

## High-pressure behavior in $\alpha$ -AlPO<sub>4</sub>: Amorphization and the memory-glass effect

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Previous studies have shown that  $\alpha$ -AlPO<sub>4</sub> (berlinite) undergoes a crystalline to amorphous transition at  $15 \pm 3$  GPa. Moreover, it has been proposed that the high-pressure amorphous phase recrystallizes upon decompression, conserving both the structure and the crystallographic orientation of the original crystal. We show in this study that this so-called memory-glass effect is instead due to a polymorphic crystal-crystal phase transition occurring between 14 and 15 GPa on compression. This transition is fully reversible, with a hysteresis of 6–7 GPa, when hydrostatic media are used for compression. When quasihydrostatic pressure media are used, the decompression history is more complex. The samples develop a rim of back-transformed material, but the interior of the grains remains in the high-pressure phase. On recovery, this interior consists of amorphous material, coexisting with the back-transformed  $\alpha$ -AlPO<sub>4</sub> phase. Quasihydrostatic runs above 18 GPa show evidence for amorphization during pressurization. In some highly nonhydrostatic runs, the recovered sample contains both amorphous material, and a crystalline phase of AlPO<sub>4</sub>. This could correspond to a rutile-structured phase, or to a phase with the InPO<sub>4</sub> structure, formed during decompression in the presence of shear stresses.

### I. INTRODUCTION

Since the discovery of static pressure-induced amorphization in hexagonal (Ih) H<sub>2</sub>O ice,<sup>1–3</sup> the phenomenon has been observed to occur for a range of crystal structures and chemistries, in particular for the analogous tetrahedral framework structures of the SiO<sub>2</sub> (quartz, cristobalite, and coesite) and GeO<sub>2</sub> polymorphs.<sup>4–7</sup> The nature of the low-temperature amorphization process has been the subject of numerous theoretical<sup>8–14</sup> and experimental investigations, using a range of experimental probes sensitive to different length scales: *in situ* x-ray diffraction and Raman, IR, and Brillouin spectroscopies, and high-resolution transmission electron microscopy on recovered samples.<sup>3–7,15–19</sup> All of these materials can be recovered in the amorphous state at room pressure. It is now apparent that the details of the amorphization process are sensitive to the state of stress undergone by the samples (hydrostatic versus nonhydrostatic loading), and the nature of the recovered samples depends upon the maximum pressure reached.<sup>3,4,7,18,19</sup>

It is now well established that the  $\alpha$ -quartz phase of SiO<sub>2</sub> gradually transforms to an amorphous state upon static compression at room temperature, in the pressure range 15–30 GPa.<sup>18,19</sup> This is followed by transformation to a crystalline rutilelike phase, containing octahedrally coordinated silicon, at pressures above 60 GPa.<sup>20</sup> In a single-crystal x-ray study of the transition in quartz,

Hazen *et al.*<sup>15</sup> observed irreversible broadening in the diffraction lines, which has been related to the occurrence of an elastic shear instability associated with softening of a zone-edge phonon mode.<sup>14</sup> This gives rise to a crystal-crystal phase transition which precedes, or perhaps accompanies, the amorphization process.<sup>14,18</sup> The experimental observation of this transition came before<sup>18</sup> the theoretical support.<sup>14</sup> This intermediate metastable crystalline phase reverts to  $\alpha$ -quartz upon decompression, which can explain some anomalous elastic behavior of SiO<sub>2</sub> recovered from pressures below 30 GPa.<sup>21</sup>

Pressure-induced amorphization has also been reported to occur for  $\alpha$ -AlPO<sub>4</sub> (berlinite) at  $15 \pm 3$  GPa, based on the disappearance of its x-ray-diffraction pattern.<sup>22</sup> This observation was not unexpected, because AlPO<sub>4</sub> is a close isoelectronic structural analog of SiO<sub>2</sub>.<sup>23</sup> During a prior high-pressure Raman study of  $\alpha$ -AlPO<sub>4</sub>, Jayaraman, Wood and Maines<sup>24</sup> had noticed that the Raman signal became extremely weak above 12 GPa. These workers considered the possibility that the onset of pressure-induced amorphization might explain the loss of signal, but did not pursue this interpretation because the original spectrum reappeared on pressure release, although with reduced intensity. In their study, Kruger and Jeanloz<sup>22</sup> observed that the x-ray-diffraction peaks of  $\alpha$ -AlPO<sub>4</sub> disappeared above  $15 \pm 3$  GPa, indicative of a crystalline to amorphous transition. During decompression, the diffraction peaks of the starting material all reappeared, indicating that, unlike the SiO<sub>2</sub> polymorphs, the crystal-

amorphous transition was reversible. Even more surprisingly, measurements of optical birefringence indicated that the sample recrystallized in its original crystallographic orientation. This interesting phenomenon was termed the memory-glass effect,<sup>22,26</sup> and has been studied theoretically via molecular-dynamics simulation.<sup>26</sup>

Because of the unusual nature of the high-pressure behavior of  $\alpha$ -AlPO<sub>4</sub> compared with its structural analogues  $\alpha$ -SiO<sub>2</sub> and hexagonal GeO<sub>2</sub>, and its implications for material properties, we undertook a study of the transition via Raman spectroscopy. Detailed *in situ* data were obtained in the pressure range where the x-ray-diffusion peaks and the Raman signal start to weaken, i.e., between 13 and 15 GPa, and particular care was taken to study the effects of hydrostatic versus nonhydrostatic compression environments on the high-pressure behavior. Our results clearly show that the amorphization and the memory-glass effect are instead due to a polymorphic crystal-crystal phase transition occurring on compression to between 14 and 15 GPa in a hydrostatic medium. This transition is fully reversible on decompression. This conclusion is in agreement with the results of a recent experimental Raman study on  $\alpha$ -GaPO<sub>4</sub> and  $\alpha$ -AlPO<sub>4</sub>,<sup>27,28</sup> which also shows that both compounds undergo crystal-crystal transitions. For  $\alpha$ -AlPO<sub>4</sub> no amorphization has been observed up to 32 GPa in experiments performed with argon as pressure-transmitting medium.<sup>27,28</sup> The present results are also in accord with the findings of the molecular-dynamics study by Tse and Klug.<sup>26</sup>

When quasi-hydrostatic pressure media are used, the behavior on pressurization and decompression is more complex. Our Raman spectroscopic results indicate that an analogous crystal-crystal transition occurs above 14 GPa. The high-pressure phase is retained to lower pressure on decompression, and samples decompressed from above 19 GPa indicate the presence of amorphous material formed from the metastable high-pressure crystal or  $\alpha$ -AlPO<sub>4</sub>. Amorphization may also occur above 18 GPa on pressurization in some nonhydrostatic runs.

## II. EXPERIMENTAL DETAILS

All the experiments were performed in a gas-driven piston cylinder type diamond-anvil cell equipped with low fluorescence diamonds. To examine possible effects of nonhydrostaticity, several pressure media were used: 16:4:1 methanol-ethanol-water mixtures (hydrostatic to 15 GPa and quasi-hydrostatic to 20 GPa), 4:1 methanol-ethanol (hydrostatic to 10 GPa), and KBr (quasi-hydrostatic to 25 GPa). The samples were fragments chipped from single crystals, grown by a hydrothermal technique.<sup>29</sup> These chips, with sizes ranging from 50 to 120  $\mu$ m in their longest dimension and initial thicknesses between 20 and 50  $\mu$ m, were loaded in 150  $\mu$ m holes drilled in preindented stainless-steel gaskets. Pressure was measured with the ruby fluorescence technique.<sup>25</sup> The pressure gradient was measured by recording fluorescence spectra from ruby grains at several points within the cell, and never exceeded 1–2 GPa at 20 GPa in the quasi-hydrostatic experiments. Care was taken that the sample never bridged the diamond anvils. Unpolarized Raman spectra

were obtained with a XY Dilor Raman spectrometer equipped with a charge-coupled-device detector. 1800 groove/mm gratings were used and the spectra were collected in a backscattering geometry through a long working distance Mitutoyo microscope objective. Raman scattering was excited with the 514.5 or 488 nm lines of an argon-ion laser.

## III. EXPERIMENTAL RESULTS

$\alpha$ -AlPO<sub>4</sub> is isomorphous to  $\alpha$ -SiO<sub>2</sub> quartz, but the doubling of the unit cell along the *c* axis (due to the alternance of AlO<sub>4</sub> and PO<sub>4</sub> tetrahedra) results in the appearance of additional peaks in the Raman spectrum compared with quartz.<sup>23,24,30</sup> Because of the similarity in crystal structures, and in atomic masses and interatomic force fields, the Raman peaks of  $\alpha$ -AlPO<sub>4</sub> can be easily correlated with those of  $\alpha$ -SiO<sub>2</sub>.<sup>23,24,30</sup>

Between room pressure and 12 GPa, in runs with alcohol-water mix, the changes in the Raman spectrum of  $\alpha$ -AlPO<sub>4</sub> are similar to those reported by Jayraman, Wood, and Maines<sup>24</sup> (Fig. 1). The *A*<sub>1</sub> soft mode (220 cm<sup>-1</sup> at room pressure) which drives the  $\alpha$ - $\beta$  transition in

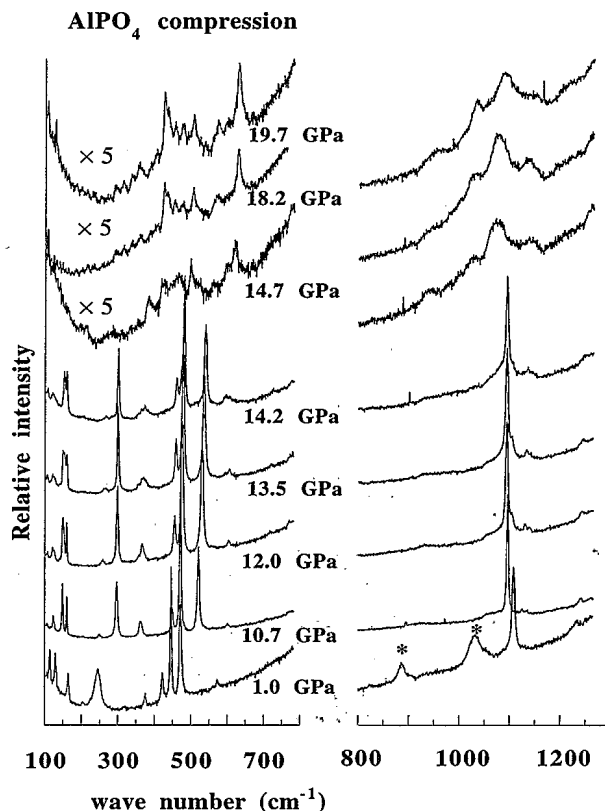


FIG. 1. High-pressure Raman spectra of  $\alpha$ -AlPO<sub>4</sub> taken during compression in hydrostatic pressure transmitting medium (16:4:1 methanol/ethanol/water mix). Between 14 and 15 GPa the samples undergo a polymorphic transition to a crystalline phase which is highly disordered. The spectrum contains too much structure to be amorphous, and the crystalline peaks become better defined as the pressure is increased. The peaks labeled by stars are due to the pressure-transmitting medium.

$\text{AlPO}_4$  has a very large positive frequency shift, as is the case in  $\text{SiO}_2$  quartz,<sup>4</sup> and the linewidth decreases rapidly with applied pressure. The pressure-induced shifts of the order modes are in close agreement with the previous measurements.<sup>24</sup> The evolution of the Raman modes with pressure (frequency shifts and bandwidths) up to 12–13 GPa was found to be nearly independent of the nature of the pressure-transmitting medium used, although some shear-induced TO–LO splitting of *E*-type modes<sup>23,30</sup> was observed in quasihydrostatic runs (Fig. 2), as noted previously by Jayaraman, Wood, and Maines.<sup>24</sup>

Above approximately 14 GPa there is a rapid decrease in the absolute intensity of the Raman signal. In this pressure range, we were forced to increase the recording time by a factor of 5, in order to obtain useful signals (Figs. 1 and 2). These experiments revealed a Raman spectrum quite different from that of  $\alpha$ - $\text{AlPO}_4$ , consisting of series of discrete well-defined bands occurring in two groups: one between 100 and 700 wave numbers with a more intense band around 620  $\text{cm}^{-1}$ , and a second between 1000 and 1200  $\text{cm}^{-1}$  (Figs. 1 and 2). On continued pressurization, the new bands which appear weakly at the

transition pressure become more intense and better defined at higher pressure, and have been monitored in this study up to 20 GPa. These results are in agreement with the recent Raman study by VerHelst-Voorhees and Wolf.<sup>28</sup> The transition is also accompanied by the appearance of different sets of parallel birefringent lines as already observed during the compression of  $\alpha$ -quartz.<sup>19</sup>

The abrupt loss of Raman signal above 14 GPa is consistent with the previous observation of Jayaraman, Wood, and Maines,<sup>24</sup> with the x-ray observations of Kruger and Jeanloz,<sup>22</sup> with the Brillouin results of Polian, Grimsditch, and Philippot,<sup>16</sup> and indicates the occurrence of a pressure-induced transition in the sample. However, the appearance of a large number of well-defined peaks in the Raman spectrum is indicative of the presence of a crystalline phase, rather than an amorphous material. The Raman peaks of this phase are all broadened compared with the low-pressure starting material, indicating that the high-pressure crystal is disordered. In all hydrostatic experiments, the spectrum of the disordered high-pressure crystalline phase is retained on decompression to 7–8 GPa, and then reverts completely to the low-pressure phase (Fig. 3). Micro-Raman spectra obtained from different regions within the high-pressure sample showed no difference between points, suggesting that the high-pressure material is homogeneous, and entirely crystalline.

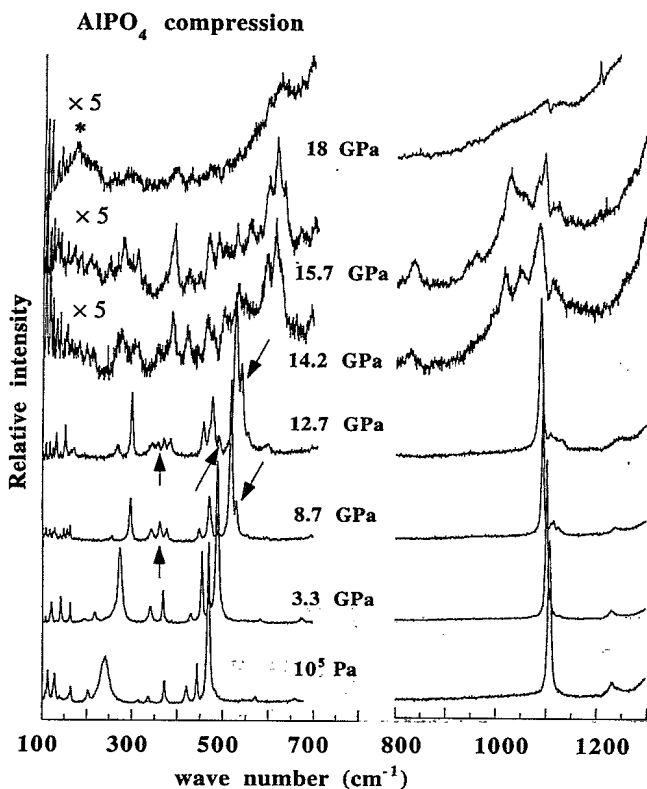


FIG. 2. High-pressure Raman spectra of  $\alpha$ - $\text{AlPO}_4$  taken during compression in KBr. Note the splitting of some modes (arrows) due to shear stresses developed in the sample because of the quasihydrostatic nature of the pressure-transmitting medium. Above 13 GPa the sample undergoes a polymorphic transition similar to that observed in the hydrostatic runs. The spectra of the high-pressure phases obtained in the hydrostatic and quasihydrostatic experiments are similar, but not identical. Above 18 GPa in the quasihydrostatic experiment, the broad Raman bands indicate the sample may be amorphous. Bands labeled by stars are second-order features of KBr.

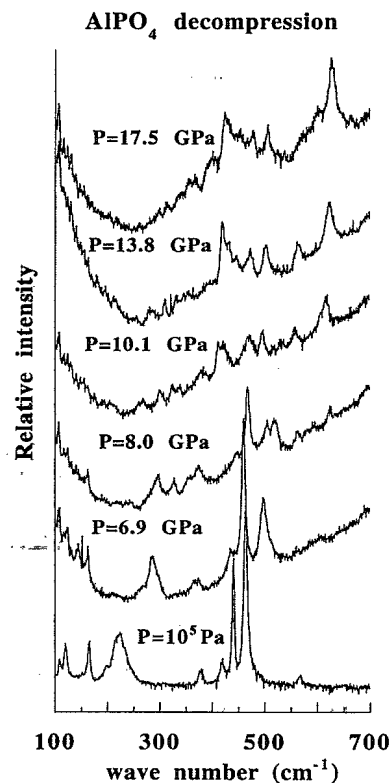


FIG. 3. Raman spectra of  $\text{AlPO}_4$  taken during decompression in hydrostatic pressure media (ethanol:methanol:water mix). The backtransformation from the high-pressure phase to  $\alpha$ - $\text{AlPO}_4$  occurs below 8 GPa. The room-pressure spectrum is similar but weaker than that of the starting material.

The high-pressure and decompression behavior become more complicated when a less hydrostatic pressure medium is used. When KBr is used as pressure medium, some degree of nonhydrostaticity is revealed at pressures below 12 GPa by the appearance of TO-LO splitting in the  $\alpha$ -AlPO<sub>4</sub> spectrum (Fig. 2). On compression to above 13 GPa, the Raman intensity due to the first-order peaks of  $\alpha$ -AlPO<sub>4</sub> is lost, and the spectrum is replaced by a series of weak crystalline peaks, as is observed in hydrostatic compression. However, the number, positions, and relative intensities of these peaks appear to differ slightly from those obtained on hydrostatic compression, for comparable pressures (Fig. 1). The transition is also accompanied by the appearance of different sets of parallel birefringent lines as already observed during the compression of  $\alpha$ -quartz.<sup>19</sup> Upon decompression, this high-pressure crystalline phase is retained throughout the sample to 10–11 GPa, as for the hydrostatic case. Below this pressure, an interesting phenomenon is observed to occur. The crystals develop a rim with different birefringence to their interior, which is observed in samples returned to room pressure (Fig. 4). This behavior is not observed in corresponding hydrostatic runs. *In situ* Raman spectra were taken during the decompression path, with the laser beam focused on the rim or the interior of the back-transforming sample. For pressures below 10 GPa, the Raman spectrum of the rim corresponds to that of  $\alpha$ -AlPO<sub>4</sub> but the spectrum of the interior is still that of the disordered high-pressure crystalline

phase (Fig. 4). Below approximately 9 GPa, the spectrum of the interior is masked by the much stronger Raman scattering of the  $\alpha$ -AlPO<sub>4</sub> phase, but the rim structure is still observed optically, and is retained to ambient pressure. The weak peaks due to the high-pressure phase can no longer be unambiguously detected below approximately 9 GPa (Fig. 4). On unloading the sample, the birefringent rim shows a Raman spectrum corresponding to  $\alpha$ -AlPO<sub>4</sub>, but the bands of this phase are broadened and slightly (by 2–4 cm<sup>-1</sup>) shifted to higher frequency, compared with the sample before compression (Fig. 5). The interior of the decompressed grain is optically isotropic, and shows mainly weak broad bands in the 350–550 cm<sup>-1</sup> and 1000–1150 cm<sup>-1</sup> regions (Figs. 4 and 6). These features are generally reminiscent of the Raman spectra of pressure-densified SiO<sub>2</sub> glass which was reported by Hemley<sup>4</sup> and GeO<sub>2</sub> (Ref. 7) and aluminophosphate glasses,<sup>31</sup> and we assign them to formation of an amorphous phase of AlPO<sub>4</sub> during decompression.

Our observation indicate that the disordered high-pressure AlPO<sub>4</sub> crystalline phase, formed during nonhydrostatic compression, reverts to a  $\alpha$ -AlPO<sub>4</sub> or a glassy material on decompression between 8–9 GPa and room pressure.  $\alpha$ -AlPO<sub>4</sub> is recrystallized at the rims of grains decompressed nonhydrostatically, most likely under the influence of shear stresses concentrated at the boundary between the grain and the pressure medium, but the berillite phase formed differs from that before pressurization, or recovered in hydrostatic experiments. The peak

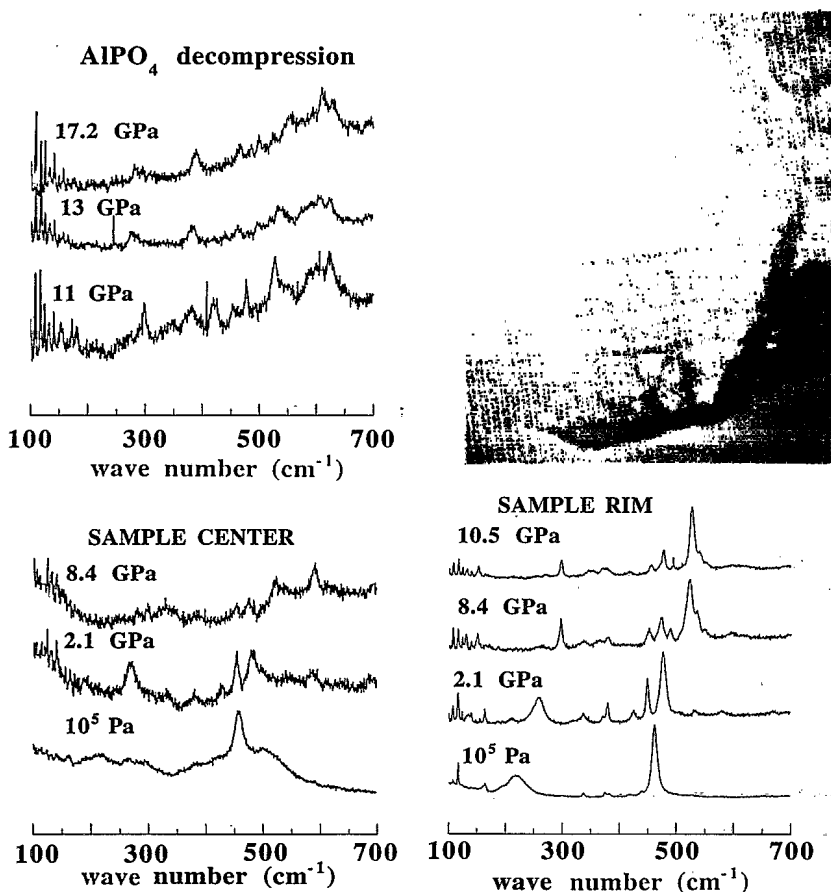


FIG. 4. Raman spectra recorded during sample decompression in quasihydrostatic (KBr) runs. From 18 to 10.5 GPa Raman spectra are identical throughout the sample. The back transformation of the sample begins below 10.5 GPa, with the reappearance of peaks of the  $\alpha$ -AlPO<sub>4</sub> spectrum. At this point, the rim of the sample develops a different birefringence from the interior of the grain. Systematic differences in the Raman spectra are observed on the same grain between the rim and the interior. On recovery, the grain center is isotropic, and exhibits a broad band Raman spectrum due to amorphous AlPO<sub>4</sub>. The superimposed sharper peaks are due to  $\alpha$ -AlPO<sub>4</sub> either coexisting with the glassy material in the interior of the grain, or in the surrounding rim. The  $\alpha$ -AlPO<sub>4</sub> peaks are shifted and broadened compared with their starting values (see details in Fig. 5). The photomicrograph shows a sample recovered after compression in KBr to 27 GPa but similar features are observed in samples compressed to 18 GPa and subsequently decompressed. The sample is examined in crossed polars with a gypsum plate. Note also the cracks developed from the edge of the sample, indicating the release of tensile stresses developed within the sample. The grain size is 120  $\mu$ m.

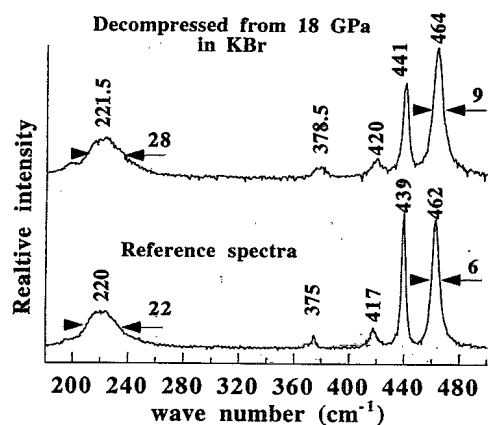


FIG. 5. Raman spectrum of  $\alpha$ -AlPO<sub>4</sub> after decompression from 18 GPa and KBr (sample rim, see Fig. 4) compared to the Raman spectrum of an uncompressed sample. The peak wavenumbers as well as the bands full width at half maximum are indicated.

broadening and frequency shifts (Fig. 5) could correspond to this phase being in a state of stress, or containing structural defects. The cracks observed in Fig. 4 are formed during decompression and may be caused by internal tensile stresses. Similar phenomena have also been observed in  $\alpha$ -quartz decompressed from 25 GPa in similar quasi-hydrostatic conditions. Analogous peak shifts have been observed for SiO<sub>2</sub> quartz recovered from shock experiments<sup>32</sup> and on decompression from between 21 and 30 GPa in static experiments,<sup>18,19</sup> and also for MgSiO<sub>3</sub> perovskite phase heated metastably to above 650 K at room pressure.<sup>33</sup> In each case, the crystalline material was intimately associated with an amorphous phase.

For compression runs carried out in KBr, the Raman spectrum of the high-pressure phase formed above 14 GPa could no longer be followed above 18 GPa. Instead, a set of weak, broad bands which could indicate the appearance of an amorphous phase are observed in the spectrum (Fig. 2). This observation indicates that AlPO<sub>4</sub> can in fact be amorphized, from the high-pressure structure rather than the  $\alpha$ -berlinite phase, during pressurization in a nonhydrostatic environment. Decompression of such samples gives rise to mixture of amorphous material and  $\alpha$ -AlPO<sub>4</sub> (Fig. 6).<sup>34</sup>

We have also conducted compression experiments up to 25 GPa in the absence of a pressure transmitting medium, to provide an extremely nonhydrostatic environment. The loss of Raman intensity of the  $\alpha$ -AlPO<sub>4</sub> phase and the accompanying crystal-crystal transition was observed to occur at  $14 \pm 1$  GPa, as before. However, the Raman spectra of the recovered samples are different from those obtained on samples compressed with a soft pressure-transmitting medium (Fig. 6). The spectra contain several broad bands which could be assigned to an amorphous phase, but the form of this broad band spectrum is different from that described above: in particular, a strong broad band occurs at  $650 \text{ cm}^{-1}$ , in a region which does not contain any features for samples

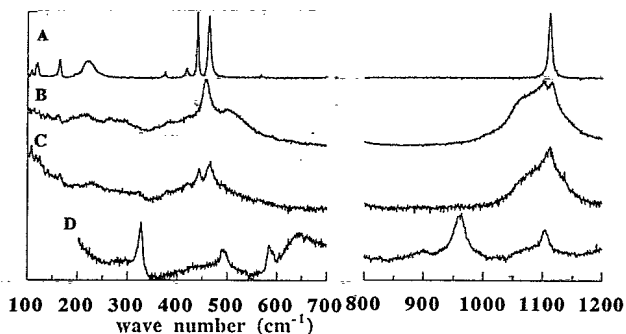


FIG. 6. Raman spectra of AlPO<sub>4</sub> recovered from compression experiments of  $\alpha$ -AlPO<sub>4</sub> using different pressure-transmitting media: (A) compressed to 20 GPa in 16:4:1 methanol/ethanol/water mix. (B) compressed to 18 GPa in KBr. Note the broad bands due to the recovered amorphous phase. (C) compressed to 27 GPa in KBr. (D) compressed to 25 GPa without pressure-transmitting medium. Note the additional sharp peaks in the spectrum, due to appearance of a crystal phase on decompression. These could be due to a rutile-like phase, or to a phase with the InPO<sub>4</sub> (*Cmcm*) structure.

decompressed in alcohol-water mixes of KBr. In addition, a series of new sharper peaks is observed (at 326, 492, 585, 958, and  $1100 \text{ cm}^{-1}$ ), which correspond to the appearance of a new crystalline phase. The likely identity of this phase is discussed in the following section. In no case was  $\alpha$ -AlPO<sub>4</sub> recovered in pure form from such highly nonhydrostatic compression experiments in contrast with similar experiments performed earlier.<sup>22</sup>

#### IV. COMPARISON BETWEEN BERLINITE AND QUARTZ

There are very strong parallels between the observations of this study on AlPO<sub>4</sub> berlinite and previous observations on SiO<sub>2</sub> quartz. Recently, a crystalline-crystalline transformation was found to precede or accompany amorphization in quartz.<sup>18</sup> The present results demonstrate similar effects in berlinite, at least in the runs performed with KBr as a pressure-transmitting medium (quasi-hydrostatic runs). In both cases, the Raman signal significantly weakens at the transition and the high-pressure spectrum with broad bands is indicative of a disordered crystalline solid. It must also be noticed that in their Raman study, Jayaraman, Wood, and Maines<sup>24</sup> stopped their measurements due to signal weakening at 12 GPa for berlinite and 20 GPa for quartz; these pressures correspond to the pressures of the phase transitions reported in the present study for berlinite and by Kingma *et al.*<sup>18</sup> for quartz. In the x-ray-diffraction pattern obtained by Kruger and Jeanloz<sup>22</sup> on  $\alpha$ -AlPO<sub>4</sub> at 25 GPa, weak broad peaks do appear in the  $12$ – $16^\circ$   $2\theta$  range, which could correspond to this phase. In quasi-hydrostatic runs (with KBr) the new phase of AlPO<sub>4</sub> experiences partial amorphization on decompression before or during the back transformation in  $\alpha$ -AlPO<sub>4</sub>, an effect also observed for SiO<sub>2</sub> quartz.<sup>18</sup>

On hydrostatic compression in alcohol the crystalline phase of AlPO<sub>4</sub> is retained at pressures in excess of 20

GPa. VerHelst-Voorhees and Wolf<sup>28</sup> have compressed hydrostatically in argon this phase to 32 GPa and never observed amorphization. It thus appears that nonhydrostatic stresses play an important role in the formation of the amorphous phase during compression. Such a sensitivity of amorphization to shear stresses is also observed in quartz.<sup>4</sup>

McNeil and Grimsditch<sup>21</sup> have measured the Brillouin scattering of  $\text{SiO}_2$  quartz up to 25 GPa. Brillouin data reveal significant elastic anisotropy in the quenched samples which were assumed to be perfectly amorphous by the authors. It has been concluded that the pressure-induced amorphous phase was elastically anisotropic and thus different from fused silica. More recent microscopic characterization of samples pressurized between 20 and 30 GPa as well as the *in situ* observation of a phase transition before the onset of amorphization have led Kingma and co-workers<sup>18,19</sup> to reinterpret the Brillouin data. They suggest that the elastic anisotropy originates from undetected crystalline material or from twinning of the residual high-pressure crystalline phase.<sup>35</sup> This reinterpretation has been commented by McNeil and Grimsditch.<sup>36</sup>

As for  $\text{SiO}_2$  quartz, the present Raman results on  $\text{AlPO}_4$  are in disagreement with the interpretation of Brillouin-scattering measurements. Polian, Grimsditch, and Philippot<sup>16</sup> have found that at 15 GPa  $\text{AlPO}_4$  undergoes a reversible transformation. Based on the previously reported loss of diffraction pattern<sup>22</sup> and Raman spectra,<sup>24</sup> they assumed that the transition is from a crystal to an amorphous material. Furthermore, they concluded from the Brillouin data that the high-pressure (amorphous) material is elastically anisotropic. However, results of the present study indicate that Polian, Grimsditch, and Philippot<sup>16</sup> were instead recording the crystalline-crystalline transition at 15 GPa and that above this pressure the anisotropy in the Brillouin signal originates from the disordered phase and not from an anomalous amorphous phase.

## V. STRUCTURE OF THE HIGH-PRESSURE PHASE

In their molecular-dynamics study of the low-temperature pressurization and decompression of  $\alpha$ - $\text{AlPO}_4$ , Tse and Klug<sup>26</sup> concluded that the transformation occurs as  $\text{PO}_4$  unit from one spiral chain is tilted and forced into an interstitial site near an adjacent Al atom, and one of its O atoms enters the coordination sphere of that Al, increasing its coordination. A similar type of mechanism has been described for the pressure-induced amorphization transition in  $\alpha$ - $\text{SiO}_2$ , based on both empirical molecular-dynamics and *ab initio* calculations.<sup>9,10,14,15,37</sup> For  $\text{SiO}_2$ , it is emphasized that compression of the quartz structure results in the oxygen atoms adopting a near-bcc arrangement. The tetrahedral silicon atoms sites are then in close proximity to vacant octahedral sites, with a low-energy pathway connecting the two types of site.<sup>14</sup> Occupation of the octahedral and tetrahedral sites in a more or less ordered or random pattern leads to a pressure-induced crystal-crystal transformation or to amorphization, associated with relaxation of a shear instability.<sup>9,14</sup>

In the case of  $\alpha$ - $\text{AlPO}_4$ , there is an important constraint on this process, determined by local atomic valency requirements. For example, the normal valencies of Al, Si, and P in oxides are +3, +4, and +5, respectively. In  $\text{SiO}_2$  quartz, oxygen is bonded to two silicon atoms in tetrahedral coordination. Each contributes  $4/4=1$  valence unit to the bonded oxygen, with the result that the valency at oxygen sums correctly to  $-2$ . In the case of  $\alpha$ - $\text{AlPO}_4$ , each tetrahedrally coordinated Al atom contributes  $3/4=0.75$ , and each tetrahedral P contributes  $5/4=1.25$ , with the result that the Al and P atoms must be perfectly ordered within the structure to achieve the correct valency at oxygen.

The stable high-pressure phase of  $\text{SiO}_2$  is stishovite (rutile structure), in which silicon is in octahedral coordination, and each oxygen is bonded to three  $\text{Si}^{\text{VI}}$  atoms. Each silicon-oxygen bond contributes  $4/6=0.33$  valence units, so that the oxygen valency is satisfied. The  $\text{AlPO}_4$  composition poses a problem, because there are now two different metal cations. The oxygen environments in a hypothetical rutile structure could be an average of  $\text{OAl}_2\text{P}$  and  $\text{AlP}_2\text{Al}$  sites. However, each octahedral Al and P will contribute  $3/6=0.5$  and  $5/6=0.83$  valence units, respectively, to the bonded oxygen. The resulting bond valence sums at oxygen would be 1.83 and 2.17, unacceptably under- and overbonded for a regular structure. If the rutile structure were adopted by  $\text{AlPO}_4$ , it would be highly distorted, or the metal oxidation states would differ considerably from their usual values. The main problem for the structure is then the occurrence of the high valency phosphorous atoms in octahedral coordination. For this reason, we believe that the coordination transformation is likely to be restricted to the Al atoms, at least on initial pressurization, and occurs in a more ordered fashion than in  $\text{SiO}_2$ , due to the ordered arrangement of  $\text{AlO}_4$  and  $\text{PO}_4$  groups in the crystal.

Tse and Klug<sup>26</sup> concluded that the resulting pressure-densified phase in  $\text{AlPO}_4$  was not in fact a random network material comparable to a quenched liquid, but was best described as a solid with considerable short-range order, although disordered over the long range. We concur with this suggestion.

The Raman spectra of the high-pressure phase obtained in runs performed in KBr are not identical to those obtained in hydrostatic experiment with alcohol although the two are most likely closely related (Figs. 1 and 2). The differences may be interpreted by small structural differences; the pressure of shear stresses may favor another structure for the high-pressure phase. These differences may also be related to polarization effects induced by orientational differences of the starting crystals.

We can conclude that the "memory glass" obtained when  $\alpha$ - $\text{AlPO}_4$  is pressurized to above 13–14 GPa is a disordered crystalline phase, and that the changes in the vibrational spectra, x-ray pattern, and Brillouin scattering are indicative of a crystal-crystal phase transition which is easily reversible on decompression when hydrostatic pressure media are used. As noted by both Kruger and Jeanloz<sup>22</sup> and Tse and Klug,<sup>26</sup> the atomic displacements associated with the transition are small, and occur in a semicoherent fashion throughout the crystal due to

the Al/P ordering, so that the original crystalline orientation is recovered when the samples reverts to  $\alpha$ -AlPO<sub>4</sub> on decompression.

## VI. DECOMPRESSION AND QUENCHED SAMPLES

The decompression history of the sample is sensitive to the nature of the pressure medium used. With alcohol, decompression from 20 GPa shows that the transition  $\alpha$ -AlPO<sub>4</sub>-disordered phase is reversible (Fig. 3). With KBr the Raman spectral features of the quenched samples indicate a mixture of crystalline and glassy material. The amorphous material is produced from amorphization of the high-pressure phase or from amorphization of  $\alpha$ -AlPO<sub>4</sub> formed by backtransformation of the high-pressure phase. The nonhydrostatic stresses are concentrated at the exterior of the sample, and presumably provide the energetic driving force for recrystallization of the rim to the low-pressure  $\alpha$ -AlPO<sub>4</sub> phase (Fig. 4). However, once it is recovered, the Raman peaks of this rim phase are shifted from their room-pressure positions, because of the partially relaxed high-pressure stresses stored within the sample interior. Finally, the present results are in agreement with those of Cordier, Doukhan, and Peyronneau,<sup>38</sup> who observed by electron microscopy the coexistence of amorphous and crystalline domains in samples of AlPO<sub>4</sub> pressurized under nonhydrostatic pressure conditions.

It was noted above that the spectrum of the sample compressed with no pressure medium contained a set of five new peaks on decompression, in addition to the broad bands of the amorphous phase (Fig. 6). These peaks were assigned to the appearance of a crystalline phase. There are several possibilities for the identity of this phase. The first is that they could correspond to a rutile-structured phase with AlPO<sub>4</sub> composition, analogous to SiO<sub>2</sub> stishovite. Wolf and co-workers have described nucleation of rutile from amorphous GeO<sub>2</sub>, during the decompression step following pressure-induced amorphization of the  $\alpha$ -quartz phase,<sup>7</sup> and stishovite has been observed within glassy patches found in quartz subjected to shock treatment.<sup>39</sup> The isochemical compounds AlAsO<sub>4</sub> and GaAsO<sub>4</sub> have been reported to form rutile-structured compounds, with a doubled *c*-axis repeat, in synthesis runs at high pressure and temperature.<sup>40</sup> If it were possible to form such a structure during decompression from the amorphous phase of AlPO<sub>4</sub>, the Raman spectrum would contain a large number of peaks. A second possibility is the orthorhombic (*Cmcm*) phase taken by InPO<sub>4</sub>. This has been proposed as an intermediate structure for SiO<sub>2</sub> at high pressure, in response to shear

instability in the  $\alpha$ -quartz structure.<sup>9,14</sup> The new crystal peaks observed in decompressed berlinite in the absence of a pressure medium could be due to crystallization of AlPO<sub>4</sub> with this structure, in the highly nonhydrostatic stress environment. It is possible that the broad band in the 600–700 cm<sup>-1</sup> region is the signature of VI-coordinated aluminium within the amorphous phase found in these samples. Previous workers have attributed intensity in this region in Raman and infrared spectra of aluminosilicate glasses to vibrations of octahedrally coordinated Al atoms.<sup>41,42</sup>

## VII. CONCLUSIONS

The present data indicate that the memory-glass effect in AlPO<sub>4</sub> is not a reversible crystal-amorphous phase transition, as was previously thought,<sup>22</sup> but instead corresponds to a reversible first-order crystal-crystal transition in hydrostatic compression runs. This observation is consistent with the results of a previous molecular-dynamics simulation,<sup>26</sup> and with the results of a recent parallel Raman spectroscopic study.<sup>27,28</sup> Compression in hydrostatic and quasihydrostatic media leads to a similar crystal-crystal transition at 13–15 GPa, but the transition is only partly reversible in the quasihydrostatic runs. The sample recrystallizes to the starting phase around the rim of each grain, but the center of the grains become amorphous during the quench. Amorphization also appears to occur in quasihydrostatic runs above approximately 18 GPa. Decompression of samples pressurized in a highly nonhydrostatic environment, with no pressure medium, give rise to an additional set of Raman lines due to appearance of a crystal phase at ambient pressure. This could correspond to a rutile-structured phase of AlPO<sub>4</sub>, or a phase with the InPO<sub>4</sub> structure.

Finally the present results emphasize the care that must be taken in the study of pressure-induced transformations. Disappearance of the Raman signal may be due to a phase transition to a weakly Raman-scattering crystalline polymorph. It should be important to reinvestigate by Raman spectroscopy the other compounds for which pressure-induced amorphization has been reported.

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