



First-order polyamorphic phase transition in boron nitride



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ABSTRACT

A first-order polyamorphic (amorphous–amorphous) phase transition is often observed in amorphous materials that have a tetrahedral structure, such as ice, carbon, or silicon, but it has yet to be observed in amorphous boron nitride (a-BN). We investigated the existence of a first-order phase transition in a-BN by means of first-principles molecular dynamics (MD) simulations at a constant temperature and various pressures. At 300 K, the volume of a-BN gradually decreases at applied pressures of 0 to 18 GPa; it then rapidly decreases by about 3% at pressures of 18 to 24 GPa, providing evidence of a first-order phase transition. The structure remains amorphous throughout the transition. As the pressure is released from 24 to 0 GPa, the volume gradually increases with preservation of the difference at the phase transition, showing that the structure of the high-density phase is maintained at 0 GPa. An analysis of the coordination number revealed that a-BN consists mainly of sp^2 -hybridized B–N bonds at 0 GPa. At the phase transition, sp^2 bonds are rapidly converted into sp^3 bonds, which subsequently account for about 30% of all bonds. This mechanism resembles that of the phase transition of amorphous carbon, in which the conversion rate is almost 100%. The low conversion rate in a-BN is probably attributable to the relative inflexibility of the structure.

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1. Introduction

Polyamorphism is the phenomenon whereby a material displays several amorphous phases. Most studies on this phenomenon have been made since its discovery in ice by Mishima and co-workers [1], although the phenomenon was mentioned in a previous study by Rapoport [2]. Various materials have been shown to exhibit a polyamorphic phase transition. In particular, materials such as C [3–5], Si [6–10], Ge [6,11,12], SiO_2 [13–15], GeO_2 [16,17], $GeSe_2$ [18], $GeSe_4$ [19], and AlN [20], in which a tetrahedral structure is favored, as in ice, have been extensively studied. The polyamorphism of these substances is related to the fact that tetrahedral structures have low atomic-packing factors that facilitate their transition into denser structures at high pressures.

Besides tetrahedral materials, B_2O_3 [21], TiO_2 [22–24], Al_2O_3 – SiO_2 [25], Al_2O_3 – Y_2O_3 [26], V_2O_5 [27], $LaBGeO_5$ [28], $CaCO_3$ [29], zeolites [30], and metallic glasses [31–33], have been investigated. Recently, polyamorphism of molecular materials such as CO_2 [34], H_2CO_3 [35], toluene [36], butanol [37] and D-mannitol [38] has also been reported. Polyamorphism in liquids is closely related to that in solids, and has been observed in C [39–41], Si [42], P [43], SnI_4 [44], Y_2O_3 – Al_2O_3 [45], $ZnCl_2$ [46], and triphenyl phosphate [47], among others.

Although BN has a tetrahedral structure, it has not previously been shown to display a first-order polyamorphic transition. BN has a

graphite-like hexagonal structure (h-BN) at low pressures, and a diamond-like (zincblende) cubic structure (c-BN) at high pressures [48–50]. c-BN, which can exist under normal conditions once it is formed, is the next hardest material after diamond and is used industrially in many applications. There is therefore a demand for the synthesis of c-BN at lower temperatures and pressures that is met commercially by the use of catalysts [51]. Attempts have been made to use amorphous BN (a-BN) as a starting material for the production of c-BN [52–53], and it has been shown that in the presence of H_2O , a-BN can be converted into c-BN at a lower temperature and pressure than can h-BN [53].

a-BN is produced by mechanical milling [54], chemical-vapor deposition (CVD) [55,56], or sputtering [57]. Analyses of chemical bonding have shown that a-BN contains sp^2 - and sp^3 -hybridized bonds in a ratio that depends on the production process. Intuitively, a greater internal stress should increase the proportion of sp^3 bonds [57]. A first-principles study showed that an a-BN model produced from liquid BN by slow cooling contains mostly sp^2 bonds [58]. Another theoretical study showed that more sp^3 bonds are present in high-density a-BN than in the low-density material [59]. If all this information is taken into consideration, it seemed plausible that a-BN might exhibit a first-order polyamorphic transition, although no such transition has yet been identified.

Durandurdu [60] recently studied a-BN by means of first-principles molecular dynamics (MD) simulations, and he reported that as the pressure is increased from 0 to 200 GPa, the volume of a-BN continuously decreases and no first-order phase transitions are observed. He concluded that the transformation from the low-density phase to the high-

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density phase occurs through continuous conversion of the interatomic bonds from sp^2 to sp^3 hybridization. Although this conclusion appeared reasonable, we still felt that it was possible that a-BN might undergo a first-order phase transition, because BN is similar to carbon in many respects, and amorphous carbon exhibits a first-order phase transition. Besides, the pressure step in Durandurdu's MD simulations was 5 GPa to cover a wide range of pressures, so that a small change in the volume might have been overlooked.

The aim of this study was therefore to reinvestigate whether a-BN exhibits a first-order phase transition. Considering the transition pressures from a-BN to c-BN in experiments [51–53], an amorphous–amorphous phase transition is likely to occur at pressures below 20 GPa if such a phase transition exists. We performed isothermal–isobaric first-principles MD simulations with finer pressure steps than those of the previous study [60] and we searched for a first-order phase transition in the range from 0 to 40 GPa. In addition, we employed an amorphous model that was twice the size of that used in the previous study [60]. This effectively reduced volume fluctuations and suppressed the influence of boundaries, permitting the detection of slight changes in volume. Finally, our results were analyzed by comparison with related materials, such as carbon or silicon.

2. Computational methods

The first-principles MD simulations were conducted by using the CPMD code, Version 3.17.1 [61]. This is based on density-functional theory [62,63] using plane waves and pseudopotentials. The norm-conserving Troullier–Martins-type [64] pseudopotential was employed. The generalized gradient approximation by Becke [65] and by Lee, Yang, and Parr [66] was included. An energy cutoff of 50 Ry was sufficient to provide convergence of the total energies and geometries. It was confirmed that the difference in total energy between 50 and 60 Ry was less than 0.06%, and test calculations for a-BN produced almost identical pair-correlation functions and coordination numbers. To calculate the pressure dependence of the volume, isothermal–isobaric MD simulations with the Parrinello–Rahman Lagrangian [67,68] were performed at the Γ point with spin-restricted wave functions. The temperature of the system was controlled by scaling the total kinetic energy of the atoms.

A total of 512 atoms (256 B and 256 N) were prepared in a cubic unit cell for the a-BN model. The number of atoms was twice that used in the previous study [60]. Although the unit cell was allowed to deform in accordance with the Parrinello–Rahman Lagrangian, it hardly deviated from the cubic shape during a computational run. All the tasks were executed on a parallel computer (SGI ICE X) with a message-passing interface (MPI).

The time step for the MD simulations was 5.0 a.u. (0.121 fs), and each simulation at a given temperature and pressure consisted of 5000 steps (605 fs). The volume at a given temperature and pressure were calculated by averaging the last 1000 steps of the MD simulation. Because the total time allowed for first-principles MD simulations with a large number of atoms is much shorter than that for classical MD simulations or experiments, it is necessary to examine whether the simulation time is sufficient for the system to reach an equilibrium state. This issue will be discussed in Section 3 in relation to the results of the MD simulations.

3. Results and discussion

To generate the a-BN model, 512 atoms arranged in the c-BN structure were heated to 3500 K, which is above the melting point of h-BN (3246 K). The atoms liquefied as soon as the MD simulation started at normal pressure. After the structure had become completely random at 605 fs, the temperature was linearly lowered to 300 K in 1815 fs. The resulting structure was amorphous and contained no separate N_2 dimers, i.e. all the atoms were connected, forming a single random

network. This amorphous model was named Model A, and the appropriateness of the model is considered later by comparing it with another model, Model B.

Starting from this a-BN Model A, MD simulations were carried out to measure the dependence of the volume on the pressure, as shown in Fig. 1 A. The volume shown is relative to the value at 0 GPa. The temperature was set to 300 K throughout the MD simulations to make the results comparable with future experiments. As the applied pressure was increased from 0 to 40 GPa (solid red circles), the volume gradually decreased at pressures of up to 18 GPa, decreased sharply between 18 GPa and 24 GPa, and then gradually decreased once more at pressures above 24 GPa. The smoothness of the volume change implies that the simulation time was sufficiently long for the system to reach an equilibrium state. The structure remained amorphous, as shown later. This discontinuous change in volume provides clear evidence of a first-order phase transition. The fluctuation in the volume at 18–24 GPa tended to be enhanced, which also supports the occurrence of a phase transition. The decrease in volume was about 3%, which is less than that of carbon or silicon (15–20%) [5,8].

The transition pressure is higher than the experimental value of 6–8 GPa for the transformation of a-BN into c-BN [52–54]. In the experiments, however, the synthesis of c-BN was performed at a high temperature above 1000 °C. At room temperature, a-BN was preserved at pressures up to 15 GPa [52]. Our results are therefore consistent with the experiments.

When the pressure was released from 24 GPa (open green circles), the volume gradually increased and it exhibited no discontinuous change at pressures down to 0 GPa. It is understandable, by analogy between c-BN and h-BN, that a-BN can retain the structure of its high-pressure phase as a metastable state at 0 GPa. This agrees with the results of the previous work by Durandurdu [60]. The hysteretic behavior is also observed in the phase transition of amorphous C, Si, and Ge [5,8, 11].

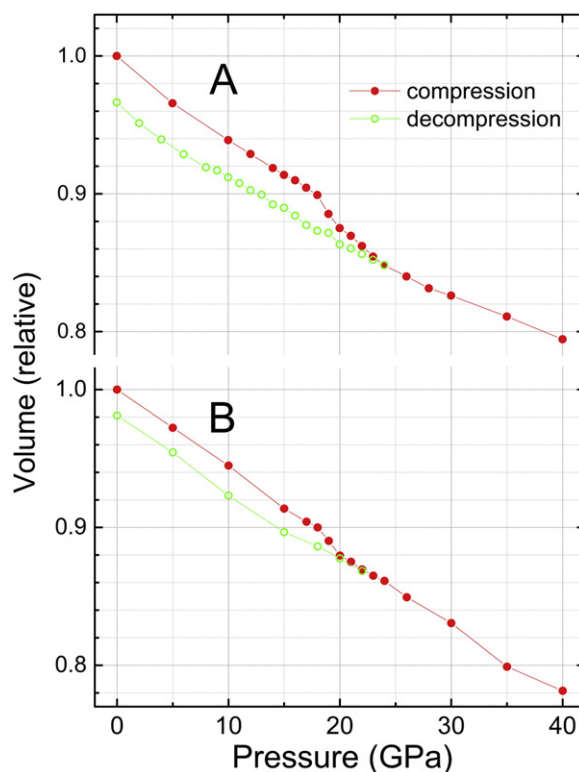


Fig. 1. Pressure dependence of the volume of a-BN Model A (upper) and Model B (lower). Solid red circles represent the compression process and open green circles the decompression process.

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