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High-pressure study of α-quartz GeO_2 using extended x-ray-absorption fine structure

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The effect of pressure on silicates and germanates is of importance to the geological sciences. Germanates generally act as models for the corresponding silicates at higher pressures in the sense that the same pressure-induced transitions occur at lower pressures in germanates. Using x-ray-absorption spectra obtained at the Stanford Synchrotron Radiation Laboratory (SSRL), we have determined the variation with pressure of the structural parameters of α-quartz GeO_2 up to 58 kbar at room temperature. Our data appear consistent with the time-of-flight powder-neutron-diffraction studies done by Jorgensen. We see no evidence of a transition from the metastable α-quartz structure to the rutile structure as is seen in SiO_2.

INTRODUCTION

Germanates generally occur in structures similar to the geologically important silicates. An interesting feature is that a given germanate structure will often undergo the same pressure-induced transitions as the corresponding silicate, but will do so at lower pressures. In this way germanates make it easier to model in the laboratory the behavior of silicates at the higher pressures found in deep-earth conditions. We have conducted a high-pressure extended x-ray-absorption fine-structure (EXAFS) study of α-quartz GeO_2. We find that, in contrast to α-quartz SiO_2,[1] and despite the fact that the rutile phase of GeO_2 is the more stable phase,[2] α-quartz GeO_2 does not undergo a change of phase in the pressure range studied, which was up to 58 kbar at room temperature.

The α-quartz structure is hexagonal with three Ge atoms per unit cell. These sit at the centers of corner-linked GeO_4 tetrahedra. The tetrahedra are distorted at 1 bar, a condition due mainly to the inequality of the O—Ge—O bond angles,[3] though there are two slightly differing Ge-O distances in the tetrahedron. This separation is about 0.04 Å, which cannot be resolved in the Fourier transforms of the EXAFS spectra (see Fig. 4).

Figure 1 shows a projection of the unit cell of α-quartz onto the basal plane.[4] Using this convention the Ge atoms sit at the positions $(u,0,0)$, $(1-u,1-u,\frac{1}{3})$, and $(0,u,\frac{2}{3})$. Each Ge atom has four nearest-neighbor Ge atoms which are at equal distances, independent of the value of c/a.

EXPERIMENT

Our Ge K-edge x-ray-absorption spectra were taken at beam line IV-1 at SSRL. The sample was pressurized in an inconel gasket between boron carbide anvils. Details of the high-pressure apparatus have been discussed elsewhere.[5] The sample was prepared by mixing powdered α-quartz GeO_2 with silicon grease, which acted as the hydrostatic medium, and was placed in the gasket along with copper foil. The compression of the copper was measured via its EXAFS and served as the pressure calibrant.[6]

RESULTS AND ANALYSIS

The EXAFS spectra at high and low pressure are shown in Fig. 2. A more detailed plot of the x-ray near-

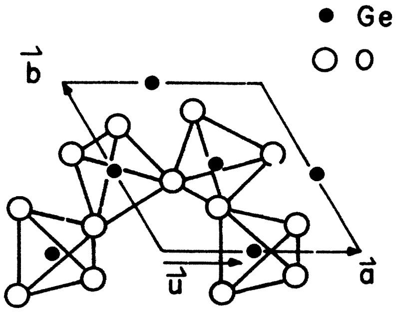

FIG. 1. Projection onto the basal plane of the GeO_4 tetrahedra. These form chains which spiral upward; successive Ge atoms have a vertical spacing of $\frac{1}{3}c$. $R_{\text{Ge-Ge}}=(1-2u,1-u,\frac{1}{3})$.

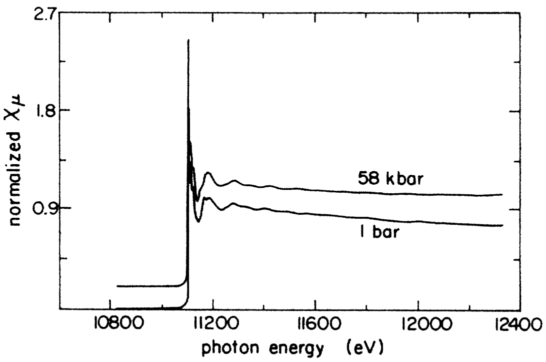

FIG. 2. X-ray-absorption spectra at the Ge K edge of GeO_2 at 1 bar and 58 kbar.

edge structure (XANES) is shown in Fig. 3. The interesting feature of the GeO_2 XANES is the triple peak structure which changes slightly with pressure. It is possible that the smoothing of the features with pressure is a manifestation of the focused multiple-scattering effect, the enhancement of the Ge-Ge scattering due to the intervening O atom.[7] The oxygen scattering amplitude is strongly dependent on both electron wave vector k and scattering angle beta,[8] where

$$k=[2m(E-E_0)/\hbar^2]^{1/2}\,, \tag{1}$$

and the scattering angle beta is defined in Fig. 5. At the angles of interest here the scattering amplitude is sensitive to angle only for small values of k ($\lesssim 4$ Å^{-1}),[8] decreasing sharply with increasing scattering angle. For larger k the amplitude is small and slowly varying. One would therefore expect to observe a decrease in the Ge-Ge scattering contribution to the XANES and little change in the EXAFS, as appears to be the case.

Figure 4 shows the Fourier transform magnitudes obtained from the EXAFS of Fig. 2. The changes in the Ge-O and Ge-Ge distances were obtained using the standard EXAFS phase difference method.[9] We also analyzed changes in σ^2, the mean-square displacement in the interatomic distance, using the log-amplitude-ratio method.[9] σ^2 arises from thermal motion and/or static disorder, and an anomalous variation with pressure or temperature often signals a phase transition. The results of these analyses are shown in Table I.

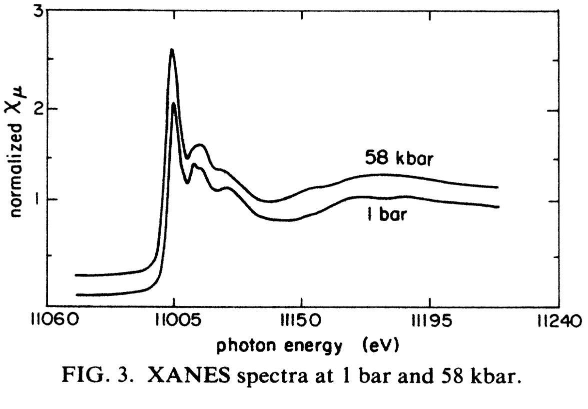

FIG. 3. XANES spectra at 1 bar and 58 kbar.

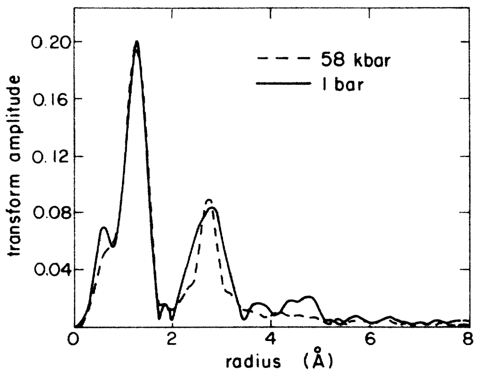

FIG. 4. Magnitudes of the Fourier transforms of $k\times\chi(k)$ at 1 bar and at 58 kbar. The transform range was 2.2–16.9 Å^{-1} using a 10% Gaussian window. The origin of the k-space scale, E_0, was determined by the inflection point in the absorption edge. No phase correction has been applied.

We note that the Ge-O distance does not change while the Ge-Ge distance decreases. Hence the tetrahedra must either undergo rigid rotations or further distortion in which the Ge-O distances are preserved. Jorgensen[10] has studied the compression of the α-quartz forms of both GeO_2 and SiO_2 up to about 25 kbar using time-of-flight powder neutron diffraction. His proposed mechanisms for compression are rigid rotation in SiO_2 and distortion in GeO_2. Although we lack the angular resolution to distinguish between these two mechanisms, we believe that the GeO_4 tetrahedra simply continue their distortion up to 58 kbar. There is certainly no evidence of an onset of another phase.

The $\Delta\sigma^2$'s of the Ge—O bond do not show any significant variation with pressure but those for the Ge-Ge distance exhibit a decrease with increasing pressure, corresponding to the narrowing of the Ge-Ge peak in the transform (Fig. 4). Though the estimated uncertainties of $\Delta\sigma^2$'s are large, the trend for the Ge-Ge distance is reasonable, as the structure is expected to stiffen with increasing pressure. The lack of an abrupt change in the trend of $\Delta\sigma^2$ with pressure reinforces the conclusion of no phase transition. We note here that there is an apparent decrease in the area of the Ge-Ge peak in Fig. 4.

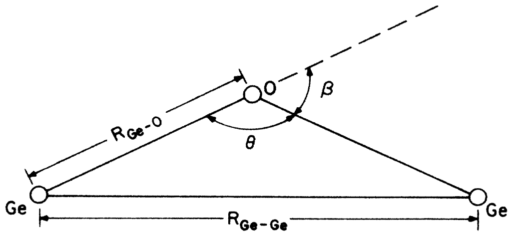

FIG. 5. Ge—O—Ge bond angle geometry, assumed identical for all such bonds. θ is the bond angle; β is the scattering angle.

TABLE I. The parameters extracted from analysis of the EXAFS spectra. All changes referenced to 1-bar standard.

	Ge-O		Ge-Ge	
P (kbar)	ΔR (Å)	$\Delta\sigma^2$ (Å^2)	ΔR (Å)	$\Delta\sigma^2$ (Å^2)
8 (2)	0.001 (0.005)	a	−0.022 (0.005)	−0.0005 (0.0008)
12	0.002	a	−0.033	−0.0012
24	0.002	a	−0.048	−0.0021
39	0.003	a	−0.064	−0.0024
44	0.003	a	−0.068	−0.0025
58	0.008	a	−0.076	−0.0025

[a] Values much smaller than uncertainties.

Our analysis indicates that this decrease does not correspond to a decrease in the coordination number, and is most likely a transform artifact.

The rutile phase would be marked by a change in the coordination number from 4 to 6 in the oxygen shell as well as a distinguishable splitting in the nearest-neighbor germanium peak. These features are clearly absent from the data, indicating that 58 kbar is not sufficient to force the considerable atomic rearrangement that must take place to affect this particular transition.

One may calculate the Ge—O—Ge bond angle using the simple geometry shown in Fig. 5. The average Ge-O distance[10] was used, along with the assumption that the bonds form an isosceles triangle. The variation of the bond angle with pressure is shown in Fig. 6.

The change in the unit-cell volume cannot be found with only the variation of the nearest-neighbor distance. One must include the change in the ratio of c/a and the change in u (Fig. 1). The relation between the nearest-neighbor germanium distance and unit-cell volume is

$$V=\frac{\sqrt{3}}{2}\left[\frac{c}{a}\right]R^{3}_{\text{Ge-Ge}}\left[1-3u+3u^{2}+\left[\frac{c}{3a}\right]^{2}\right]^{-3/2} \qquad (2)$$

Using values extrapolated from Jorgensen's data,[10] the compression curve was obtained and is shown in Fig. 7, along with the compression curve obtained by Jorgensen. There is an apparent discrepancy in the curvature; otherwise the agreement is good.

A basis for quantitative comparison of these results can be had by fitting to the Murnaghan equation of state,

$$P=\frac{B_0}{B_0'}\left[\left[\frac{V_0}{V}\right]^{B_0'}-1\right], \qquad (3)$$

where B_0 and B_0' are the zero pressure values of the bulk modulus and its pressure derivative, respectively. One must bear in mind that the high curvature means that the bulk modulus is not a linear function of the pressure, and thus the fit of our data to the Murnaghan equation of state is simply a convenient parametrization of the P-V relation. The fit parameters for our data are $B_0=265$ kbar and $B'=16.8$, which are to be compared to $B_0=391$ kbar and $B'=2.2$ for Jorgensen's.

The bulk modulus may be calculated directly with a linear fit using the lowest three pressures (including 1 bar); this yields $B_0=343$ kbar. Sound velocity measurements[11] give $B_0=347$ kbar.

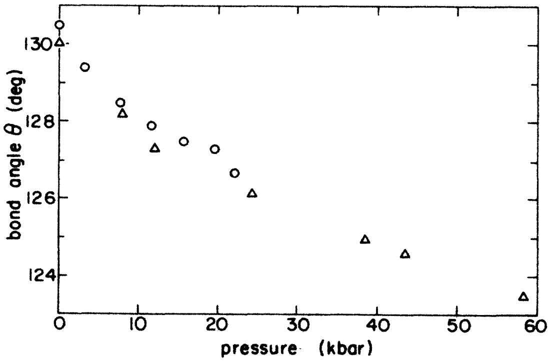

FIG. 6. Bond angle θ vs pressure. (△, this work; ○, Jorgensen's data.)

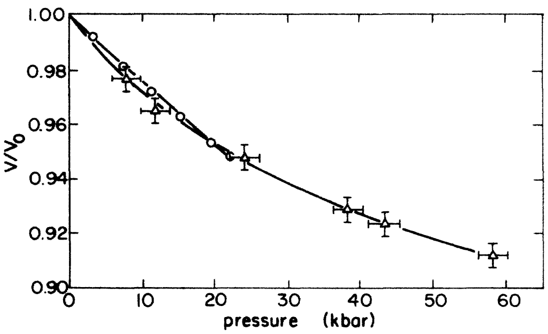

FIG. 7. V/V_0 vs pressure. Solid curves are the fits to the Murnaghan equation of state. (△, this work; ○, Jorgensen's data.)

CONCLUSION

We clearly do not see a transition to the rutile phase of GeO_2 below 58 kbar at room temperature. The duration of the experiment was approximately nine hours, and perhaps a longer time under pressure or the simultaneous application of high temperature, or both, is required to facilitate the rather substantial structural transformation.

The compression mechanism is interpreted as a continued distortion of the tetrahedra. The degree of curvature in the compression curve seems reasonable in view of this mechanism and the associated steric hindrance as the bonds bend.

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