High resolution synchrotron x-radiation diffraction imaging of crystals grown in microgravity and closely related terrestrial crystals

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ABSTRACT

Irregularities in three crystals grown in space and four terrestrial crystals have been compared by high resolution monochromatic synchrotron x-radiation diffraction imaging. For two of the materials, mercuric iodide and lead tin telluride, features consistent with the presence of additional phases in terrestrial samples have been suppressed in the comparable crystals grown in microgravity.

Comparison of the images of highly purified terrestrial mercuric iodide with those of lower purity space and terrestrial material suggests specific detector performance models. These models ascribe the improved performance of detectors made from space-grown mercuric iodide to reduction in a widely dispersed impurity phase rather than to extreme macroscopic lattice regularity.

While the general grain structure of lead tin telluride is not strongly affected by growth in microgravity, the subgrain uniformity of the space crystal is substantially higher than that of the comparable terrestrial crystal. The greater uniformity is associated with suppression of the second phase that appears to be characteristic of the terrestrial crystal examined.

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The terrestrial seed crystal of triglycine sulfate displayed an unexpected layered structure, which propagated during space growth.

Terrestrial Bridgman growth of gallium arsenide revealed a mesoscopic structure substantially different from that of the Czochralski seed.

1. INTRODUCTION

1.1 Motivation for crystal growth in space

The performance of x and gamma-ray detectors made from space-grown mercuric iodide has been reported to be far superior to similar devices made from similar ground-grown material. This improved performance was traced to enhanced charge carrier mobility in the space-grown crystals, which was at least six times as high as that for similar detectors made from ground-grown crystals\(^1,2\). More recently, detectors made terrestrially from purer material also have displayed improved energy resolution. Further enhancement in radiation detectors through careful crystal growth thus seems feasible.

1.2 Role of high resolution x-radiation diffraction imaging

The nature of the variation associated with the enhanced performance of these crystals is not yet clear. Since effective optimization and control of the performance of such materials require this information, identification of irregularities now takes a high priority.

Fortunately, recent advances in diffraction imaging with nearly parallel monochromatic synchrotron x-radiation present a timely opportunity: 1) to observe individual defects with maximum sensitivity, 2) to determine their distribution and structure, 3) to correlate them with specific differences in performance, and 4) ultimately to optimize their formation\(^3,4,5\). High-defect-sensitivity monochromatic diffraction experiments, carried out on beam line X23A3 at the National Synchrotron Light Source at Brookhaven National Laboratory, are reported here on seven crystals, three of which contained material grown in microgravity.

2. MERCURIC IODIDE

2.1 Terrestrial crystal compared with Spacelab III crystal

A terrestrial mercuric iodide crystal vapor-grown in the same way and from the same source material as on Spacelab III incorporates irregularities that cause it to diffract over an angular range of one half degree. However a large central portion of this terrestrial crystal is sufficiently regular to diffract only over a few minutes of arc. Indeed the (1 1 10) diffraction image in Bragg geometry in figure 1 demonstrates lattice regularity of the order of a few arc seconds with respect to rotation around a [110] axis. The absence of diffraction in a wide [110] (vertical) stripe in the center of figure 1 shows a lattice deformation of about 10 minutes of arc around an axis defined by this stripe. This twist of the crystal lattice is evident indirectly also in
(0 1 10) diffraction in Bragg geometry, figure 2, for which the crystal was rotated azimuthally 45°, because in this orientation the lattice twist precludes bringing the two parts simultaneously into diffraction. Examination of these images and of a sequence of real-time images of the (008) diffraction indicates that the principal lattice twist axis itself bends gradually through several minutes of arc.

Another principal aspect of all images of this crystal is a set of textural bands oriented in the [110] direction. Close examination of these bands shows them to consist of a high density of discrete features that are out of diffraction in all images. We ascribe them to one or more additional phases, although the possibility of severe misorientation of grains of the same phase cannot be entirely eliminated. Some of these features appear as thin (100) stripes, sometimes in crossed pairs, while others are generally round. In the bands containing a high density of these features, diffraction appears to be restricted to small (∼5 μm) cells of the type observed in scanning cathodoluminescence.

Other areas of the crystal contain similar features, but with a much lower density. These regions also contain thin, curved features marked by higher diffraction, lower diffraction, or alternating regions of higher and lower diffraction intensity in tandem, which may be dislocations.

Six observations all indicate that the sharp lattice twist occurred during growth. 1) The twist axis does not extend across the entire crystal. 2) The magnitude of the apparent separation of the two parts of the images is uniform throughout its length. It is difficult to conceive of such a partial lattice twist, one lying precisely in the (001) plane, developing through inadvertant mishandling. The twist

Figure 1. High-resolution (1 1 10) 8 keV diffraction image in Bragg geometry of (001) surface of terrestrial HgI₂ crystal comparable to that grown on Space lab III. Lighter areas diffract more strongly.

Figure 2. High-resolution (0 1 10) 8 keV diffraction image in Bragg geometry of (001) surface of terrestrial HgI₂ crystal comparable to that grown on Spacelab III. Lighter areas diffract more strongly.
axis is normal to the [110]-banded texture. These bands thus appear to be formed during growth; the [110] lattice twist axis is aligned with the crystal growth direction. 4) The curved nature of the linear features in the vicinity of the lattice twist is more consistent with growth than with post-growth bending. 5) The onset of the lattice twist immediately precedes a major textural change that appears to be growth-related. 6) The bending noted in the lattice twist axis differs in the two resulting subgrains.

All of these observations are consistent with a growth model in which growth begins in the vicinity of the extreme [110] corner of this crystal (in figure 1, for example, this is the top corner) and proceeds relatively uneventfully in the [110] direction (downward in figure 1, for example), until just before the onset of the band of high density features, one of which initiated the sharp lattice twist. This twist then propagated for the remainder of the growth. During this subsequent growth, briefer periods of relatively high feature density alternate with periods of relatively low feature density.

During the evaporation of such crystals, small specks of foreign material similar in size to the features observed in this study accumulate on the surface at an irregular rate. Chemical analysis indicates these specks are neither mercury nor iodine precipitates but rather consist of metalorganic impurities with a carbon content of the order of 70% and a wide variety of metals. It is tempting to associate these observed impurity features with the features observed in diffraction and therefore to conclude that impurities reside in such crystals in discrete form.

The morphology of the diffraction images permits us to develop two alternative growth models that tie together all of these observations. In both, growth over a region of a few micrometers forms a crystal with a relatively high degree of purity and crystal perfection, creating small regions that diffract strongly. Impurities are rejected during this stage of the growth process, in a manner similar to constitutional supercooling, accumulating near the growth surface. In a faceted model, the level of impurities after growth of a few micrometers accumulates to such an extent that they precipitate out, marking the local {100} growth surface. At reentrant corners of such surfaces a globular precipitate possibly forms. In the second model, the rejection of impurity stimulates full dendritic growth, which leaves the linear features observed. None of our observations to date permit us to distinguish absolutely between these two models. Either model must be modulated by an as yet unidentified process that controls the general impurity level.

2.2 Spacelab III crystal

A crystal grown in Spacelab III in the same way and from the same material as the crystal described above contains lattice irregularities causing it to diffract also over an angular range of about one and one half degrees. A high-resolution (008) diffraction image of this crystal in Bragg geometry appears in figure 3. It is clear from the filamentary appearance of this image as well as from the one and one half degree acceptance angle for diffraction that the lattice orientation or lattice
parameter of the space crystal is less uniform than for the comparable terrestrial crystal shown in figures 1 & 2: that is, no large region of the space crystal appears in diffraction as does the center of the comparable terrestrial crystal.

Perhaps closely related, but potentially far more important however, is the absence in this and other images of the Spacelab III crystal of the arrays of features that are out of diffraction, characteristic of the terrestrial crystal. The formation of these features is suppressed in microgravity.

The Spacelab III sample differed from the terrestrial sample not only by its growth in microgravity but also by the superposition of graphite electrodes so that its performance as a neutron and x-ray detector could be measured. Since graphite is relatively transparent to x-rays, these electrodes were not expected to interfere with the imaging process. We found no evidence for unusual surface strain.

However, this crystal was not encapsulated. With the passage of the 5 years that this crystal has been in the laboratory, some deterioration in electronic performance of the device made from it actually has been observed, a deterioration that is characteristic also of unencapsulated devices made in terrestrial environments.

2.3 Terrestrial crystal to be compared to a future flight crystal

A third mercuric iodide crystal, one grown from higher purity material similar to that to be used on a future flight, also contains irregularities that cause it to diffract over a full two degrees. A high-resolution (1 1 10) diffraction image of this crystal in Bragg geometry appears in figure 4. The regularity displayed in this image

Figure 3. High-resolution (008) 8 keV diffraction image in Bragg geometry of (001) surface of Spacelab III HgI₂ crystal. Lighter areas diffract more strongly.

Figure 4. High-resolution (1 1 10) 8 keV diffraction image in Bragg geometry of (001) surface of high purity terrestrial HgI₂ crystal. Lighter areas diffract more strongly.
resembles much more that of the Spacelab III crystal than that of its terrestrially-grown counterpart. The complete absence of evidence for additional phases in this high purity crystal is consistent with the thesis that the features that are out of diffraction in images of the earlier terrestrial crystal are impurities.

3. LEAD TIN TELLURIDE

3.1 Terrestrial crystal comparable to Space Shuttle STS 61A crystal

Various regions of the terrestrially grown Bridgman sample of lead tin telluride, similar to one grown on Space Shuttle STS 61A, diffract as the crystal is rocked over a full two degrees. A high-resolution (220) diffraction image of this crystal in Bragg geometry is shown in figure 5.

The sample was a full right half cylinder. The sharply delineated irregular outlines of the image in figure 5 thus indicate immediately that several grains are present: the curvature of the [110] (right hand) edge shows that a subsidiary grain started to grow almost simultaneously with the main grain. Then, after 1 centimeter, a third grain started between the center of the boule and the opposite edge of the main grain. It grew laterally more rapidly than the nucleating grain, however, completely overtaking the growth of the nucleating grain. The new grain is brought into diffraction by a 33 arc minute rotation of the sample about the boule (growth) axis.

Subgrains within each of the main grains are clearly visible through terraced variation in contrast. The diffraction from a 1.5 cm length of each of the two principal grains observed is notable, however, in light of the increase in tin level from 14% to 18% during the first 3 centimeters of growth visible in these images. The fractional change in lattice constant over the 1.5 cm length of the grains is $4 \times 10^{-4}$, which affects the Bragg angle by 90 arc seconds. Nevertheless, because of the presence of kinematic scattering, we cannot use the area of diffraction to evaluate the degree of local compositional variation.

Other important aspects of this variation are evident on closer examination. Cellular regions of high diffraction intensity varying in size from 10 to several hundred micrometers are observed. They are separated by lines of reduced diffraction that are 10-50 μm wide. Many of these lines at first glance appear to be scratches because of their gentle curvature and random orientation. However, three characteristics typical of surface scratches, such as those visible for example in the gallium arsenide images to which we turn later, are not observed in these linear features. First, instead of the constant width typical of scratches, the lines in the present images vary in width, both from line to line, and even over the length of a given line. These lines separate cellular regions of high diffraction. Second, instead of the sharp boundaries characteristic of scratches, the edges of these lines are indistinct. And third, the contrast reversal typical of scratches is never observed in these lines. They are invariably out of diffraction over their entire length, even as the crystal is rotated while it is observed by video camera. Thus, while we cannot rule out scratches, the
linear features here differ markedly from the images of scratches in other materials. Moreover, these lines are not observed in the image of the space-grown sample.

We are thus left with the postulate that the highly diffracting cells are separated by material of another phase. The indistinctness of the boundaries between these regions strongly suggest gradual change in chemical composition. The pseudobinary phase diagram parallel to the lead-tin axis predicts complete miscibility. However, the observation of similar structure following electrolytic etching led earlier to a series of experiments on the metal/tellurium ratio, which delineated its importance in the growth of this material. This earlier work provides a satisfactory model for the current observations as well. While the metal constituents are widely recognized to be interchangeable, a single phase is preserved only with tellurium concentration in excess of 51%. Below this value, two or more phases are formed, differing in metal/tellurium ratio. Since the tellurium concentration of the current crystals is 50.1%, two phases or more are actually to be expected. Constitutional supercooling may also play an important role, depending on the temperature gradients imposed.

Figure 5. High-resolution (220) 8 keV diffraction image in Bragg geometry of approximately (220) surface of terrestrial PbSnTe crystal. The growth direction is [001]. Lighter areas diffract more strongly.

Figure 6. High-resolution (220) 8 keV diffraction image in Bragg geometry from approximately (220) surface of PbSnTe crystal grown on STS 61A. The growth direction is [001]. Lighter areas diffract more strongly.
3.2 Space Shuttle STS 61A crystal

A (220) image of a crystal grown on Space Shuttle flight STS 61A, oriented in Bragg geometry, appears in figure 6. The multigrain nature of the STS 61A crystal is superficially similar to that of the terrestrial crystal. But, while these images appear qualitatively similar to the full images for the corresponding terrestrial crystal, they differ in important ways.

Each grain is more generally uniform than those of the terrestrial crystal. This uniformity follows a drastic reduction in the incidence of linear features and subgrains. Thus, while the granular structure resembles that for the terrestrial crystal, variation within individual grains from the intrusion of a distinct second phase is suppressed in microgravity.

4. TRIGLYCINE SULFATE

A normal slice from a disc-shaped terrestrial triglycine sulfate seed crystal with additional growth achieved on Spacelab III diffracts in Laue geometry into images, each of which appears over less than half of an arc minute. The character of the diffraction from this crystal is very different from that of the others. First, this crystal was thin enough and low enough in atomic number to allow diffraction in Laue geometry. Second, superimposed images of this crystal taken as it was rotated about its [100] and [001] axes appear in closely spaced groups, each associated with the diffraction directions expected for diffraction from one set of (h00) or (00l) planes, respectively. The various images have similar, but not identical, shapes. A (200) high-resolution diffraction image of this crystal in Laue geometry is shown in figure 7. Members of a given group of images appearing

| Layer | Fig. | (hkl) | Angle (°) |
|-------|------|-------|-----------|
| C2    |      | 300   | +6.6      |
| B3    |      | 200   | +2.1      |
| B1    | 7    | 200   | +2.5      |
| A2    |      | 001   | -19.2     |
| A3    |      | 001   | -36.8     |

Figure 7. High-resolution (200) 10 keV diffraction image in Laue geometry from grain B1 of TGS crystal from Spacelab III. Lighter areas diffract more strongly.
at nearly identical diffraction (i.e. detector) angles come into dif-
fraction serially as the sample is rotated, as summarized in table 1.

The appearance of images in groups at similar diffraction angles
indicates that this crystal consists of layered grains whose lattices
are similar but rotated with respect to one another by rotation about
the [100] and [001] axes. Since each image is ostensibly nearly "com-
plete," the grain boundaries are roughly parallel to the (010) crystal
surface. In an optically thick material, transmission through such a
layered crystal would be precluded by the misalignment of the successive
grains. However, this crystal is optically thin, permitting the
observation of symmetrical diffraction from each of the grains in turn.

From the occurrence of similar features in pairs of images, which
can be ascribed to features shared by adjacent grains at their interface
and the degree of clarity, we can assign a tentative order to the
various grains as intersected by the x-ray beam. This is the order
indicated in table 1. Most of the features thus appear to be associated
with irregularities at the granular interfaces, although radiographic
effects from other layers are present in each image.

The space-grown portion of this crystal is much smaller than the
seed. Space growth was in a narrow (0.1 mm) stripe in the [001] direc-
tion along that one edge of the seed. The absence of a clear demarka-
tion between the seed and new growth in most of the images is in
contrast to the terrestrial growth of comparable material. The
interface between the seed and the new growth is visible in figure 7,
because defects in the seed grain appear not to propagate into the new
growth in the central portion of the disc. Toward the edge of the disc,
the irregularity observed in all of the grains is consistent with rapid
growth anticipated from the defects observed near the edge of the seed.

One image differs slightly from the others in shape along the
growth edge. It thus appears that new growth did not occur uniformly on
all layers. On this one layer, growth appears to have been much slower
than on the others, although this may represent initial etching of the
seed crystal associated with premature contact with the solution.

5. GALLIUM ARSENIDE

A terrestrial crystal of selenium-doped Bridgman-grown gallium ar-
senide diffracts over several degrees. A low resolution diffraction
image, achieved by rocking the crystal 4° around a [112] axis during
(220) diffraction is shown in figure 8. This is remarkably similar to
infrared images of the same crystal. The additional information in a
high-resolution (220) diffraction image of this crystal in Bragg
geometry, figure 9, is striking by contrast.

The demarkation of the Czochralski seed from the new Bridgman
growth is very clear in those images in which this region is in dif-
fraction (for example, a horizontal line in the middle of figure 9).
The seed/growth boundary is delineated in two ways. First, toward the
periphery of the boule it marks a smooth limit to diffraction, past which the lattice does not diffract under the same conditions. Thus, either the lattice constant, or orientation, or both differs in the new growth. Second, the mesoscopic structure of the growth is observed to be transformed at the interface. The cellular structure of the seed is characteristic of diffraction images of Czochralski-grown undoped gallium arsenide. In the new Bridgman growth, the formation of cells appears to be completely suppressed. Nevertheless, the two lattices merge without visible interruption. The lattice mismatch appears to set up a gradual warping of the crystal lattice. Further analysis of the features observed is precluded by the inability to observe diffraction in Laue geometry.

6. SUMMARY OBSERVATIONS

6.1 Mercuric iodide

Observation of a terrestrial specimen grown from material similar to that of the Spacelab III crystal are consistent with the presence of
more than one phase. Nondiffracting features dominate the mesoscopic structure, and one of these appears to have initiated a sharp lattice twist by 10 minutes of arc around an axis aligned with the growth direction. Formation of these features is suppressed both in a comparable Spacelab III crystal and in a high purity terrestrial crystal. At the same time, the general regularity of the lattice of these latter crystals is lower than in the earlier terrestrial crystal.

The performance of devices made from new high purity material is improved by enhanced carrier lifetime, while the improved performance of the Spacelab III crystal is traceable to the higher mobility of its charge carriers. Thus, although the electronic improvements are quite distinct in these two cases, in neither of them do we find the features that we have observed in the first terrestrial crystal and ascribe to impurity phases. Absence of additional phase precipitates may thus be much more important to device performance than the uniformity of lattice orientation that we observe in the first terrestrial crystal.

6.2 Lead tin telluride

The mesoscopic structure of terrestrial lead tin telluride appears also to be influenced strongly by the intrusion of material of a differing phase. But in this instance the available evidence surprisingly suggests an additional phase with a different alloy of the major constituents. This observation is consistent with prediction of a second phase for systems with tellurium concentration very close to 50%, such as the current samples.

Although the STS 61A crystal has grain structure that appears to be similar to that of the comparable terrestrial crystal, the formation of the subgrain variation characteristic of the terrestrial sample is suppressed in microgravity. This suppression is correlated with the predicted thermo-solutal stability in microgravity.

6.3 Triglycine Sulfate

Interpretation of the space-growth of triglycine sulfate is complicated by the inadvertent contact between the seed and the solution prior to space growth and by the layered structure that we observe in the seed. Defects in one of these layers appear not to have propagated in the central portion of the disc in microgravity, while defects in the other seed layers appear indeed to have propagated into the new growth. In addition, one of the seed layers appears to have grown at a rate slower than the others.

6.4 Gallium Arsenide

Although gallium arsenide has not yet been grown in space, the mesoscopic structure of a terrestrial Bridgman-grown boule has been observed to differ from that of the Czochralski-grown seed. The Bridgman-grown lattice also appears to be warped more than that of the Czochralski-grown seed. Neither observation is yet understood, and their resolution will require a sample thin enough to sustain anomalous transmission.
7. ACKNOWLEDGEMENT

The collaboration described in this report would have not have been possible without the multifaceted support of the NASA Microgravity Sciences and Applications Division. Thanks to this strong NASA support, important guidance has been given to the growth of several important crystal systems.

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