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### RAPID COMMUNICATIONS

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#### Ferroelastic phase transition in rutile-type germanium dioxide at high pressure

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Rutile-type  $\text{GeO}_2$  was found to undergo a proper ferroelastic transition at 26.7(2) GPa from Raman spectroscopic measurements. The  $B_{1g}$  optic mode softens up to this pressure and then becomes a hard  $A_g$  mode. The square of these mode frequencies varies linearly with pressure in accordance with the soft-mode theory of second-order phase transitions. The present results have enabled a systematic relationship between the square of the soft-mode frequency at ambient pressure and the critical pressure in the homologous series  $\text{SiO}_2$ ,  $\text{GeO}_2$ , and  $\text{SnO}_2$  to be identified. [S0163-1829(98)50230-5]

#### I. INTRODUCTION

There is a great deal of interest in the high-pressure transitions of silica due to the possible geophysical repercussions of such transitions. Stishovite (the high-pressure, tetragonal, rutile-structured phase of silica) was found to transform reversibly to an orthorhombic,  $\text{CaCl}_2$ -type phase at a pressure of about 100 GPa by x-ray powder diffraction.<sup>1</sup> In contrast, theoretical calculations and Raman spectroscopic experiments<sup>2,3</sup> indicate that this transition occurs at 50 GPa. Landau theory predicts that a transition from the rutile-type [ $P4_2/mnm(D_{4h}^{14})$ ,  $Z=2$ ] to a  $\text{CaCl}_2$ -type [ $Pnmm(D_{2h}^{12})$ ,  $Z=2$ ] structure should be a second-order, proper ferroelastic transition and involve the softening of the Raman-active  $B_{1g}$  mode.<sup>4,5</sup> The order parameter for this transition is the spontaneous strain  $e_{ss}=(a-b)/(a+b)$ , which is of  $B_{1g}$  symmetry ( $a$  and  $b$  are unit cell constants of the orthorhombic  $\text{CaCl}_2$ -type phase). The  $B_{1g}$  mode does indeed soften in stishovite<sup>3,6</sup> and at the transition it becomes a hard  $A_g$  mode. There is considerable disagreement, however, between the results of different studies using various techniques, concern-

ing the transition pressure and the second-order nature of the rutile to  $\text{CaCl}_2$  transition in silica.<sup>1-3,7,8</sup> In particular, the reported transition pressure varies greatly as a function of the pressure-transmitting medium used. Values of 50 GPa,<sup>3</sup> 56 GPa,<sup>7</sup> and 100 GPa (Ref. 1) were reported for experiments using neon, hydrogen, and no medium, respectively. Studies of ferroelastic transitions at high pressure are difficult as they are highly sensitive to deviatoric stress.<sup>8-10</sup> In all such studies, it is essential to use pressure-transmitting media that approximate as closely as possible hydrostatic conditions. The transition in silica presents particular problems as it occurs well above the solidification pressure of all potential, pressure-transmitting media. It is thus of interest to investigate the behavior of silica analogs, which undergo the same transition at lower pressures. The most appropriate model compound for stishovite is rutile-type  $\text{GeO}_2$ . Rutile-type to  $\text{CaCl}_2$ -type transitions at high pressure have been reported for the other group 14 dioxides,  $\text{SiO}_2$ ,<sup>1,3,7</sup>  $\text{SnO}_2$ ,<sup>10</sup> and  $\text{PbO}_2$ .<sup>11</sup> Preliminary, x-ray diffraction experiments under nonhydrostatic conditions indicate that rutile-type  $\text{GeO}_2$  also transforms to an orthorhombic  $\text{CaCl}_2$ -type phase at high

TABLE I. Raman data for GeO<sub>2</sub> at high pressure.

Rutile type (0.1 MPa)			CaCl <sub>2</sub> type [34.2(2) GPa]		
Mode	$\nu$ (cm <sup>-1</sup> )	$d\nu/dP$ (cm <sup>-1</sup> /GPa)	Mode	$\nu$ (cm <sup>-1</sup> )	$d\nu/dP$ (cm <sup>-1</sup> /GPa)
$B_{2g}$	873(1)	4.25(3)	$B_{1g}$	1012(1)	3.4(2)
$A_{1g}$	701(1)	3.46(3)	$A_g$	815(1)	2.8(2)
$B_{1g}$	171(1)	*	$A_g$	155(1)	*

\*See discussion in the text.

pressure,<sup>12</sup> however, due to the lack of hydrostaticity, the equilibrium transition pressure could not be determined. Raman experiments<sup>13</sup> up to a maximum of 11.7 GPa indicate that the  $B_{1g}$  mode in GeO<sub>2</sub> softens with pressure. The present Raman spectroscopic results obtained using helium as a hydrostatic, pressure-transmitting medium indicate that this compound transforms at 26.7(2) GPa and that the transition is second order. These results permit systematic behavior in the homologous series SiO<sub>2</sub>, GeO<sub>2</sub>, and SnO<sub>2</sub> to be identified.

## II. EXPERIMENT

High-pressure experiments were performed in a membrane-type, diamond-anvil cell. Rutile-type GeO<sub>2</sub> was prepared from the quartz-type phase (Produits Touzart & Matignon, purity 99.999%) in a belt-type apparatus at 3.0 GPa and 585 °C. The grey material recovered was subsequently annealed at 900 °C in air at ambient pressure. The resulting white product was entirely in the rutile-type phase and no impurities were detected by x-ray diffraction or Raman spectroscopy indicating a chemical and phase purity of at least 99.9%. The widths of the x-ray diffraction lines of this phase are consistent with a crystallite size of the order of 70 nm. Samples were loaded along with a ruby crystal using helium as a pressure transmitting medium in 50–100- $\mu$ m-diameter holes of stainless steel gaskets, which had been preindented to a thickness of about 60  $\mu$ m. Several loadings were performed and great effort was made in order to avoid contact between the sample and the gasket or the diamond anvils. Such contact was easily detected as it yielded asymmetric peak shapes and, in extreme cases, additional peaks shifted to positions at which they would be expected at lower pressures. Pressures were measured based on the shifts of the ruby  $R_1$  and  $R_2$  fluorescence lines.<sup>14</sup> No broadening of the ruby lines was observed up to the maximum pressure reached of 34.2 GPa. Raman experiments were performed in back-scattering geometry using a Jobin Yvon Model U 1000 double monochromator with a supernotch filter and a liquid-nitrogen-cooled CCD. The 488.0 and 514.5 nm lines of an argon-ion laser were used for excitation. The spectrometer was calibrated using a standard neon lamp. The Raman scattering and ruby fluorescence data were fitted to Lorentzians and the resulting peak positions have an uncertainty of less than  $\pm 1$  cm<sup>-1</sup>. The contribution to the pressure error due to measurement uncertainty is less than  $\pm 0.2$  GPa. Uncertainties in measured values and standard deviations for calculated values are given in parentheses.

## III. RESULTS AND DISCUSSION

Rutile-structured germanium dioxide is composed of columns of edge-sharing GeO<sub>6</sub> octahedra along **c**, which are crosslinked along the [110] and  $[\bar{1}\bar{1}0]$  directions. Group theory predicts that a rutile-structured crystal [ $P4_2/mnm(D_{4h}^{14})$ ,  $Z=2$ ] will have four Raman active modes:  $\Gamma_{\text{Raman}} = A_{1g} + B_{1g} + B_{2g} + E_g$ . Up to the present, only the first three modes have been observed for GeO<sub>2</sub>.<sup>13</sup> In this study, Raman lines were observed at 873(1), 701(1), and 171(1) cm<sup>-1</sup> at ambient pressure, which are, respectively, the  $B_{2g}$ ,  $A_{1g}$ , and  $B_{1g}$  modes. As in previous work,<sup>13</sup> the  $E_g$  mode was too weak to be detected. The two higher-frequency modes involve Ge-O stretching in the GeO<sub>6</sub> octahedra, whereas the  $B_{1g}$  mode corresponds to the libration of the columns of octahedra about their twofold axes along **c**. The condensation of this libration at high pressure would yield a static, orthorhombic, CaCl<sub>2</sub>-type distortion of the rutile-type structure as found by x-ray diffraction.<sup>12</sup> The two former modes were found to harden with increasing pressure. Their pressure dependences, Table I, were found to be linear within experimental error and are in agreement with the values obtained previously in experiments up to 11.7 GPa.<sup>13</sup> The soft  $B_{1g}$  mode exhibited a nonlinear pressure dependence and was found to decrease in frequency up to 26.7(2) GPa (Fig. 1). Above this pressure, this mode began to harden, thereby indicating that the transition had occurred. The soft-mode behavior and the absence of discontinuities in the frequencies of the hard modes are consistent with a second-order phase transition. In addition, no hysteresis was observed on decompression. No new modes appeared above the transition pressure. Group theory predicts that the CaCl<sub>2</sub>-type phase identified by x-ray diffraction<sup>12</sup> [ $Pnmm(D_{2h}^{12})$ ,  $Z=2$ ] should have six Raman-active modes:  $\Gamma_{\text{Raman}} = 2A_g + 2B_{1g} + B_{2g} + B_{3g}$ . The two  $A_g$  modes corresponds to the  $A_{1g}$  and the  $B_{1g}$  modes of the tetragonal phase, while one  $B_{1g}$  mode corresponds to the tetragonal  $B_{2g}$  mode. The other three predicted modes arise from the unobserved tetragonal  $E_g$  mode and an inactive  $A_{2g}$  mode which could explain why they were not detected.

The decrease in  $d\nu/dP$  for the hard modes above the phase transition indicates reduced compression of the Ge-O bonds in the octahedra. This reduction in compressibility of the Ge-O bonds is a consequence of the additional compression mechanism available above the transition pressure. Whereas in the rutile-type phase the columns of edge-sharing octahedra are fixed, in the high-pressure phase they gradually tilt about their two-fold axes. This process is favored by the application of pressure as the gradual increase in angle to

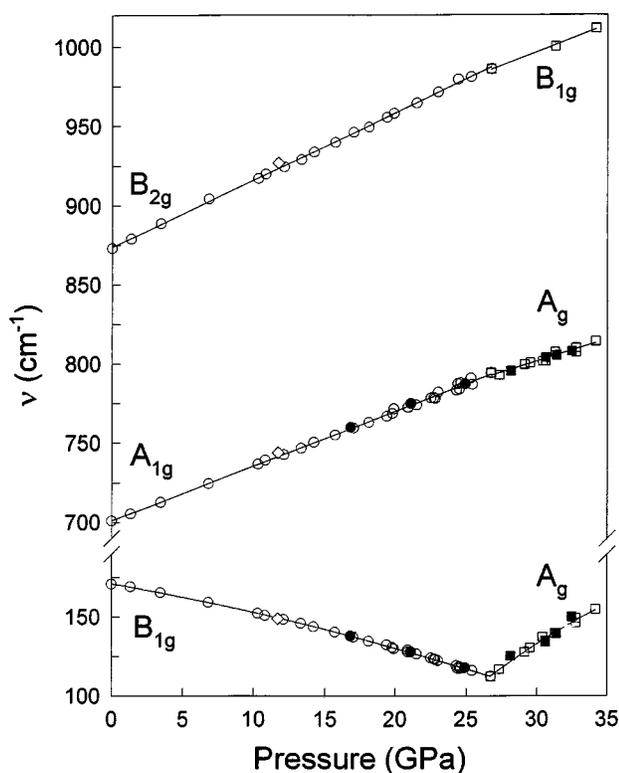


FIG. 1. Observed Raman modes of  $\text{GeO}_2$  as a function of pressure. Open symbols refer to points obtained upon compression and solid symbols to those obtained on decompression. Symbols  $\circ$  and  $\square$  correspond to the rutile-type and  $\text{CaCl}_2$ -type phases, respectively. Solid lines represent least-squares fits to the data. The spectral region containing the very weak  $B_{2g}$  mode was not investigated in all runs due to the long acquisition time needed. Diamonds ( $\diamond$ ) represent the values obtained in Ref. 13 at the maximum pressure attained of 11.7 GPa.

close to  $10^\circ$  yields a hexagonal close-packed oxygen sublattice.<sup>9,10</sup>

The soft-mode theory of second-order phase transitions predicts that the soft mode in the paraelastic phase ( $p$ ) should have the following pressure dependence:  $\nu_p^2 = k_p |P - P_p|$ , while for the corresponding mode in the ferroelastic phase ( $f$ ):  $\nu_f^2 = k_f |P - P_f|$ , where  $P_p$  and  $P_f$  are the pressures at which the modes for each phase become unstable and  $k_p$  and  $k_f$  are constants. These relationships hold for both the paraelastic low-pressure phase and the ferroelastic high-pressure phase over the entire pressure ranges that they are observed (Fig. 2). The lines intersect at the critical pressure ( $P_c$ ) of 26.7(2) GPa and the slopes  $k_p$  and  $k_f$  are  $-631(4)$  and  $1503(52)$   $\text{cm}^{-2}/\text{GPa}$ , respectively.  $P_p$  and  $P_f$  were found to be 46.9(2) and 18.2(4) GPa, respectively. The ratio  $k_f/k_p = -2.4(1)$ , which is close to the value of  $-2$  predicted by Landau theory<sup>15</sup> and the critical pressure is close to the predicted value,  $P_c = 1/3(P_p + 2P_f) = 27.8(3)$  GPa. The soft-mode frequency at  $P_c$  is 112(1)  $\text{cm}^{-1}$ , which is 0.66(1) times its ambient pressure value,  $\nu_0$ . The behavior in silica is very similar with the soft-mode frequency decreasing to 70% of its ambient pressure value.<sup>3</sup> Calculations for silica<sup>2</sup> are in agreement with this observation as they indicate that the elastic shear modulus  $(C_{11} - C_{12})/2$  goes to zero well before the soft-mode fre-

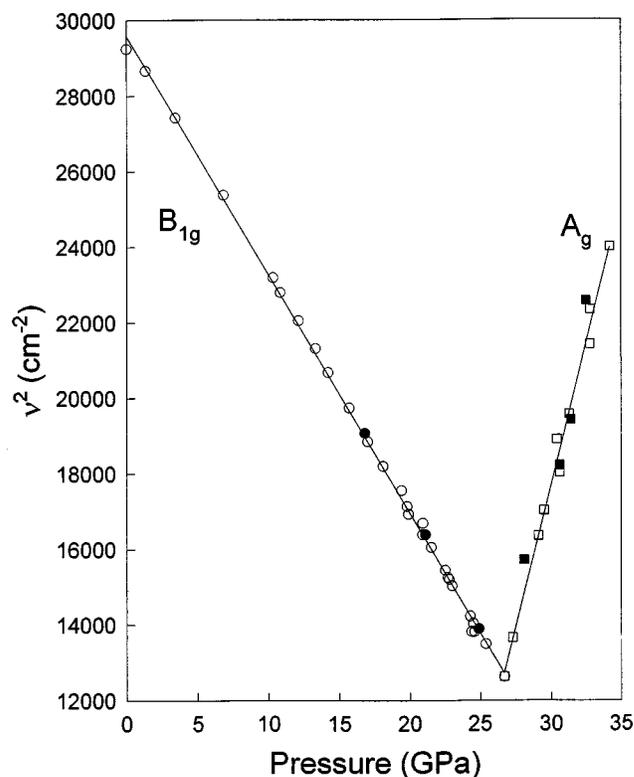


FIG. 2. Square of the  $B_{1g}$  soft-mode and corresponding  $A_g$  hard-mode frequencies in  $\text{GeO}_2$  as a function of pressure. Legend as for Fig. 1.

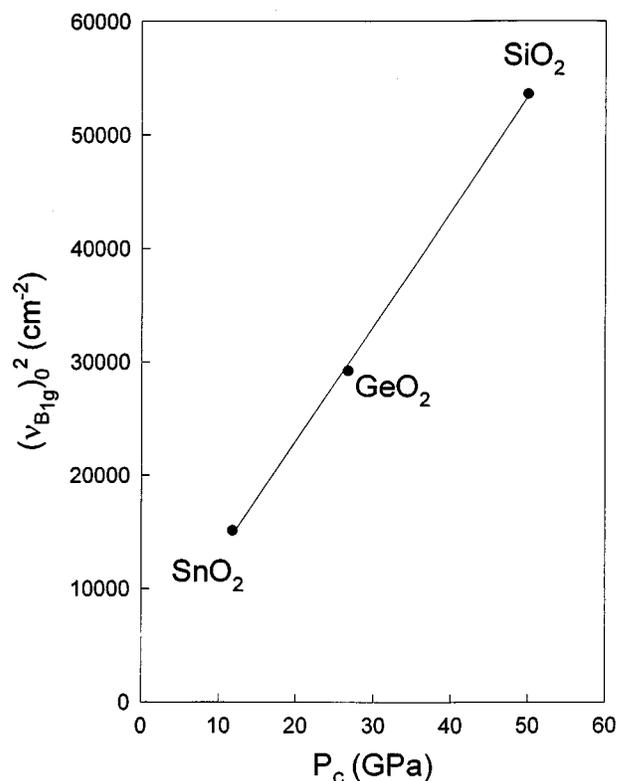


FIG. 3. Square of the  $B_{1g}$  soft-mode frequency at ambient pressure as a function of critical pressure for rutile-type  $\text{SiO}_2$ ,  $\text{GeO}_2$ , and  $\text{SnO}_2$ . Note:  $P_c$  was obtained from Raman spectroscopic measurements for  $\text{SiO}_2$  and  $\text{GeO}_2$  and from x-ray diffraction for  $\text{SnO}_2$ .

quency. This implies the softening of a transverse acoustic mode. Similarly, at the well-known, second-order,  $\text{CaCl}_2$ -type to rutile-type transition in  $\text{CaCl}_2$  at high temperature, the optic-mode softening was also incomplete and a significant difference between  $T_c$  and  $T_p$  was found.<sup>15</sup> It can be noted that a rather unusual ratio of the slopes,  $d\nu^2/dT$  below and above  $T_c$  of  $-6.5$ , was obtained. The present results indicate that  $\text{GeO}_2$  undergoes a second-order, ferroelastic phase transition at  $26.7(2)$  GPa and the behavior of this compound mirrors that of silica.

Rutile-type to  $\text{CaCl}_2$ -type phase transitions are observed in the homologous group 14 dioxides  $\text{SiO}_2$  and  $\text{SnO}_2$ . The critical pressure in silica obtained under the conditions closest to hydrostatic is 50 GPa using neon as a pressure-transmitting medium in a Raman spectroscopic study.<sup>3</sup>  $\text{SnO}_2$  was found from x-ray diffraction measurements to transform at 11.8 GPa under hydrostatic conditions.<sup>10</sup> The  $B_{1g}$  soft mode is observed at  $231.6\text{ cm}^{-1}$  in  $\text{SiO}_2$  (Ref. 3) and  $123\text{ cm}^{-1}$  in  $\text{SnO}_2$  (Ref. 16) at ambient pressure. The following relationship is obtained from soft-mode theory:  $\nu^2 \propto |P - P_c|$ . If we select ambient pressure in order to compare these dioxides, the experimental results on the homologous series  $\text{SiO}_2$ ,  $\text{GeO}_2$ , and  $\text{SnO}_2$  indicate that  $(\nu_{B_{1g}})_0^2 \propto |P_0 - P_c|$ , which reduces to  $(\nu_{B_{1g}})_0^2 \propto P_c$  (Fig. 3). There is thus systematic behavior in this series of homologous compounds, which undergo a second-order phase transition driven by a soft mode, with the critical pressure being pro-

portional to the square of the soft-mode frequency at  $P=0$ . As the soft modes do not go to zero at the critical pressure, systematic behavior in  $k_p$ ,  $k_f$ ,  $P_p$ , and  $P_f$  is also implied, which is due to the similarities in the structural and vibrational properties of these dioxides. The present result also supports the validity of the phase transition pressure of 50 GPa obtained for  $\text{SiO}_2$  from Raman scattering measurements using neon as a pressure-transmitting medium.<sup>3</sup>

#### IV. CONCLUSIONS

The present Raman spectroscopic investigation of  $\text{GeO}_2$  up to  $34.2(2)$  GPa indicates that a second-order, proper ferroelastic transition occurs at  $26.7(2)$  GPa. The square of the frequencies of the  $B_{1g}$  soft mode and the corresponding  $A_g$  hard mode varies linearly with pressure over the entire pressure range that they are observed as predicted by the soft-mode theory of second-order phase transitions. A systematic relationship between  $(\nu_{B_{1g}})_0^2$  and  $P_c$  is identified for  $\text{SiO}_2$ ,  $\text{GeO}_2$ , and  $\text{SnO}_2$ . This result indicates that the behavior of stishovite at high pressure closely mirrors that of its heavier homologues  $\text{GeO}_2$  and  $\text{SnO}_2$ .

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