Amorphous-to-Amorphous Phase Transition in Zeolites

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A transition between two amorphous phases with different densities has been detected in zeolites at high pressures using Raman scattering. The Raman spectra measured at amorphous-to-amorphous phase transitions in zeolites and silicon are almost identical; this fact suggests a common nature of these transitions in both singleand multicomponent materials.

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The studies of polyamorphism (the coexistence of different amorphous phases with the same composition but different densities) began with the detection of a high-density amorphous phase of water [1]. Recently, Greaves and coworkers [2, 3] studied the dynamics of amorphization of crystalline zeolites under increasing pressure or temperature using x-ray diffraction and small-angle x-ray scattering techniques. They detected the appearance of low-density amorphous (LDA) and high-density amorphous (HDA) phases in the course of amorphization. They also found that the temperature dependence of amorphization times τ_A for the LDA phases of zeolites obeyed the Arrhenius law, whereas the temperature dependence of structural relaxation times τ for the HDA phases (ordinary glasses of the same composition) obeyed the Vogel-Fulcher-Tamman law. Greaves et al. [2, 3] noted that ordinary liquids approached a glass-transition temperature from low viscosities η as the melt temperature was decreased, whereas a glass-transition temperature was approached from the other side in the amorphization of zeolites, from high viscosities η_A as the crystal temperature was increased. Therefore, limitations for reaching low configurational entropy as pressure or temperature varies are different for ordinary glasses and zeolites. Greaves et al. [2, 3] stated that, if the rate of change in pressure is chosen so that the dynamics of amorphization of zeolites is much faster than the dynamics of formation of ordinary glass with the same composition, that is, $\tau_A \ll$ τ and $\eta_A \ll \eta$, an LDA glass is formed. This LDA glass exhibits a more perfect structure with complete Al-Si ordering and a low configurational entropy. This ordered glass can exhibit physical properties other than the properties of glass prepared by ordinary methods even with the slowest cooling of a melt. For example, it can be harder, less dense, and less reactive than ordinary glasses with the same composition. The LDA glass is also of theoretical interest because its entropy is

nient for us for the reason that they knowingly have a driving force for amorphization, because they can be considerably compacted by compression [4]. We studied the time dependence of amorphization

we studied the time dependence of antiophization for two zeolites with different densities: natrolite $(Na_2Al_2Si_3O_{10} \cdot 2H_2O)$ and leucite $(KAlSi_2O_6)$. Natrolite is a brittle hydrated zeolite, in the cavities of which small-radius cations of Na occur in addition to water. Leucite is practically anhydrous and exhibits a high density; as compared with other minerals, it is closer to quartz rather than zeolites (because of its strength, it is widely used for the preparation of artificial teeth). Because of its high density, leucite is more difficult to subject to amorphization than natrolite. The Raman spectra were recorded on a Dilor OMARS 89 spectrometer equipped with an LN/CCD-1100 PB multichannel detector (Princeton Instruments). Samples of size

similar to the entropy of the parent crystal (dehydrated

zeolite). Thus, because this amorphous phase is pro-

duced from material with a lower (or the same) entropy

rather than from a higher entropy phase (melt), it avoids

the Kauzmann paradox: limitations of the possible convergence of entropy observed on cooling a melt.

phases in zeolites had still not been observed, we also

studied the dynamics of zeolite amorphization under

increasing pressure using Raman spectroscopy. It is

well known that this technique is more sensitive to crys-

tallinity on a small scale than x-ray diffraction. There-

fore, the regions of zeolite instability evaluated by

Greaves et al. [2, 3] with the use of x-ray diffraction

techniques may be underestimated. Zeolites are alumi-

nosilicates whose crystal structure is formed by SiO₄

and AlO₄ tetrahedra joined into a corner-shared three-

dimensional framework with cavities and channels,

which are occupied by water molecules and metal cat-

ions. These low-density porous crystals were conve-

Because in situ transitions between LDA and HDA



Fig. 1. Raman spectra of natural natrolite and leucite measured under increasing pressure until amorphization.

~ $0.1 \times 0.05 \times 0.15$ mm were placed in an apparatus with diamond anvils in a hydrostatic medium (methanol–ethanol in a ratio of 4 : 1). The pressure was determined to within ± 0.03 GPa from the shift of the ruby R_1 band.

Figure 1 shows the Raman spectra recorded in natrolite at a high rate of increasing pressure and in leucite at a low rate until amorphization. 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. For simplicity, we did not show intermediate spectra in Fig. 1. The most intense band at 443 cm⁻¹ in the spectrum of natrolite was ascribed to a mode that corresponds to the vibrations of eightfold aluminosilicate rings, and the second most intense band at 534 cm⁻¹ belongs to a mode that corresponds to the vibrations of fourfold rings. The doublet shape of this spectrum was changed to a quadruplet upon a phase transition at 3.7 GPa. The complete amorphization occurred at 7.2 GPa, when a low-intensity broad band due to a glassy phase appeared. According to Greaves et al. [2, 3], the rate of pressure change of $\sim 1.7 \times 10^{-3}$ GPa/s can be considered sufficiently fast in order for the condition $\tau_A \gg \tau$ to be fulfilled, and an ordinary disordered HDA glass results from the amorphization of natrolite. As for the spectrum of leucite, it exhibits a doublet of strong Raman bands, which correspond to the vibration modes of fourfold aluminosilicate rings. The shape of this spectrum changed to a triplet upon a phase transition at 2.3 GPa. As the pressure was increased, all three bands shifted to the right; however, no signs of amorphization were detected even at 13.6 GPa: the bands were not broadened, and the band intensities remained almost unchanged. The enhanced stability of leucite to amorphization at high pressures is due to the rigid framework, the absence of water, and the special arrangement of potassium. Bulky potassium cations, which occur in the W positions at the centers of sixfold rings, support the framework to significantly enhance the stability of the structure. Therefore, a longer time is required for leucite to reach an equilibrium state at this pressure. We decided to use the slow kinetics of this transition because, as mentioned above, slow amorphization at $\tau_A \ll \tau$ and $\eta_A \ll \eta$ results in an LDA glass with a more perfect structure, complete Al-Si ordering, and a low configurational entropy. Thus, we ceased to increase the pressure and managed to observe changes in the spectrum on keeping a leucite sample at a constant pressure of 13.6 GPa. We obtained an amorphized glass-type spectrum after two weeks, when the intensity of crystalline Raman bands decreased by a factor of about 20. The energy H_A of leucite conversion into an amorphous phase can be found from the Arrhenius function $\tau_A = \tau_0 \exp(H_A/k_B T)$, where τ_A is the amorphization time of leucite, k_B is the Boltzmann constant, T is the temperature, and the multiplier τ_0 is ~10⁻¹² s. In our case, $H_A = k_B T \ln(\tau_A/\tau_0)$, and $\tau_A \approx 1296 \times 10^3$ s (15 d); $H_A = 1.08$ eV. This value is much lower than that required for bond rupture, and it is most likely that this value results from the diffusion of cations. Greaves et al. [2, 3] also noted that zeolite amorphization under



Fig. 2. Raman spectra of amorphous natrolite and leucite at various pressures.

pressure resulted from changes in the local structure of charged compensation cations.

As a result of this slow leucite amorphization due to slow kinetics, an energetically more favorable and more ordered LDA glass would be formed. To support the hypothesis that the resulting HDA phase of natrolite and LDA phase of leucite are shown in Fig. 1, we recorded Raman spectra on applying additional pressure to these two amorphous samples, as shown in Fig. 2. Because the LDA structure with stronger bonds and a lower entropy is converted into a denser and more disordered HDA phase under compression, we would see changes in the spectra of amorphous leucite corresponding to the LDA-HDA phase transition. At the same time, the spectra of natrolite would remain unchanged, because its HDA structure is already disordered. It can be seen in Fig. 2 that, as we expected, considerable changes occurred only in the spectra of leucite.

The LDA–HDA phase transition in zeolites was not observed previously with the use of Raman spectroscopy. To identify the resulting changes, we compared our spectra with the spectra of amorphous silicon [5], in which the LDA–HDA phase transition was observed as the pressure was increased. This comparison seems reasonable, because silicon and zeolites exhibit a similarity of tetrahedrally coordinated structures formed by joined tetrahedra. Figure 3 compares these spectra. The Raman spectrum of amorphous silicon at 6.4 GPa con-

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sists of two bands: a tetrahedral Si-Si vibration mode at 500 cm⁻¹ and a weaker bending angular mode near 300 cm⁻¹. These special features reflect an extended version of the vibrational density of states of crystalline silicon. As the pressure was increased to 13 GPa, Si-Si stretching vibrations became weaker because of a distortion of tetrahedra; however, silicon remained an LDA polymorph. The optical properties of silicon dramatically changed between 13 and 18 GPa: its reflectance strongly increased. This was likely due to the onset of its metallization. In this case, the only broad band with a maximum at about 400 cm⁻¹ remained in the Raman spectrum. It is similar to the spectral envelope of vibration modes in silicon with the β -Sn structure at a high pressure and, possibly, other high-density polymorphs. Therefore, McMillan et al. [5] ascribed the appearance of this band to a higher coordinated high-density HDA phase.

The Raman spectrum of amorphous leucite consists of three bands: a band at 1100 cm^{-1} due to Si–O stretching vibrations; a band at 600 cm⁻¹ attributed to (O–T– O) (T = Si, Al) bending vibrations; and a weak band below 400 cm⁻¹ most likely due to T–O rotational vibrations. Because the silicon content of leucite is twice as high as the aluminum content, we consider that silicon tetrahedra mainly contribute to the Raman spectrum. Small peaks at 600 cm⁻¹ can be due to either residual crystallites or four-membered rings of tetrahe-



Fig. 3. Raman spectra of amorphous leucite and silicon [5] measured at the LDA–HDA phase transitions. The dashed lines indicate the shifts of tetrahedral band maxima as the coordination of silicon increases.

dra suspended in an amorphous matrix [6]. It can be seen in Fig. 3 that the spectra of amorphous leucite changed with pressure in almost the same manner as the spectra of silicon. Therefore, it is believed that the LDA–HDA phase transition also occurred in leucite between 15.8 and 18.3 GPa. In this case, the maxima of tetrahedral amorphous bands in the spectra of both leucite and silicon shifted toward lower frequencies (as indicated by dashed lines) because of bond weakening as the coordination of silicon increased. It is likely that Greaves et al. [2, 3] did not detect coordination changes because amorphization occurred at ~4 GPa in their experiments, whereas it occurred at much higher pressures of ~18 GPa in this work.

In addition to silicon, amorphous-to-amorphous phase transitions were also observed in tetrahedrally coordinated materials such as H_2O and SiO_2 [1, 7]. It was found that these transformations were substantially different: in H_2O , this was a first-order transition, which occurred with a discontinuous change in volume [8], whereas the transition observed in SiO₂ occurred gradually and continuously [9]. Because the Raman spectra measured at the LDA–HDA phase transition in leucite and silicon were identical, it is believed that this transition in leucite is also a first-order phase transition.

In conclusion, we can state that the LDA-HDA phase transition in zeolites at high pressures was detected using Raman spectroscopy; this phase transi-

tion occurred with increasing coordination of silicon. We found that the Raman spectra measured at the LDA–HDA phase transitions in zeolites and silicon were almost identical. This fact suggests a common nature of these transitions in both single- and multicomponent materials.

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REFERENCES

- 1. O. Mishima and H. E. Stanley, Nature 396, 329 (1998).
- G. N. Greaves, F. Meneau, A. Sapelkin, et al., Nature Mater. 2, 622 (2003).
- G. N. Greaves and F. Meneau, J. Phys.: Condens. Matter 16, S3459 (2004).
- 4. P. Richet and P. Gillet, Eur. J. Mineral. 9, 907 (1997).
- 5. P. F. McMillan, M. Wilson, D. Daisenberger, and D. Machon, Nature Mater. 4, 680 (2005).
- A. Pasquarello and R. Car, Phys. Rev. Lett. 80, 5145 (1998).
- P. H. Poole, T. Grande, C. A. Angell, and P. F. McMillan, Science 275, 322 (1997).
- O. Mishima, L. D. Calvert, and E. Whalley, Nature 314, 76 (1985).
- 9. Q. Williams and R. Jeanloz, Science 239, 902 (1988).

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