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DELTA[SUB]2 -YC[SUB]2 SI[SUB]2 O[SUB]7 STRUCTURE CONFIRMED BY PROCESSING AND SIMULATION OF ATOMIC-RESOLUTION IMA6ES

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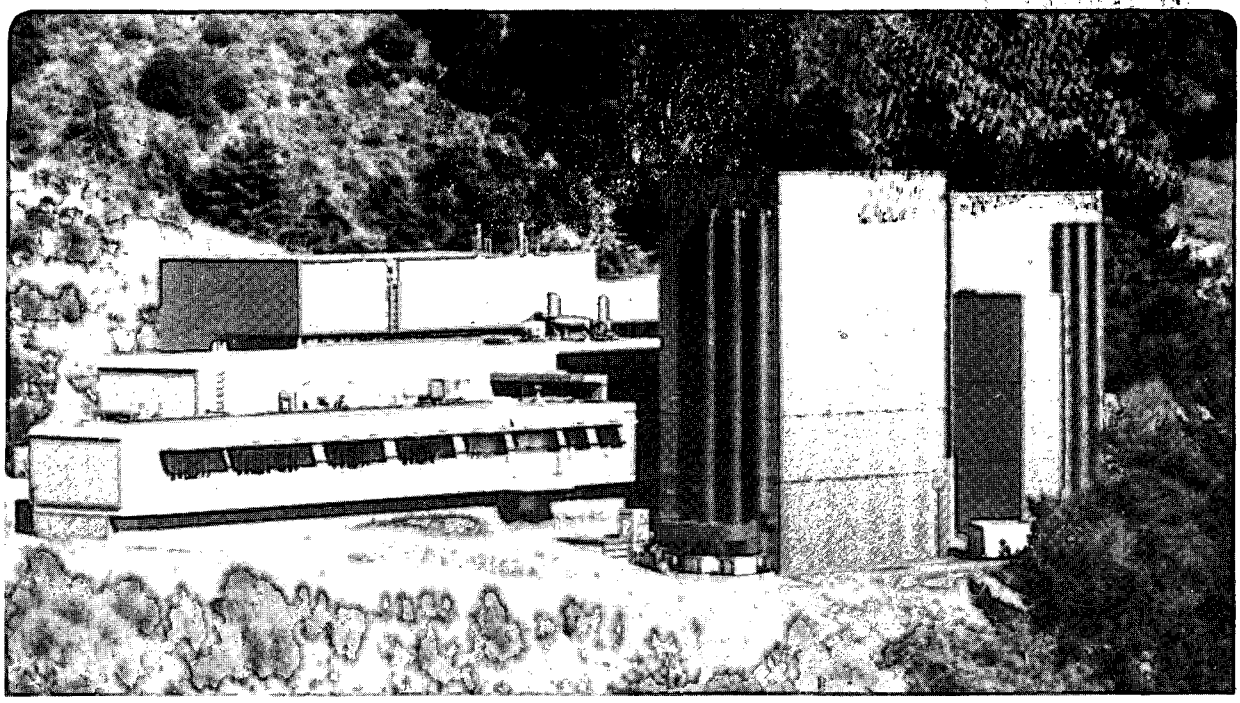

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DISCLAIMER

δ_2-$Y_2Si_2O_7$ STRUCTURE CONFIRMED BY PROCESSING AND SIMULATION OF ATOMIC-RESOLUTION IMAGES.

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ABSTRACT

High resolution electron micrographs have been obtained in various orientations for δ_2-$Y_2Si_2O_7$ using the Atomic Resolution Microscope (ARM) at the National Center for Electron Microscopy (NCEM). These ARM images were processed by masking the diffractogram of the digitized image in Fourier space and applying an inverse transform (using the SEMPER program at the NCEM Image Analysis Facility) in order to reveal details obscured by amorphous contrast originating in the glassy matrix. Processed experimental images from very thin regions of the crystalline phase were compared with images simulated from postulated models (SHRLI images); close agreement was obtained.

INTRODUCTION

Yttrium disilicate has been studied previously in relation to its application in laser materials and high energy phosphors based on rare earth silicates doped with yttrium. However, recently more attention is being focussed on yttrium silicate because it remains as a product phase after firing the Si_3N_4 based ceramics with densifying aids such as Y_2O_3, Al_2O_3 and rare earth oxides [1,2]. In spite of its importance, the crystallographic data available on the basis of x-ray powder diffraction studies are not reliable. The main reason for this unreliability is the extensive polymorphism exhibited by yttrium silicate; in fact, six different modifications, each with large low symmetry unit cells, have been reported [3]. Hence structural studies in this material are highly desirable.

The occurence of two similar δ–phases, namely δ_1 and δ_2–$Y_2Si_2O_7$, was reported recently [4,5]. These structures were found during a systematic study aimed at crystallization behavior of glass having a nominal composition of $Y_{0.26}Si_{0.30}Al_{0.11}ON_{0.11}$ (4). Employing complementary techniques, i.e. convergent beam electron diffraction (CBED), X-ray diffraction (XRD), and selected area electron diffraction (SAED), the structures of phases were differentiated [4,5], and a model structure for δ_2–$Y_2Si_2O_7$ was proposed. This structural model was found to be isostructural with that proposed for $Gd_2Si_2O_7$ [6]. Further structural details, for the δ_2–phase, were studied using high resolution transmission electron microscopy by imaging using various orientations. However, due to the presence of the glassy matrix in partially vitrified samples, most structural details of the crystalline phase were obscured, particularly in the thinner regions. Therefore, experimental high resolution electron micrographs were first processsed and then interpreted with the help of simulated images. This paper reports the results of these efforts for the structure analysis of the δ_2–$Y_2Si_2O_7$ phase.

EXPERIMENTAL DETAILS

Samples of the heat-treated crystallized glass described by Dinger et al [4] were used in this research. Specimens for high resolution imaging were prepared by cutting thin slices, mechanical grinding to approximately 50um and finally ion beam thinning. A thin layer of carbon was deposited onto one side of the specimen to reduce the effect of charging. The samples were examined in the Berkeley NCEM Atomic Resolution Microscope, and experimental images digitized and processed at the NCEM image analysis facility [7] using the SEMPER [8] program in order to improve the visibility of the crystalline phase. SHRLI [9] images were simulated for comparison with experiment.

RESULTS AND DISCUSSION

From the convergent beam diffraction data, the structure of $\delta_2 Y_2Si_2O_7$ was found to be orthorhombic, having cell parameters **a** = 13.60Å, **b** = 5.01Å, and **c** = 8.15Å; $\alpha = \beta = \gamma = 90^\circ$ and space group $Pna2_1$. It is isostructural to $Gd_2Si_2O_7$ which belongs to the pyrosilicate structural group [6]. In the δ_2-$Y_2Si_2O_7$ structure, each of the Y atoms is coordinated by seven oxygen atoms, i.e. the basic structural unit is the Si_2O_7 double tetrahedra with two yttrium atoms on either side of it. Coordination polyhedra of yttrium ions are formed by both the terminal and the bridge oxygen atoms. A model of δ_2-$Y_2Si_2O_7$ projected aong [001] direction is shown in Figure 1; in this figure the yttrium atoms are represented by the larger spheres, silicon by the smaller and oxygen by the smallest spheres. The results of atomic resolution studies used to further study the structural details at atomic level, are described below.

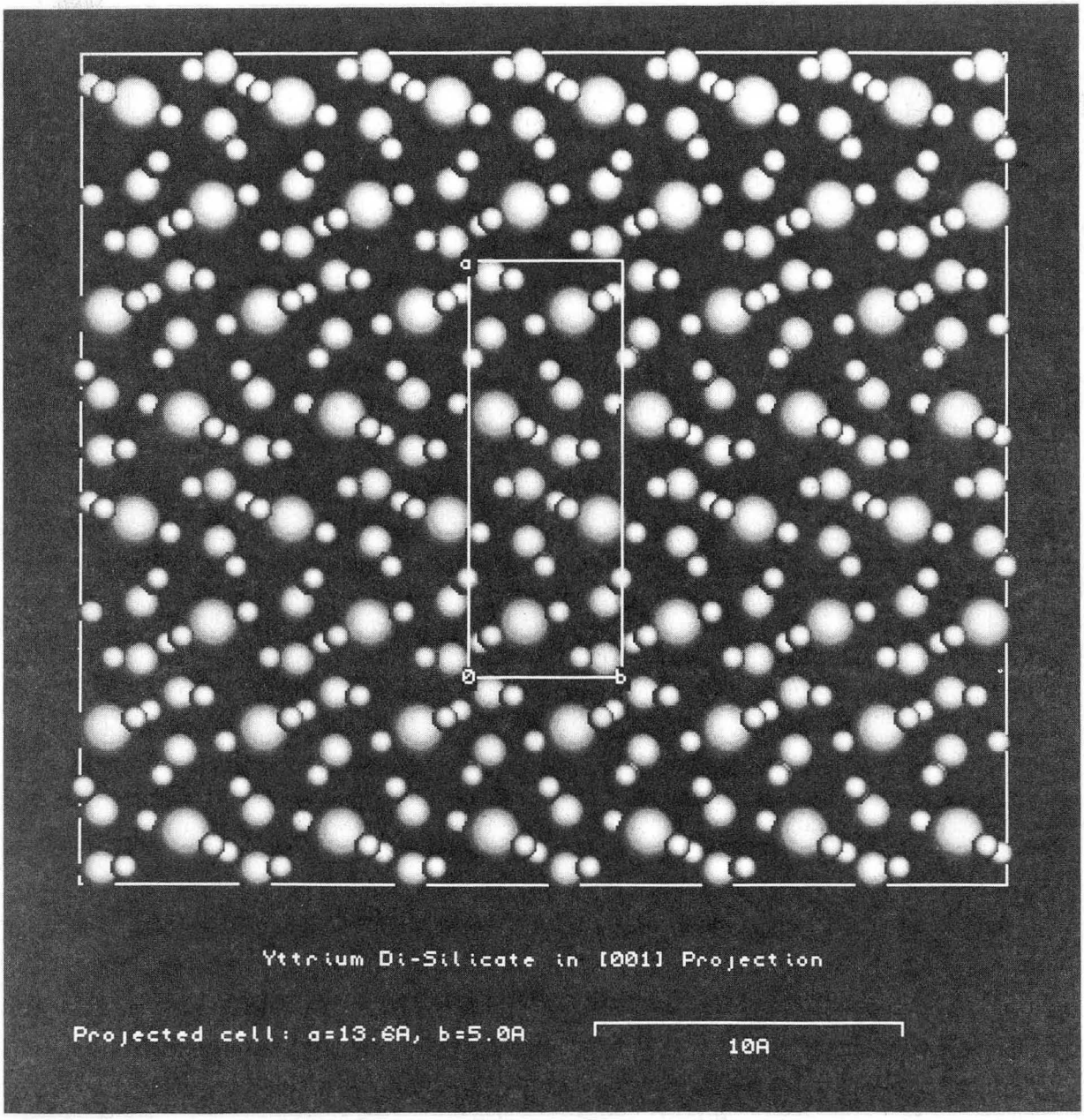

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Figure 1. Computer-generated display of the postulated structure of δ_2-$Y_2Si_2O_7$ in [001] orientation. Large spheres represent yttrium atoms, mid-size spheres silicon atoms, and small spheres oxygen atoms. The unit cell is marked.

Figure 2 shows a high resolution electron micrograph in [001] orientation. The details in the image vary from thin to thick regions very drastically. In the thicker regions, a 13.60Å periodic arrangement of dot patterns corresponding to the **a**-parameter of δ_2-$Y_2Si_2O_7$, is clearly seen. On the other hand, the thinner regions, for example the encircled region marked 3 in Figure 2, give merely the impression of an amorphous structure. The great proportion of amorphous material present, compared with the smaller amount of crystalline material, is due to some of the original material remaining when the δ_2-$Y_2Si_2O_7$ is crystallized from the original glassy phase.

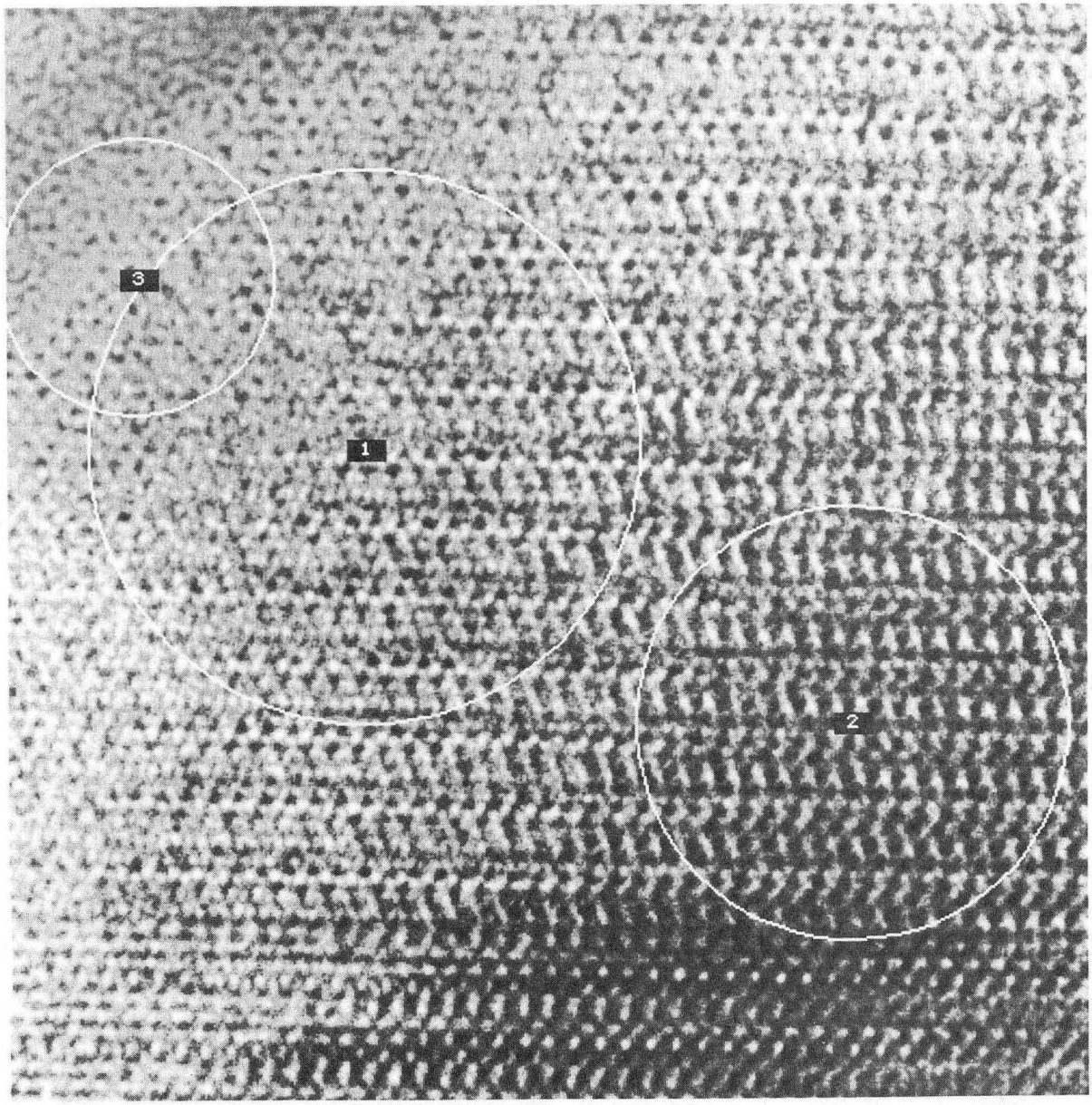

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Figure 2. High-resolution image of δ_2-$Y_2Si_2O_7$ obtained with the NCEM atomic-resolution microscope and digitized for processing. The thin edge of the crystalline region is towards top left, and the three regions chosen for processing are circled. Repeat distances in the periodic image (most easily seen in the lower half of the thick-crystal region marked 2) are 5Å in the horizontal direction and 13.6Å vertically.

Image Simulations

In order to confirm the postulated δ_2-$Y_2Si_2O_7$ structure, simulations of high-resolution images were carried out for the proposed model (fig.1). We used the SHRLI [9] programs for the same ARM conditions as were used for the experimental images (1000keV, Cs of 2.8mm, aperture radius corresponding to 0.65Å^{-1}, incident beam convergence semiangle of 0.6millirad., halfwidth of spread of focus of 100Å, and halfwidth of specimen vibration of 0.5Å); images were simulated over a range of defocus from 0 to -1200Å, and specimen thicknesses to 410Å. Most of the simulated images showed arrangements of strong black spots corresponding approximately to those in the thicker regions of figure 2, especially near the optimum defocus of -600Å (fig.3).

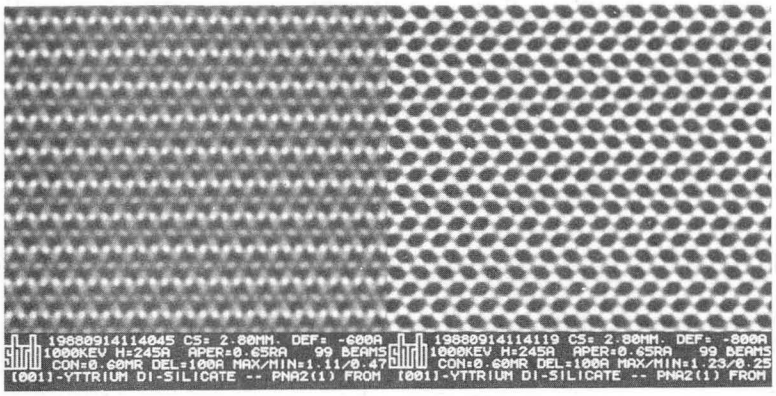

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Figure 3. Simulated images (SHRLI) of [001] δ_2-$Y_2Si_2O_7$ under ARM conditions for a specimen thickness of 245Å with defocus values of -600Å and -800Å. The black spots in these images correspond only approximately to the positions of those in the experimental image.

Image Processing

In the presence of an amorphous phase, high-resolution images of crystalline phases become degraded because of the contribution of amorphous contrast to the image [10]. In the case of δ_2-$Y_2Si_2O_7$ the presence of a glassy phase due to incomplete vitrification contributes non-periodic contrast to the image; for this reason, a simple image-processing technique was applied to decrease the amorphous contribution and to enhance the periodic component of the image. A large area (area 1 in figure 2) was extracted from the digitized image and Fourier transformed to produce its diffractogram or image intensity spectrum (fig.4a). Using the SEMPER [8] program, rectangular windows were placed around positions that fell on a reciprocal lattice corresponding to the δ_2-$Y_2Si_2O_7$ spacings in [001] projection (fig.4b). Subsequent inverse transformation then produced a processed image containing much less non-periodic component than the original (unprocessed) image.

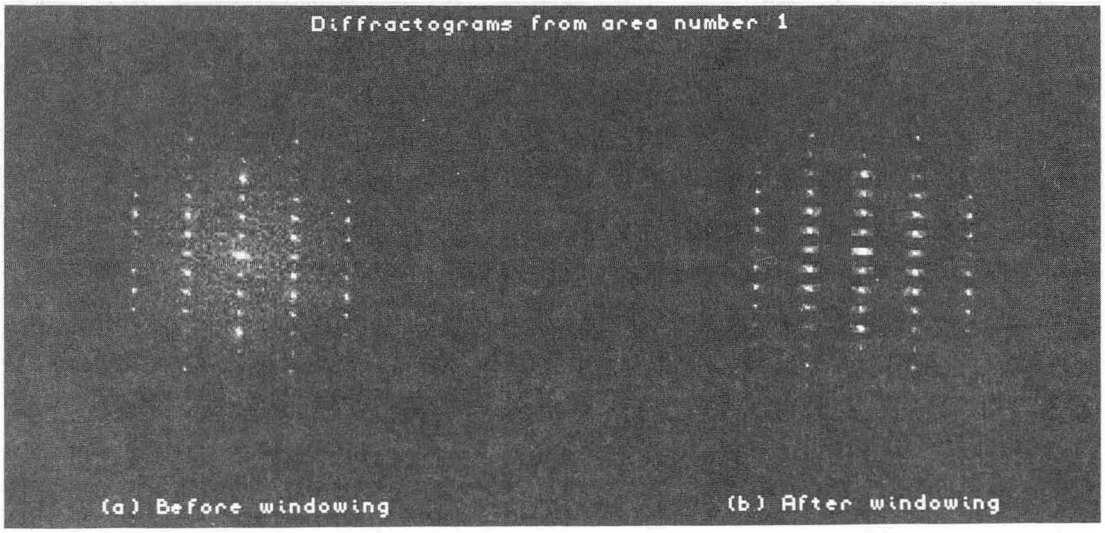

Figure 4. (a) Diffractogram (intensity spectrum) obtained by Fourier transformation of area 1 of figure 2. (b) After most of the non-periodic spectrum has been suppressed by windowing.

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Although the processed image from area 1 of figure 2 contained less non-periodic component than the original, its pattern of black spots did not correspond to that of the simulation (fig.3). However, the thicker regions of the original (unprocessed) image (fig.2) show a clearer periodic component due to the (presumably) greater proportion of periodic (crystalline) material present. For this reason, an area from the thicker region (area 2 in figure 2) was extracted and processed (fig.5a). The result of the processing of area 2 shows a pattern similar to the simulations (fig.3), but with some variations from the expected symmetry (fig.5b).

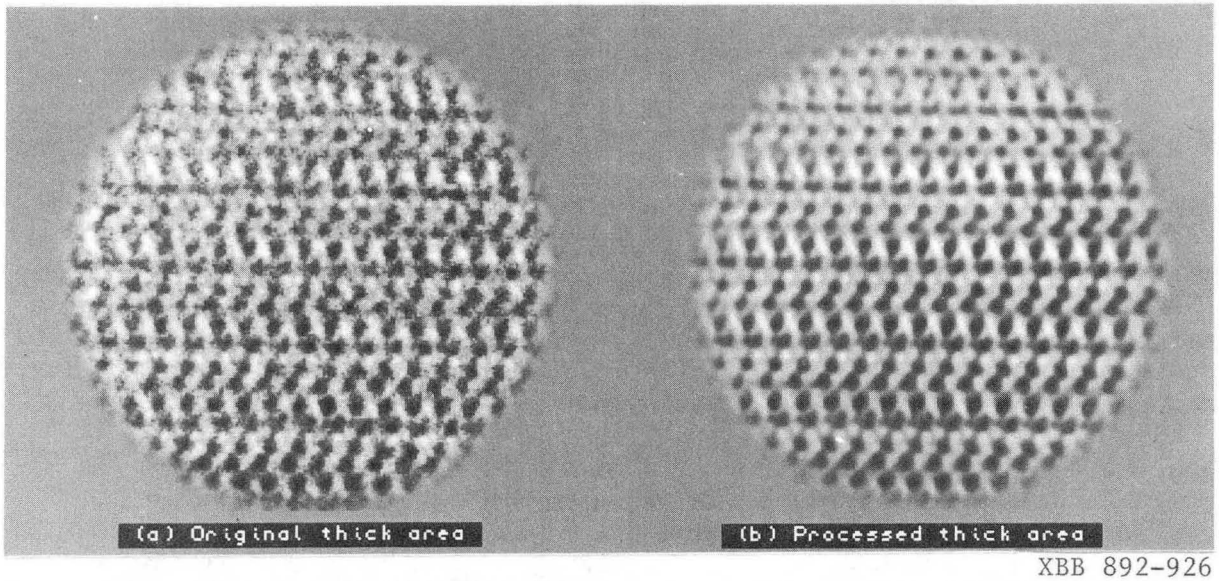

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Figure 5 (a) Original thick-crystal image extracted from area 2 of figure 2.
(b) Processed image after windowing of the diffractogram.

The variations visible in the thick-crystal image are typical of those due to crystal tilt [11] or microscope misalignment [12]. If misalignment is the problem, then the entire micrograph will show the effect; however, if crystal tilt is the factor destroying image symmetry, then its effect will be much less in the thinner regions [11]. Accordingly, we extracted the image of the thinnest-possible region (area 3 in figure 2), and processed it.

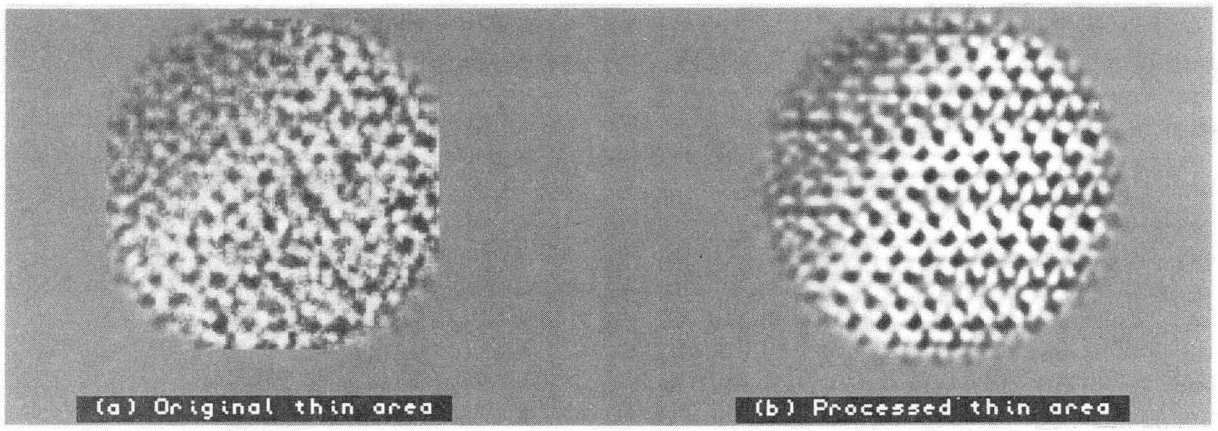

Figure 6 (a) Original thin-crystal image extracted from area 3 of figure 2. XBB 892-927
(b) Processed image after windowing of the diffractogram.

The processing technique applied to the thin region (fig.6a) produced a result (fig.6b) that shows very little of the asymmetry present in the images from thicker areas, proving that the latter is due to crystal tilt. More importantly, the (processed) thin-crystal image matches an image simulated for a thin (41Å) crystal of the postulated model. To demonstrate this match, the center square of the processed area (fig.6b) was extracted, adjusted in magnification, and inserted into the simulated image. The result (fig.7) confirms the postulated model, and shows that the large black spots are at the positions of the yttrium atoms.

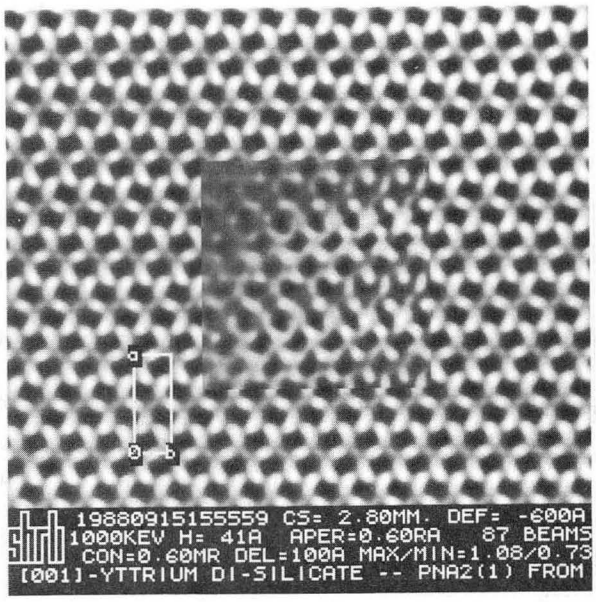

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Figure 7. Inset of thin-crystal processed image into an image simulated for ARM conditions at a defocus of -600Å and a specimen thickness of 41Å. The unit cell is marked. The inserted processed image matches the simulation best at its right edge. However, the left edge of the processed image, coming from a very thin area of the specimen, and containing very little periodic information, is a much poorer match to the simulation.

CONCLUSIONS

Although high-resolution images of δ_2-$Y_2Si_2O_7$ are extremely "noisy" due to the presence of a non-crystalline glassy phase, it is possible to extract the periodic component of the image sufficiently well to enable a structural model based on CBED, XRD and SAED to be confirmed by matching of experimental and simulated images. This procedure can be carried out even for the case of a crystal tilted off exact orientation, provided that a sufficiently-thin crystal edge can be found. In this case, high-resolution TEM imaging has confirmed the model postulated for the structure of the phase δ_2-$Y_2Si_2O_7$.

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