Atomistic modeling of multiple amorphous-amorphous transitions in SiO_2 and GeO_2 glasses at megabar pressures

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We present molecular dynamics simulations of SiO_2 and GeO_2 glasses up to megabar pressures, 120 and 160 GPa, respectively, and show direct parallels between polyamorphism of glasses and polymorphism of their crystalline counterparts under compression. The glasses undergo a set of several smooth transformations in much the same manner as the corresponding crystals at nearly the same pressures, where coordination numbers of Si and Ge atoms considerably exceed 6, reaching 6.4 and 7.6, respectively, at maximum simulation pressures. The transformations in glasses, unlike those in crystals, occur with rather small hysteresis. High coordination states are not retained in a metastable form at room pressure.

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Polymorphism in crystals under compression, or the existence of pressure-induced phase transformations to denser structures, is a fairly well-studied phenomenon. In contrast to transitions in crystals, the transformations between different amorphous states is not well understood.[1–3] The pressure treatment of glasses and amorphous solids leads, in most cases, to glass densification and a change of the intermediate range order of an amorphous network. Nevertheless, some examples of coordination transformations in disordered media can be provided: for instance, transformations in glassy SiO_2, GeO_2, B_2O_3; amorphous H_2O ice,[4–6] amorphous zircon,[7] and some others. For oxide glasses, transformations under compression for the SiO_2 and GeO_2 glasses are well studied. During these transformations, the glass structure changes from fourfold coordinated, as in quartz, to sixfold coordinated. Very recent molecular dynamics simulation of GeO_2[8] thoroughly considers the tetrahedral-octahedral transition in the glass under pressure.

Recall that under compression, the SiO_2 crystal undergoes a set of transitions (see Ref. 4 for corresponding references): α-quartz (coordination number $Z = 4$) → coesite ($Z = 4$, transition pressure $P \approx 3$–4 GPa) → stishovite (rutile structure) ($Z = 6$, $P \approx 9 \pm 1$ GPa) → $CaCl_2$-structure type ($Z = 6$, $P \approx 60$–70GPa) → α-PbO_2-structure type ($Z = 6$, $P \approx 80$–120 GPa) → pyrite-structure type ($Z = 8$, $P \approx 210$–260 GPa). The pressure-temperature diagram of GeO_2 is similar to that of SiO_2 or perhaps even simpler as it lacks a number of four-coordinated phases, including a coesite-like one. A rutilelike phase of GeO_2 ($Z = 6$) transforms to the $CaCl_2$ structure type ($Z = 6$, $P \approx 30$ GPa), then to the α-PbO2-structure type ($Z = 6$, $P \approx 45$–50 GPa) and finally to the pyritelike structure ($Z = 8$, $P \approx 70$–85 GPa) (see Ref. 4 for corresponding references). The metastable phase of GeO_2 with a quartzlike structure ($Z = 4$) transforms under pressure into the phase with a rutilelike structure ($Z = 6$) at $P \approx 10$ GPa.[9] Note that the α-PbO_2 structure is the densest of those belonging to the rutile group and, in a certain sense, intermediate between the structures with the coordination number 6 and those of the fluorite group with the coordination number of $6 + 2 = 8$.

Of considerable interest is the question as to how far the analogy between polymorphism and polyamorphism can be drawn. That is, can SiO_2 and GeO_2 glasses undergo transformations to short-range order packings which are even denser than those in rutilelike structures? Very recently, spectroscopic evidence for the transformation of the SiO_2 glass to a denser modification at pressures higher than 140 GPa has been provided.[10]

Another issue of special interest is whether the dense modifications of the SiO_2 и GeO_2 glasses with increased coordination can be retained in the metastable state at normal pressure. It is known for crystalline prototypes that many high-pressure phases, for example, stishovite and SiO_2 with the α-PbO_2 structure, can be retained in the metastable state under normal conditions.

For the SiO_2 and GeO_2 substances, adequate intermolecular interaction potentials have been developed; using these potentials, experimental data for both glasses and crystalline phases can be well reproduced in wide temperature and pressure ranges.[11,12] Note that most of the previous computer simulations of the SiO_2 and GeO_2 glasses have been conducted at pressures below 50 GPa (see Ref. 4 for corresponding references); however, first-principles simulations of the SiO_2 melt were performed up to 150 GPa.[13]

In this paper, we deal with the above problems by performing high-pressure molecular dynamics (MD) simulations of SiO_2 and GeO_2 glasses to the pressures exceeding 100 GPa. We have used, as in the earlier work,[11] fully connected tetrahedral structures with 1536 atoms and employed well-studied interatomic potentials for SiO_2 and GeO_2.[14,15] We have used DL_POLY MD package.[16] Each pressure point was simulated for 50 ps in the Berendsen ensemble. We note that increasing simulation time as well as the system size does not affect the results.

The SiO_n and GeO_n polyhedron representations of the fragments of silica and germania glasses under pressure are shown in Figs. 1 and 2. The average cation coordination number $Z = \langle n \rangle$ and system volume are shown in Figs. 3 and 4. The cutoff distance for determining the cation coordination number Z_{Si} was taken as the halfway distance between the

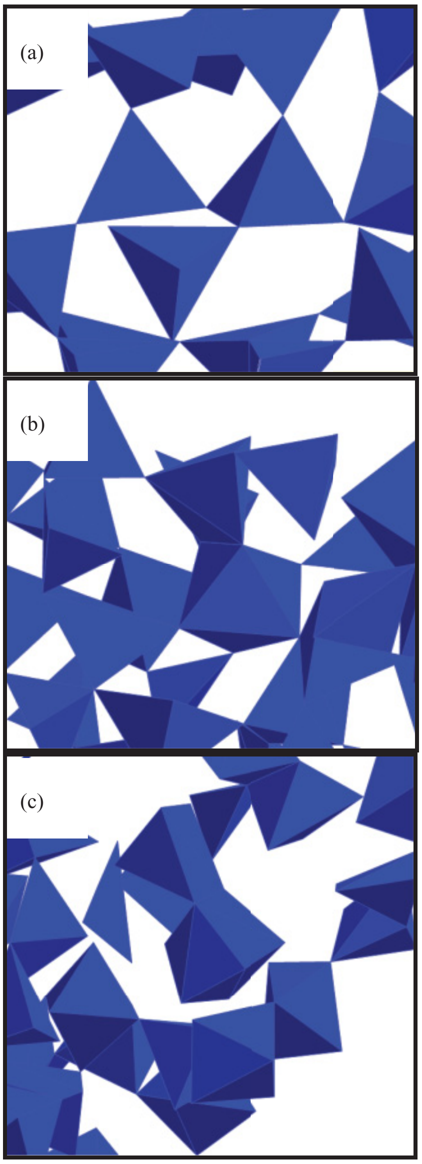

FIG. 1. (Color online) Polyhedron representation of the simulated SiO_2 glass network fragments (a) at zero pressure (tetrahedrons SiO_4 are visible), (b) at $P = 20$ GPa (SiO_4, SiO_5, and SiO_6 units), and (c) at 110 GPa (highly distorted SiO_5, SiO_6, and SiO_7 units).

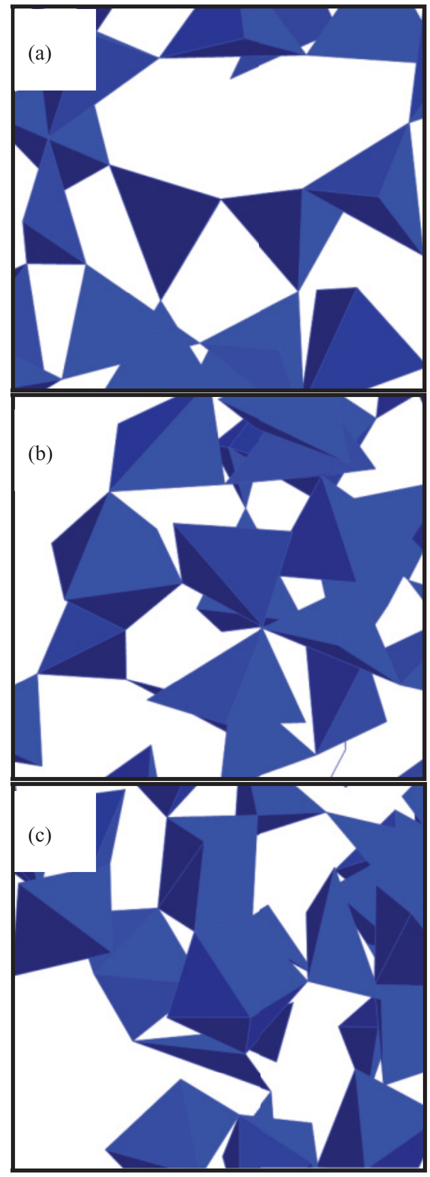

FIG. 2. (Color online) Polyhedron representation of the simulated GeO_2 glass network fragments (a) at zero pressure (tetrahedrons GeO_4 are visible), (b) at $P = 40$ GPa (GeO_4, GeO_5, and GeO_6 units), and (c) at 160 GPa (highly distorted GeO_5, GeO_6, GeO_7 and GeO_8 units).

average Si-O and O-O distances, i.e., equal to 1.9 angstroms. For the germanium coordination Z_{Ge}, the similarly found cutoff distance is 2.3 angstroms.

One can see that at megabar pressures there are seven-coordinated states of Si in the SiO_2 glass [Fig. 1(c)] and eight-coordinated states of Ge in the GeO_2 glass [Fig. 2(c)].

The principal result of this work is the discovery of several regions of transformations which are characterized by higher slopes of the increase of average cation coordination numbers in both glasses. In a-SiO_2 under compression, a smeared transformation with an increase in the Si coordination number from 4 to 6 was observed in a wide pressure range. Most changes in coordination from 4.5 to 5.7 take place in the 10- to 40-GPa (Fig. 3) pressure range, similarly to what is seen in the experiments[5] and previous simulations.[17]

Under further compression, the number of Si-O nearest neighbors continues to grow to 6.4 at 120 GPa. The most intensive changes occur at 80–100 GPa, close to the transformation pressure to the α-PbO_2 structure in SiO_2 [80–120 GPa depending on the temperature (Fig. 3)]. It is likely that the coincidence between the pressure values of the additional increase in Z in the glass and those of the transformation in the crystalline SiO_2 into the α-PbO_2 type structure is not accidental. Close values of the coordination number $Z \approx 6.5$ at 150 GPa have recently been obtained by first-principles simulations of liquid silica,[13] consistent with the present results with empirical potentials.

According to our simulations, the transformation pattern in GeO_2 glass is more varied. The main part of transformation takes place in the 5- to 25-GPa pressure range with an increase

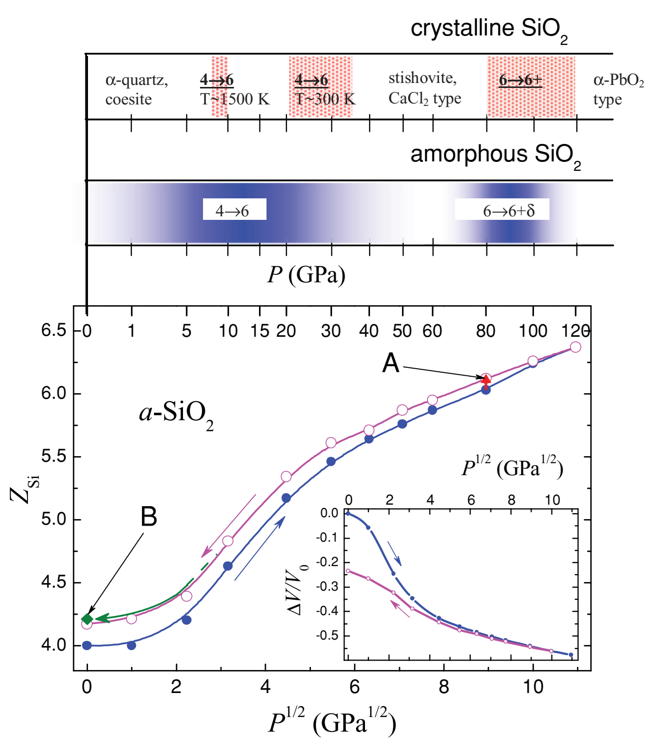

FIG. 3. (Color online) Pressure dependence of the average coordination number for Si (Z_{Si} versus $P^{1/2}$) in compression-decompression cycle for the simulated SiO_2 glass (at the bottom) and the transition pressure interval diagrams for the simulated amorphous and real crystalline SiO_2 (at the top). For the amorphous state the pressure diagram illustrates intervals of intensive increase of Z_{Si} in the simulation, whereas for crystalline phases the diagram shows pressure intervals of the key phase transitions. The inset at the bottom presents the relative volume versus $P^{1/2}$ dependence. Point A corresponds to the glass state obtained after isobaric (80 GPa) heating up to 1000 K. Point B corresponds to the final state of the glass obtained during additional decompression cycle at low temperature (10 K).

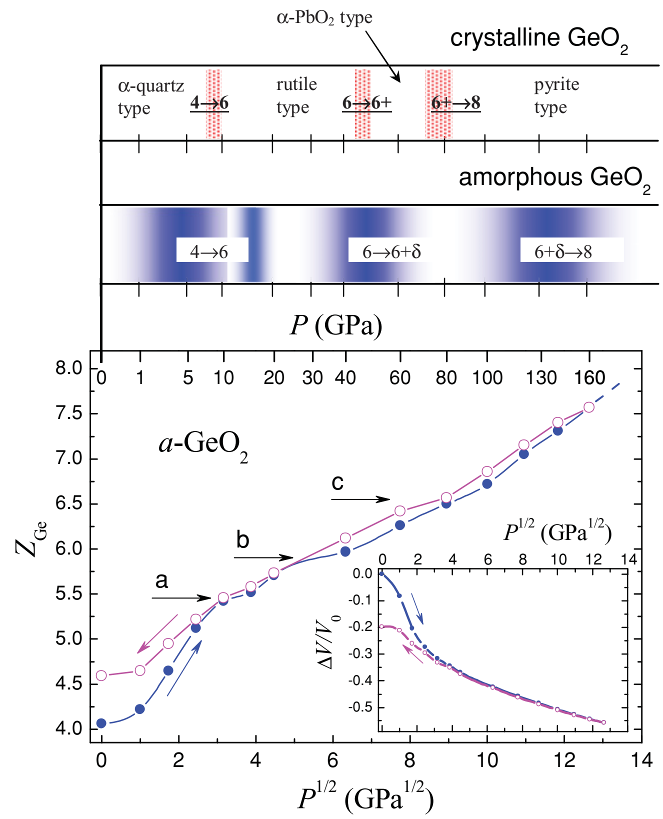

FIG. 4. (Color online) Pressure dependence of the average coordination number for Ge (Z_{Ge} versus $P^{1/2}$) in compression-decompression cycle for the simulated GeO_2 glass (at the bottom) and the transition pressure interval diagrams for the simulated amorphous and real crystalline GeO_2 (at the top). For amorphous state the pressure diagram illustrates intervals of intensive increase of Z_{Ge} in the simulation, whereas for crystalline phases the diagram shows pressure intervals of the key phase transitions. The α-quartz type GeO_2 phase is metastable at normal conditions, and the shown transition to the rutile type phase (at 300 K) is nonequilibrium. The inset at the bottom presents the relative volume versus $P^{1/2}$ dependence. The levels a, b, and c ($Z_{\mathrm{Ge}} \approx 5.5$, 5.9, and 6.5, respectively) correspond to relatively stable (with respect to pressure change) states of GeO_2 glass.

in the coordination number from 4 to 6 (Fig. 4), consistent with the experimental data and simulation results (see Refs. 4 and 8 and references therein). According to Ref. 18, there exists an intermediate fivefold coordinated state of α-GeO_2; however, it is more likely that this intermediate state includes Ge atoms of different coordinations of 4, 5, and 6.[8,19–21] With further pressure increase, we find two more regions of smeared coordination transformations: from 6 to 6.3 at 40–60 GPa and from 6.5 to 7.4 at 90–140 GPa (Fig. 4). Interestingly, again, these pressure intervals are close to transformation pressures in the crystalline GeO_2 into the α-PbO_2-type and pyrite-type structured phases (Fig. 4). The maximum coordination number value for the room temperature compressed a-GeO_2 is 7.6 at $P = 160$ GPa.

The transformations in both glasses are almost reversible in terms of coordination numbers. It is of interest that the transformations in the glasses occur with a sufficiently small hysteresis. We checked the effect of temperature on the hysteresis by releasing pressure at 10 K and found no considerable increase in the hysteresis. As a result, high coordinated numbers are not retained in both glasses at normal pressure, even at very low temperatures (see Fig 3 for SiO_2). This constitutes the important difference between the glassy and crystalline states. We find that final average coordination numbers for SiO_2 on decompression from megabar pressures are $Z \approx 4.17$ at $T = 300$ K and $Z \approx 4.21$ at $T = 10$ K. For GeO_2 glass, a larger fraction of five- and six-coordinated states is retained after decompression, $Z \approx 4.6$ both at $T = 300$ K and 10 K. These values are in good agreement with experimental values.[4]

We note that the residual densification in a-SiO_2, $\Delta V/V \approx 23$–26%, is larger than the values of the maximum densification for a-GeO_2, $\Delta V/V \approx 20\%$, despite the lower values of the residual increase in the coordination number (see Figs. 3 and 4). This is due to the fact that the residual densification in a-SiO_2 is to a large extent determined by the change in the amorphous network topology without a change in coordination numbers.[22]

If we interpret the observed picture from the simulation as a set of transformations between different polyamorphs, the small hysteresis of the transformations testifies that the regions of the loss of stability of glassy states are located close to the pressures of the metastable equilibrium of different polyamorphs. The closeness of the transition pressure intervals for the crystalline and amorphous states is evidently related to similarities between structural units in the crystalline and amorphous counterparts.

The small hysteresis of the transformations show that the coordination number Z is roughly an increasing temperature-independent function of pressure. This means that the transformations of amorphous SiO_2 and GeO_2 have a pressure-driven dynamics. In turn, the most adequate microscopic approach to the observed dynamics seems to be based on the local instability modes[17] and consideration of atomic clusters, which can be recognized as groups of atoms involved into instability-driven reconstructions. Molecular dynamic simulation[17] and empirical analysis[23] suggest that a typical cluster in amorphous SiO_2 and GeO_2 involves a number of atoms of the order of 10. The detailed experimental study of kinetics of amorphous-amorphous transformations in a-GeO_2 is in accord with the cluster approach.[24] In the present simulation, the coexistence of differently coordinated SiO_n and GeO_n polyhedrons (Figs. 1 and 2), i.e., the coexistence of parent and final atomic configurations with respect to the densification process, also proves that small ($\sim$10 atoms) clusters are involved in the local instability modes for reconstructions up to $Z = 8$.

The pressure-driven dynamic nature of the $Z(P)$ function can be recognized if we consider that the average coordination of the whole amorphous SiO_2 or GeO_2 network is equal to $2Z/3$, i.e., the maximum of the whole coordination riches $\approx$4.2 for SiO_2 and $\approx$5.05 for GeO_2 in the current simulation. So both glass networks remain under pressure quite open packed. The majority of stable (i.e., relaxed to the ideal glass state) ion-covalent atomic glasses under normal pressure have the average coordination close to the rigidity percolation threshold[25] stabilized by covalent and ionic forces.[26] With the pressure increase, the covalent and ionic forces have a weaker interatomic distance scaling $\sim 1/r^2$ in comparison with sharply increasing repulsive forces between nearest neighbors.[27] In this case, the open-packed structure should be destabilized with pressure increase even from simple geometrical arguments.[28] So, the local instability reconstructions result in an increase of the averaged $Z(P)$ function, which can be considered as a rough measure of an increasing role of the nearest neighbor repulsive forces stabilizing the amorphous network. On the contrary, at decompression the glasses with higher coordination become overconstrained and overstressed, and, consequently, follow nearly the same $Z(P)$ coordination dependence.

Our simulation results, therefore, suggest interesting future experiment. It might be expected that structural studies of GeO_2 glass at pressures of about 1.5 Mbar will detect the transformation into the high-density glass with eightfold coordinated Ge atoms.Our results suggest that that a similar set of transformations may exist in other glasses. For example, amorphous a-SnO_2 should experience several successive coordination transformations under compression. Recall that crystalline SnO_2 undergoes four phase transformations with the increase in the Sn coordination numbers from 6 to 9 at $P < 1$ Mbar.[29] Finally, the existence of several coordination transformations in glasses suggests that similar transformations take place in corresponding melts.

In summary, high-pressure molecular dynamics simulations show that the GeO_2 and SiO_2 glasses undergo several successive coordination transformations. The glass structure in the megabar region represents highly distorted polyhedrons with high ($n = 5, 6, 7$, and 8) coordination numbers for cation atoms. The transformations in glasses, unlike those in crystals, occur smoothly with rather small hysteresis. Finally, most of high coordination states ($n = 6, 7$, and 8) are not retained in glasses after decompression.

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[1] V. V. Brazhkin *et al.* (eds.), *New Kinds of Phase Transitions: Transformations in Disordered Substances* (Kluwer, Dordrecht, The Netherlands, 2002).
[2] V. V. Brazhkin and A. G. Lyapin, J. Phys.: Condens. Matter **15**, 6059 (2003).
[3] P. F. McMillan, J. Mater. Chem. **14**, 1506 (2004).
[4] Th. Loerting *et al.*, Adv. Chem. Phys. **43**, 29 (2009).
[5] T. Sato and N. Funamori, Phys. Rev. Lett. **101**, 255502 (2008).
[6] V. V. Brazhkin *et al.*, Phys. Rev. Lett. **101**, 035702 (2008).
[7] K. Trachenko *et al.*, Phys. Rev. Lett. **98**, 135502 (2007).
[8] D. Marrocchelli *et al.*, J. Phys.: Condens. Matter **22**, 152102 (2010).
[9] V. V. Brazhkin *et al.*, JETP Lett. **71**, 293 (2000).
[10] M. Murakami and J. D. Bass, Phys. Rev. Lett. **104**, 025504 (2010).
[11] K. Trachenko *et al.*, Phys. Rev. Lett. **93**, 135502 (2004).
[12] M. Hawlitzky *et al.*, J. Phys.: Condens. Matter **20**, 285106 (2008).
[13] B. B. Karki *et al.*, Phys. Rev. B **76**, 104205 (2007).
[14] S. Tsuneyuki *et al.*, Phys. Rev. Lett. **61**, 869 (1988).
[15] T. Tsuchiya *et al.*, Phys. Chem. Miner. **25**, 94 (1998); **27**, 149 (2000).
[16] W. Smith and T. Forester, J. Mol. Graphics **14**, 136 (1996).
[17] D. J. Lacks, Phys. Rev. Lett. **80**, 5385 (1998).
[18] M. Guthrie *et al.*, Phys. Rev. Lett **93**, 115502 (2004).
[19] M. Micolaut *et al.*, J. Phys.: Condens. Matter **18**, R753 (2006).
[20] G. Shen *et al.*, Proc. Natl. Acad. Sci. USA **104**, 14576 (2007).
[21] Q. Mei *et al.*, Phys. Rev. B **81**, 174113 (2010).
[22] S. Susman *et al.*, Phys. Rev. B **43**, 1194 (1991).
[23] V. V. Brazhkin *et al.*, JETP Lett. **78**, 542 (2003).
[24] O. B. Tsiok *et al.*, Phys. Rev. Lett. **80**, 999 (1998).
[25] J. C. Phillips, J. Non-Cryst. Sol. **34**, 153 (1979); M. F. Thorpe, *ibid.* **57**, 355 (1983).
[26] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).
[27] Here we used the atomic potentials[11,12] containing only the central repulsive and ionic terms. But, for reliability of these potentials at high pressure, it important that both covalent and ionic forces have the same interatomic distance scaling $\sim 1/r^2$ (Ref. 26).
[28] A. G. Lyapin and V. V. Brazhkin, Phys. Rev. B **54**, 12036 (1996).
[29] S. R. Shieh *et al.*, Phys. Rev. B **73**, 014105 (2006).