New high-pressure phase of GaSb

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A new high-pressure phase has been found in GaSb. This phase is observed at room temperature after heating samples to ~473 K from the *Imma* phase taken above ~20 GPa. The structure is face-centered orthorhombic with *Ammm* symmetry and as for the previously observed high-pressure phases in GaSb, it is site-disordered.

Because gallium antimonide is the least ionic of the III-V semiconductors, its high-pressure behavior is expected to be the most similar to that of silicon and germanium.[1–3] This has stimulated many high-pressure studies of GaSb over the past 40 years.[4–6] At ambient conditions, GaSb has the site-ordered zinc-blende structure. At 7 GPa and room temperature, it has been found to transform to a site-disordered orthorhombic structure with *Imma* symmetry.[7] This phase remains stable to at least 50 GPa. However, more recent work[8] has shown that under highly hydrostatic conditions the zinc-blende phase transforms to a β-tin-like phase and that β-tin is also obtained by heating the *Imma* phase (at 7 GPa and 500 K), suggesting that the *Imma* phase is only stabilized under nonhydrostatic conditions.[8,9] Further measurements at higher pressures and room temperature have shown a transition between 63 and 71 GPa to a phase that has not yet been fully characterized, but appears to be site-disordered body-centered cubic.[10] This may be the transition reported earlier in an energy-dispersive x-ray-diffraction study by Weir, Vohra, and Ruoff at 61.0(7) GPa (Ref. 11).

We have now performed simultaneous high-pressure/high-temperature (hp/nt) experiments, where samples starting in the *Imma* phase were heated to ~473 K for approximately 2 h at pressures up to 25.5 GPa. Two different behaviors were observed: for samples at pressures up to ~13 GPa, the *Imma* phase transforms to the β-tin structure, while for samples taken above ~20 GPa, a new orthorhombic phase with the space group *Ammm* was found. Between ~13 GPa and ~20 GPa, a mixture of the β-tin and *Ammm* was observed. The new orthorhombic phase has been refined and it is presented here.

Samples suitable for high-pressure powder-diffraction experiments were produced by finely grinding a starting material of 99.99% stated purity, from the Aldrich Chemical Company. Data were collected on station 9.1 at the Synchrotron Radiation Source, Daresbury Laboratory, using an image-plate-area detector.[12] The incident wavelength was 0.4654(1) Å. The samples were loaded into a Mao-Bell-type diamond-anvil cell[13] with 4:1 methanol:ethanol as a pressure-transmitting medium[14] and chips of ruby for pressure measurement.[15] Samples were heated in an off-line furnace. Diffraction patterns were recorded before and after heating. The fully integrated profiles were refined using the least-squares Rietveld method[16] with the GSAS program.[17]

All data were collected after cooling the sample back to room temperature. The new orthorhombic *Ammm* phase was first observed along with a small proportion of the β-tin phase on recovering back to room temperature at 17.1 GPa. A sequence of the results obtained from 10.5 to 22.5 GPa is illustrated in Fig. 1. Each profile has been collected from a different initial sample of the *Imma* phase. The profile in Fig. 1(a) shows a typical pattern of the *Imma* phase obtained on pressure increase from the zinc-blende phase at room temperature before heating. At 10.5 GPa, the *Imma* phase has transformed to the β-tin structure on heating and this remains stable on recovering back to room temperature as shown in profile (b). At pressures above about 12.7 GPa, the (100)
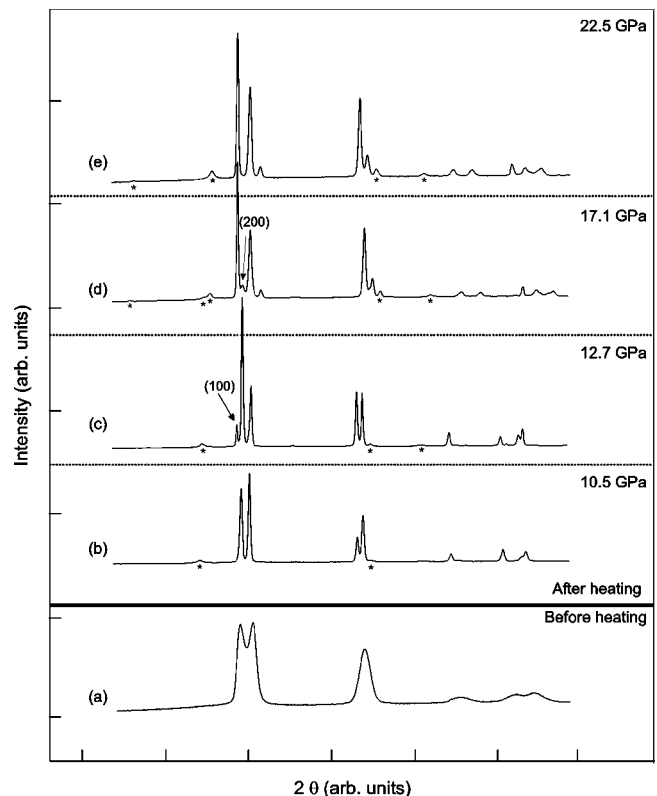

FIG. 1. Diffraction patterns observed in GaSb after heating samples taken from the *Imma* phase [profile (a)] at four different pressures: (b) the β-tin profile obtained at 10.5 GPa, (c) the first appearance of the *Ammm* phase as indicated by the emergence of the (100) peak at 12.7 GPa, (d) the *Ammm* phase at 17.1 GPa with the remaining (200) peak of the β-tin phase shown by the arrow, and (e) the *Ammm* profile obtained at 22.5 GPa. The peaks marked by an asterisk are discussed in the text.
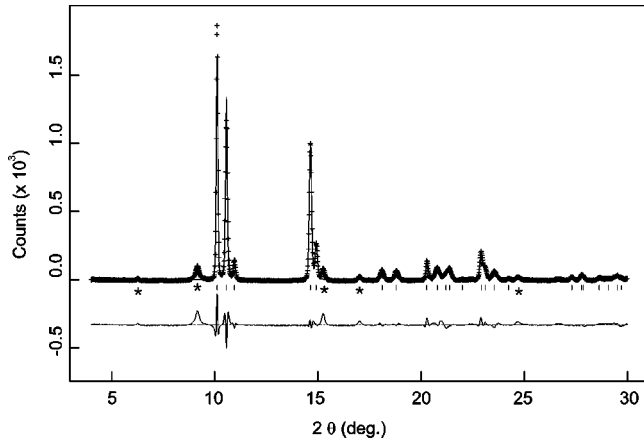
FIG. 2. Rietveld refinement fit of the *Ammm* structure to a profile of GaSb at 22.5 GPa. The difference between the observed and fitted profiles is shown. Tick marks indicate the positions of *Ammm* reflections. The peaks marked with asterisks are discussed in the text.

peak of the new phase becomes visible as indicated by the arrow in Fig. 1(c). At 17.1 GPa, the profile is mainly dominated by the new phase with a small residue of the β-tin structure shown by the (200) peak in Fig. 1(d). A complete transformation to the new phase was observed at 22.5 GPa. The profile is illustrated in Fig. 1(e) and like β-tin, the new phase remains stable indefinitely at room temperature. The profile in Fig. 1(e) was successfully indexed on an orthorhombic unit cell with $k+l=2n$, indicating that the structure is *A*-face-centered. Density considerations require that the unit cell contains just two atoms, which must then be located at $(0, 0, 0)$ and $(0, 1/2, 1/2)$, in a randomly disordered way as discussed below. The space group of this structure is *Ammm*. The full integrated profile has been fitted at 22.5 GPa with $a = 2.6432(1)$ Å, $b = 4.8813(7)$ Å, and $c = 2.9583(2)$ Å giving a volume $V = 38.171(5)$ Å^3. A Rietveld refinement of the *Ammm* phase is shown in Fig. 2 and the structure is illustrated in Fig. 3.

It is interesting to note that profile (d) in Fig. 1 bears some striking similarities to a profile of lnSb recorded at 2.1 GPa, as shown in Fig. 4. This has been previously identified as a mixture of the *Immm* and β-tin phases.[18] Both profiles contain a very small amount of the β-tin structure as indicated by the (200) peak. The *Immm* phase of InSb is characterized
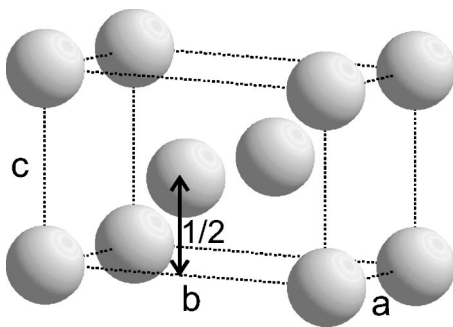

FIG. 3. The unit cell of the *Ammm* structure. Each site has a 50:50 occupancy of Ga and Sb atoms.
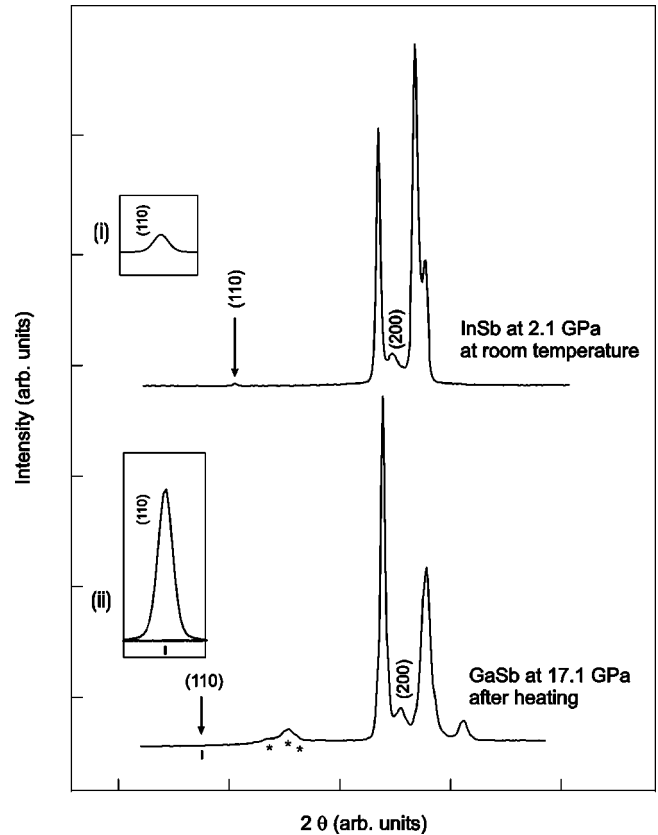

FIG. 4. A comparison between a profile of InSb at 2.1 GPa (Ref. 18) and a profile of GaSb at 17.1 GPa. The presence of the (200) β-tin peak is indicated in both profiles. The peaks marked by asterisks are discussed in the text. Inset (i) shows the (110) reflection of InSb enlarged. Inset (ii) compares the (featureless) measured profile and the calculated profile at the position of the (110) reflection in GaSb. The calculated profile is taken from a best fit to the whole pattern with the equivalent site-ordered structure. The enlargement is approximately the same as in inset (i).

by the weak (110) peak, the so-called difference reflection peak, indicating that the structure is site ordered. The structure has the same general arrangement of sites as in Fig. 3, but with In at $(0, 0, 0)$, Sb at $(0, 1/2, 1/2)$ and an *a* axis twice as large (relative to *b* and *c*). The intensity of the (110) peak depends on the difference in scattering strength between the atomic species, which is very small for InSb.[18] In the GaSb profile, this peak is absent. The complete absence of the difference reflection, despite the large difference in scattering strength between Ga and Sb, indicates that this new structure is site-disordered. Recent extended x-ray-absorption fine structure (EXAFS) studies, using the HI-PREXX facility[19] on station 9.3 at Daresbury Laboratory, have shown that there is not complete order even over distances comparable to one unit cell.[20] Further details of site-ordering in all the hp and hp/ht phases of GaSb along with details of the EXAFS experiments, will be published elsewhere.[21]

Finally, it has been noted that every profile, collected after heating, contains some additional peaks, as marked by asterisks in Figs. 1, 2, and 4, over a range of pressures. The origin of these peaks is not clear. Data have been collected with and without the pressure-transmitting medium and with different

gasket materials (W and Re) to investigate possible contamination or reaction with sample environment on heating. The patterns subsequently collected still exhibit these additional weak peaks in all cases. Sample contamination is, therefore, excluded. It could, thus, be the presence of a new minority phase, only formed at high temperature, but the weak intensities of the peaks make it very difficult to solve.

The discovery of this site-disordered *Ammm* phase adds to the growing evidence that GaSb is very unusual amongst the II-VI and III-V semiconductors in exhibiting site-disorder in *all* its several high-pressure and high-pressure/high-temperature phases. The only other known examples to date are the *Cmcm* phase of GaP, the highest pressure body-centred-cubic phases of InSb, HgTe, and some intermediate

phases in InSb.[10] The fact that the samples have been heated for some time at $\sim$473 K indicates that kinetic effects are not responsible for the site-disordering. This suggests that GaSb is behaving as a disordered metallic alloy or exhibiting frustrated ordering behavior.[21] Further *in situ* hp/ht studies and new computational work are needed to gain insight into this interesting new aspect of structural stability in these systems.

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[1] J. C. Philips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973), p. 42.

[2] S. C. Yu, I. L. Spain, and E. F. Skelton, Solid State Commun. **25**, 49 (1978).

[3] S. B. Zang and M. L. Cohen, Phys. Rev. B **35**, 7604 (1987).

[4] S. Minomura and H. G. Drickamer, J. Phys. Chem. Solids **23**, 451 (1962).

[5] J. C. Jamieson, Science **139**, 845 (1963).

[6] A. Jayaraman, W. Klement, and G. C. Kennedy, Phys. Rev. **130**, 540 (1963).

[7] M. I. McMahon, R. J. Nelmes, N. G. Wright, and D. R. Allan, Phys. Rev. B **50**, 13 047 (1994).

[8] M. Mezouar, H. Libotte, S. Deputier, T. LeBihan, and D. Hauserman, Phys. Status Solidi B **211**, 395 (1999).

[9] H. Libotte and J.-P. Gaspard, Phys. Rev. B **62**, 7110 (2000).

[10] R. J. Nelmes and M. I. McMahon, in *High Pressure in Semiconductor Physics 1*, edited by Tadeusz Suski and William Paul, Vol. 54 of *Semiconductors and Semimetals* (Academic Press, San Diego, 1998), p. 145.

[11] S. T. Weir, Y. K. Vohra, and A. L. Ruoff, Phys. Rev. B **36**, 4543 (1987).

[12] R. J. Nelmes and M. J. McMahon, J. Synchrotron Radiat. **1**, 69 (1994).

[13] H. K. Mao and P. M. Bell, Year Book—Carnegie Inst. Washington **79**, 409 (1980).

[14] G. J. Piermarini, S. Block, and J. S. Barnett, J. Appl. Phys. **44**, 5377 (1973).

[15] G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, J. Appl. Phys. **46**, 2774 (1975).

[16] H. M. Rietveld, J. Appl. Crystallogr. **2**, 65 (1969).

[17] A. C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report LAUR, 86-748, 2000 (unpublished).

[18] R. J. Nelmes, M. I. McMahon, P. D. Hatton, J. Crain, and R. O. Piltz, Phys. Rev. B **47**, 35 (1993).

[19] A. V. Sapelkin, S. C. Bayliss, D. Russel, S. M. Clark, and A. J. Dent, J. Synchrotron Radiat. **7**, 257 (2000).

[20] C. B. Vanpeteghem, R. J. Nelmes, D. R. Allan, M. I. McMahon, A. V. Sapelkin, and S. C. Bayliss, Phys. Status Solidi B **223**, 405 (2001).

[21] C. B. Vanpeteghem, R. J. Nelmes, G. J. Ackland, D. R. Allan, M. I. McMahon, A. V. Sapelkin, and S. C. Bayliss (unpublished).