Amorphization Induced by Pressure: Results for Zeolites and General Implications

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We report an *ab initio* study of pressure-induced amorphization (PIA) in zeolites, which are model systems for this phenomenon. We confirm the occurrence of recently reported low-density amorphous phases that preserve the crystalline topology, and explain the role of the zeolite composition regarding PIA. Our results support the correctness of existing models for the basic PIA mechanism, but suggest that energetic, rather than kinetic, factors determine the irreversibility of the transition.

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Many minerals can be turned amorphous by mere application of pressure, a phenomenon known as pressure-induced amorphization (PIA) [1]. Our understanding of PIA is only partial. The so-called "size criterion" explains PIA in many systems composed of unconnected ionic units [2], but lacks generality. Simulations of materials like α-quartz [3] and α-berlinite [4] suggest a more universal picture: PIA would be the result of a first-order transition associated with very localized, weakly interacting structural distortions that become unstable upon compression. In such a transition, domain nucleation would overwhelm growth and destroy the long-range order [5]. Cohen, Íñiguez, and Neaton [5] (CIN) further propose the PIA transition will be *reversible* (i.e., the long-range order will be recovered upon decompression) if the crystalline *topology* (i.e., the atomic coordination and bonding) is preserved in the amorphous phase.

Recent work [6] on the nanoporous aluminosilicates known as zeolites has renewed the interest in PIA. It was shown that a zeolite may present two distinct PIA phases: a low-pressure (≈ 2 GPa) low-density amorphous phase (LDA), which might constitute a "perfect" glass with negligible configuration entropy, and a high-pressure (≈ 6 GPa) high-density amorphous phase (HDA). Further, the crystalline topology is found to be preserved in the LDA phase and lost in the HDA phase, which, according to the CIN picture, implies amorphization will be reversible in the former case and irreversible in the latter. These results, together with other studies [7,8] that, for example, show a striking dependence of the PIA reversibility on the zeolite composition, clearly point at these systems as ideal to test general PIA theories.

Here we report an *ab initio* study that reveals the mechanisms controlling PIA in zeolites and provides important insights pertaining PIA phenomena at large.

We used the generalized gradient approximation (GGA) to density functional theory [9] as implemented in the code SIESTA [10]. We wanted to study amorphization occurring in spite of negligible thermal activation and thus focused on low temperature simulations. We proceeded as follows: we started from the experimentally known zero-pressure

phase and increased (or decreased) the pressure p by a Δp of 0.25 GPa. At each new pressure $p + \Delta p$, we started from the structure obtained for the previous pressure p, performed a short (100 fs) molecular dynamics simulation at 100 K, with random initial velocities, and relaxed the resulting structure. In this way, we were able to compute the pressure dependence of a phase up to its (meta)stability limit, where it transforms into a new phase that is directly obtained from the calculation. Discontinuities in the calculated volume/enthalpy are indicative of first-order transitions; when the discontinuities appear only in the slope of the volume/enthalpy versus pressure curve, the transitions are of second-order.

Zeolites have the general formula $A_{x/n}^{n+}\mathrm{Al}_x\mathrm{Si}_{1-x}\mathrm{O}_2$, where A is a charge-compensating cation. The Si/Al atoms are at the center of corner-sharing O_4 tetrahedra. A typical zeolite structure, with the so-called "LTA" framework, is sketched in the top-right inset of Fig. 1; note the four-, double-four-, six-, and eight-member *rings* (denoted as 4MR's, D4R's, etc.), also known as *secondary building units*. We studied three LTA zeolites with different percentages of Al and Na as the charge-compensating cation: an Al-free "all-SiO_2" system, Na-ZK4 with a 1-to-5 Al-Si ratio, and Na-A where the ratio is 1-to-1. Following experimental information [11], we considered primitive cells containing 72, 76, and 168 atoms, respectively, for all-SiO_2, Na-ZK4, and Na-A.

All-SiO_2 *results*.—The all-SiO_2 LTA zeolite exhibits most of our key findings. Figure 1 shows the pressure dependence of the unit cell volume and the evolution of an 8MR that captures the typical structural distortions. The slope changes and volume discontinuities indicate a series of phase transitions. It is sufficient for our purposes to describe the structure in terms of the average values and standard deviations of the relevant angles (Si-O-Si and O-Si-O) and distances (Si-O). For example, for the reference LTA structure at 0 GPa we obtained $\bar{d}_{\mathrm{SiO}} = 1.63 \pm 0.01$ Å, $\bar{\theta}_{\mathrm{OSiO}} = 109 \pm 1°$, and $\bar{\theta}_{\mathrm{SiOSi}} = 151 \pm 8°$.

Phases I to III in Fig. 1 are connected by continuous transitions characterized by rigid rotations of the O_4 tetrahedra. Such rigid unit modes (RUM's [12]) are mainly
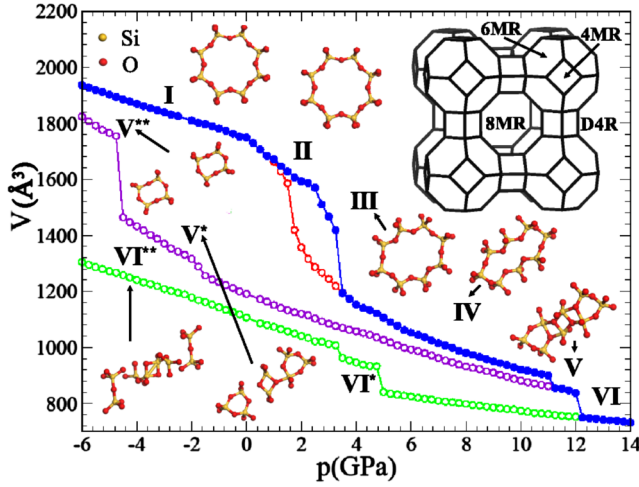
FIG. 1 (color online). Pressure dependence of the all-SiO$_2$ unit cell volume. Solid and open symbols refer, respectively, to compression and decompression. Also shown is the evolution of a representative eight-member ring. The top-right inset is a sketch of the LTA-framework structure as defined by the Si/Al atoms.

reflected in $\bar{\theta}_{\mathrm{SiOSi}}$. For example, for phase III at 2.75 GPa we obtained $\bar{d}_{\mathrm{SiO}} = 1.62 \pm 0.01$ Å, $\bar{\theta}_{\mathrm{OSiO}} = 109 \pm 2°$, and $\bar{\theta}_{\mathrm{SiOSi}} = 142 \pm 18°$. At 3.5 GPa phase III transforms discontinuously into a phase IV of significantly smaller volume. This transition does not involve any topological change; i.e., no bonds are formed or broken. In fact, as in the previous cases, the structural changes mostly affect $\bar{\theta}_{\mathrm{SiOSi}}$; at 7 GPa we obtained: $\bar{d}_{\mathrm{SiO}} = 1.63 \pm 0.02$ Å, $\bar{\theta}_{\mathrm{OSiO}} = 109 \pm 7°$, and $\bar{\theta}_{\mathrm{SiOSi}} = 132 \pm 20°$.

At 11.25 GPa and 12.25 GPa we observe first-order transitions into phases V and VI, respectively. These phases display collapsed rings of all types and new Si-O bonds, with the corresponding loss of the LTA-framework topology. The occurrence of SiO$_5$ and SiO$_6$ groups results in a wide dispersion of distances and angles. For example, at 13 GPa we obtained $\bar{d}_{\mathrm{SiO}} = 1.70 \pm 0.10$ Å, $\bar{\theta}_{\mathrm{OSiO}} = 107 \pm 23°$, and $\bar{\theta}_{\mathrm{SiOSi}} = 117 \pm 17°$. Note the increase in the average Si-O distance, which reflects the existence of high-coordination defects.

Figure 1 also shows our results regarding the reversibility of the transitions. The transitions to phases II and III are reversible, with no hysteresis in the $V(p)$ curve. Phase IV can also transform back to the crystalline phase, but hysteresis occurs in this case. Note that the presence or absence of hysteresis agrees with the observed character, first or second order, of the transition. Finally, upon decompression from phases V and VI, the system undergoes a number of structural changes but does not find its way back to the low-pressure stable phases. The transitions to phases V and VI are thus irreversible.

Our simulations reveal the atomistic origin of this irreversibility. The metastable phases V** and VI** in Fig. 1 present the right first-neighbor coordination and can thus be viewed as formed by SiO$_4$ units. However, the ring

structure is not the LTA one. For example, in phase V** the original 8MR has transformed into two disconnected 4MR's, and phases V* and VI** contain Si pairs sharing two oxygens (see Fig. 1). Note that phases V** and VI** are robustly metastable: while their excess energy with respect to phase I is relatively large (about 0.35 eV *per* formula unit at 0 GPa), a transition to the crystalline phase would require multiple Si-O bond breakings within SiO$_4$ units, which is energetically very costly.

The origin of the defects affecting the ring topology is easily identified. Phases V and VI exhibit collapsed rings in which bonds form between Si and O atoms on opposite sides of the original rings. The resulting SiO$_5$ and SiO$_6$ groups break upon decompression and the atoms recover their original coordination. However, this defect breaking can happen in a variety of ways from which *only one* allows the ring to fully recover at low pressures. In addition, this unique *right way* involves the largest volume expansion and, thus, is energetically favorable only at relatively low pressures. For example, for phase VI we obtained that above 2 GPa the SiO$_5$ and SiO$_6$ groups find it energetically favorable to break in ways that restore the original atomic coordination but, at the same time, destroy the 8MR.

Our simulated system is defined by the unit cell of the LTA structure and, thus, cannot capture the translational-symmetry breaking characterizing amorphization. Hence, in a few cases we considered larger supercells and simulated the translational-symmetry loss directly. More precisely, we considered the relaxed structures obtained at pressures neighboring transition points (i.e., 0 GPa, 3.5 GPa, etc.), created the corresponding $2 \times 2 \times 1 \times$ 72-atom supercells, and increased the pressure to simulate the transformation. Interestingly, for the second-order transitions to phases II and III, the translations within the supercell are preserved. On the other hand, as shown in Fig. 2, the translational symmetry within the supercell is completely lost in the transitions to phases IV and V, both of which are first order in character. We can thus conclude that phases IV and V are genuine amorphous phases, the crystal topology being preserved in the former and lost in the latter.

Na-ZK4 and Na-A results.—We consider first the case of Na-A, which is more informative. Figure 3 shows the pressure dependence of the 168-atom primitive cell and the evolution of a characteristic D4R. (Note that the Si and Al atoms are intercalated in Na-A.) Phase I is the reference phase, which at 0 GPa is characterized by $\bar{d}_{\mathrm{SiO}} = 1.65 \pm 0.01$ Å, $\bar{d}_{\mathrm{AlO}} 1.76 \pm 0.02$ Å, $\bar{\theta}_{\mathrm{OSiO}} = 109 \pm 5°$, $\bar{\theta}_{\mathrm{OAlO}} = 109 \pm 3°$, and $\bar{\theta}_{\mathrm{SiOAl}} = 148 \pm 10°$. Phases II and III are the product of two transitions that are, respectively, continuous and discontinuous. Both transformations are characterized by RUM's that involve rotations of the O$_4$ tetrahedra and mainly affect the Si-O-Al angles. For example, for phase III at 5 GPa we obtained $\bar{d}_{\mathrm{SiO}} = 1.66 \pm 0.05$ Å, $\bar{d}_{\mathrm{AlO}} = 1.82 \pm 0.09$ Å, $\bar{\theta}_{\mathrm{OSiO}} = 109 \pm 10°$,
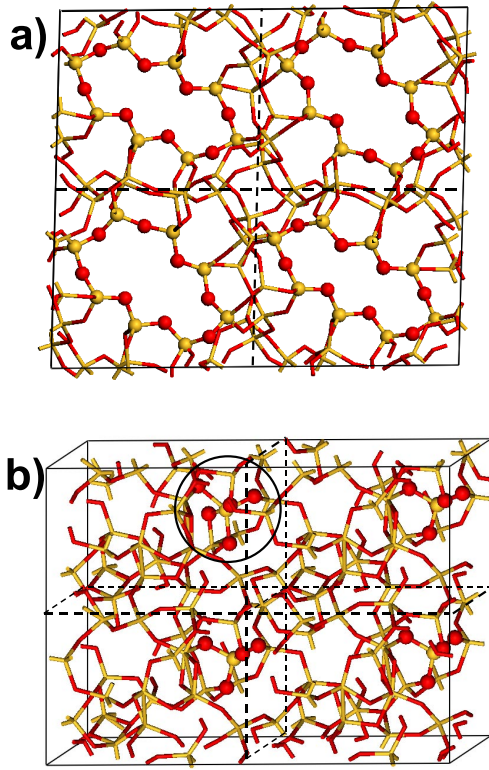
FIG. 2 (color online).   All-SiO$_2$ $2 \times 2 \times 1$ supercells (see text) resulting from transitions at 3.50 GPa [panel (a)] and 11.25 GPa [panel (b)]. Dashed lines sketch the cell from which we start. We highlight examples of atoms that were translationally related before the transition; a SiO$_5$ group is circled in panel (b).

FIG. 3 (color online).   Same as Fig. 1 for the Na-A zeolite.

$\bar{\theta}_{OAlO} = 108 \pm 21°$, and $\bar{\theta}_{SiOAl} = 118 \pm 18°$. Note that phase III preserves the LTA topology, clearly resembling what we found for phase IV of all-SiO$_2$.

At 5.25 GPa we find a second discontinuous transition to a phase IV in which the D4R's collapse and the LTA topology is lost. Comparison with all-SiO$_2$ suggests the Al atoms reduce the pressure at which the coordination defects appear, which is consistent with the fact that Al is more likely than Si to have a five or sixfold oxygen coordination. Interestingly, only the D4R's collapse in phase IV; since in Na-A the centers of the 6 and 8MR's are occupied by Na atoms, this suggests the cations are responsible for the preservation of the large rings. The structure of phase IV at 7 GPa is characterized by $\bar{d}_{SiO} = 1.67 \pm 0.06$ Å, $\bar{d}_{AlO} 1.85 \pm 0.10$ Å, $\bar{\theta}_{OSiO} = 109 \pm 12°$, $\bar{\theta}_{OAlO} = 107 \pm 24°$, and $\bar{\theta}_{SiOAl} = 116 \pm 20°$. The relatively large standard deviations reflect the structural disorder.

As shown in Fig. 3, we found that *all* the transitions in Na-A are reversible. Hysteresis does not occur in the case of the second-order transition (to phase II), but it does for the first-order transitions (to phases III and IV). Note that the reversibility from phases II and III, in which the ideal LTA topology is preserved, is consistent with our results for all-SiO$_2$. However, the obtained reversibility from phase IV, in which the LTA topology is lost, is clearly at
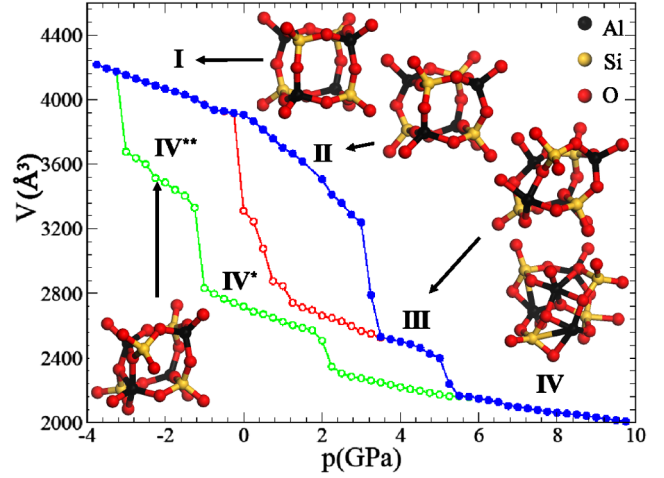
odds with what we found in the all-SiO$_2$ case. Note also that, unlike phases V** and VI** of all-SiO$_2$, phases VI* and VI** of Na-A present coordination defects and are not robustly metastable at low pressures.

Our results for Na-ZK4 (not shown here) can be summarized as follows. (1) At low pressures there are continuous transitions dominated by RUM's. (2) A first-order transition, at 4.25 GPa, causes coordination defects, most of which involve neighboring Si-Al atom pairs that approach to share two O atoms. All the Al atoms in the system give rise to coordination defects, while only a small fraction of the Si atoms do. (3) Upon further compression we find discontinuous transitions to phases in which rings of all types collapse. (4) The second-order transitions are reversible without hysteresis, and all the first-order transitions are irreversible. Thus, as in Na-A, the presence of Al in Na-ZK4 reduces the pressure at which the coordination defects appear. On the other hand, at variance with all-SiO$_2$ and Na-A, Na-ZK4 does not present any first-order transition to a topology-preserving phase.

Discussion.—Our simulations render a wealth of conclusions that pertain not only zeolites, but PIA phenomena at large. First of all, our results strongly support the existence of the LDA phases reported by Greaves *et al.* [6]. Two of the considered zeolites (all-SiO$_2$ and Na-A) present an LDA phase, which supports the claim that such phases are common. Further, for all-SiO$_2$ the LDA phase is predicted to be stable in a wide range of pressures. Our results thus suggest that this zeolite, which has been recently synthesized [13] and is relatively simple, would be ideal for detailed experimental and theoretical studies of the perfect glass proposed in Ref. [6].

Our simulations confirm PIA is a first-order transition, thus supporting the above-mentioned nucleation-overwhelms-growth mechanism [5]. In topology-breaking PIA transitions, the structural distortions involve formation of new bonds and, as Fig. 2(b) suggests, are rather localized and can freeze in independently from the rest. In the PIA transitions that respect topology, the localized distortions

are essentially rigid rotations of the O_4 tetrahedra. This is further confirmed by vibrational calculations showing the *whole* low-energy RUM-related band softens under compression.

The Al atoms facilitate the formation of coordination defects. Such defects are predicted to occur at about 5 GPa in Na-ZK4 and Na-A, which is consistent with experimental data [6,7], and only above 11 GPa in all-SiO_2. The Na cations, on the other hand, impede the collapse of the rings at whose centers they are located; i.e., there is no formation of new Si-O bonds between atoms on opposite sides of Na-hosting rings. This is consistent with our finding that Na-A, which contains a large amount of Na, presents an LDA phase while Na-ZK4 does not. Also, based on our results, it is reasonable to assume large cations will be more effective in preventing rings from collapsing. That is in agreement with reports that, for one particular zeolite, PIA is irreversible for small cations (e.g., H) and reversible for larger ones (e.g., Li and Na). The same rationale applies to the probable role of H_2O molecules preventing PIA [8]. These observations remind one of the ''size criterion'' mentioned above [2]; in zeolites the cation size would play a role in determining the occurrence and reversibility of the PIA transition.

Our results support the CIN picture [5] that topology-preserving PIA transitions are reversible. However, at variance with what is proposed in Ref. [5], they also show that topology-breaking PIA transitions may be reversible. That is the case of Na-A, where the topology breaking is caused by bond formation between atoms that are close neighbors in the crystalline phase. We find in such conditions the coordination defects can be *correctly undone* upon decompression, and the crystalline structure recovered. We find the PIA transition to be irreversible in cases in which the coordination defects involve atoms that are away from each other in the crystalline phase (i.e., when the 6M and 8M rings collapse). In such cases, the atoms recover their preferred low-pressure coordination upon decompression, but the resulting ring topology differs from the crystalline one.

Our simulations also refine the CIN picture in what regards the mechanism for irreversibility. According to Ref. [5], irreversibility occurs because the system is *unable* to find the *transition path* to its most stable (crystalline) phase. To some extent our results support such a kinetics-related explanation, as we find that, for amorphous phases with collapsed rings, only a small number of transition paths allow the system to recover both the ideal coordination to first neighbors and the LTA ring structure. However, our work also suggests a second and more important cause for the irreversibility: we find that at high pressures (e.g., above 2 GPa) it is energetically favorable to recover the ideal first-neighbor coordination in ways that break the crystalline ring structure. Thus, in addition to being more numerous, the *wrong* transition paths (i) are energetically preferred at moderately high pressures and (ii) lead to

phases that are robustly metastable at low pressures. This *thermodynamics-related* mechanism constitutes an alternative cause, probably the main one in zeolites, for PIA irreversibility.

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