$ is thought to produce metastable phase separation in the $ZrO_2$-$SiO_2$ subsystem (21,22). It must be emphasized, however, that at the present stage these explanations are merely hypothetical. The TEM results do show, however, that crystallization is promoted by phase separation, since regions in which the glass is richer in $Y^{3+}$ are those which tend to crystallize.

## V. Summary

Two Y-Si-Al-O-N glasses have been investigated with respect to the influence of nitrogen on the glass properties and the crystallization behavior of the glass. The results show:

1) Nitrogen diminishes the tendency of the glass to crystallize compared to a pure oxide glass.
2) Nitrogen raises the transition temperature of the glass, thus it strengthens the glass network.
3) $ZrO_2$ additions, whilst dissolving in the glass, promote crystallization. The most likely explanation for this phenomenon is that $ZrO_2$ promotes phase separation in the glass.

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Table 1. Chemical Composition, Fabrication Parameters and Phase Analysis

| Sample Designation | Composition wt% | | | | | Eq.% | | | | | fabrication parameters temp. (°C) | atmos. | time (h) | weight-loss (wt%) | phases |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $Si_3N_4$ | $SiO_2$ | AlN | $Al_2O_3$ | $Y_2O_3$ | Si | Al | Y | O | N | | | | | |
| A | 6.61 | 27.84 | 3.84 | 9.41 | 52.30 | 5.1 | 17.6 | 31.5 | 70.8 | 29.2 | 1600 | $N_2$ | 30 | 15 | glass |
| A | 6.61 | 27.84 | 3.84 | 9.41 | 52.30 | 5.1 | 17.6 | 31.5 | 70.8 | 29.2 | 1600 | $N_2$ | 5 | 4.3 | glass |
| A | 6.61 | 27.84 | 3.84 | 9.41 | 52.30 | 5.1 | 17.6 | 31.5 | 70.8 | 29.2 | 1450 | $N_2$ | 30 | 5.5 | glass |
| B | - | 23.15 | - | 22.31 | 54.54 | 34.9 | 29.7 | 35.3 | 100 | - | 1450 | $N_2$ | 30 | 4.9 | $\beta Y_2Si_2O_7$ vvw<br>$Al_2O_3$ vw |
| B | - | 23.15 | - | 22.31 | 54.54 | 34.9 | 29.7 | 35.3 | 100 | - | 1600 | $N_2$ | 30 | 10.4 | glass |
| B | - | 23.15 | - | 22.31 | 54.54 | 34.9 | 29.7 | 35.3 | 100 | - | 1600 | air | 30 | 0 | YAG s |
| A+1wt% $ZrO_2$ | | | | | | | | | | | 1450 | $N_2$ | 30 | 2.4 | $\beta Y_2Si_2O_7$ vw |
| A+5wt% $ZrO_2$ | | | | | | | | | | | 1450 | $N_2$ | 30 | 6.0 | YAG m,<br>$\beta Y_2Si_2O_7$ m |

starting powders: $Si_3N_4$, AlN: H. C. Starck, $Al_2O_3$ Alcoa, $Y_2O_3$ Merck

$ZrO_2$: ultrafine by use of $ZrO(CH_3COO)_2$ Roth

Table 2. Results of the secondary heat treatment, the starting material was X-ray pure glass (i.e. the 2nd, 3rd and for B the 5th of the samples, listed in Table 1)

| Sample | Heat Treatment temp. (°C) | time (h) | Phase Analysis |
|---|---|---|---|
| A | 1100 | 0.1 | YAG vvw, $Y_2SiO_5$ vvw |
| | 1100 | 2 | $Y_2SiO_5$ vvw |
| | 1100 | 24 | $\beta Y_2SiO_7$ vw, YAG vvw |
| B | 1100 | 0.1 | YAG vw, $Y_2SiO_5$ vvw |
| | 1100 | 2 | $Y_2SiO_5$ vw |
| | 1100 | 24 | $Y_2SiO_7$ w, YAG vvw, YAG w |
| A+1wt% $ZrO_2$ | 1100 | 2 | $Y_2SiO_5$ w, $Y_2Si_2O_7$ w, YAG vvw |
| | 1100 | 24 | YAG vw, $Y_2Si_2O_7$ w, $ZrO_2$ mvw, $YSiO_2$ Nvw |
| A+5wt% $ZrO_2$ | 1100 | 2 | YAG w, $Y_2Si_2O_7$ w, $Y_2SiO_5$ vw |
| | | 24 | YAG vw, $Y_2SiO_7$ vw, $ZrO_2$ mvw, $YSiO_2$ Nvw |

## Figure Captions

Fig. 1. (a) Electron micrograph of glass of composition A treated 0.5h at 1450°C and annealed 24h at 1100°C (650kV: bright field); (b) selected area diffraction pattern showing diffuse ring from the glass. Spots are Bragg reflections from the small crystal particles (Si or $Si_3N_4$) resolved in A (see Figs. 5,6).

Fig. 2. Glass of composition B: 0.5h at 1600°C in nitrogen (650kV: bright field).

Fig. 3. Electron microscopy results on glasses doped with $ZrO_2$ (a) 1% $ZrO_2$ dark field image of Bragg spot from crystal phase. Notice unusual morphology of the crystals. (b) 5% $ZrO_2$; (c) selected area diffraction pattern showing crystallization has occurred--see also Bragg contours in crystal phase; (d) dark field image of one of the spots shown in (c). Treated 1/2h at 1450°C and 2h at 1100°C.

Fig. 4. Electron micrograph (bright field: 650kV) and microanalysis of characteristic x-ray spectrum from glass phase (dotted lines) and crystalline phase (solid line).

Fig. 5. Energy dispersive x-ray microanalysis of glass matrix (a) and crystal phase (c) shown in the micrograph (b). (d) is the EELS spectrum. Specimen A with 5% $ZrO_2$.

Fig. 6. As Fig. 5.

Fig. 7. EDS spectrum from sample A showing large number of different cations detected in these glasses.

Fig. 8. In-situ heating experiment: glass A containing 5% $ZrO_2$ bulk treated 0.5h at 1450°C and 2h at 1100°C (a) foil after temperature raised to

1100°C, (b) after further heating ~ 1h to a maximum of 1230°C and cooled in-situ. Arrows point to growth of crystals in (b) and new nucleation due to the in-situ heating; bright field images taken at 2meV.

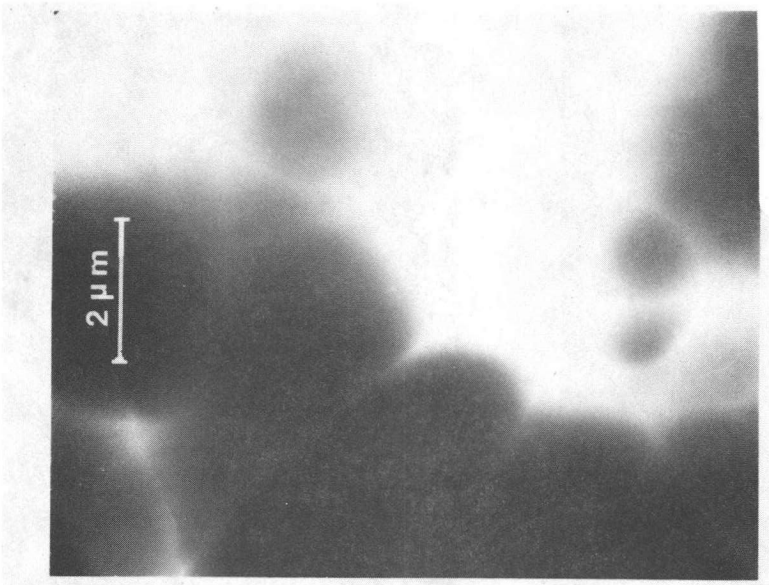


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Fig. 2

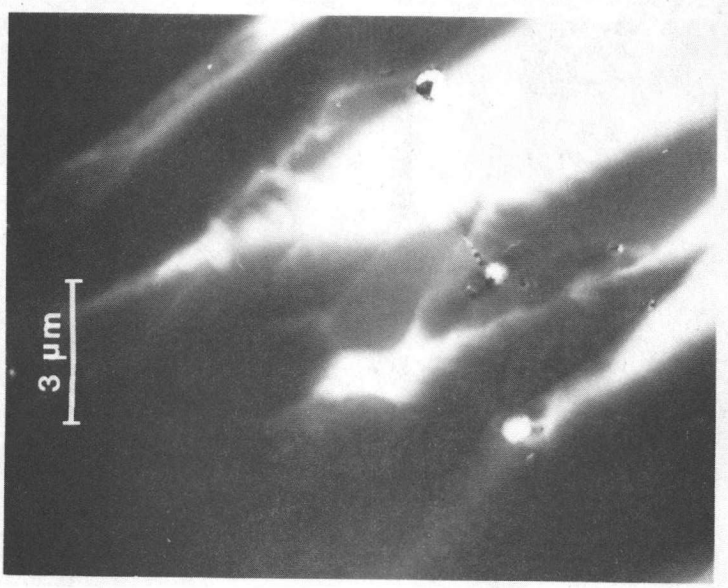
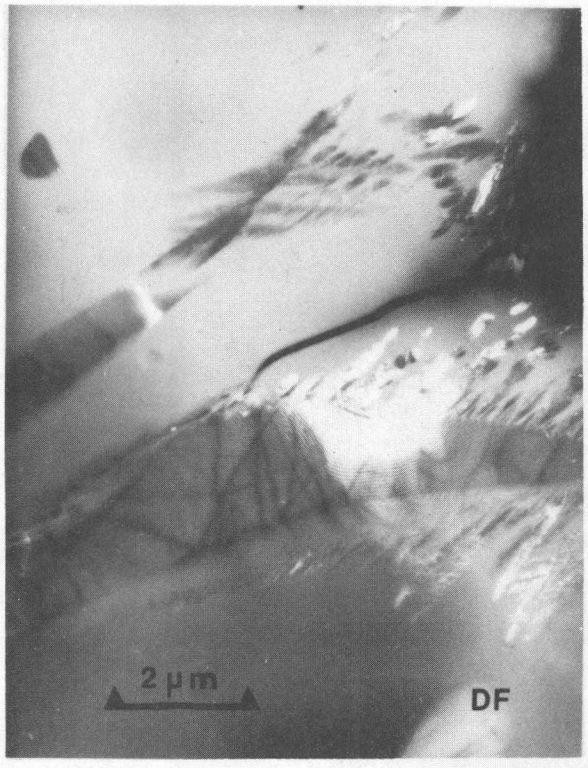
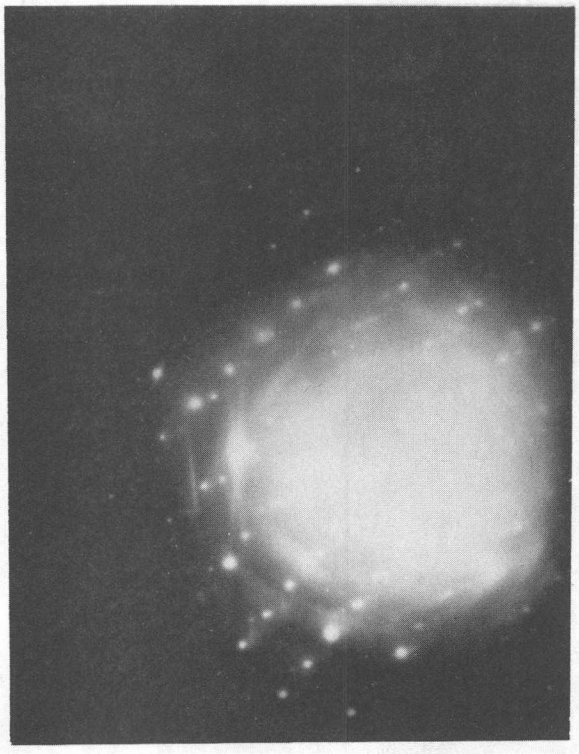



Fig. 1




A


B



C


D

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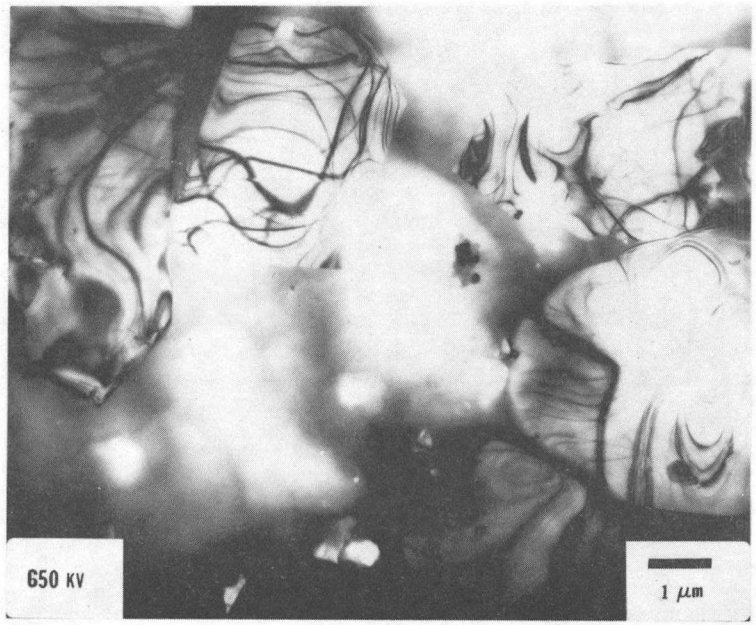
Fig 3



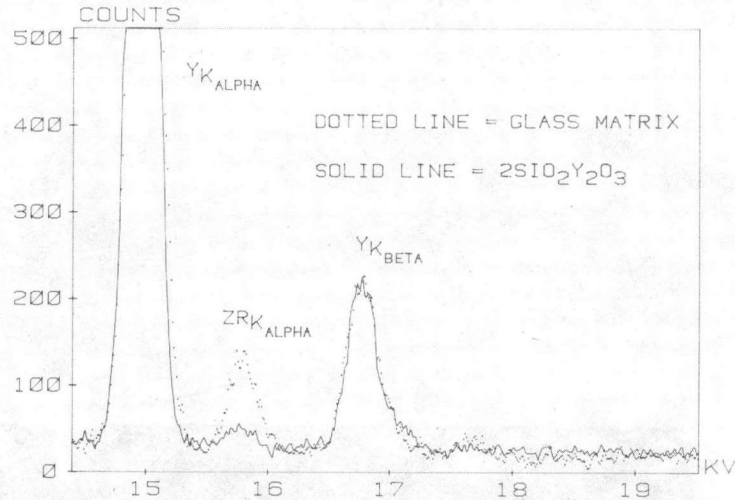




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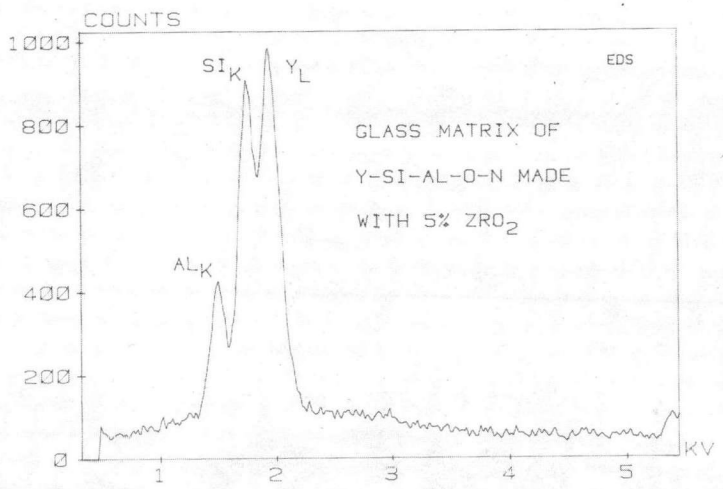
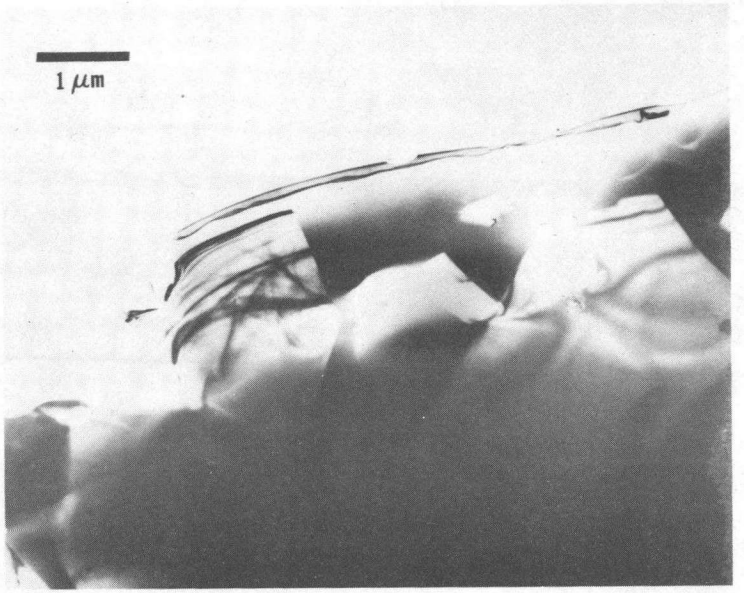
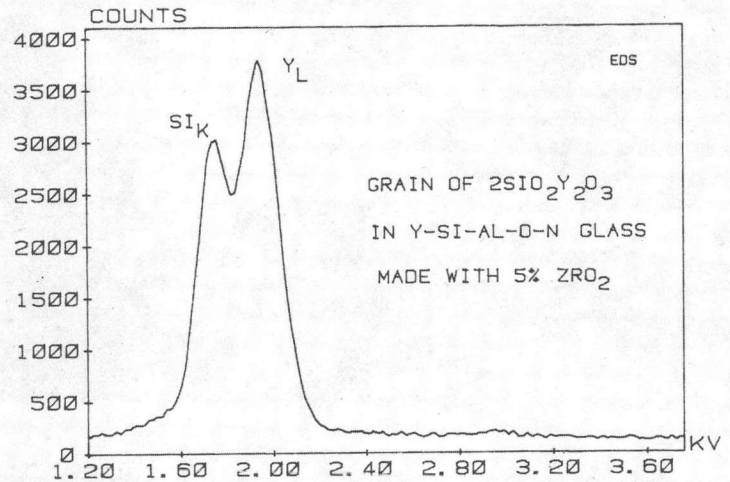
**Fig. 4**



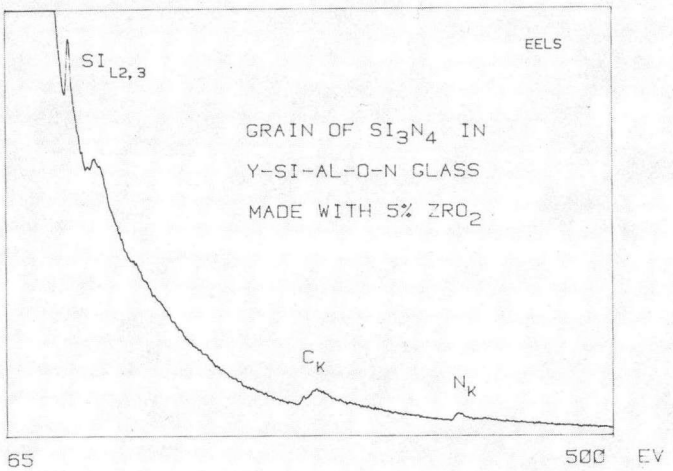




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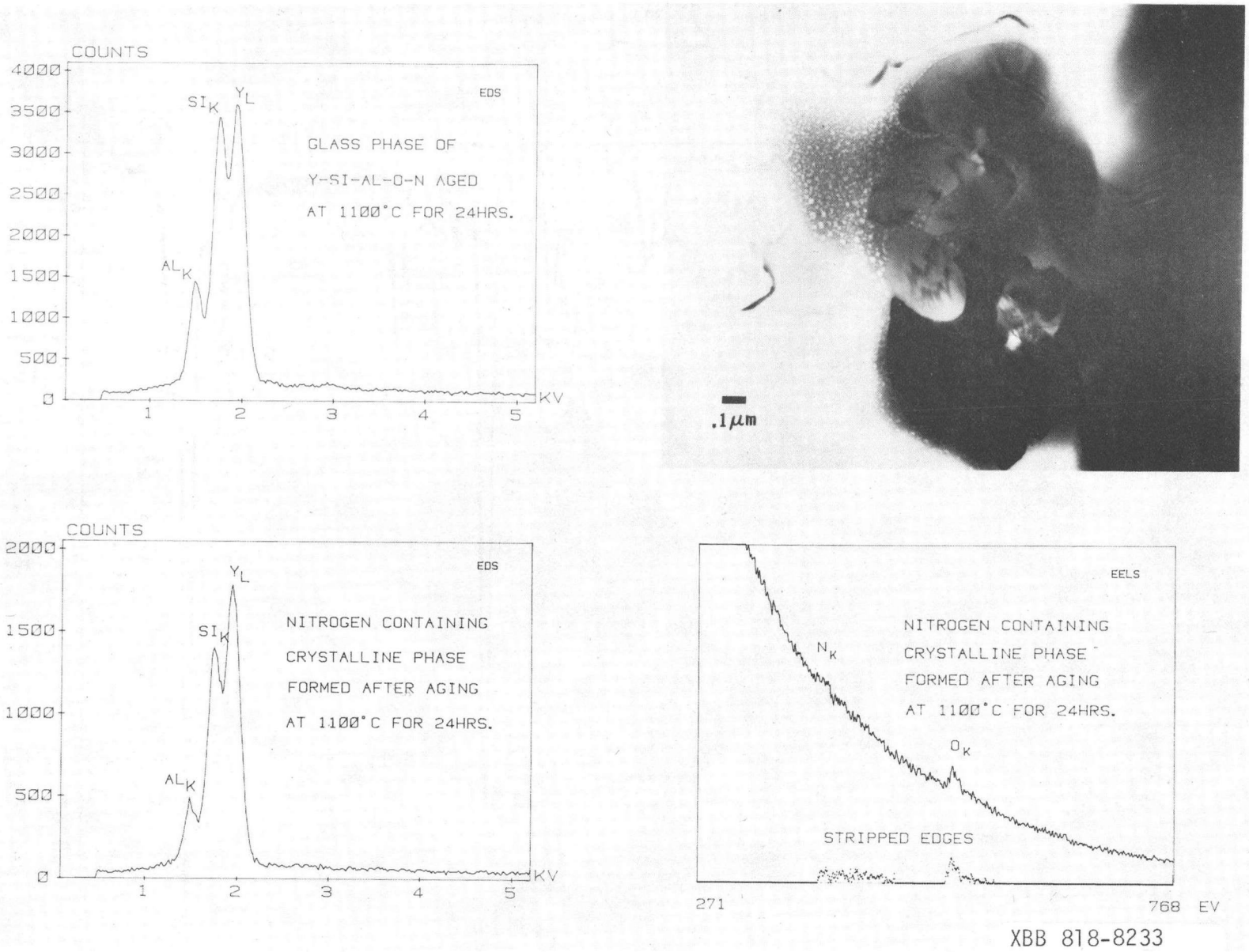
**Fig. 5**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GLASS PHASE OF
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AT 1100°C FOR 24HRS.
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AL K
EDS
NITROGEN CONTAINING
CRYSTALLINE PHASE
FORMED AFTER AGING
AT 1100°C FOR 24HRS.
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**Fig. 6**

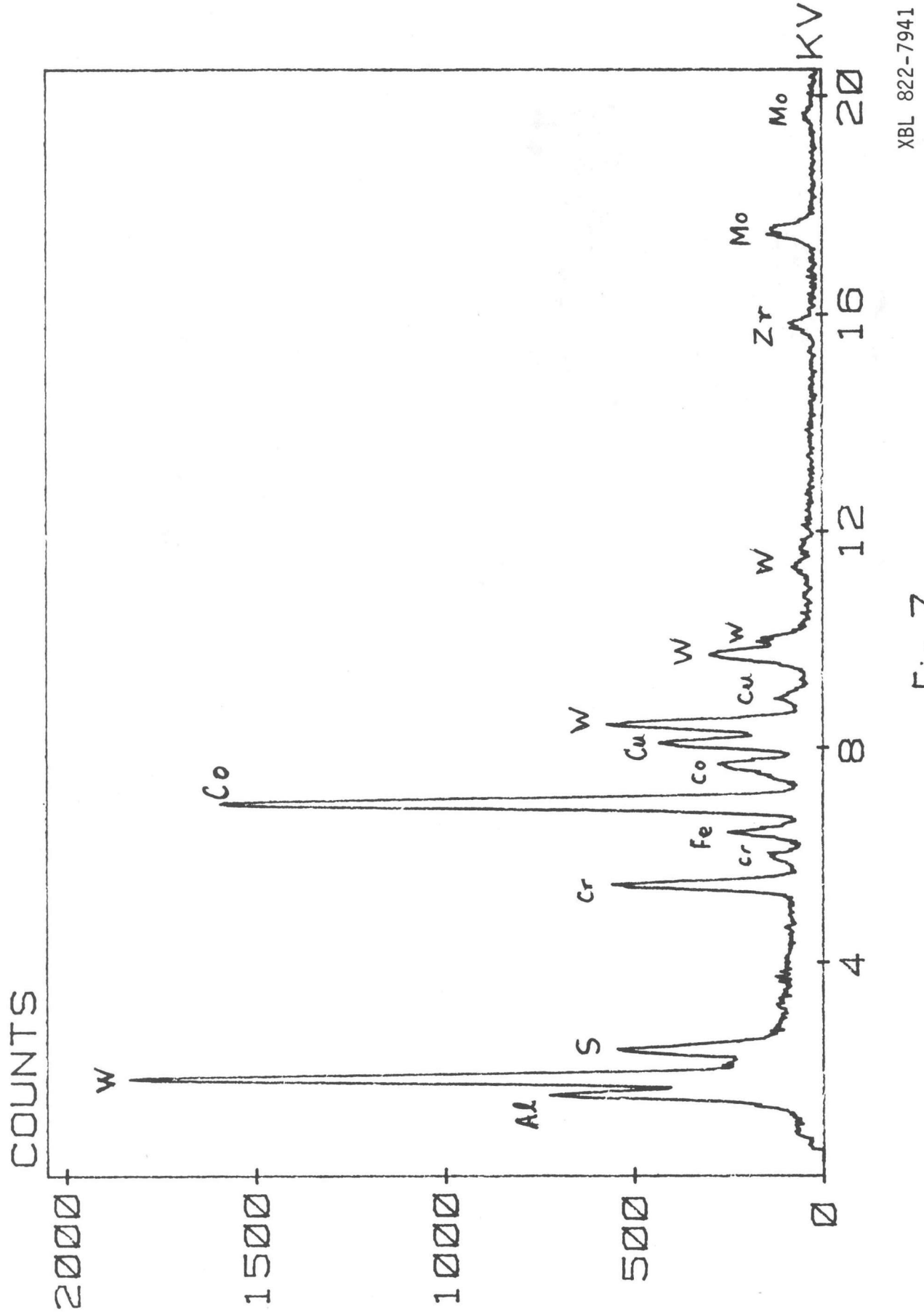


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Fig. 7

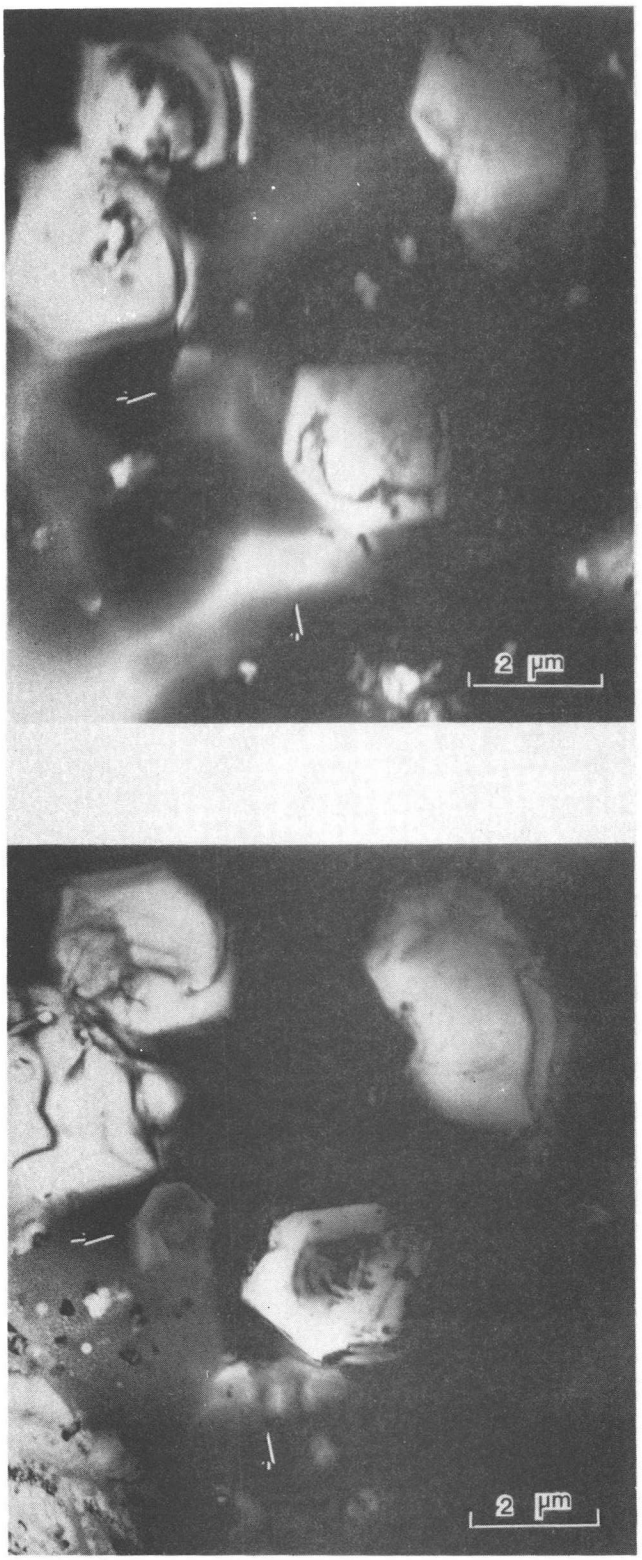


Fig. 8 a & b

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