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Stability and crystal structure of BC8 germanium

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It is found that samples of crystalline germanium brought rapidly (<1 s) to ambient pressure from 14 GPa transform to the so-called BC8 structure rather than to the ST12 structure that is found on slower pressure decrease. The BC8 phase is unstable at atmospheric pressure, but we have been able to record angle-dispersive powder patterns within less than 30 minutes of pressure release using an image-plate detector on a synchrotron source. The refined crystal structure of BC8-Ge is very similar to that found previously for BC8-Si.

I. INTRODUCTION

Silicon and germanium both form relatively complex metastable phases on pressure release from their high-pressure β-tin phase.[1-4] In the case of silicon, a body-centered cubic structure with eight atoms in the basis (denoted BC8) is obtained on slow pressure decrease,[2] while two other phases (Si-VIII and Si-IX) are obtained on very fast (<0.1 s) pressure decrease.[4] For germanium, a simple tetragonal structure with 12 atoms in the unit cell (ST12) is obtained.[1-3]

The crystal structures of both BC8-Si and ST12-Ge have been determined by Kasper and Richards.[5] The BC8-Si structure is composed of sixfold rings. Each atom has four nearest neighbors, three at 2.39(1) Å and one at 2.30(1) Å, in a distorted tetrahedral arrangement. The structure of ST12-Ge is also composed of distorted tetrahedra, but with the atoms in fivefold and sevenfold rings. The angular distortions of the ST12-Ge tetrahedra are greater than in the BC8-Si structure, but the four nearest-neighbor bonds appear to be closer in length, with two at 2.49(4) Å, one at 2.48(4) Å, and one at 2.49(5) Å. The larger uncertainties in these bond lengths reflect the greater complexity of the ST12 structure, and may conceal some significant differences.

There has never been any report of silicon in the ST12 form, but there is evidence for the existence of BC8 germanium at room temperature. Bates, Dachille, and Roy[3] found two weak reflections after pressure release which the dominant ST12 phase could not account for, and which disappeared within a few hours. However, pressure release at dry-ice temperature produced a stable pattern in which the same two lines and two further (weaker) lines were detectable, and all four were shown to correspond to the strongest lines obtained from BC8 silicon. The best-fitting lattice parameter, $a=6.92$ Å, gave a density $\sim 1\%$ less than that of ST12-Ge. Later, Qadri, Skelton, and Webb[6] reexamined the behavior of germanium on release of pressure and obtained an ST12 pattern with just one very weak additional line which could be interpreted as the strongest line of the BC8 phase. Most recently, Menoni, Hu, and Spain[7] have reported that extra lines attributed to BC8-Ge in preliminary work[8] were later found to be a contamination of the data. Thus in all work done to date with crystalline starting material, the evidence rests principally on the few lines seen by Bates, Dachille, and Roy.[3] More definite BC8 patterns have been obtained after starting with *amorphous* germanium. Minomura and co-workers[9] obtained first a crystalline β-tin phase at 10 GPa and then an almost pure BC8 pattern on return to ambient pressure. As found by Bates, Dachille, and Roy,[3] the BC8 phase disappeared quite quickly under ambient conditions, and after two days had almost completely transformed to a phase giving a very broadened hexagonal pattern. However, some later work on amorphous germanium has yielded less clear results.[10,11]

The existence of BC8-Ge is a matter of considerable interest because it allows experimental as well as theoretical studies of silicon and germanium in the same metastable form, and germanium in the two different forms. But progress has been limited by the elusiveness and instability of the BC8-Ge phase, characteristics which have also prevented a determination of its crystal structure. We now report the reproducible production of the BC8 phase, by sufficiently rapid pressure release, and present the results obtained from a refinement of the crystal structure.

II. EXPERIMENTAL TECHNIQUES

Diffraction data were collected on station 9.1 at the Synchrotron Radiation Source, Daresbury, using angle-

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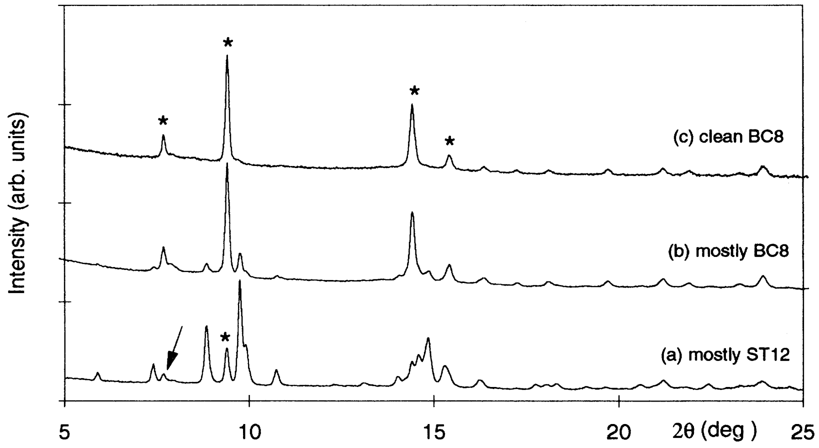

FIG. 1. The integrated profiles of the patterns recorded from germanium on pressure release to ambient. (a) From a sample of mostly ST12-Ge, (b) from a sample of mostly BC8-Ge, and (c) from a sample containing only BC8-Ge. The asterisk in (a) indicates the single BC8 reflection observed by Qadri, Skelton, and Webb (Ref. 6), while the asterisks in (c) indicate the four BC8 reflections observed by Bates, Dachille, and Roy (Ref. 3) at dry-ice temperatures. In all three profiles, $\lambda = 0.4650$ Å, and the sample-plate distance is ~365 mm. The exposure times were (a) 20 min, (b) 40 min, and (c) 16 min.

dispersive diffraction techniques and an image-plate area detector. The incident wavelength was 0.4650(1) Å. The two-dimensional powder patterns collected on the image plates were read on a Molecular Dynamics 400A PhosphorImager and then integrated to give conventional one-dimensional diffraction profiles. Details of our experimental setup and pattern integration program have been reported previously.[12–14]

The germanium sample was a finely ground powder prepared from starting material of 99.9999% purity supplied by the Aldrich Chemical Company. Two Diacell[15] diamond-anvil pressure cells, having full conical apertures of 50° half angle, were used. Their design allows the pressure to be decreased rapidly to ambient. Samples were loaded with a 4:1 mixture of methanol:ethanol as the pressure-transmitting medium, and the pressure was measured using the ruby-fluorescence technique.[16] To obtain single-phase BC8 samples, the pressure was first raised to 14 GPa and a diffraction pattern was collected to confirm that the samples were fully into the β-tin phase. The cells were then quickly brought down to ambient pressure. As the BC8 samples rapidly transformed to another phase (see below), a diffraction pattern with an exposure time of ~15 min was collected immediately; no significant transformation could be detected in these patterns. Only the incident-beam half of the pressure cells was used in order to maximize the recorded signal in short exposures and to remove possible errors arising from angle-dependent cell absorption. The structural results described were all obtained from full Rietveld[17] refinement of the integrated profiles using the program MPROF.[18]

III. RESULTS AND DISCUSSION

During preliminary work we found that the proportion of the BC8 phase increases with the rate of pressure release. Figure 1 shows three patterns of germanium obtained on pressure decrease from the β-tin phase at different rates. The profile in Fig. 1(a) contains approximately twice the (small) amount of BC8 phase (relative to the ST12 phase) observed by Qadri, Skelton, and Webb,[6] and the single reflection observed by them is indicated by an asterisk. The other low-angle BC8 peak observable in Fig. 1(a)—marked by an arrow— was hidden by a peak

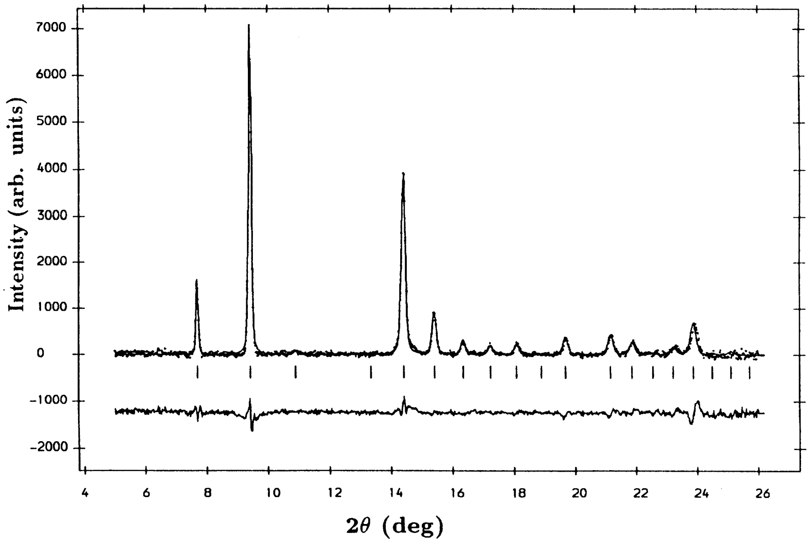

FIG. 2. A Rietveld refinement of the BC8-Ge profile in Fig. 1(c). The tick marks show the positions of the allowed reflections. The difference between the observed and calculated profiles is shown below the tick marks.

from the cubic diamond structure in their diffraction patterns.

The profile in Fig. 1(b) was obtained from a slightly faster pressure release and the BC8 component is sharply increased. A two-phase Rietveld refinement of this pattern gives lattice parameters of $a=5.932(1)$ Å and $c=6.979(1)$ Å for the ST12 phase [atomic volume $=20.47(1)$ Å^3], and $a=6.932(1)$ Å for the BC8 phase [atomic volume $=$ 20.82(1) Å^3]. These values are in good agreement with those obtained previously by Kasper and Richards[5] for ST12-Ge [$a=5.93(1)$ Å and $c=6.98(1)$ Å], and by Bates, Dachille, and Roy[3] for BC8-Ge ($a=6.92$ Å) and show the ST12 structure to be 1.7(1)% denser than BC8 at atmospheric pressure.

It was possible to obtain patterns containing only BC8-Ge lines by decreasing the pressure from 14 GPa very rapidly (in less than 1 s), as shown in Fig. 1(c). The four BC8 reflections seen previously by Bates, Dachille, and Roy[3] (at low temperature) are indicated by asterisks. Figure 2 shows the fit obtained from a Rietveld refinement of this pattern using the structure of BC8-Si (Ref. 5) as a starting model, with atoms on the 16(c) positions of spacegroup $Ia3$ at (x,x,x) and $x=0.1003$. The refined lattice parameter is $a=6.932(1)$ Å and the atomic coordinate refines to $x=0.1008(3)$. A second clean BC8 pattern, collected and refined in an identical manner, gave a unit-cell dimension of $a=6.932(1)$ Å and an atomic coordinate $x=0.1000(4)$. To ensure that the refined atomic coordinate was not biased by the trial structure (that of BC8-Si), refinements were carried out with the initial value of x set to 0.1036 (the value at which all four nearest-neighbor bond lengths become equal).[19] In both cases, the coordinate refined back to the value already given.

The average BC8 structure from the two refinements has $a=6.932(1)$ Å and $x=0.1004(3)$. The structure is essentially the same as that found previously for BC8-Si [$a=6.636(3)$ Å, $x=0.1003(8)$], in agreement with recent calculations.[20] As for BC8-Si, the BC8-Ge structure has distorted tetrahedra containing three long bonds of 2.498(1) Å [2.39(1) Å in BC8-Si] and one short bond of 2.411(7) Å [2.30(1) Å in BC8-Si]. The average nearest-neighbor bond length is thus 2.477(2) Å, slightly longer than the nearest-neighbor distance of 2.4497(1) Å found in the diamond structure of germanium.[21] The six tetrahedral angles of the BC8-Ge structure are also distorted from their ideal values, with three angles of 117.56(5)° and three of 99.07(10)°. This compares with values of 117.9(2)° and 99.2(3)°, respectively, in BC8-Si.[5]

As said in Sec. II, exposures of the BC8 phase had to be made immediately on recovery to ambient pressure because the samples rapidly transformed to a different phase characterized by very broad reflections. This process is illustrated in Fig. 3, which shows how the initial profile in Fig. 1(c) evolved over the following 17-h period. In an exposure begun only 30 min after pressure release, a broad feature has appeared as a shoulder on the lowest-angle BC8 peak, and extra features have just started to appear at 8.5° and 13° (2θ). The latter features become more prominent in Fig. 3(c) and after 17 h [Fig. 3(d)] there is only the faintest trace of the BC8 phase remaining. This behavior is in accord with the observations of Bates, Dachille, and Roy[3] who noted that although the BC8 phase remained indefinitely at dry-ice temperatures, 90% disappeared in 3 h at 30°C. They also reported the appearance of some ST12-Ge, but we have not observed this when the initial pattern is entirely BC8.

Comparison of the time evolution illustrated in Fig. 3 with that obtained by Minomura[9] for BC8-Ge prepared from initially amorphous germanium shows transformations to remarkably similar broadened-phase patterns in both cases. The instability of BC8-Ge is in contrast to the ST12-Ge phase; samples of the latter left at room temperature for approximately two months are partially transformed back to the cubic-diamond structure, but ~80% of the ST12 phase remains. The BC8-Si phase is even more stable, with a "lifetime" of more than 100 years at room temperature.[22] But the lifetime is very temperature dependent. At 470 K, BC8-Si transforms in only a few minutes to a phase identified as hexagonal diamond,[2,22,23] and the pattern appears to be a sharper version of the *same* profile as in Fig. 3(d). This similarity, and the results of Bates, Dachille, and Roy[3] for the stability of BC8-Ge as a function of temperature (above), suggest that BC8-Ge and BC8-Si behave in the same way except that the activation energy is higher for the transfor-

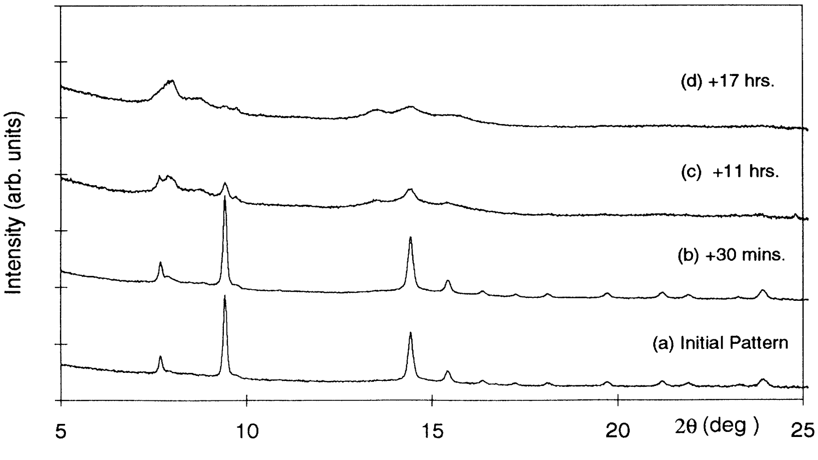

FIG. 3. The time evolution of the profile shown in Fig. 1(c) over a 17 h period. In all profiles, $\lambda=0.4650$ Å and the sample-plate distance is ~365 mm. The exposure times were (a) 16 min, (b) 54 min, (c) 29 min, and (d) 20 min.

mation of BC8-Si.

We have also made a preliminary investigation of the effect of pressure on the stability of BC8-Ge. Results suggest that the transformation shown in Fig. 3 is reversed at pressures above ~7 GPa, but further work is needed to reach definite conclusions.

In summary, germanium brought rapidly (< 1 s) to ambient pressure from ~14 GPa transforms completely to the BC8 phase. The crystal structure is essentially the same as that of BC8-Si. At room temperature, BC8-Ge transforms in less than a day to another phase that appears to be the same as that obtained by heating BC8-Si.

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