Pressure-Induced Transformations of the Low-Cristobalite Phase of $GaPO_4$

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(Received 6 May 1994)

Tsuneyuki *et al.* predicted a new high pressure phase of silica using a molecular dynamics calculation; this calculation was novel in that it predicted a new crystal structure using only a knowledge of the chemical composition [Nature (London) **339**, 209 (1989)]. We report that the low-cristobalite phase of $GaPO_4$ undergoes a pressure-induced transition at 15.9 GPa to this novel phase, which contains tetrahedral and octahedral coordination shells of oxygen atoms around the phosphorus and gallium atoms, respectively. This pressure-induced coordination change in $GaPO_4$ verifies a mechanism proposed for the tetrahedral-to-octahedral coordination change in minerals that occurs in the transition zone between the upper and lower mantle.

PACS numbers: 62.50.+p, 61.10.−i, 62.40.+i, 64.70.Dv

One of the goals of condensed matter theory is to predict crystal structures from first principles with a knowledge of only the chemical composition [1–3]. Tsuneyuki *et al.* recently predicted a new high pressure phase of silica using a molecular dynamics calculation [1]. In this Letter we investigate the ambient temperature, high pressure behavior of the low-cristobalite phase of gallium phosphate, designated c-$GaPO_4$. $GaPO_4$ is one of many isostructural analogs of silica which can be produced by substituting M^{3+} and X^{5+} ions for Si^{4+}; these analogs mimic the phase behavior of silica very closely [4].

A modified Merrill-Bassett style diamond anvil cell was used to generate high pressures. Inconel gaskets, with a 0.25–0.3 mm hole, were used to contain the samples and 4:1 methanol/ethanol was used as the pressure transmitting fluid. Upon compression c-$GaPO_4$ undergoes a continuous phase transition. It is clear at 15.9 GPa that a new diffraction pattern has developed indicative of the formation of a new crystalline phase (hp-$GaPO_4$) (see Fig. 1). This phase is stable to the highest pressure reached, namely, 22.0 GPa. Upon release of the pressure the hp-$GaPO_4$ phase is retained although the major diffraction feature of the original c-$GaPO_4$ returns weakly indicating the displacive nature of the transformation.

The diffraction pattern of hp-$GaPO_4$ does not resemble that of any known SiO_2 structure. In order to index the diffraction pattern of c-$GaPO_4$ we measured it at high pressure using angle-dispersive x-ray methods [5] (see Fig. 2). Its diffraction pattern closely resembles that of a new crystal structure of SiO_2 predicted by Tsuneyuki *et al.* from a first principles calculation [1,6]. This structure, hp-SiO_2, was predicted to form when cristobalite was compressed to 16.5 GPa at ambient temperature. The hp-SiO_2 phase that formed belongs to the orthorhombic, *Cmcm* space group and contains equal numbers of four- and six-coordinated silicon atoms (see Fig. 3). The reported lattice constants are $a = 5.20$ Å, $b = 7.44$ Å, and $c = 5.58$ Å [1]. Because of the differences in both atomic size and bonding between gallium and silicon atoms, we would expect small changes in the unit cell parameters as well as slight shifts in the peak positions for the hp-$GaPO_4$ structure from that of the hp-SiO_2 structure of Tsuneyuki *et al.* Although precise unit cell parameters cannot be calculated from the hp-$GaPO_4$ diffraction pattern obtained, the best fit of our data occurs for $a = 5.12$ Å, $b = 7.31$, and $c = 5.92$ Å. More precise diffraction techniques are required to determine the minor differences in bond angles, etc., between hp-$GaPO_4$ and the phase predicted by Tsuneyuki *et al.*

We would expect the calculation of Tsuneyuki *et al.* for SiO_2 to apply to the silica analog c-$GaPO_4$ [1]. Their calculation is based on an ionic two-body potential; the reason the silica analogs form is that their average ionicity

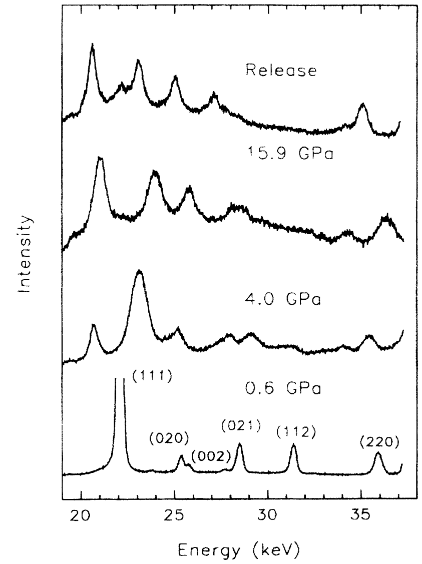

FIG. 1. The change with pressure of the x-ray diffraction pattern of c-$GaPO_4$. The diffraction patterns were measured at CHESS (the Cornell High Energy Synchrotron Source) using a Ge solid state detector [27]. *Ed*, determinated with a piece of gold foil, was 88.36 keV Å.

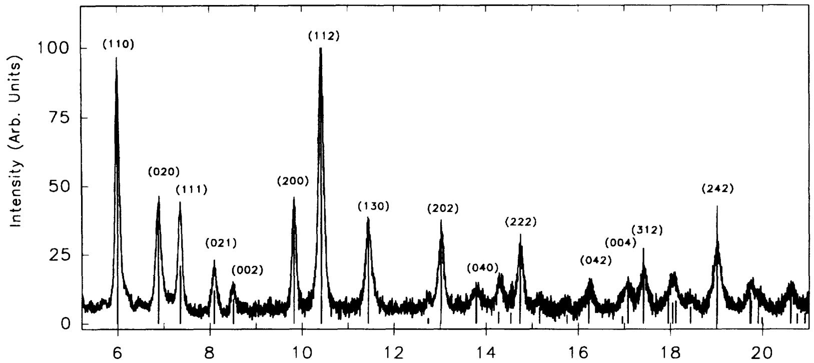

FIG. 2. Angle-dispersive x-ray diffraction (ADXD) pattern of c-GaPO$_4$ at a pressure of ~17.5 GPa. The x-ray diffraction pattern of the high pressure phase reported by Tsuneyuki *et al.* is shown underneath the experimental diffraction pattern [1]. The pattern was calculated with gallium atoms on the 4(a) sites, phosphorous atoms on the 4(c) sites, and the lattice constants reported in the text. (If the sites of the phosphorous and gallium atoms are switched the intensities of the calculated diffraction pattern are significantly different than those observed experimentally, thus showing that it is the gallium atom that becomes six coordinated.) The ADXD measurements were performed on the X17-B1 beam line at NSLS using 0.439 Å wavelength radiation. HR-IIIN Fuji image plates were placed ~210 mm from the diamond cell. This cell is similar to the one described above, but was fitted with a rectangular pyramidal slot with included angles of 60° and 22°. The sample to plate distance was calibrated using the NIST α-Al$_2$O$_3$ (SRM676) standard. The two-dimensional diffraction patterns on the plates were integrated using the methods described by Nelmes and co-workers [5].

is close to silica, although the ionicity of an individual M-O or X-O bond may be different from an Si-O bond [7]. Although the two-body potential of Tsuneyuki *et al.* has been successfully used to study the known polymorphs of silica, it does not account for both ionic and covalent elements of the Si-O bond [8]. One drawback of the two-body potential is that it does not reproduce the covalency of the Si-O bond, and therefore the pressure response, correctly [9]. In fact, Tsuchida and Yagi found experimentally that cristobalite did not transform into the hp-SiO$_2$ phase, but instead transformed to an unknown phase at 10.0 GPa [10]. Chelikowsky, King, and Glinnemann modified the potential of Tsuneyuki *et al.* to include bond-bending forces. Their results showed that the dominating factor in the pressure response of SiO$_2$ was the rigidity of the Si-O-Si bond [9]. Our results suggest, then, that bond-bending forces are less important in GaPO$_4$ than in SiO$_2$.

We have also measured the effect of pressure on the Raman spectrum of c-GaPO$_4$ (see Fig. 4). The Raman spectrum of c-GaPO$_4$ is dominated at ambient pressure by a peak at 395 cm^{-1}, while at the highest pressures the central feature is located at 572 cm^{-1}. The 395 cm^{-1} vibration in isomorphic cristobalite has been assigned to Si-O and Si-O-Si stretching of the SiO$_4$ tetrahedra [11]. We suspect that the 572 cm^{-1} peak is associated with the vibrations of six-coordinated MO$_6$ units. In isomorphic and polymorphic forms of silica exhibiting sixfold coordination around the silicon atoms, the characteristic Raman peaks appear ~250 cm^{-1} higher than the central feature in their tetrahedrally coordinated counterparts. Two examples are four-coordinated α-quartz versus six-coordinated stishovite, and the quartz form of GeO$_2$ versus its octahedral rutile polymorph [12]. In addition, the Raman features of octahedrally coordinated rutile structures appear between 600 and 800 cm^{-1} [12,13]. The results we see for the GaPO$_4$ sample are similar, giving further evidence that a pressure-induced coordination change is responsible for the phase transformation. The Raman scattering from the sample after the pressure is released is a superposition of c-GaPO$_4$ and hp-GaPO$_4$. These Raman results are consistent with the x-ray diffraction measurements: c-GaPO$_4$ undergoes a partially reversible phase transformation to an octahedrally coordinated phase. The fourfold-to-sixfold coordination change is reminiscent of that calculated by Tse and Klug for the pressure-induced amorphization of the silica analog AlPO$_4$ [14]. This observation of a coordination change with pressure has significant implications for the mechanism of pressure-induced amorphizations [15,16].

Several researchers have suggested that the amorphizations of silica polymorphs occur because of a mechanical instability driven by a fourfold to sixfold coordination change around the cations [17,18]. This work provides additional evidence to support this claim as c-GaPO$_4$ undergoes a continuous phase transition, while isostructural c-AlPO$_4$ (Robeson and Hammack, unpublished) amorphizes. The reason for this may lie in the differences in the M-O-X bond angles among low-cristobalite isomorphs: Si-O-Si = 150° in cristobalite, Al-O-P = 143° in c-AlPO$_4$, and Ga-O-P = 135° in c-GaPO$_4$ [19]. The M-O-X bond angle in c-GaPO$_4$ is considerably less than the other two isomorphs. Hazen and Finger have noted that the pressure-induced amorphization of α-quartz occurs when there is a dramatic reduction in the Si-O-Si bond angle [20,21]. The bond angle strain is so severe that amorphization occurs. Because of its already small bond angles, c-GaPO$_4$ may be able to accommodate the

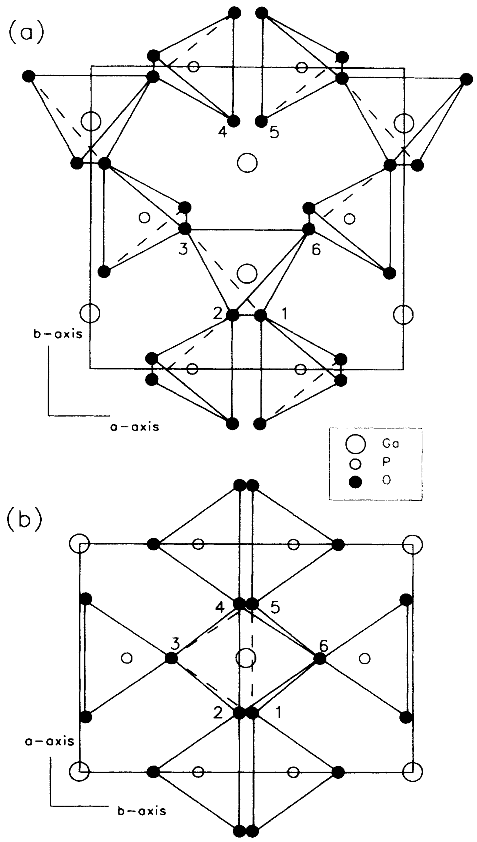

FIG. 3. (a) The unit cell of c-GaPO$_4$. The structure contains only four-coordinated gallium and phosphorous atoms [19]. (b) The unit cell of the high pressure phase predicted by Tsuneyuki *et al.* The gallium atoms are now six coordinated, while the phosphorus atoms stay four coordinated. Note that the c axes of the cells are collinear, although inverted so that the a and b axes interchange. The formation of the octahedrally coordinated gallium atoms is consistent with the transformation proposed by Stolper and Ahrens: The rings of GaO$_4$ and PO$_4$ tetrahedra shown in (a) rotate and bend until (b) two oxygen atoms from PO$_4$ tetrahedra are added to the gallium coordination shell.

bond angle strain required to form the hp-GaPO$_4$ phase, whereas c-AlPO$_4$ and cristobalite cannot.

The phase transformation of c-GaPO$_4$ also has geophysical significance as minerals containing six-coordinated silicon atoms are thought to make up the bulk of the Earth's interior [22,23]. Of interest is how these coordination changes occur in the transition zone between the upper and lower mantle and how these changes may affect the seismic response of this region [22,24,25]. Stolper and Ahrens have proposed a model for these transformations in silicate glasses based on the folding up of rings or chains of tetrahedra [26] (see Fig. 3). They suggest that the transformations are displacive rather than thermally activated allowing them to occur at low temperatures. The mechanism of the four-to-sixfold coordination change observed in the molecular dynamics study of Tsuneyuki *et al.* is that proposed by Stolper and Ahrens [1,6]. Thus our experimental observations add some support to their ideas as the GaPO$_4$ phase transformation is a displacive one occurring slowly with pressure at room temperature.

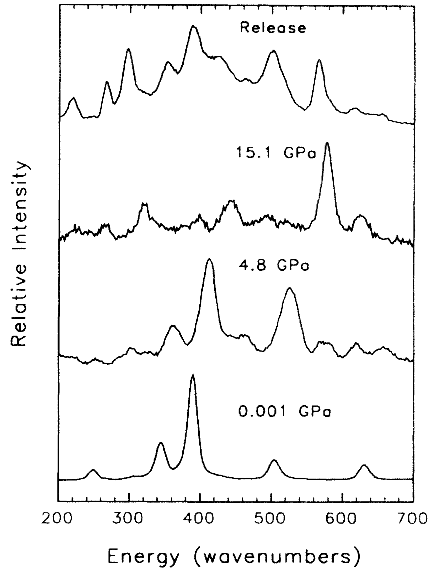

FIG. 4. Raman scattering from c-GaPO$_4$ at pressures of 0.001, 4.8, and 15.1 GPa and upon release of the pressure. The 514.5 nm line of a Spectra-Physics model 2020-5W argon laser was used for the excitation of Raman effects; the scatted light was gathered at 160° to the incident exciting beam by a Spex 1403 double monochromator. The ruby calibration method was used to monitor the pressure in the diamond anvil cell [28].

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy. The authors thank Dr. K. Brister and the staff at CHESS for their assistance with the high pressure EDXD experiments, Dr. Mark Rivers at the National Synchrotron Light Source for assistance with the ADXD measurements, K. M. Meyer and P. Klabnik for technical assistance, and G. C. Serghiou for critical comments. W. S. H. thanks C. S. Harris for assistance.

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