

SHOCK-SYNTHESIZED GLASSY AND SOLID SILICA: INTERMEDIATES BETWEEN FOUR- AND SIX-FOLD COORDINATION

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Upon compression, many materials undergo major reconstructions of their structure and bonding, including increases in coordination of atoms and changes in bonding character. While transforming, the materials pass through intermediate states, which are often too transient to be captured and examined. Here we discuss the coordination change in silica as an example of a system where such interesting intermediate structural states have been quenched from shock-experiments. On the basis of these results we suggest a relation between the formation of one of these phases and the extension of the liquid–liquid transition boundary into the stability field of solid silica. We report Raman spectra of shock-retrieved vitreous silica which indicate different compression mechanisms for shock-generated amorphous silica and vitreous silica compressed at 300 K. Static recompression of shock-generated glass leads to an amorphous-crystal transition above 13 GPa.

INTRODUCTION

Major reconstructive changes in the structure and bonding character of condensed matter influence phase relations and properties of materials relevant in geoscience, material science, physics, and chemistry. For example, the boundary between upper and lower mantle in the Earth, which certainly affects the propagation of seismic waves and plays an eminent role as a major barrier for global mass and heat transport, is determined by the change of coordination of silicon in magnesium silicates from four to six [1]. The insulator-metal transition in hydrogen is another example of a major change in bonding that is relevant for convection and heat balance in giant planets [2, 3]. The graphite–diamond and fullerite–graphite–diamond transitions in carbon, as well as the change in hydrate

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shell coordination in compressed water [4] are other well-known examples of major changes of coordination in important and abundant materials.

Although there is a fully developed, well-established theory for continuous phase transitions [5], reconstructive transitions are much less understood. Intermediate states of such transitions are keys to better understanding of their mechanisms. Furthermore, materials in such transitory states may display unusual properties which are interesting and desirable by themselves.

It turns out, however, that in most cases such intermediate states are very hard to capture. This is due to the intrinsic kinetics of reconstructive transitions and accompanying effects like internal strain, heat release, and generation of boundaries upon seed formation, which trigger catastrophic breakdown of the pristine structure. In experiments, such effects often evoke extreme response to external probes and irreversible ultrafast transformation. Recent advances in computational physics allow for simulations of such intermediate states [6], but finite size effects [7] complicate the extrapolation of such simulations to real systems.

Shock-experiments provide a tool for generation of high pressures and temperatures on the time scale of reconstructive transitions [8]. This is illustrated by the fact that the hysteresis of transitions upon shock is much larger than that along corresponding static pressure–temperature paths [9]. Here, we discuss examples of intermediate states of structure in an important system characterized by a pressure-induced change in coordination in the solid state and a correlated liquid–liquid transition, silica.

SHOCK-SYNTHESIS OF NOVEL SILICA PHASES OF SILICON-COORDINATION INTERMEDIATE BETWEEN FOUR- AND SIX-FOLD

Silica forms three-dimensional tetrahedral networks at ambient pressure. Upon compression, these polymorphs transform into much denser networks constituted by octahedral units with six-fold coordinated silicon [10]. The transformation is kinetically hindered at 300 K and tetrahedrally coordinated silica phases become amorphous [11] upon room temperature compression to densities where six-fold coordinated silica in the stishovite-structure is the thermodynamically stable phase [12]. Recently, it turned out that upon further compression to pressures above 45 GPa [13–15] these amorphous materials recover crystalline structures with six-fold coordinated silicon. However, these six-fold coordinated silica phases deviate from the stishovite-structure by noticeable distortion of the octahedra leading to partially even higher coordination of Si and by different topologies of octahedral arrangement [13, 15]. Such distorted phases are expected to become thermodynamically stable at pressures around 100 GPa [16, 17].

There has been a long debate on the detailed mechanism of the four- to six-fold coordination change in silica [18–20] and its transitory states. Both calculational work [18, 21] and sterical models [22] proposed five-fold coordination as an intermediate step during the transition. So far, a five-fold coordinated silica phase has not been observed.

The reconstructive transition in silica is of further interest because the equivalent change coordination has to occur in silicate melts as well. The P–T range of the liquid–liquid transition in silicate melts and the nature of transitory states are highly relevant for generation, viscosity, and buoyancy of melts in the mantle of the Earth [23]. It has been inferred that the amorphization of quartz corresponds to the extension of the melting curve of quartz into the stishovite-field [11], by analogy to the formation of high-density amorphous ice in the H₂O system [4] at the metastable extension of the melting curve of Ice I into the Ice VI field.

Stolper and Ahrens [24] suggested a compression mechanism whereby progressive tilting between the tetrahedral units in silicate eventually transforms the network into a chain of distorted octahedra. However, they noticed that such a mechanism requires unphysically small Si—O—Si bond angles. An alternative model by Stixrude and Bukowinski [25] suggests changes of topology of tetrahedral rings as a compression mechanism. However, the predictions of this model are at odds with experimental observations in that they predict a decrease rather than an increase in the number of small (four- and three-membered) tetrahedral rings upon compression of the melt [26]. Recently, another topological model predicts correctly the increase in the number of such small rings upon compression and indicates that coordination defects linked to higher connectivity within the network constituted by short-membered tetrahedral rings lead to breakdown of the tetrahedral into octahedral units [27]. Both mechanisms, formation of small rings and higher connectivity along with coordination defects, are then responsible for the density inversion in molten silica above 8 GPa [27]. Here, we examine if transitory states of coordination can be retrieved from shock-experiments on silica, and how they relate to these models of the liquid–liquid transition and to the aforementioned proposed mechanisms of transition in cold compressed silica.

Macroscopically Disordered Silica Phase and its Relation to the Structure of Dense Silica Melt

In a recent paper [28], we reported shock-experiments on quartz and coesite and short-term CO₂-laser-heating experiments on compressed tridymite which led to the discovery of a new dense silica phase intermediate between four- and six-fold coordinated silica. This polymorph is the first observed silicate composed of face-sharing polyhedra. It has a density similar to stishovite and occurs metastably within the stability field of stishovite and CaCl₂-type silica [16, 17]. The strong sterical constraints on the Si—O—Si bond angles in face-sharing units are overcome by disorder of the Si-sublattice, and by distortion and expansion of the polyhedral units from regular tetrahedra and octahedra into pyramidal and bipyramidal units. Since the occupation of available Si-sites in each polyhedron depends on the occupation in the adjacent polyhedra [25], hence allowing for large areas of correlated site occupancy, the disorder of Si is macroscopic in analogy to proton-disorder in ice [4] or spin disorder in pyrochlores. Because of this macroscopic disordered state the effective coordination of Si is transitional between four- and six-fold (Fig. 1(a)). The structure therefore suggests a mechanism for this coordination change in silica and other silicates at the high temperatures of the earth's mantle that is fundamentally different from proposed mechanisms at 300 K, which suggest static five-fold coordination as a transitory state between tetrahedrally and octahedrally coordinated silica. Since the new phase was formed in shock-experiments on various materials (quartz, coesite) and in laser-heating experiments on tridymite, we suggest that it plays a fundamental role in the change of coordination. The new polymorph also illustrates how the face-sharing polyhedra can be constructed without inferring unphysical small bond angles. Face-sharing polyhedra occur naturally in tilt-compression of tetrahedral networks and had been suggested to control the change of coordination in silica [24, 29]. However, the importance of macroscopic disorder of Si within such face-sharing units had so far been overlooked.

We examine if there are indications of a relation between the structure of the new phase and molten dense silica with respect to the mechanism of coordination change. In Figure 1b, we show the phase diagram of silica, simplified by omitting the low-pressure phases cristobalite and tridymite. The melting curve is characterized by a sharp increase in slope at the coesite–stishovite phase-transformation, which marks the transition from tetrahedrally to octahedrally coordinated silica in the solid field and which is anticipated by a region of

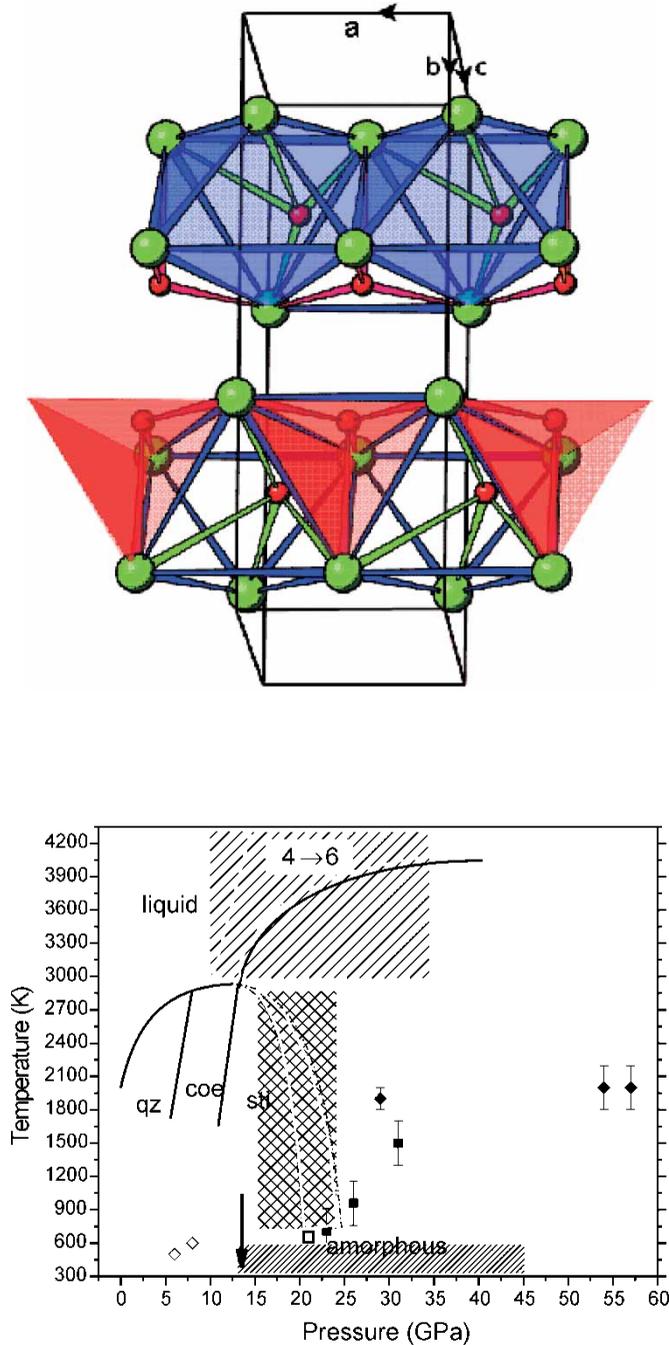


FIGURE 1 (a) Structure representation of the new silica phase [29]. Green spheres are O, red spheres are Si, red and green lines indicate Si–O bonds, and blue lines mark the edges of polyhedra. Two chains of SiO_2 run through each elementary cell along the a -axis. The chains are built from alternating bi-pyramidal and triangular pyramidal units. In the upper chains the faces of the bi-pyramids and in the lower ones the faces of the pyramids are colored blue and red, respectively. (b) Phase diagram of silica indicating the metastable extension of the low-pressure melting curve to higher pressures (shaded area between the dash-dotted lines) and the range of pressure-induced amorphization of quartz (densely hashed area). Filled symbols: experiments where the new polymorph was detected after retrieval (diamonds: [28], squares: [32]). Open symbols: no observation of the new phase. Arrow: pressure of glass–solid transition of shock-generated silica glass at 300 K.

probably negative slope on the coesite liquidus [30]. It has been argued that in this pressure range a liquid–liquid transition occurs in molten silica [11, 24, 26, 27, 30]. A change in density of the liquid upon transition then affects the volume difference between melt and solid and induces this negative slope of the melting curve [11, 24, 26, 27, 30]. Schreine-maker's rules require that the metastable extension of the coesite melting curve extends across the stability field of solid stishovite. Furthermore, extrapolating its slope and curvature suggests that, around 15–20 GPa, the extended curve approaches ambient temperature. As noticed some time ago, these are the P–T conditions where quartz amorphizes (shaded area in Fig. 1b), [11, 30]. In order to locate the new intermediate silica phase in the silica phase diagram we indicate the experimental conditions where the new phase formed as black diamonds; white diamonds indicate runs where the new phase was not observed. In the same way we indicate by black and white squares results from a parallel study on laser shocked quartz [31], where the same phase was synthesized. Here, we use the peak pressures reported in Ref. [31] and assume corresponding temperatures based on the Hugoniot of quartz, although in laser shock-experiments the temperatures can be higher. Therefore, the data points from Ref. [31] could extend the temperature window towards higher temperatures. Figure 1b shows that the low-pressure boundary of formation of the new metastable silica phase indeed matches the extension of the low-pressure melting curve into the solid field. This supports our suggestion of a relation between this phase of intermediate coordination and the structure of silica melt around the liquid–liquid transition. However, the available data points are limited to a narrow temperature window. We plan further experiments along steeper Hugoniot (*e.g.*, using porous starting materials) to probe the range of higher temperatures.

Glass–Solid Transition in Shock-Generated Silica Glass

The new phase was found as isolated, round grains of up to 10 μm diameter in a matrix of glassy silica. The distribution of the crystalline grains was not random; rather there were areas in the glass with high density of crystals, whereas other areas were completely free of crystals.

We collected Raman spectra from this glassy matrix immediately after retrieval from the shock-experiments and found various degrees of back-transformation from dense forms of vitreous silica to its known forms at ambient pressure. Figure 2a shows a spectrum almost identical to those reported from silica decompressed from above 15 GPa to ambient conditions [32–34]: Strong peaks at 495 cm^{-1} and around 600 cm^{-1} are characteristic of irreversibly densified glass and have been assigned to four- and three-membered tetrahedral rings [32–34]. The number of such rings is expected to increase with increasing density at the expense of six- and five-member rings [26, 32–34], although recent calculations indicate that the Raman shift around 500 cm^{-1} in dense vitreous silica does not receive much contribution from four-member rings [35]. Figure 2b shows another spectrum of vitreous silica retrieved from shock-experiments on CT-opal, which experienced peak pressures of 52 GPa and temperatures of ~ 3000 K. This spectrum shows quite different features: the peak at ~ 500 cm^{-1} and any features below this energy disappeared, while there is still a broad peak around 600 cm^{-1} . According to the established concept of breakdown of large rings into smaller ones [26], this spectrum indicates breakdown of four-membered rings and predominance of three-membered rings, which give rise to the spectral feature around 600 cm^{-1} . The spectral features of the present glass then indicate a very high degree of compression. We notice the similarity of this spectrum and the calculated Raman spectrum of ultradense silica glass with predominantly six-fold coordinated silicon reported in Ref. [35]. However, the spectrum in Figure 2b exhibits two further pronounced peaks

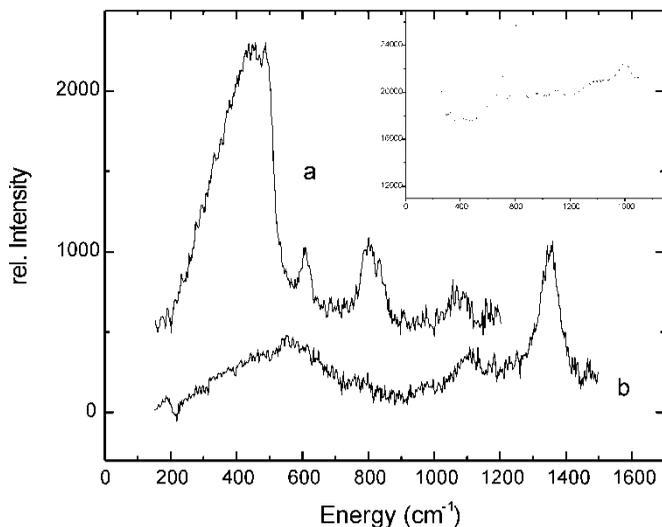


FIGURE 2 Raman spectra of shock-retrieved silica. (a) Spectrum of silica glass with features very similar to those reported for statically compressed silica glass [33–35]. (b) Glass with no spectral features of four-, five- or six-member rings of silica tetrahedra. A broad feature centered around 600 cm^{-1} indicates persistence of three-member rings. Inset: spectrum of the new dense silica polymorph from the same shock-experiments.

around 1100 and 1400 cm^{-1} . The latter is a very high energy for vibrations in silica. For comparison, Figure 2c shows the spectrum of the new transitory silica phase with Si-disorder in face-sharing pyramidal and bi-pyramidal polyhedra. This phase exhibits similar strong spectral features around 1100 and 1400 cm^{-1} also. Although these peaks could be strong second-order peaks of regular stretch vibrations of this solid around 550 and 700 cm^{-1} , we have argued that there is a contribution by first-order scattering [28] related to O-dominated Si—O stretch vibrations, where the broadness of these peaks likely reflects the intrinsic structural disorder or to an anomalously enhanced phonon density of states related to this disorder. If this is correct, the corresponding features in the spectrum of ultra-dense silica glass (Fig. 2b) indicate a similar kind of disorder. Hence, the compression-mechanism of breakdown of rings of tetrahedra from six- to three-membered rings may be followed by breakdown of tetrahedral units into face-sharing irregular polyhedra with intrinsic disorder of the Si-positions such as to maximize the Si—O—Si bond angles [28]. In fact, we will show that the ultra-dense silica glass presented in this study transforms into six-fold coordinated silica upon very moderate compression at 300 K .

We loaded a specimen of shock-generated glass into a diamond cell using Ar as pressure medium and collected diffraction patterns upon compression. Up to about 8 GPa the patterns show diffuse Bragg scattering typical for glasses (Fig. 3(a)). At 13.4 GPa these glass peaks are joined by Bragg diffraction from a crystalline phase (Fig. 3(b) and insets). The Bragg reflections from this crystalline phase are a few spots confined to a narrow angular range in the detector plane rather than extended diffraction rings. This is quite unexpected since it implies diffraction from a single-crystal-like sample rather than from randomly oriented small seeds of crystalline order, which give rise to diffraction fringes uniform in intensity. The glass–solid transition therefore does not result from growth of islands of order conserved upon vitrification but appears to be a collective process in the bulk sample occurring upon compression.

The pressure of this glass–solid transition is much lower than the corresponding transitions from amorphized quartz, cristobalite, and tridymite to post-stishovite phases

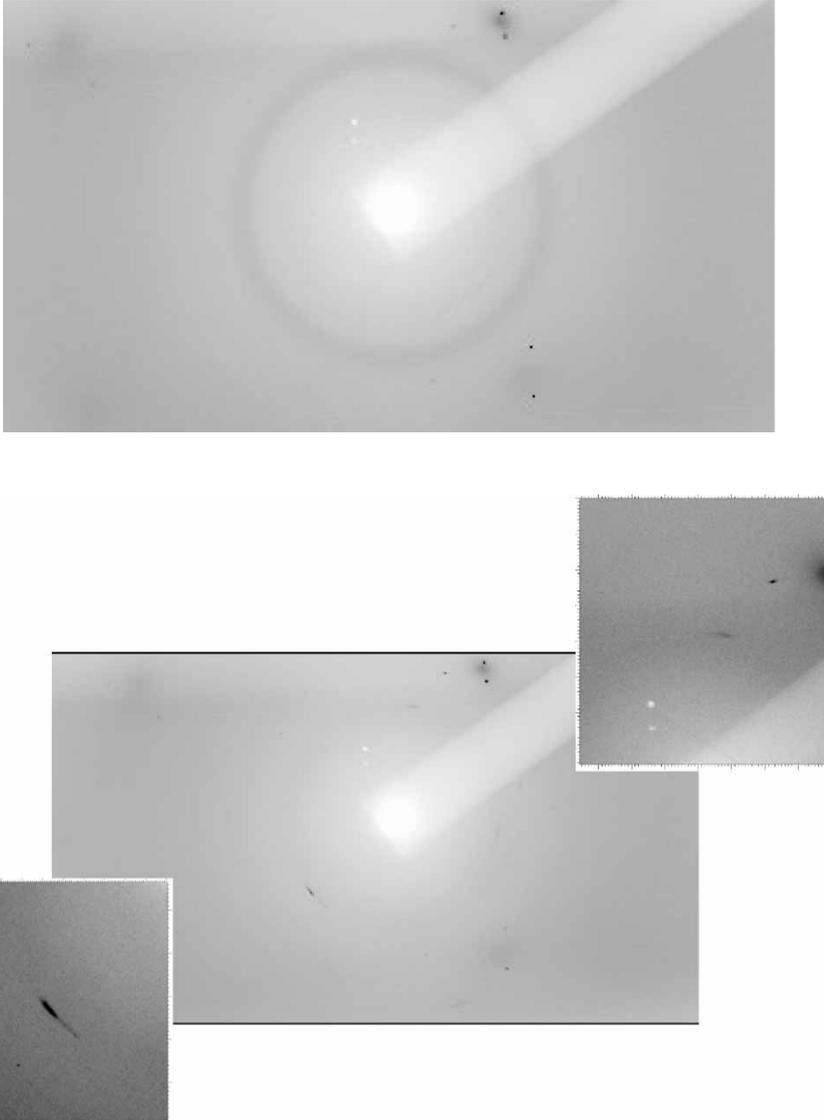


FIGURE 3 Diffraction images from shock-generated vitreous silica. The sample is embedded in Ar as pressure-transmitting medium. (a) At 1.52 GPa, (b) at 13.4 GPa. Four single-crystal spots and a further broad spot in both images are from the diamond anvils. (b) The glass peaks are superimposed by crystalline Braggpeaks (marked by white circles, zoomed insets). These peaks indicate presence of a single large crystallite under strain or with large mosaic spread. This implies onset of crystalline ordering of the bulk rather than starting from isolated seeds. The glass–solid transition therefore does not result from growth of islands of crystalline order in the starting material but is a collective process in the bulk sample.

[13–15]. This suggests that the kinetic barrier for transition of this dense glass to octahedrally coordinated solids is substantially lower.

At the pressure of onset of crystallization (Fig. 3(c)), we released and recovered the sample. Afterwards we collected diffraction patterns at ambient pressure. As we will discuss elsewhere [36], the sample exhibits an increasing degree of crystalline order with increasing irradiation by X-rays of 29 keV, although this phase cannot be stable under

ambient conditions. The patterns show characteristic features of six-fold coordinated silica with density close to stishovite, hence, much higher than the density of stable ambient pressure silica phases. The recovered material therefore keeps a memory of the dense six-fold coordinated ordered structure that it was approaching at pressures above 13 GPa.

CONCLUSIONS

We have shown by the example of silica that shock-experiments provide a useful tool to generate intermediate states of structure in materials which undergo major reconstructive transitions in bonding and coordination. On the basis of the available set of data, we suggest that fundamental structural features of a previously described [28] shock-synthesized silica polymorph of intermediate coordination and macroscopic disorder of the Si-sublattice is related to the liquid–liquid transition in silica. The lower boundary of P–T conditions of its formation match the geometric extension of the low-pressure melting curve of silica into the high-pressure solid field, which corresponds to the upper boundary of mechanic stability of liquid or glassy tetrahedral networks. The structure of this transitory phase differs from disordered dense silica phases occurring upon cold compression of amorphized silica. Hence, the compression mechanisms in silica at low temperature appear to be different from those at high temperature, which are potentially related to the mechanisms in the melt.

This conclusion is consistent with another result presented in this paper: the glass–solid transition into a dense six-fold coordinated silica phase upon compression of shock-synthesized silica glass at 300 K and above 13 GPa. Furthermore, we find that the glass–solid transition in shock-generated glass is a bulk phenomenon resulting in a large single crystallite rather than in the microcrystalline aggregates formed by growth of multiple crystalline seeds in a glassy matrix. Raman spectra of shock-retrieved vitreous silica differ from statically compressed silica in that the peak related to four-membered silicate rings is absent. Four-membered rings are predominant in statically compressed silica even to pressures above 30 GPa [37]. Raman shifts at quite high energies of $\sim 1400\text{ cm}^{-1}$ occur in both the shock-retrieved glass and the novel solid phase as well. We argue that they are of first-order and belong to vibrations in similar polyhedral units in both the glass and the solid. The irregular face-sharing bi-pyramidal units with macroscopic disorder of Si that dominate the solid may therefore also occur in the glass. These units may be intrinsic to the mechanism by which increasing coordination, increasing connectivity, and breakdown of tetrahedral rings are related to the density-inversion in the liquid–solid silica system seen in recent calculations [27].

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References

- [1] A. E. Ringwood, *Origin of the Earth and Moon*, part 1 [Springer Verlag, New York, 1979].
- [2] K. A. Johnson and N. W. Ashcroft, *Nature (London)*, **403**, 632 (2000).
- [3] D. Saumon and T. Guillot, *Astrophys. J.*, **609**, 1170 (2004).
- [4] O. Mishima, L. D. Calvert and J. Whalley, *Nature (London)*, **310**, 393 (1984).
- [5] M. E. Fisher, *Rev. Mod. Phys.*, **79**, 653 (1998).
- [6] S. Jahn, P. A. Madden and M. Wilson, *Phys. Rev. B*, **69**, 20106 (2004).
- [7] K. Binder, *Int. J. Mod. Phys. B*, **15**, 1193 (2001).
- [8] McQueen *et al.*, The equation of state of solids from shock wave studies. In: R. Kinslow (Ed.), *High-Velocity Impact Phenomena*, (Academic Press, New York, 1970), pp. 293–417.
- [9] S. N. Luo and T. J. Ahrens, *Phys. Earth Planet. Interiors*, **143**, 369 (2004).
- [10] C. T. Prewitt and R. T. Downs, High-pressure crystal chemistry. In: R. J. Hemley (Ed.), *Ultra-high-Pressure Mineralogy*, Reviews in Mineralogy 37, [Mineralogical Society of America, Washington DC], pp. 294–297
- [11] R. J. Hemley *et al.*, *Nature (London)*, **334** (1988).
- [12] J. Zhang, B. Li, W. Utsumi and R. C. Liebermann, *Phys. Chem. Min.*, **23**, 1 (1996)
- [13] J. Haines, J. M. Leger, F. Gorelli *et al.* *Phys. Rev. Lett.*, **87**, 155503 (2001).
- [14] Y. Tsuchida and T. Yagi, *Nature*, **347**, 267 (1990).
- [15] L. S. Dubrovinsky *et al.*, *Chem. Phys. Lett.*, **333**, 264 (2001).
- [16] D. M. Teter *et al.* *Phys. Rev. Lett.*, **80**, 2145 (1998).
- [17] S. Ono, K. Hirose, M. Murakami and M. Ishiki, *Earth Planet. Sci. Lett.*, **197**, 187 (2002).
- [18] J. S. Tse and D. D. Klug, *Phys. Rev. Lett.*, **67**, 3559 (1991).
- [19] J. R. Chelikowsky *et al.*, *Phys. Rev. Lett.*, **65**, 3309 (1990).
- [20] R. M. Wentzcovitch, C. da Silva, J. R. Chelikowsky and N. Binggeli, *Phys. Rev. Lett.*, **80**, 2149 (1998).
- [21] S. L. Chaplot and S. K. Sikka, *Phys. Rev. B*, **47**, 5710 (1993).
- [22] J. Badro *et al.*, *Phys. Rev. B*, **56**, 5797 (1997).
- [23] S. M. Rigden, T. J. Ahrens and M. E. Stolper, *Science*, **226**, 1071 (1984).
- [24] E. M. Stolper, and T. J. Ahrens, *Geophys. Res. Lett.*, **14**, 1231 (1987).
- [25] L. Stixrude and M. S. T. Bukowski, *Science*, **250**, 541 (1990).
- [26] X. Y. Xue, J. F. Stebbins, M. Kanzaki and R. G. Tronnes, *Science*, **245**, 962 (1989).
- [27] A. Trave *et al.* *Phys. Rev. Lett.*, **89**, 245504 (2002).
- [28] S. N. Luo, O. Tschauner, P. D. Asimow and T. J. Ahrens, *Am. Min.*, **89**, 455 (2004).
- [29] L. S. Dubrovinsky *et al.* (2004). *Phys. Earth Planet. Inter.*, **143**, 231 (2004)
- [30] J. Z. Zhang *et al.*, *J. Geophys. Res. Sol. Earth*, **98**, 19785 (1993).
- [31] T. de Resseguier, P. Berterretche, M. Hallouin and J. P. Petit *J. Appl. Phys.*, **94**, 2123 (2003).
- [32] M. Grimsditch *Phys. Rev. Lett.*, **52**, 2379 (1986).
- [33] R. J. Hemley, H. K. Mao, P. M. Bell and B. O. Mysen, *Phys. Rev. Lett.*, **57**, 747 (1986).
- [34] P. McMillan, B. Piriou and R. Couty, *J. Chem. Phys.*, **81**, 4234 (1984).
- [35] A. Rahmani, M. Benoit and C. Benoit, *Phys. Rev. B*, **68**, 184202 (2003).
- [36] O. Tschauner, S. N. Luo, P. D. Asimow and T. J. Ahrens, In press.
- [37] K. Lipinska-Kalita and R. J. Hemley, In press.