

In situ observation of amorphous-amorphous apparently first-order phase transition in zeolites

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In this letter, the authors present the observation of the phase transition between low-density amorphous (LDA) and high-density amorphous (HDA) zeolites using a high pressure Raman spectroscopy. It is found that this transition is apparently of the first order and occurs with a silicon coordination rise. It is shown that the Raman spectra of the LDA-HDA phase transitions in zeolites and in silicon are almost identical, suggesting a generality of amorphous-amorphous transformations both in simple substances and in complex polyatomic materials with tetrahedral configurations.

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Investigations of polyamorphism, the coexistence of different amorphous phases of the same composition but different densities, were triggered by the discovery of a high-density amorphous phase of water.¹ Amorphous zeolites have recently attracted great attention in view of polyamorphism: Meneau and co-workers,^{2,3} studying the dynamics of either pressure- or temperature-induced amorphization of crystalline zeolites using the x-ray diffraction and the small-angle x-ray scattering, have discovered that the dynamics of order-disorder transitions in zeolites under temperature and pressure are equivalent. They also found that the temperature dependence of the amorphization times τ_A for zeolites follows the Arrhenius law in contrast to the temperature dependence of the structural relaxation times τ for the conventional glasses of the same composition, which conforms to the Tamman-Vogel-Fulcher law. Meneau and co-workers^{2,3} associate the initial amorphous phase in a zeolite with the low-density amorphous (LDA) phase and the conventional glass of the same composition with the high-density amorphous (HDA) phase.

The nature of phase transformations in topologically disordered systems such as amorphous solids has not been adequately studied as yet,^{1,4} since the interaction between amorphous phases is rather complicated. There is a native dispersion of energies for individual elementary atomic clusters (or individual atoms for simple substances) in amorphous phases; consequently, the energy relation between two idealized amorphous phases is complicated because the transitions between elementary clusters of different structural types are possible for both directions.⁵ Moreover, the distributions of local energy minima for the amorphous basins can correspond to energy bands. This means, for example, a possibility of continuous transformation between amorphous phases, in contrast to crystals, in which the point of transition is clearly defined by intersection of the Gibbs free energy curves.

The pressure-induced transformations in amorphous phases were observed in a few tetrahedral coordinated materials. Such transformations have appeared basically different: In H_2O and Si, it is the first-order transition characterized by a discontinuous volume change,^{4,6} and the transition observed in SiO_2 and GeO_2 is gradual and continuous.^{7,8}

Brazhkin and Lyapin⁹ have drawn a conclusion that the transition type is determined by the ratio of the size of the smallest possible region with the changed short order to the correlation length of the medium-range order in a disordered medium.

The reversibility of the LDA-HDA transition observed in amorphous materials hinders the measurement on quenched samples: This transition must be investigated *in situ* at high pressures and temperatures. In view of the fact that transitions between LDA and HDA phases in zeolites *in situ* have not been observed yet, we have also investigated the dynamics of zeolite amorphization with an increase in pressure using the Raman spectroscopy. We investigate the dynamics of amorphization in two zeolites of different densities—natrolite $Na_2Al_2Si_3O_{10} \cdot 2H_2O$ and leucite $KAlSi_2O_6$. Zeolites are crystalline microporous materials with a structure formed by the corner sharing of SiO_4 or AlO_4 tetrahedra. Each tetrahedron is linked to the other four to form the framework materials which may have a different topology. Zeolites are characterized by having cages or channels, where alkaline or earth-alkaline cations and small molecules (generally water) are located. It is known that under compression, there is a driving force for amorphization if an important densification is possible, i.e., when the starting mineral has a low density, usually associated with the network-forming cations such as Si and Al in tetrahedral coordination.¹⁰ Based on the above said, zeolites as crystalline microporous materials are suitable for our experiments, because with amorphization under pressure they can become a 60% more-dense material.¹¹

Natrolite containing water in the cavities is a less rigid zeolite than leucite. In addition to water, there are Na cations of a small radius in the natrolite cavities. Leucite is, in fact, water-free and characterized by its high density. As compared to the other minerals, it is closer to quartz than to zeolites (it is widely used as a material for dental applications). Due to its high density, leucite will hardly become amorphous than natrolite. The Raman scattering spectra are recorded by Dilor OMARS 89 spectrometer with a charge-coupled-device LN/CCD-1100 PB (Princeton Instruments). The $0.1 \times 0.05 \times 0.15$ mm³ samples were compressed into a diamond anvil cell under hydrostatic conditions using a methanol-ethanol medium of 4:1 weight ratio. The pressure is determined from shifting a luminescence ruby line R_1 with an accuracy of ± 0.03 GPa. The Raman scattering is more

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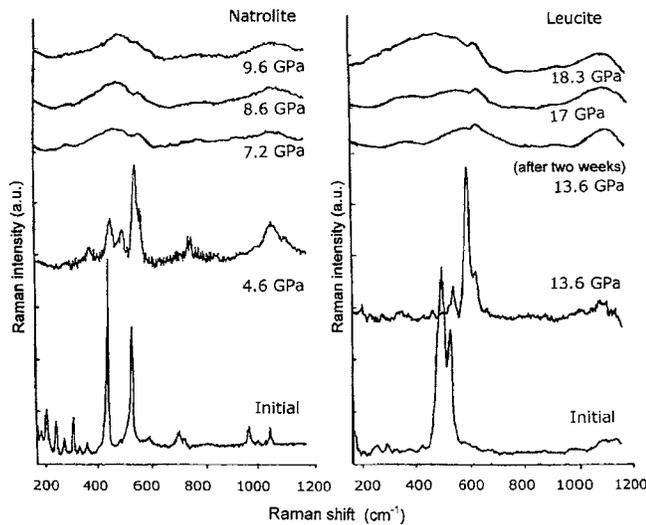


FIG. 1. Raman spectra recorded for natrolite with a fast pressure increase ($\tau_A > \tau$) to obtain the HDA phase (at 7.2 GPa) and a slow ($\tau_A < \tau$) for leucite to obtain the LDA phase (at 13.6 GPa).

sensitive than the x-ray diffraction to remaining traces of crystallinity; therefore values of the zeolite stability range obtained in Refs. 2 and 3 with the use of the x-ray diffraction can appear underestimated as compared to the values obtained using the Raman scattering.

Meneau and co-workers^{2,3} found that if the rate of compression is properly chosen to make the dynamics of zeolite amorphization much faster than that of a conventional glass of the same composition, i.e., $\tau_A < \tau$, then a LDA glass will be obtained, which may have physical properties different from any obtainable by the usual routes, even by the slowest cooling from the melt. Figure 1 demonstrates the Raman spectra recorded with a fast pressure increase ($\tau_A > \tau$) for natrolite and a slow ($\tau_A < \tau$) for leucite. We used a stepwise increase in pressure with a step of ~ 1 GPa at 10 min intervals, which was equivalent to $\sim 1.7 \times 10^{-3}$ GPa s⁻¹. For simplicity, we did not show intermediate spectra in Fig. 1. The most intensive Raman band of a natrolite spectrum at 443 cm⁻¹ is referred to as a collapse mode of the eightfold aluminosilicate rings. The second in intensity band at 534 cm⁻¹ is referred to as a breathing mode of the fourfold aluminosilicate rings. The spectrum doublet form converts to the quadruplet one at 3.7 GPa during the phase transition. The complete amorphization occurs at 7.2 GPa, when a weak broad glass similar to a hump appears. According to Refs. 2 and 3, the rate of pressure change of $\sim 1.7 \times 10^{-3}$ GPa s⁻¹ can be considered as sufficiently fast to meet the condition $\tau_A > \tau$. Therefore, a conventional disordered high-density HDA glass must be obtained at 7.2 GPa as a result of natrolite amorphization. At further increase in pressure up to 9.6 GPa, the natrolite spectra did not change, because the HDA structure has already been completely disordered.

As for a leucite spectrum, it contains a doublet of strong bands that correspond to the breathing modes of the fourfold aluminosilicate rings. The spectrum form is changed to a triplet at 2.3 GPa during the phase transition. All the three bands shift to the right with an increased pressure, but no evidence of features of amorphization is seen even at 13.6 GPa—the bands do not widen and their intensity is nearly unaffected. The leucite elevated tolerance for amorphization at high pressures is associated with the rigid type

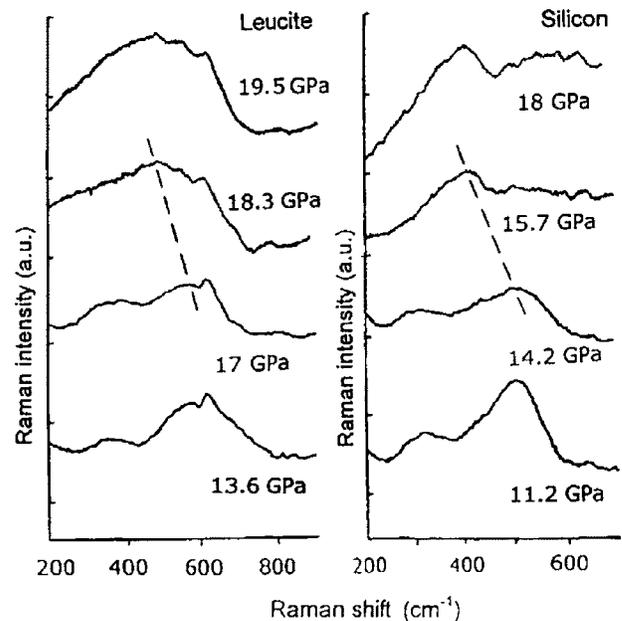


FIG. 2. Comparison of amorphous leucite and silicon Raman spectra (Ref. 12) at the LDA-HDA phase transitions. The dashed lines show the motion of maxima of tetrahedral bands with an increase in silicon coordination.

of a skeleton, water deficiency, and a special arrangement of potassium. Large cations of potassium in W positions in the middle of the sixfold aluminosilicate rings support a skeleton, thus essentially increasing the structure stability. Hence, it takes more time for leucite to come to equilibrium at such a pressure. We decided to use the slow kinetics of this phase transition, because a LDA glass was to be obtained during the slow amorphization, when $\tau_A < \tau$. That was the reason we stopped to increase the pressure and started to observe the spectrum changes keeping a leucite sample at the constant pressure of 13.6 GPa. In two weeks, in the Raman spectrum we obtained a weak broad glasslike hump when the intensity of the crystalline Raman bands has 20 times decreased. At further keeping the sample at 13.6 GPa, the spectrum is not changed, which is to say that a minimum of free energy was attained, which we attribute to the occurrence of the LDA phase. The energy H_A of the leucite transformation into the LDA amorphous phase can be found from the Arrhenian dependence $\tau_A = \tau_0 \exp(H_A/k_B T)$, where τ_A is the time of leucite amorphization, k_B is the Boltzmann constant, T is the temperature, and the factor τ_0 is equal to 10^{-12} s. In our case, $H_A = k_B T \ln(\tau_A/\tau_0)$, $\tau = 1296 \times 10^3$ s (15 days), and $H_A = 1.08$ eV, the latter value being significantly smaller than it is required for breaking bonds and is probably due to the cation diffusion. If we have used the pressure more than 13.6 GPa then for overcoming the energy barrier between the two metastable phases we would need the time less than two weeks. But, on the contrary, we wanted to reach the slowest amorphization. At further increase in pressure up to 18.3 GPa, as expected there are observed changes in the leucite amorphous spectra corresponding to the LDA-HDA phase transition, because the LDA structure is rearranged under compression to a denser HDA phase.

The LDA-HDA phase transition in zeolites with the use of the Raman scattering has not been detected yet. To identify the above-discussed changes, we have compared our spectra to those of amorphous silicon,¹² where the LDA-HDA phase transition is observed as the pressure increases.

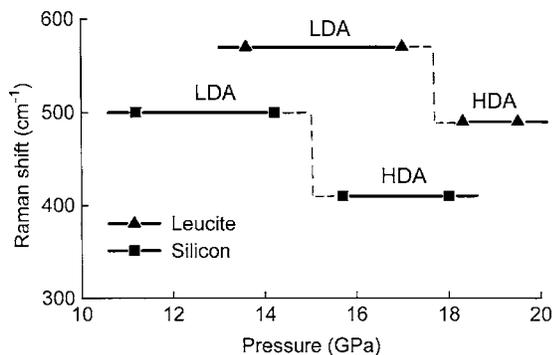


FIG. 3. Pressure dependence frequencies of maxima of tetrahedral bands in leucite (triangles) and in silicon (squares) Raman spectra taken from Fig. 2 at the LDA-HDA phase transitions.

This comparison seems to be reasonable because both silicon and zeolite have the following common characteristics: (1) locally tetrahedral coordination, (2) denser liquid than its crystalline form, and (3) decrease of the melting temperature with increasing pressure. These characteristics essentially result from the directional bonding that forms an open structure (tetrahedral configuration) at ambient pressure. It has been considered that an open atomic configuration could be the key factor of polymorphic transformations.¹³ Figure 2 demonstrates the comparison of the above-discussed spectra. Amorphous silicon Raman spectrum at 11.2 GPa includes two bands: the tetrahedral Si–Si stretching vibration features at 500 cm^{-1} and a weaker angle-bending mode at $\sim 300\text{ cm}^{-1}$. These features reflect a broadened version of the vibrational density of states of the crystalline silicon. The Si–Si stretching band became slightly weaker due to tetrahedral distortions as pressure goes higher up to 14.2 GPa; however, the spectrum remains to be a LDA polymorph. Between 14.2 and 15.7 GPa, the optical properties of silicon drastically change. Its reflection strongly increases, which is probably due to occurrence of its metallization. In this case, a single broad feature with a maximum near $\sim 400\text{ cm}^{-1}$ remains in the Raman spectrum. This is similar to the envelope of bands in the vibrational density of states calculated for crystalline silicon with the β -Sn structure at high pressure, and presumably other high-density polymorphs. Thus, McMillan *et al.*¹² ascribed the appearance of this broad feature to a higher coordinated silicon species with a denser HDA phase.

The Raman spectrum of the amorphous leucite at 13.6 GPa includes two bands: the tetrahedral (O–T–O) ($T = \text{Si, Al}$) bending vibration features at 600 cm^{-1} and a weaker librational mode of TO_4 tetrahedra below 400 cm^{-1} . Since silicon in leucite is twice as much as in aluminum, we consider silicon tetrahedra to make the dominating contribution to the Raman spectrum. Small spikes at 600 cm^{-1} can be related both to the residual crystallites or four-term tetrahedra rings embedded into an amorphous matrix.¹⁴ Figure 2 demonstrates that the amorphous leucite spectra vary with pressure in much the same way as the silicon spectra, that is to say that the LDA-HDA phase transition also occurs in leucite between 17 and 18.3 GPa. In this case, maxima of tetrahedral amorphous bands are shifted toward the lower frequencies (Fig. 2—the dashed lines) both in leucite and in silicon spectra. This is a result of weakening the bonds with an increase in silicon coordination. (As it was mentioned

above, silicon in leucite is twice as much as aluminum, thereby we consider a silicon coordination rise to make the dominating contribution to the Raman spectrum in comparison with the contribution of an aluminum coordination rise.) This transition in leucite is found to be reversible as well as the LDA-HDA transition in silicon during decompression. No coordination change was observed in Refs. 2 and 3, which is probably a result of amorphization at $\sim 4\text{ GPa}$, and in our experiment, the LDA-HDA transition takes place at higher pressures $\sim 18\text{ GPa}$. Earlier, we have discovered that the tetrahedra distortion which occurs at an increase in silicon coordination, becomes appreciable at pressures being greater than 15 GPa.¹⁵

Figure 3 demonstrates that the LDA-HDA phase transitions in silicon and leucite are transitions of the apparently first order which occur at pressures of 15.0 ± 0.7 and $17.7 \pm 0.6\text{ GPa}$, respectively.

To conclude, it may be said that the apparently first-order LDA-HDA phase transition, which occurs with a silicon coordination rise, is discovered in amorphous zeolite at high pressures with the use of *in situ* Raman scattering. The behavior of this transition cannot be predicted easily with molecular dynamics simulations (due to the long relaxation times). The connection between LDA and HDA phases depends on a possible existence of a route between them in the phase space. If there is no route or is only a “narrow” route like first-order transition, we may conclude they are not related to each other. The point is that no one can easily discover such routes by experiments or theoretical calculations. Therefore, the physics of the amorphous-amorphous phase transitions induced by pressure is still far from a clear knowledge, and the additional experimental result is an important contribution to the development of this physics.

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