Pressure Induced Metastable Amorphization of BAs: Evidence for a Kinetically Frustrated Phase Transformation

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A transformation from the zinc blende (zb) to an amorphous crystal structure was observed at 125 GPa, just slightly above the calculated equilibrium transition pressure to the rock salt phase [Phys. Rev. B **36**, 6058 (1987)]. This is the first evidence that pressure induced amorphization in AB compounds is a kinetically frustrated process. The amorphous state persisted on further loading to 165 GPa, and throughout down-loading to 0 GPa. The Birch coefficients of the equation of state for the zb phase were determined to be $B_0 = 148 \pm 6$ GPa and $B_0' = 3.9 \pm 0.3$, in good agreement with theoretical calculations.

We have performed a high pressure experimental study of the structure of BAs to test theoretical predictions of its high pressure behavior and also as a first step in measuring the transition pressure on up-loading P_t from the zinc blende (zb) structure for the important sequence BAs, BP, BN, and diamond.

Before this study there had been no high pressure structural phase transformations observed in the boron III-V compounds. BAs is of particular interest because it is the most covalent III-V compound. It has the lowest Phillips ionicity $f_i = 0.002$ and shares the lowest Pauling ionicity $f_i = 0.00$ with BP [1].

Wentzcovitch, Cohen, and Lam [2] have done a theoretical study of BN, BP, and BAs at high pressure. Unusual properties are attributed to these compounds due to the lack of p electrons in the boron core. One of these properties is the reversal of anion and cation roles for BAs (and BP) from their standard assignments in the other III-V compounds. Also of interest are the predictions of high P_t from the fourfold coordinated zb to the sixfold coordinated rock salt (rs) structures of 110, 160, and 1110 GPa for the sequence BAs, BP, and BN. In another study, they have calculated the valence charge-density contours along the (110) plane of BAs, with the result being a covalently distributed charge with two humps along the bond, similar to diamond [3].

Excluding the boron III-V compounds, P_t is usually in the range of 2 to 22 GPa. The next highest P_t for a III-V compound belongs to GaN, which transforms from the zb to rs structure at 50 GPa experimentally (average of Refs. [4] and [5]) and 55 GPa based on calculations [6]. No phase transformation has been observed in BP to 110 GPa [7], and this study is the first on BAs.

The predicted P_t from zb for the boron III-V compounds are approximately an order of magnitude higher than for the non-boron III-V compounds. It is not *a pri-*ori obvious whether new structure or phenomena will occur in the phase transitions from these strongly covalent materials at very high pressures. Only experiments can answer these questions. This study demonstrating a zb amorphous transition in BAs at 125 GPa supports the idea that novel phenomena may indeed take place in strongly covalent materials at extreme compression.

BAs was prepared from the elements in a sealed, evacuated quartz tube at 850 °C for 24 h [8]. The Boron was 99.9% pure, 60 mesh crystalline powder and the arsenic 99.9999% sublimed chunk. The BAs was single phase zb by x-ray powder diffraction and indexed to an fcc cell with $a_0 = 4.777$ Å in agreement with the literature value [8].

For the high pressure experiments a finely ground BAs powder was prepared. The pressure vessels consisted of diamond anvil cells (DAC's) of the controlled displacement type [9]. Three separate experiments were performed.

In the first experiment single beveled diamond anvils with 100 μm flats were used. The sample chamber was a 75 μm diameter hole drilled in a rhenium gasket preindented to 50 μm thickness. A small amount of gold powder was also placed in the sample chamber to be used as a pressure marker. This experiment achieved 165 GPa on up-loading and down-loading to 0 GPa without catastrophic anvil failure. The second experiment was similar to the first except the anvils had 60 μm flats and a 50 μm hole was used. This experiment ended when an anvil surprisingly failed at 90 GPa. In the third experiment the anvils has 450 μm flats (nonbeveled), and the gasket was spring steel preindented to 65 μm thickness with a 125 μm diameter hole. This hole was approximately one-half filled with powder sample and one-half filled with a 4:1 methanol-ethanol mixture to serve as a quasihydrostatic pressure medium. A few small

ruby chips were also added. This experiment achieved 41 GPa and was used to measure low pressure equation of state (EOS) as accurately as possible (quasihydrostatic vs nonhydrostatic conditions). The EOS results of all three experiments were within experimental error of each other.

Energy dispersive x-ray diffraction (EDXD) experiments were performed at the Cornell High Energy Synchrotron Source (CHESS) to measure the EOS of the BAs sample. Further details of the experimental techniques and apparatus are given in references [9] and [10]. The size of the incident x-ray beam into the DAC was collimated to 20 μm $\times$ 20 μm with a set of tungsten apertures. This aperture set is important to minimize both gasket diffraction and pressure gradient effects [11]. Also the slit downstream of the DAC which defines the diffraction angle was moved as close to the sample as possible, about 35 mm, to minimize the Compton scattering from the diamonds. This effect is important for experiments over 100 GPa where the sample becomes quite thin.

The diffraction angle was calibrated with a gold foil; 2θ was 14.905° for experiments 1, 2, and 12.171° for 3. Typical collection time for a spectrum was about 20 min. The pressure for spectra of experiments 1 and 2 was

determined from the isothermal EOS of gold by Jamieson, Fritz, and Manghnani [12] from the x-ray measured gold cell volume. For experiment 3 the pressure for each x-ray spectrum was measured with a ruby fluorescence spectrum based on the nonhydrostatic ruby scale [13]. The sample cell volume was also obtained from each x-ray spectrum. Thus each spectrum represents a point of EOS of the sample. The pressure was then increased (decreased) by decreasing (increasing) the anvil separation and the measured EOS was generated. Micro-Raman spectroscopic measurements on the recovered sample and ruby florescence measurements were performed on a Spex model 1877C triple monochromator with a cooled optical multichannel detector. Raman and fluorescence signals were excited using the 488 nm line from an Ar^+ laser.

The following sequence occurred in experiment 1 with increasing pressure. The zb phase was stable at each pressure step-up to 120 GPa. Above 120 GPa the area of the sample diffraction peaks decreased dramatically. Above 135 GPa, and continuing to the highest pressure achieved in this study of 165 GPa, no sample diffraction peaks from BAs were present. Figure 1 shows this phenomena with a set of diffraction spectra at 118, 127, and 148 GPa. A series of down-loading spectra were then taken. No sample diffraction was observed at lower pressures, even upon the complete release of pressure. The ratio of the area of the BAs (111) diffraction peak to the area of the As $K\alpha$ fluorescence peak is used as a relative measure of the amount of sample diffraction and is plotted in Fig. 2. The sharp transition at $P = 125$ GPa between the region of constant and zero diffraction on uploading is evidence of a crystalline to amorphous phase transition at 125 GPa in BAs.

The diffraction from the gold powder used as a pressure marker remained strong throughout the experiment. The relative volumes of BAs and gold sampled by the x-
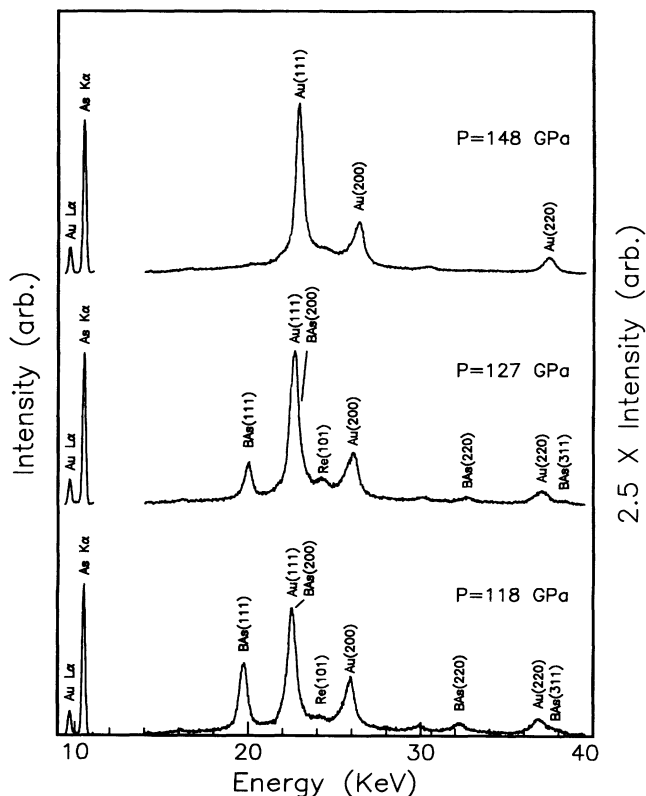

FIG. 1. EDXD diffraction spectra of BAs vs pressure P normalized to As $K\alpha$ fluorescence. The Au peaks are from the gold powder used as a pressure marker and the peaks labeled Re are from the rhenium gasket.
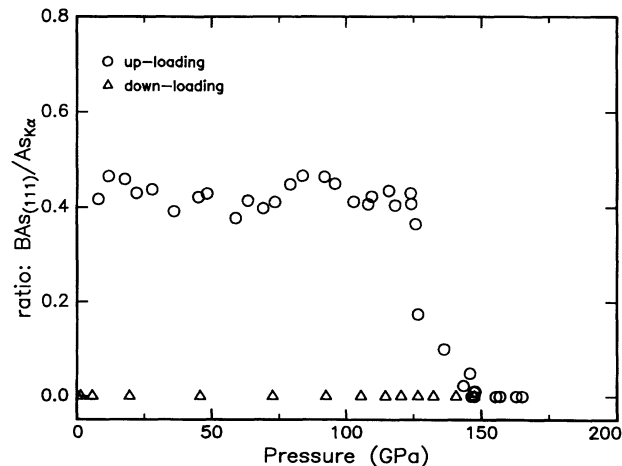

FIG. 2. Intensity ratio of BAs (111) diffraction to As $K\alpha$ fluorescence vs pressure.
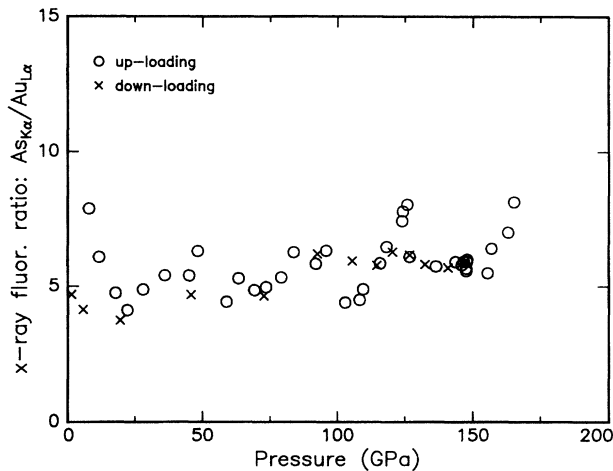
FIG. 3. Intensity ratio of As $K\alpha$ to Au $L\alpha$ x-ray fluorescence lines vs pressure.

ray beam remained constant through both up-loading and down-loading. This is measured by the ratio of areas of the As $K\alpha$ to Au $L\alpha$ fluorescence peaks as plotted in Fig. 3. Strong gold diffraction and a constant ratio of sample of gold volumes imply that there was sufficient sample thickness even at the highest pressures to detect BAs diffraction.

The down-loaded DAC was opened and the gasket moved. One of the diamond anvil tips was covered with a thin layer of opaque material. Raman spectra were taken on this recovered sample and also on a powder BAs sample. The zb BAs spectrum had strong Raman and the recovered sample had no detectable Raman. These spectra are plotted in Fig. 4. This is taken as further indication of a nonreversible phase transformation of the zb BAs. The measured values for the TO and LO modes
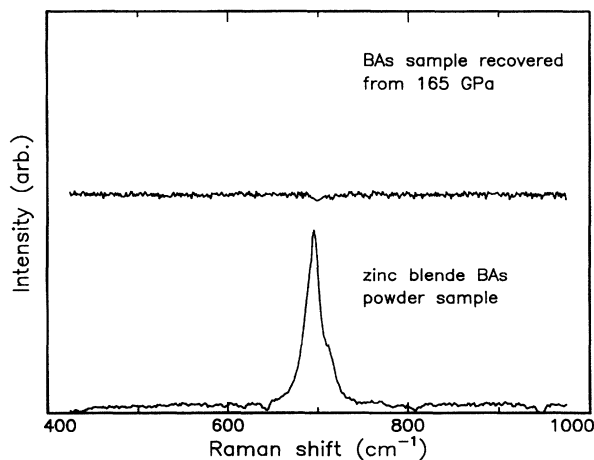
of the room temperature BAs were 695 and 714 cm^{-1}, respectively, in good agreement with the calculated TO value of 670 cm^{-1} of [3].

Figure 5 is a plot of the measured BAs EOS data, and the curve generated by the fitting of this data to the two parameter Birch EOS (BE2):

$$P = \tfrac{3}{2}B_0(x^{7/3} - x^{5/3})\left[1 + \tfrac{3}{4}(B_0' - 4)(x^{2/3} - 1)\right], \quad (1)$$

where $x = V_0/V$, B_0 is the isothermal bulk modulus at zero pressure, and B_0' is the pressure derivative of the isothermal bulk modulus evaluated at zero pressure [14]. The resulting values of the two parameters are $B_0 = 148 \pm 6$ GPa and $B_0' = 3.9 \pm 0.3$, in good agreement with the calculated value of $B_0 = 145$ GPa [2].

In a review of pressure induced amorphous phases, Ponyatovsky and Barkalov discuss a thermodynamic model of solid state amorphization (SSA) based on the PT phase diagram of a material as formulated independently by many researches [15]. In this model the amorphous phase is the product of a process where P and/or T is varied in such a way that the extrapolated melting curve between the liquid and a crystalline phase is crossed. Such thermobaric processes may be classified into three broad categories: (1) SSA resulting in a phase less dense than the crystalline phase which would form under equilibrium conditions with increasing pressure, (2) SSA resulting in a denser phase than the crystalline phase which would form under equilibrium pressure with decreasing pressure, and (3) increasing the temperature of a high pressure metastable phase. A necessary condition for such a PT phase diagram is that the slope of the liquidus be negative, i.e., the liquid is more dense than the solid phase, and the melting temperature decreases with increasing pressure. This ice-type phase diagram
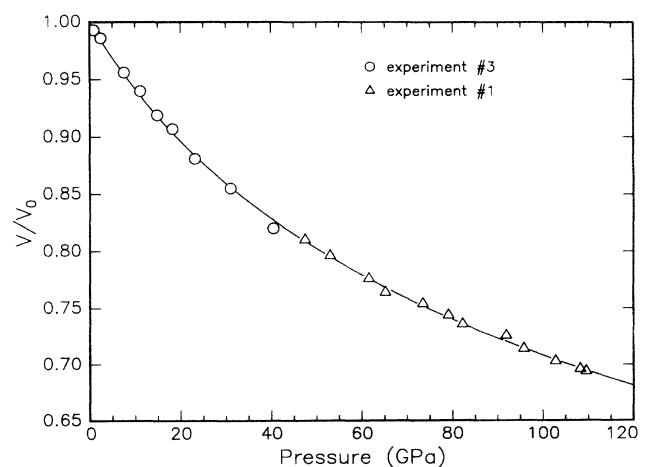

FIG. 4. Raman spectra of the BAs sample recovered from 165 GPa and from a powder zb BAs sample.

FIG. 5. Plot of reduced atomic volume, V/V_0 of BAs, vs pressure on up-loading. V is the measured atomic volume and V_0 is the atomic volume at zero pressure. Fit of the data points to the BE2 equation of state are shown by the curve.

(Ref. [16]) is not unusual in the group IV elements and III-V compounds.

Amorphization of some group IV elements and III-V compounds through such thermobaric treatments is well documented. Examples include Si, Ge, and GaSb [17,18]. The only other III-V compound where complete amorphization at room temperature through application of high pressure has been achieved is GaAs. GaAs transforms to a completely amorphous phase that is an insulator on decompression from Mbar pressures [19]. At Mbar pressures GaAs is in a sixfold coordinated simple hexagonal structure [20] and metallic state [19]. Using the above classification scheme the SSA of GaAs on decompression is type (2).

There are no known examples of phase transitions with increasing pressure of the group IV elements and III-V compounds from their ambient condition fourfold coordinated structures (zb or wurtzite) that are not strongly first order (fifteen cases). It is reasonable to assume that the zb to amorphous transition observed in BAs with increasing pressure is also first order. If this is true then it would be the first room temperature example of type (1) SSA in this class of materials, supporting the proposed classification scheme for SSA.

The calculated equilibrium transition for BAs is 110 GPa from fourfold (zb) to sixfold (rs) coordination [2]. Such calculations have an excellent record in accurately predicting the equilibrium transition pressure [21]. The actual transformation pressure on loading is somewhat higher, and this may be due to hysteresis (i.e., kinetics) [22,23]. We believe that in general shear and nonhydrostatic pressure effects reduce the amount of hysteresis in polymorphic pressure induced solid state phase transformations. This observation is based on the experience of our laboratory with dozens of materials over decades of high pressure experiments. The fact that we find pressure induced amorphization to begin at 125 GPa (just above the pressure of 110 GPa for the expected transition to the crystalline rs structure) is evidence that pressure induced amorphization in *AB* compounds is a kinetically frustrated process.

It would be interesting to do a high pressure optical study of BAs to discover if the amorphous phase is insulating or metallic. By analogy with their amorphization work on ice, Mishima, Calvert, and Whalley suggested BP (among others) as a candidate for SSA [20]. A high pressure study of BP to 2 Mbar would be appropriate to determine if it too transforms to an amorphous phase.

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