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 low-density amorphous phases like the one reported by Greaves et al. [Science 308, 1299 (2005)], which preserves the crystalline topology and might constitute a new type of glass. The role of the zeolite composition regarding PIA is explained. 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.

PACS numbers: 61.50Ks,61.43.Fs,64.70.Pf,82.75.-z

Many minerals can be turned amorphous by mere application of pressure, an intriguing phenomenon known as pressure induced amorphization (PIA) [1]. The concrete realizations of PIA can be quite diverse. Remarkably, upon release of the applied pressure some materials recover their crystalline order, thus exhibiting reversible amorphization, while others remain amorphous. Our understanding of PIA is only partial. Simulations of systems like α-quartz [2], silica [3], and α-berlinite [4] suggest PIA is 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 if the crystalline topology is preserved in the amorphous phase, i.e., if the amorphization does not involve bond formation or breaking. While physically plausible, this picture is yet to be confirmed.

The recent work of Greaves et al. [6] on the nanoporous aluminosilicates known as zeolites has renewed the interest in PIA. These authors have shown a zeolite may present two distinct PIA phases: a low-pressure ($≈ 2$ GPa) low-density amorphous phase (LDA), which they argue may constitute a new type of glass, and a high-pressure ($≈ 6$ GPa) high-density amorphous phase (HDA). Further, they claim the crystalline topology is 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 present an ab initio study of PIA in three representative zeolites with different compositions. Our results (i) confirm the occurrence of the above mentioned LDA and HDA phases, (ii) show how the zeolite composition controls the nature of the PIA transition, and (iii) essentially confirm, and perfect, the CIN picture regarding PIA reversibility. While obtained for zeolites, our results clearly pertain PIA phenomena at large.

We used the Generalized Gradient Approximation to Density Functional Theory [9] as implemented in the code SIESTA [10]. Note that we wanted to study amorphization occurring in spite of negligible thermal activation, and thus focused on low temperature simulations. We proceeded as follows: at each considered pressure, we performed a short (100 fs) molecular dynamics simulation at 100 K, starting with random velocities, and relaxed the resulting structure. Zeolites have the general formula $A_{x/n}Al_xSi_{1-x}O_2$, where $A$ is a charge-compensating cation (e.g. Li or Na). The Si and 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. 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 low-density amorphous phases like the one reported by Greaves et al. [Science 308, 1299 (2005)], which preserves the crystalline topology and might constitute a new type of glass. The role of the zeolite composition regarding PIA is explained. 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.
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 $\theta_{\text{SiOSi}}$; at 7 GPa we obtained: $d_{\text{SiO}}=1.63\pm0.02$ Å, $\theta_{\text{OSiO}}=109\pm7^\circ$, and $\theta_{\text{SiOSi}}=132\pm20^\circ$.

At 11.25 GPa phase IV transforms discontinuously into a phase V, and at 12.25 GPa there is another first-order transition to a phase VI. Phases V and VI display collapsed rings of all types and new Si–O bonds (see the 8MR depicted in Fig. 1), 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 $d_{\text{SiO}}=1.70\pm0.10$ Å, $\theta_{\text{OSiO}}=107\pm23^\circ$, and $\theta_{\text{SiOSi}}=117\pm17^\circ$. 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 can be 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 break up 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 this case, and for phase VI, the ring has a width of 8.4 Å, and the Si pairs are not adjacent. Therefore, 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.

We also investigated if these transitions involve true amorphization. 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 selected cases we consid-
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$^\ast$ and VI$^\ast$ of all-SiO$_2$, phases IV$^\ast$ and IV$^{\ast\ast}$ 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 raise 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. Maybe most importantly, we confirm the existence of the LDA phases reported by Greaves et al. Two of the considered zeolites (all-SiO$_2$ and Na-A) present an LDA phase, which supports the claim that such phases may be quite 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 new type of glass proposed in Ref. [6].

Our simulations confirm PIA is a first-order transition, thus supporting the above mentioned nucleation-overswhelms-growth mechanism [6]. In topology-breaking PIA transitions, the structural distortions involve formation of new bonds and, as Fig. 2b, suggests, are rather

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**FIG. 3:** Same as Fig. I for the Na-A zeolite.
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 O4 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-SiO2. The Na cations, on the other hand, impede the collapse of the rings at whose centers they are located. As a result, there is no formation of new Si–O bonds between atoms on opposite sides of Na-hosting rings. This seems 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 seems 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 H2O molecules preventing PIA.

Our results support the CIN picture 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 irreversible. 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, so that the crystalline structure is 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 reversibility. 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.

We thank J. Junquera for his help with the basis optimization and R.L. Cappelletti for his comments on the manuscript. We thank the financial support of the Spanish Ministry of Science and Education through the “Ramón y Cajal” program, MEC grants MAT2002-02808 (IP) and BFM2003-03372-C03-01 (JI), the Catalan Government grant SGR-2005-683 (JI), and FAME-NoE. We used the facilities of the CESGA supercomputing center.

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