Pressure-Induced Crossover between Diffusive and Displacive Mechanisms of Phase Transitions in Single-Crystalline α-GeO$_2$

V. V. Brazhkin, A. G. Lyapin,* R. N. Voloshin, S. V. Popova, E. V. Tat'yanin, and N. F. Borovikov
Institute for High Pressure Physics, Russian Academy of Sciences, Troitsk, Moscow region, 142190, Russia

S. C. Bayliss and A. V. Sapelkin
Department of Chemistry, School of Applied Sciences, De Montfort University, The Gateway, Leicester, LE1 9BH, United Kingdom

(Received 15 August 2002; published 11 April 2003)

We present the first example of the phase transition occurring via the different kinetic mechanisms, displacive or diffusive, competing with each other in quartzlike α-GeO$_2$ single crystals. Upon room-pressure heating, α-GeO$_2$ transforms to the rutile-type phase (the $\alpha \rightarrow r$ transition) via the diffusive mechanism. With increase of the treatment pressure the diffusive mode of the temperature-induced $\alpha \rightarrow r$ transition is substituted at ≈ 4 GPa by a displacivelike mode, and then at ≈ 6 GPa the transition type changes from the $\alpha \rightarrow r$ sequence to a displacive martensiticlike transition to a distorted rutilelike phase ($\alpha \rightarrow r'$. A crossover between diffusive and displacive transition modes suggests a new way to control the meso- and nanometer-scale morphology of high-pressure phases.

DOI: 10.1103/PhysRevLett.90.145503 PACS numbers: 61.50.Ks, 64.60.My, 81.30.Kf

The commonly accepted classification of first-order phase transitions in solids is based on the concepts of diffusive and martensitic or, more generally, displacive mechanisms [1,2]. The first type of transition takes place, at sufficiently high temperatures, as a diffusion-driven nucleation and crystal growth, whereas the latter corresponds to cooperative atomic rearrangement due to elastic or phonon softening. However, no information on phase transitions that take place via both of the mechanisms, competing with each other in the same substance, has been as yet available.

At room and low pressures, martensitic transitions are typically accompanied by small volume changes that ensure coherent atomic displacements throughout large domains, on a scale much larger than the lattice constants [1,2]. However, under pressure the situation can be quite a different one, since many crystals undergo polymorphic transitions with a considerable volume change, typically from 5% to 50% [3]. At low temperatures, when diffusion freezes, the phase transition can occur only via displacive rearrangement, but elastic stresses, arising due to the large volume jump, prevent any coherent martensitic transition in large crystal domains. On the contrary, at high temperatures near T_m, the diffusive mechanism is kinetically efficient. Thus, it would be natural to expect for many high-pressure transformations, first, a competition between different transition mechanisms and, second, the existence of complicated mechanisms comprising both displacive and diffusive features. Solid-state amorphization under pressure is an example of a low-temperature transformation with the nanometer-scale displacive origin; however, it cannot be reduced to an ordinary martensitic transition [4,5].

Information on the mechanisms of high-pressure transitions over wide temperature intervals is very scanty. We present the first systematic study of the crossover competition between different transition mechanisms in the same substance, here α-GeO$_2$. α-GeO$_2$ initially attracted attention as the closest structural isotype of silica, and it has a simple pressure-temperature phase diagram (Fig. 1) consisting of two solid phases at pressures less than 10 GPa, α-GeO$_2$ (the hexagonal α-quartz-type structure, space group $P3_121$, $a = 0.4987$ nm and $c = 0.5652$ nm, $Z = 2$, $\rho = 4.28$ g/cm^3) and r-GeO$_2$ (the tetragonal rutile-type structure, space group $P4_2/mnm$, $a = 0.4395$ nm and $c = 0.2860$ nm, $Z = 2$, $\rho = 6.28$ g/cm^3) [3]. Unlike SiO$_2$, the stable GeO$_2$ phase at ambient conditions is the rutile-type r phase similar to stishovite SiO$_2$. α-GeO$_2$ phase is stable at high temperatures (Fig. 1), although the α phase can be retained at ambient conditions in the metastable state. This provides an uncommon opportunity to compare the temperature- and pressure-induced modes of transformation from the open packed α-quartz structure of GeO$_2$ to denser modifications.

The $\alpha \rightarrow r$ transition at room pressure occurs upon heating via the typical diffusive mechanism [Fig. 2(a)] and is accompanied by a large negative volume jump $\sim$50% [5]. The diffusion-driven kinetics of the $\alpha \rightarrow r$ transition was studied under pressure at 2 GPa [9]. When compressed at room temperature, polycrystalline α-GeO$_2$ exhibits solid-state amorphization, the coordination of Ge atoms being changed from fourfold to sixfold [10,11]. Recently [12–14], it has been shown that crystalline α-GeO$_2$ reveals upon room-temperature compression a transition to a new r' phase [Fig. 2(b)] with a distorted rutile-type $P2_1/c$ monoclinic structure [Fig. 3(a); at ambient conditions $a = 0.815$ nm, $b = 0.436$ nm, $c = 0.535$ nm, $\alpha = \gamma = 90°$, and $\beta = 118°$ [13]] based on 3×2 octahedral chains [15] [Fig. 3(b)]. The lamellar morphology of the r' phase [Fig. 3(b)] and crystallographic orientational relations between the parent and

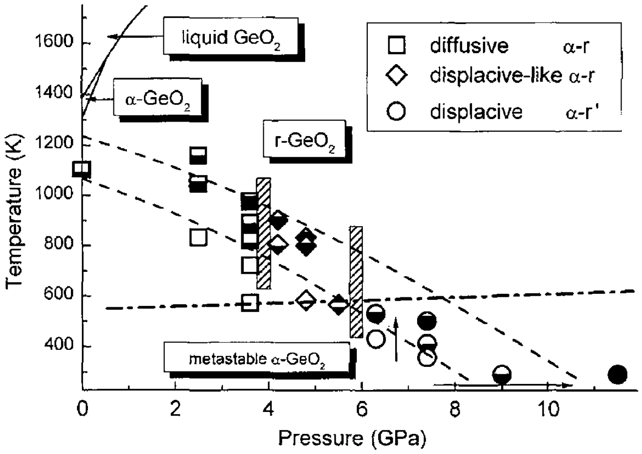

FIG. 1. Transitional diagram for metastable α-GeO$_2$ plotted on the equilibrium phase diagram of germanium dioxide. The equilibrium phase diagram was reconstructed from Refs. [3,6–8]. The symbols correspond to the points of pressure-temperature treatment of α-GeO$_2$ samples. They display the results of the scanning electron microscopy (SEM), transmission electron microscopy (TEM), and x-ray diffraction studies of the samples quenched to ambient conditions, which allowed us to identify the diffusive $\alpha \rightarrow r$ (squares), displacivelike $\alpha \rightarrow r$ (diamonds), and displacive $\alpha \rightarrow r'$ (circles) transitions. The degree of symbol filling corresponds to the share of the high-pressure r or r' phase, estimated on the basis of x-ray diffraction. The dashed lines approximate the region of pressure-temperature–induced transitions from metastable α-GeO$_2$, serving as its kinetic stability boundary, and, in turn, the vertical bars separate the pressure intervals with different transition modes. The dash-dotted line approximates the region of $r' \rightarrow r$ recrystallization, obtained in the separate quenching experiments.

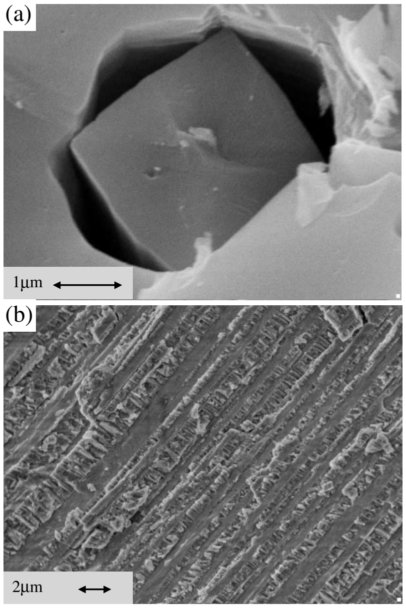

FIG. 2. SEM photographs of the r-GeO$_2$ crystallite grown by diffusion in the α-GeO$_2$ surroundings upon room-pressure heating to 1100 K (a) and of the r'-GeO$_2$ phase obtained via the displacive mechanism upon room-temperature compression of α-GeO$_2$ to 11.5 GPa (b).

product phases [Fig. 4(c)] [13] directly point to the displacive (martensiticlike) nature of the $\alpha \rightarrow r'$ transition. According to our measurements, r'-GeO$_2$ gradually transforms to the stable r-GeO$_2$ [Figs. 4(a) and 4(b)] at about 500 to 700 K, when it is heated at both ambient and high pressures.

The totally different mechanisms of transitions in heated and compressed α-GeO$_2$ (Fig. 3) to the similarly packed structures with nearly the same densities make it imperative to study the crossover between these two transition modes. In the present work we studied in detail the transitions from single-crystalline α-GeO$_2$ to more stable modifications upon heating at various pressures. Large ($3 \times 3 \times 1$ mm^3) single crystals of GeO$_2$ were grown by the hydrothermal method on SiO$_2$ substrates. Pressures up to 12 GPa were generated in the toroid chambers using both hydrostatic (the 4:1 methanol-ethanol mixture, only at room temperature) and quasihydrostatic (NaCl and hexagonal BN) pressure-transmitting media. After 1 min pressure-temperature treatments the samples were quenched to ambient conditions. Subsequently, the structure of phases obtained was investigated by x-ray and electron diffraction, and the morphology was examined by SEM.

From TEM studies, we established the crystallographic orientational relations between the initial quartzlike α-GeO$_2$ and final r' phase obtained at compression, namely, $(100)^{\alpha}$ nearly parallel to $(100)^{r'}$ and $(\bar{1}20)^{\alpha}$ nearly parallel to $(010)^{r'}$. The $\alpha \rightarrow r'$ transition seems

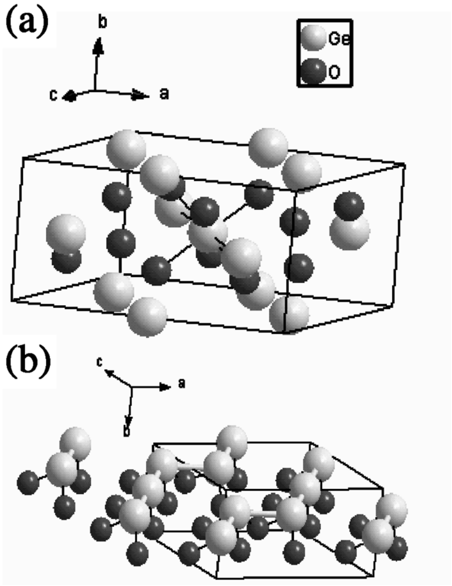

FIG. 3. Elementary cell of the distorted rutilelike monoclinic r' phase (a) and layer packing of germanium atoms over oxygen layers in the r' phase which is 3×2 octahedrally chained (b).

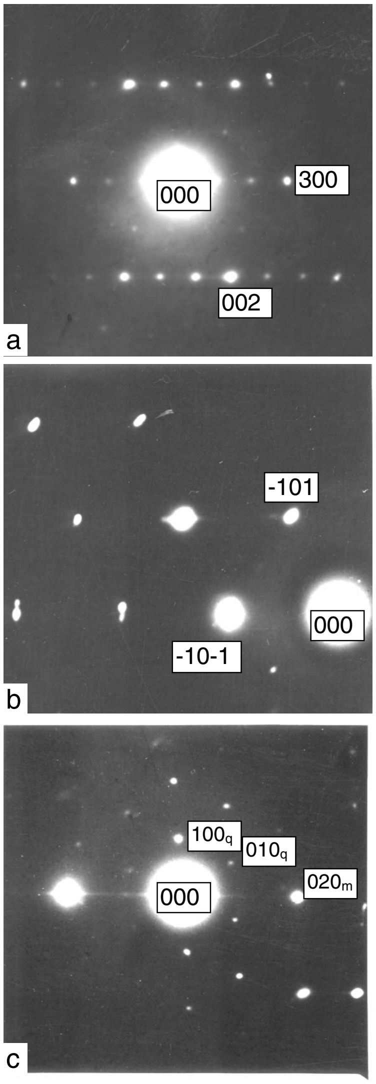

FIG. 4. Electron diffraction pattern (a) from the single crystallite of the monoclinic phase of GeO_2 for the 010 zone (reciprocal lattice plane), (b) from rutile phase (010 zone of rutile structure) obtained upon annealing of the same crystallite as in (a), and (c) from the partly transformed area revealing both initial α quartz (001 zone, index "q" for reflections) and new monoclinic modification [the reflections (index "m") for the $\bar{1}07$ and 001 zones can be observed] related transitionally and crystallographically to one another.

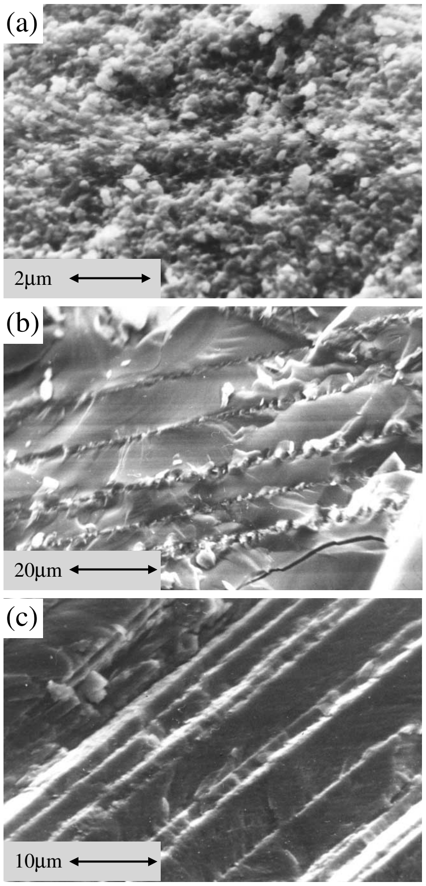

FIG. 5. SEM photographs of samples quenched upon pressure-temperature treatment. Image (a) illustrates diffusive-grown r-GeO_2 grains (the sample treated at 2.6 GPa and 1170 K); (b) nucleated layers of the r phase in the α-GeO_2 surroundings (5.5 GPa and 570 K); (c) the final stage of growth for the layered r phase (4.8 GPa and 800 K).

to be connected to a displacive crystallographic relation between the r' phase and the tetrahedrally networked α-quartz structure. For the compressed α-quartz structure theoretical calculations [16] showed a dynamic instability at $(1/3, 1/3, 0)$ in the Brillouin zone, which suggests a $3 \times 3 \times 1$ supercell in the parent phase for the martensiticlike rearrangement.

The crossover between different mechanisms of temperature-induced transitions in α-GeO_2 is clearly illustrated by the SEM morphology of samples quenched after transitions at various pressures (Fig. 5). The results of the morphology study and x-ray diffraction (see examples in Fig. 6) for different samples are mapped on the phase diagram (Fig. 1). First, these data provide the information on the low-temperature kinetic stability region for α-GeO_2, where it is conserved as a metastable phase, and, second, indicate three pressure intervals of different transition modes (Fig. 1). At pressure $P < 4$ GPa the morphology of samples displays the diffusive mechanism of the $\alpha \rightarrow r$ transition, although under pressure the average size of r-GeO_2 crystallites [Fig. 5(a)] is smaller than that for crystallites growing at ambient pressure [Fig. 2(a)]. Starting from 3.5–4 GPa, the $\alpha \rightarrow r$ transition mechanism becomes at least partially displacive, which is illustrated by the lamellar morphology for the r-phase nucleation and for the final stage of the transition [Figs. 5(b) and 5(c)]. The diffraction data are indicative of a change from the $\alpha \rightarrow r$ to $\alpha \rightarrow r'$ transition mode near 6 GPa, the $\alpha \rightarrow r'$ transition mechanism being displacive as argued on the basis of the TEM and SEM data.

The observed sequence of transitions can be interpreted as follows. At high temperatures, $T \sim 900$ to 1200 K, and low pressures, the transition in α-GeO_2 is efficiently accomplished through diffusion. With temperature decrease, $T \sim 600$ to 900 K (this corresponds

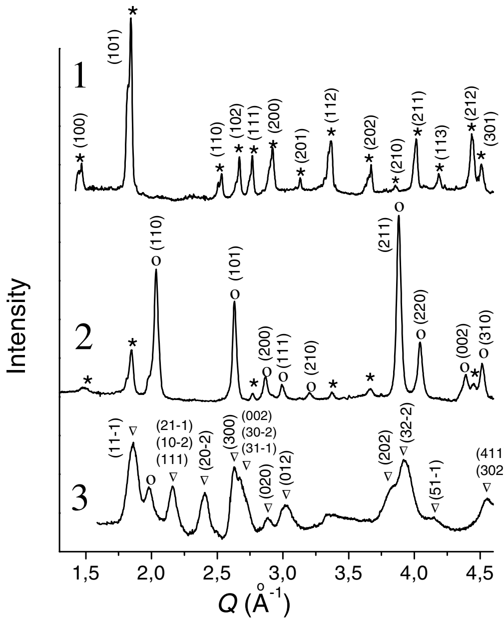

FIG. 6. The x-ray diffraction patterns obtained from GeO_2 samples upon pressure-temperature treatment at 4.8 GPa and 580 K (curve 1), 2.6 GPa and 1050 K (curve 2), and 11.5 GPa and 290 K (curve 3). The patterns reveal the α phase (reflections of which are marked by asterisks), the r phase (circles) with admixture of the α phase, and the r' phase (triangles) with admixture of the r phase, respectively. The indexes correspond to the dominant phases.

to $0.3T_m$–$0.45T_m$), diffusion becomes slower, and the displacive mechanism seems to trigger the onset of transition, but the contribution of diffusion remains still significant, since the transition temperatures are above the line of the $r' \rightarrow r$ transition (Fig. 1). At $T \sim 300$ to 600 K (0.15–0.3 of T_m), diffusion becomes mainly frozen, so the martensiticlike $\alpha \rightarrow r'$ transition occurs instead of the $\alpha \rightarrow r$ one.

Similar crossovers between equilibrium and nonequilibrium modes of high-pressure transformations were previously found for H_2O ice [17], Si, and Ge [18]. A crossover between the thermodynamic and nonequilibrium dynamic scenarios should be also expected for carbon and BN [19]: here graphite or hexagonal BN transform to the lonsdaleite or wurtzite structures through the martensitic mechanism upon compression, and to the diamond or sphalerite modifications via diffusion upon heating. Summarizing, it would be reasonable to believe that the observed change of transition kinetics should be a rather common phenomenon for the high-pressure polymorphism of solids.

From the practical point of view, the crossover between different mechanisms can serve as efficient tools for governing the morphology of final high-pressure phases, changing, in particular, the grain size or shape and phase texture [compare, e.g., Figs. 2(a) and 5(a) or Figs. 2(b) and 5(c)]. Therefore, the control of the morphology for many high-pressure phases, such as diamond and boron nitride, seems very promising for high-pressure technology, e.g., in producing new nano- and microstructured materials. In turn, the morphology of many geological and space specimens may serve as a signature of the formation conditions.

The authors are grateful to D.V. Balitskii for the α-GeO_2 single crystals, to I. Fletcher for experimental assistance in SEM experiments, and to S.M. Stishov, P. McMillan, J. Haines, and M.V. Kondrin for helpful discussions. The work was supported by the Russian Foundation for Basic Research and by the UK Royal Society.

---

*Electronic address: alyapin@hppi.troitsk.ru

[1] J.W. Christian, *The Theory of Transformations in Metals and Alloys* (Pergamon, Oxford, 1975), 2nd ed., Pt. 1.
[2] A.G. Khachaturyan, *The Theory of Structural Transformation in Solids* (Wiley, New York, 1983).
[3] E. Yu. Tonkov, *High Pressure Phase Transformations: A Handbook* (Gordon and Breach, Philadelphia, 1992), Vols. 1–2.
[4] K.J. Kingma, C. Meade, R.J. Hemley, H.-K. Mao, and D.R. Veblen, Science **259**, 666 (1993).
[5] V.V. Brazhkin and A.G. Lyapin, High Press. Res. **15**, 9 (1996).
[6] P. Richet, Phys. Chem. Miner. **17**, 79 (1990).
[7] M. Madon, Ph. Gillet, Ch. Julien, and G.D. Price, Phys. Chem. Miner. **18**, 7 (1991).
[8] I. Jackson, Phys. Earth Planet. Interiors **13**, 218 (1976).
[9] N.S. Brar and H.H. Schloessin, High Temp. High Pressures **13**, 313 (1981).
[10] J.P. Itie, A. Polian, G. Calas, J. Petiau, A. Fontaine, and H. Tolentino, Phys. Rev. Lett. **63**, 398 (1989).
[11] N. Suresh, G. Jyoti, S.C. Gupta, S.K. Sikka, and S.C. Sabharwal, J. Appl. Phys. **76**, 1530 (1994).
[12] V.V. Brazhkin, E.V. Tat'yanin, A.G. Lyapin, S.V. Popova, O.B. Tsiok, and D.V. Balitskii, in *Science and Technology of High-Pressure: Proceedings of the International Conference on High-Pressure Science and Technology (AIRAPT-17), Honolulu, 1999*, edited by M.H. Manghnani, W.J. Nellis, and Malcolm F. Nicol (Universities Press, Hyderabad, India, 2000), p. 861.
[13] V.V. Brazhkin, Ye. V. Tat'yanin, A.G. Lyapin, S.V. Popova, O.B. Tsiok, and D.V. Balitskii, Pis'ma Zh. Eksp. Teor. Fiz. **71**, 424 (2000) [JETP Lett. **71**, 293 (2000)].
[14] J. Haines, J.M. Leger, and C. Chateau, Phys. Rev. B **61**, 8701 (2000).
[15] D.M. Teter, R.J. Hemley, G. Kresse, and J. Hafner, Phys. Rev. Lett. **80**, 2145 (1998).
[16] G.W. Watson and S.C. Parker, Phys. Rev. B **52**, 13 306 (1995).
[17] E.L. Gromnitskaya, O.V. Stal'gorova, V.V. Brazhkin, and A.G. Lyapin, Phys. Rev. B **64**, 094205 (2001).
[18] V.V. Brazhkin, A.G. Lyapin, S.V. Popova, and R.N. Voloshin, Phys. Rev. B **51**, 7549 (1995).
[19] V.F. Britun and A.V. Kurdyumov, Superhard Materials (Kiev) No. 2, 3–14 (2001).