## **Preparation of Perfect Glasses from Zeolites**

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**Abstract**—When glasses are traditionally formed from melts, due to slow crystallization dynamics, the configuration and free volume of the liquid state are frozen in a random structure with high entropy. The amorphous state can also be attained directly from a crystalline solid under pressure. In this case, at a certain rate of change in the pressure, some structural elements can remain ordered; i.e., the amorphous material can retain the crystalline topology. As a result, the amorphous material will have a very low entropy, close to that of the crystal, i.e., will be a "perfect" glass with new physical properties. The method for preparing such a perfect glass from zeolites and its properties are discussed.

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The mechanical properties of glasses have been significantly improved during the last decade using new technologies; in particular, by increasing the melt homogeneity, applying more uniform heating and cooling during the glass formation and annealing, qualitative monitoring to eliminate surface defects, performing various tests, using special coatings, etc. However, the glass strength is still far from its theoretical limit. The theoretical ultimate strength of glass under compression is between 14 and 35 GPa, while the best steels have an ultimate strength of 0.7 GPa; i.e., the glass strength may exceed the steel strength by a factor of 20–50. Nevertheless, the glasses produced now for airplanes and spacecrafts have a strength of about 0.7 GPa, i.e., the same value as for the best steels. Concerning the strength of the glass for conventional applications, it is lower than the theoretical limit by a factor of 100–1000. Hence, one can see that glasses have a very large reserve for improving their properties.

In recent years, in the study of new unconventional approaches, an important step was made in preparation of more perfect glasses. In 2005, Greaves et al. (the United Kingdom) [1], investigating the amorphization of crystalline zeolites under the action of pressure or temperature by X-ray diffraction methods, revealed that, choosing the rate of change in pressure or temperature such as to ensure the zeolite amorphization dynamics to be much faster than the dynamics of formation of a conventional glass from an melt of the same composition (i.e.,  $\tau_A < \tau$ ), one can obtain a low-density amorphous (LDA) phase, which has a fairly perfect structure with complete Al-Si ordering and low configuration entropy. Upon further heating or compression, this phase is transformed into a denser, more disordered fragile high-density amorphous (HDA) phase, which is a conventional glass.

In the case of slow amorphization, the condition  $\tau_A < \tau$  is satisfied for a simple reason. The point is that the

LDA phase is a stronger phase with low fragility (in the terminology proposed by Angell [2]), because it has a large free-volume fraction. Therefore, local relaxation processes of activation type may always occur in it; i.e., a local atomic rearrangement does not require participation of other atoms in this process. In other words, if some atom has to jump (obviously, overcoming the activation barrier), there will always be a free place nearby for this atom to do it. Hence, the temperature dependence of the relaxation time has only activation character. In conventional glasses (HDA phase), the situation is different. In this case, the atomic density is high; the free volume is small; and, therefore, the number of free sites is insufficient for local atomic jumps over the barrier, especially near the glassy transition temperature  $T_g$ . To initiate the relaxation process, it is necessary to rearrange the configuration of the entire ensemble of neighboring atoms. In other words, the relaxation process in the HDA phase is collective. However, when an ensemble of atoms is rearranged, the effective barrier energy is very high; this process is more difficult to occur in comparison with an individual rearrangement. Moreover, the higher the pressure, the smaller the free volume and the larger number of atoms should be involved to ensure a significant displacement of an atom. Therefore, the effective activation energy increases with an increase in pressure and is generally described by the Vogel–Fulcher law.

Thus, the structure of the LDA phase obtained from crystalline minerals at slowly increasing temperature or pressure has physical properties different from those of a glass obtained by conventional methods, even upon slowest melt cooling. For example, it can be more solid and less chemically active, than the conventional glass of the same composition. The LDA phase is also interesting from the theoretical point of view because its entropy is similar to that of the initial crystal. When a glass is obtained not from a melt but from a crystal, some structural elements can remain ordered. The transition occurs at low temperatures (at which everything is frozen in a conventional liquid or glass, and relaxation may occur for several thousand years). Disordering during solid-phase amorphization occurs in a certain phonon mode and certain structural elements. As a result, the entropy of an amorphous solid may exceed the entropy of a crystal by a very small value.

Thus, since this amorphous phase was obtained from a material with a lower entropy rather than from a melt with a higher entropy, it should avoid the Kauzmann paradox: limitation on the possible entropy convergence, which is observed upon melt cooling.

Using Raman scattering, we observed in situ the transitions between the LDA and HDA phases with an increase in pressure in zeolites (in 2006) [3, 4]. The Raman spectra were recorded on a DILOR OMARS 89 spectrometer with a multichannel LN/CCD-1100 PB detector (Princeton Instruments). The samples  $\sim 0.1 \times$  $0.05 \times 0.15$  mm in size were placed in chamber with diamond anvils, in a hydrostatic medium (methanolethanol in the ratio 4:1). The pressure was determined from the shift of the  $R_1$  band of ruby with an error of  $\pm 0.03$  GPa. We investigated the amorphization dynamics for two zeolites of different densities: natrolite  $Na_2Al_2Si_3O_{10} \times 2H_2O$  and leucite KAlSi<sub>2</sub>O<sub>6</sub>. Natrolite is a more brittle aqueous zeolite, whose cavities, along with water, contain Na cations of small radius. At the same time, leucite is almost anhydrous and has a high density; in comparison with other minerals, it is closer to quartz than to zeolites (due to its strength, it is widely used in stomatology). Since leucite has a high density, it should be more difficult to amorphize in comparison with natrolite.

We decided to use the slow kinetics of the transition to the amorphous phase for leucite, since slow amorphization (when  $\tau_A < \tau$ ), as was mentioned above, should yield an LDA glass with a higher quality structure, complete Al-Si ordering, and low configuration entropy. We observed the changes in the spectrum, keeping a leucite sample under a constant high pressure (13.6 GPa). An amorphized glasslike spectrum was obtained after two weeks, when the intensity of crystalline Raman bands decreased by a factor of about 20. If the pressure exceeded 13.6 GPa, it would take us less than two weeks to overcome the energy barrier between the two metastable phases. However, our purpose was, vice versa, to obtain the slowest amorphization. Further exposure of the sample under 13.6 GPa did not lead to changes in the spectrum, a fact indicating attainment of the free-energy minimum. We attribute this minimum to the formation of the LDA phase. The energy of leucite transformation to the amorphous LDA phase  $H_A$ can be found from the Arrhenius dependence  $\tau_{\rm A}$  =  $\tau_0 \exp(H_A/k_BT)$ , where  $\tau_A$  is the leucite amorphization time,  $k_{\rm B}$  is the Boltzmann constant, T is temperature, and the factor  $\tau_0 \sim 10^{-12}$  s. In the case under consideration,  $H_A = k_B T \ln(\tau_A/\tau_0)$ ,  $\tau_A \approx 1296 \times 10^3$  s (15 days),

and  $H_A = 1.08$  eV. The latter value is much smaller than that necessary for breaking bonds; therefore, the initial crystalline topology should remain after attaining the LDA phase. A short time after the above-described experiments, also in 2006, Iniguez et al. (Spain) [5] confirmed by ab initio calculations that zeolites are amorphized under pressure and that LDA and HDA phases indeed belong to two different classes of amorphous materials. It was concluded in [5] that the structure of the LDA phase is determined by random displacements of the nucleation sites of the amorphous phase, which do not destroy the topology of the initial zeolite crystal structure, while the HDA phase is a conventional "thermal" glass, whose atomic structure is not topologically equivalent to any crystal structure.

A further increase in pressure in the LDA phase (to 18.3 GPa), as was expected, lead to a change in the Raman spectra of amorphous leucite, which corresponds to the LDA-HDA phase transition, because the LDA structure is rearranged under compression to the denser and more disordered HDA phase (see figure). The LDA-HDA phase transition in zeolites has not been observed by Raman spectroscopy. Therefore, to identify the pressure-induced changes, we compared our spectra with the spectra of amorphous silicon [6], in which this transition was definitely observed. We believe such a comparison justified, because silicon and zeolites have the following common characteristics: (i) local tetrahedral coordination is present, (ii) the liquid phase is denser than the crystalline one, and (iii) the melting temperature decreases with an increase in pressure. These characteristics are in essence due to the directed bonds, which form an open structure (tetrahedral configuration) at atmospheric pressure. It is believed that an open atomic configuration is a key factor of polyamorphous transformations [7]. The above-mentioned spectra are compared in the figure. It can be seen that spectra of amorphous leucite change with pressure almost in the same way as the silicon spectra; this similarity indicates that leucite, as well as silicon, undergoes the LDA-HDA phase transition between 17 and 18.3 GPa. In this case, in the spectra of both leucite and silicon, the peaks of the tetrahedral amorphous bands are red-shifted (indicated by the dashed line) due to bond weakening with an increase in the silicon coordination.

In 2007, an analogous concept of amorphous structure ordering was used by the researchers from the Wisconsin Madison University (the United States) to obtain a superstrong glass. Ediger et al. [8] developed a technology allowing one to make the molecular structure of organic glass more organized, and, therefore, stronger. To obtain a glass with an extraordinary thermodynamic and kinetic stability, it was formed in the layer-by-layer way, using vapor-phase deposition. A glass was heated to the evaporation point, and the evaporated molecules were condensed on a cold substrate in the form of a very thin liquid-glass film; this process was multiply repeated. When this "puff pastry" was finally hardened, the periodic summary amorphous structure acquired the





Comparison of the Raman spectra of amorphous leucite and silicon [6] at the LDA–HDA phase transitions. The dashed lines indicate the shift of the tetrahedral band peaks with an increase in the silicon coordination. These spectra confirm that the LDA phase is observed in leucite at 17 GPa. crystal properties. The researchers ascertained that they obtained the most stable glass that had ever been prepared under laboratory conditions, because the potential-energy surface for such glasses was much lower than for conventional glasses (a circumstance controlling the thermodynamics and kinetics of the amorphous system). Ediger and his colleagues supposed that they could obtain for several hours glasses whose preparation would require at least 4000 years using the conventional technique. Such a stable glass can have direct technological applications, for example, to stabilize amorphous medicinal preparations. These stable glasses, as well as the above-mentioned LDA phase, are an ideal object for studying the fundamental problems of glass formation, such as the entropic Kauzmann paradox, using the properties of the potential-energy surface (energy landscape) of these glasses. Note that these glasses have been developed from only organic materials and have "crystalline" properties in only one direction. The glasses that we propose to obtain by amorphizing crystalline minerals under pressure increasing at a certain rate should be free of such limitations.

Currently, we cannot make any quantitative estimates of the enhancement of mechanical properties, because the analytical expressions relating the mechanical strength of glass (Young's modulus) to the parameters characterizing the local crystalline topology or the configuration energy landscape (configuration entropy) of glass are absent in the literature. However, we can state at the qualitative level that, the larger the topological disorder (fluctuations of bond angles and lengths), the smaller the elastic moduli at the same density. Large fluctuations lead to a decrease in the average angular hardnesses. Generally, Young's modulus of glass can be several times smaller than that of crystal at similar densities. A density deficit makes this difference even more considerable.

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## REFERENCES

- 1. Greaves, G.N., Meneau, F., et al., *Science*, 2005, vol. 308, p. 1299.
- Angell, C.A. et al., J. Non-Cryst. Solids, 2000, vol. 274, p. 319.
- Ovsyuk, N.N. and Goryainov, S.V., *Pis'ma Zh. Eksp. Teor. Fiz.*, 2006, vol. 83, no. 3, p. 138 [*JETP Lett.* (Engl. Transl.), vol. 83, no. 3, p. 109].
- Ovsyuk, N. and Goryainov, S., Appl. Phys. Lett., 2006, vol. 89, 134 103.
- 5. Peral, I. and Iniguez, J., *Phys. Rev. Lett.*, 2006, vol. 97, 225 502.
- McMillan, P.F., Wilson, M., et al., *Nat. Mater.*, 2005, vol. 4, p. 680.
- 7. Poole, P.H., Grande, T., Angell, C.A., and McMillan, P.F, *Science*, 1997, vol. 275, p. 322.
- Swallen, S.F., Kearns, K.L., et al., Science, 2007, vol. 315, p. 353.