

Search for a precursor crystal-to-crystal phase transition to amorphization in α -GeO₂ and α -AlPO₄ under pressure

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Abstract. Recent X-ray diffraction studies on α -quartz (SiO₂) by Kingma *et al* [1], have shown the occurrence of a reversible, crystalline-to-crystalline, phase transition just prior to amorphization at ≈ 21 GPa. This precursor transition has also been confirmed by our recent molecular dynamics simulation study [2]. In order to investigate the possibility of a similar behaviour in other isostructural compounds, which also undergo pressure induced amorphization, α -GeO₂ and α -AlPO₄ (berlinite form) were studied using energy dispersive X-ray diffraction. In either of these materials, no such phase transition is detected prior to amorphization. The onset of amorphization and its reversal is found to be time dependent in GeO₂.

Keywords. Precursor phase transition; pressure-induced amorphization; α -GeO₂; α -AlPO₄; high pressure energy dispersive X-ray diffraction.

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1. Introduction

Over the last few years there have been a number of theoretical and experimental studies on the pressure-induced amorphization in α -quartz. Some of the striking features of the amorphization have been the direct observation of the change in Si coordination from 4 to ≈ 6 by IR spectroscopy [3], anisotropy of elastic constants in the amorphous phase [4], and the occurrence of a reversible, crystalline-to-crystalline phase transition just prior to amorphization [5]. Various molecular dynamics simulation studies have also supported these experimental observations [5–8, 2, 9]. The observation of the reversible phase transition at ≈ 21 GPa in α -quartz phase of SiO₂ has added a new dimension to this problem [1]. These authors have attributed the Brillouin scattering results regarding the anisotropy of amorphous phase as due to the presence of traces of the precursor crystalline phase in the amorphous phase [1]. We have shown through our MD results that the precursor phase in SiO₂ is a distorted superstructure of α -quartz phase. The super-structure is consistent with a recent proposal that $(\frac{1}{3}, \frac{1}{3}, 0)$ phonon mode goes soft in α -quartz phase prior to amorphization [6]. The d values in the diffraction patterns generated from our MD results are in good agreement with those from the experiments of Kingma *et al*.

α -GeO₂ is an excellent high pressure model for α -quartz (SiO₂), since the GeO₂ tetrahedra are more deformed in comparison to SiO₂ in the α -quartz phase [10, 11]. In fact the ambient structure of α -GeO₂ compares well with the structure of α -SiO₂ at 10 GPa. At this pressure the intertetrahedral Si–O–Si and Ge–O–Ge angles have

an average value of 130° . Although changes in Ge–O coordination from four to six is observed at 6 GPa [12, 11] complete amorphization is observed to occur above 20 GPa at which pressure the Raman spectrum is found to be similar to the GeO_2 glass. Interestingly selective area, HREM studies on decompressed samples of polycrystalline GeO_2 (decompressed from 20 GPa) shows new, non-quartz like diffraction spots [13]. Recent shock experiments on $\alpha\text{-GeO}_2$, show the existence of new diffraction peak at $d = 4.04 \text{ \AA}$ and 3.11 \AA , in the sample recovered from 6.8 GPa [14]. However, the sample shocked to 10 GPa does not show these additional lines.

The berlinite phase of AlPO_4 is isostructural to α -quartz, with the Al and P atoms replacing Si atoms in alternating polyhedra. The room pressure structure of berlinite AlPO_4 is closer to $\alpha\text{-SiO}_2$ (as compared to $\alpha\text{-GeO}_2$) in that the Al–O–P angle is 142° [15], (Si–O–Si angle in $\alpha\text{-SiO}_2$ is 144°). AlPO_4 has been shown to become 'X-ray amorphous' at 12 GPa [16] at which pressure the Raman spectrum also disappears [17]. Single crystal studies [18] indicate the amorphization to be complete around 18 GPa. In contrast to $\alpha\text{-GeO}_2$ and $\alpha\text{-SiO}_2$, AlPO_4 reverts back to the crystalline phase on pressure release at ~ 7 GPa. In fact, the reversibility has been shown to have memory, since the single crystal reverts back to an identical crystallographic configuration when decompressed from the amorphous phase [18]. Recent Brillouin scattering studies on AlPO_4 [19] have confirmed the existence of elastic anisotropy in the pressure-amorphized phase (above 15 GPa) and the subsequent reversal to the starting crystalline phase on decompression. However, lack of complete reversibility has been noted in recent non-hydrostatic experiments [20].

Both of these compounds exist not only in the isostructural forms of α -quartz but also in other polymorphic forms of SiO_2 . This underlying similarity of the three materials $\alpha\text{-SiO}_2$, $\alpha\text{-GeO}_2$ and $\alpha\text{-AlPO}_4$ is also expected to show up in the similar nature of pressure-induced amorphization brought about by distortion of the inter-tetrahedral angles and change in coordination from four to six [21]. This prompted us to carefully investigate the existence of any new precursor transformation in these materials.

2. Experimental

High pressure energy dispersive X-ray diffraction (EDXRD) studies on polycrystalline samples of $\alpha\text{-GeO}_2$ and AlPO_4 were done using the system described elsewhere [22]. Samples were loaded into stainless steel gaskets with a hole size of $\approx 150\text{--}200 \mu$. $\alpha\text{-GeO}_2$ was prepared by S C Sabharwal of Technical Physics and Prototype Engineering Division of BARC by keeping crystalline GeO_2 in the high temperature stability field of α -phase and then quenching it. For GeO_2 , in one experiment, methanol-ethanol and in two experiments Si oil (trade name DC704) was used, as the pressure medium. The latter was used, as in some experiments at high pressures, GeO_2 samples were reported to react with methanol-ethanol mixture [23]. However, in our study we find that, visually, GeO_2 particles in the methanol-ethanol medium do not undergo any substantial change in the range of pressure of our interest (≈ 11 GPa). Also in the case of retrieval, we get back the initial diffraction pattern of $\alpha\text{-GeO}_2$. Sample pressure was determined using the ruby pressure scale [24, 25]. In an effort to investigate the possibility of phase transformations occurring during decompression, X-ray data on pressure release were also collected from various terminal pressures.

3. Results

The diffraction data from our experiments on α -GeO₂ are presented in figures 1–4. The data have been scaled with respect to the MoK _{β} fluorescence peak. As is evident from figure 1, the α -GeO₂ becomes 'X-ray amorphous' at ≈ 10 GPa. We also find that in GeO₂, both the onset of amorphization as well as its reversal/irreversal has considerable time dependence. Figure 2, shows the evolution of diffraction pattern at 9.4 GPa in experiment #5, which uses DC704 oil as a pressure medium. The data of first three hours show clear diffraction pattern. Subsequently the diffraction pattern deteriorates progressively. For example, after about 44 hours diffraction patterns is

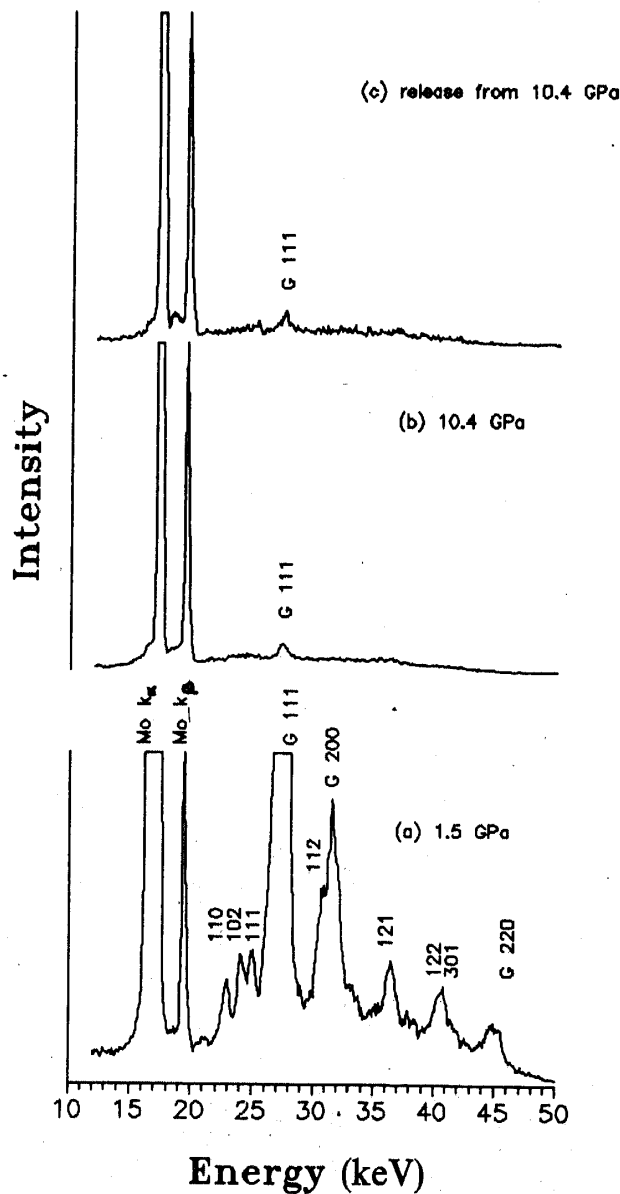


Figure 1. Diffraction pattern of α -GeO₂ at (a) 1.5 GPa, (b) 10.4 GPa and (c) after the release of pressure from 10.4 GPa. Gasket peaks are marked as G hkl. At higher pressures, the intensity of these peaks decreases due to widening of the gasket hole which was initially comparable to the collimated X-ray beam of $\sim 200 \mu$. Pressure medium in this experiment was Si oil.

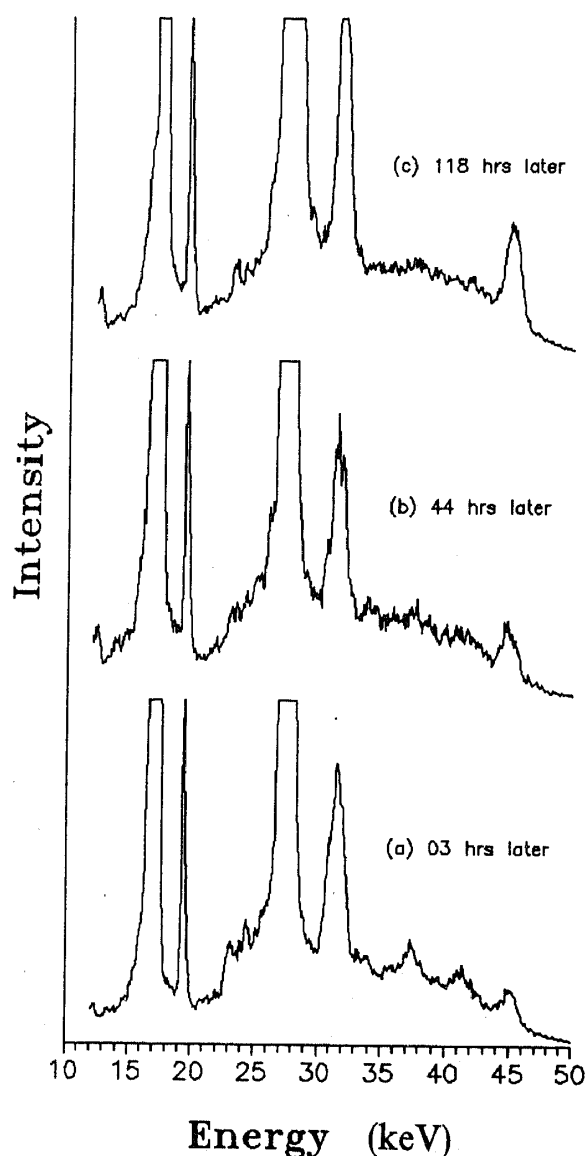


Figure 2. Time evolution of amorphous phase from α -GeO₂ at 9.4 GPa. (a) After 3 hrs of raising the pressure to 9.4 GPa, (b) after 44 hrs. and (c) after 118 hrs. Remnant peaks are MoK _{α} , MoK _{β} and gasket peaks as in figure 1. Higher intensity of gasket diffraction peaks here is due to the smaller gasket hole ($\sim 150 \mu$) compared to that of figure 1 and figure 3. Si oil was used as a pressure medium in this run.

barely visible and even this is completely lost after about 116 hr. And on release of pressure, even after 17 hours there is no reappearance of diffraction pattern. The ruby spectrum at 9.4 GPa shows that the pressure was non-hydrostatic as the R_1 - R_2 separation was $\approx 7 \text{ \AA}$ in constant to $\approx 14 \text{ \AA}$ in truly hydrostatic medium ([26]). The time dependence of emergence of crystalline phase on decompression depends on both the peak pressure as well as the deviation from the hydrostatic environment. We find that the samples pressurized beyond 11 GPa do not show re-emergence of the crystalline phase to within a few hours, but the ones loaded to smaller peak pressures do show reversibility. For example in run # 3, in which methanol-ethanol is used as a pressure medium, we find that amorphous phase reverts back to crystalline phase after some time. Figure 3a shows complete loss of diffraction pattern at high

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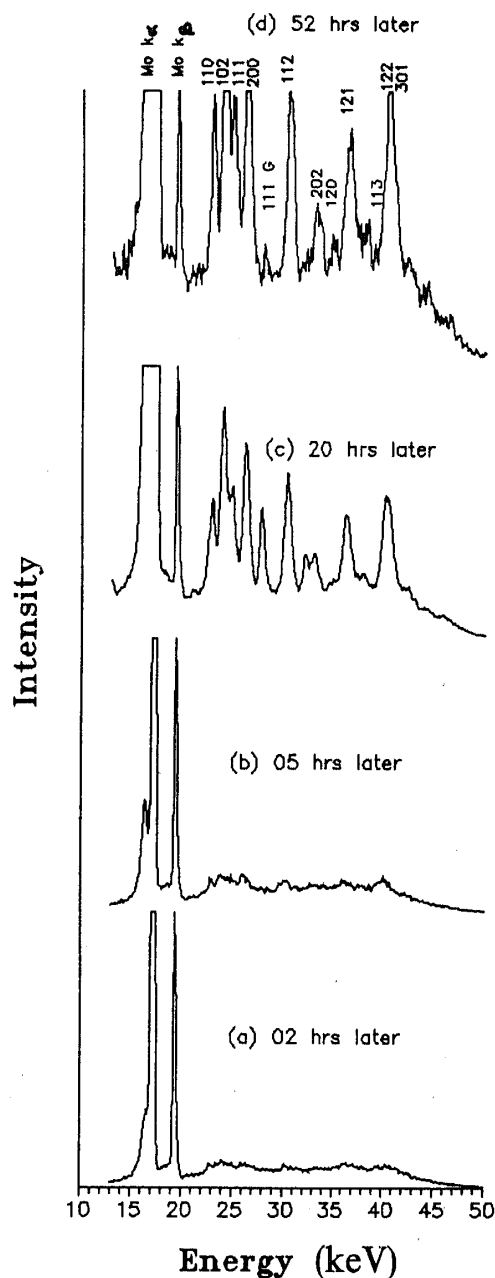


Figure 3. Evolution of crystalline α -GeO₂ from the amorphous phase after the release of pressure. (a) 2 hrs after the pressure release, (b) 5 hrs after the pressure release, (c) 20 hrs after the pressure release and (d) 52 hrs after the release of pressure. Methanol-ethanol mixture was used as a pressure medium in this experiment.

pressures. On unloading this, up to two hours there is no diffraction pattern, and therefore stays amorphous. But after about five hours a weak diffraction pattern appears which becomes substantially strong after 20 hr. After about 48 hr the material seems to have returned completely to crystalline form. Figure 4 shows the diffraction patterns at 1.5 and 7 GPa on compression and on release from 7 GPa. The decompressed sample is then raised to a pressure of 8.4 GPa which is also shown here. The diffraction pattern at still higher pressure viz. 9.4 GPa of this run has been given above in figure 2. On raising the pressure to 7 GPa, the background rises substantially

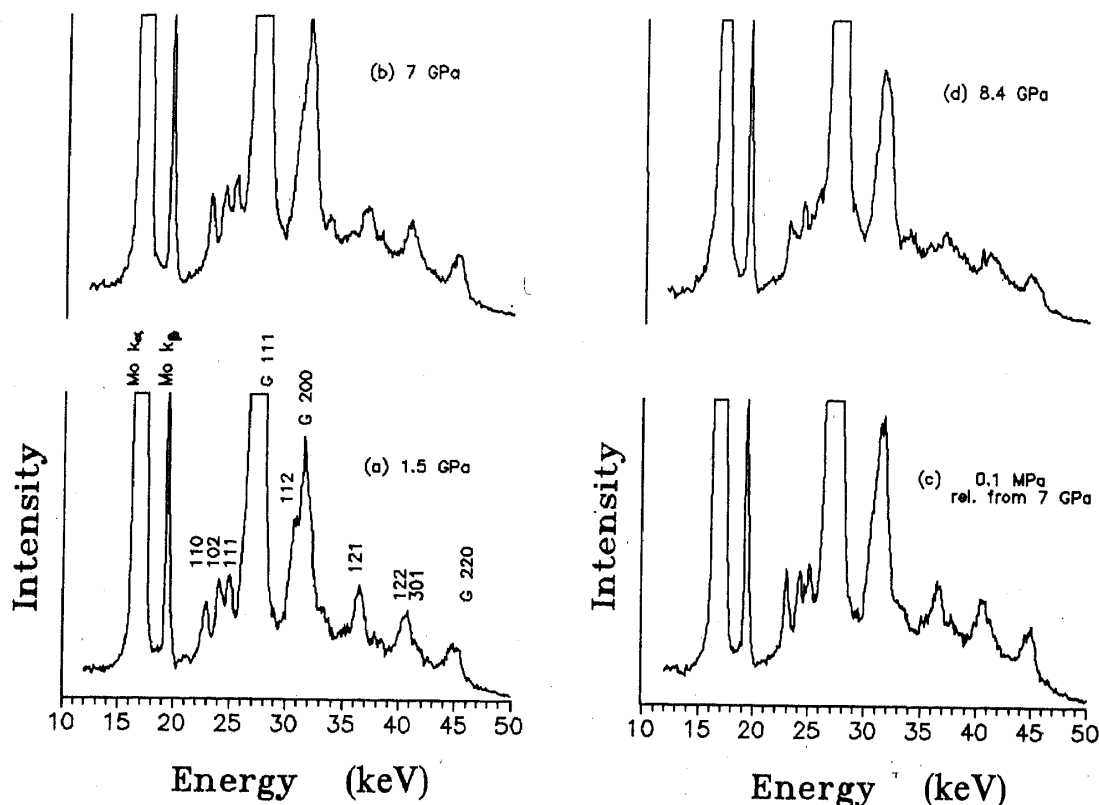


Figure 4. The diffraction pattern of α -GeO₂ at (a) 1.5 GPa, (b) 7 GPa, (c) after the release from 7 GPa and (d) the decompressed phase of (c) is raised to 8.4 GPa. Gasket peaks are marked as G hkl as in figure 2.

and irreversibly around 30 keV, but without much change in the FWHM of the overriding diffraction peaks. This should be contrasted with the observations of Suresh *et al* [14] who find irreversible broadening of all Bragg peaks on shock loading to 6.8 GPa. We also carefully checked the d values reported in the shock experiments and found no evidence of these additional diffraction lines in our experiments. In fact in all our experiments, no new diffraction lines are observed in α -GeO₂ prior to amorphization, or on decompression from various terminal pressures.

AlPO₄ is observed to become 'X-ray amorphous' between 13 and 15 GPa in complete agreement with the results of Sankaran *et al* [16]. As in the case of α -GeO₂, no new diffraction lines are observed prior to amorphization. On decompression, the crystalline X-ray pattern of the starting phase re-emerges with some hysteresis. Since the X-ray data for AlPO₄ is no different from our earlier data [16], we have chosen not to show the X-ray data from the current set of experiments. It may be noted that the AlPO₄ sample used for this run is from the same batch used by Sankaran *et al* [16].

4. Discussion

The present study on α -GeO₂ and AlPO₄ indicates that there exists no precursor phase prior to amorphization in either of the two materials. In contrast to the results of shock loading of GeO₂ [14], our studies show no new diffraction peaks on compression or decompression from pressures in the region 7–9 GPa. We also find that irreversibility of crystalline to amorphous phase transition may be dependent on the pressure as well as the amount of non-hydrostatic stresses present in an experiment.

It is particularly interesting to note that when the ruby spectrum shows the existence of non-hydrostatic stresses, GeO_2 transforms slowly but irreversibly to an amorphous phase at 9.4 GPa. A more hydrostatic medium like ethanol-methanol raises the pressure of irreversible amorphization to beyond 10 GPa. This signifies the importance of shear stresses in aiding the crystal to amorphous phase transition. Our experimental results suggest that the existence of non-hydrostatic stresses not only reduces the pressure of transformation, it also brings in irreversibility. Role of shear stresses in bringing about irreversibility in amorphization has also been noted earlier [27]. In fact a substantial amorphization of $\alpha\text{-GeO}_2$ on shock loading this material to less than 7 GPa supports our suggestion. It should be noted that high resolution electron microscopy (HREM) studies of Wolf *et al* [13] indicate the disorder present even in the samples recovered from 7 GPa. Their Raman scattering results also indicate substantial irreversible change at 8.7 GPa. Present studies indicate that these results are likely to be both time dependent as well as significantly dependent on the presence of non-hydrostatic stresses. This study points out another result that whenever there is irreversible pressure induced amorphization, the limit of irreversibility may have kinetics dependence. Alternatively, the irreversibility within the time period of measurement may have either large shear stresses or a pressure considerably higher than the equilibrium value. Therefore, there is a limiting compression, from where the crystalline phase could re-emerge thereby indicating a reversible amorphization. A similar feature has also been noted in lithium triborate by Lin *et al* [28] though they have not stated this categorically.

Also in two of our experiments where we used Si oil, there may be a large amount of non-hydrostatic stresses present at about 10 GPa. Therefore it is reasonable to presume that $\alpha\text{-GeO}_2$ does not transform to any new phases prior to amorphization even under non-hydrostatic conditions. The decompression also does not lead to any new phases.

Single crystal optical micrography studies on the behaviour of $\alpha\text{-AlPO}_4$ under pressure, have been extensively carried out by Kruger and Jeanloz [18]. They report the occurrence of twin bands close to the amorphization pressure. Similar formation of twin walls has also been shown to precede the new crystalline to crystalline phase transformation in $\alpha\text{-quartz}$ (SiO_2) [1]. The absence of a similar transition in AlPO_4 , therefore, suggests that the two phenomena are not necessarily correlated.

The presence of precursor phase in $\alpha\text{-SiO}_2$ and its absence in $\alpha\text{-GeO}_2$ and in AlPO_4 may be understood by the following arguments. It is well known that the pressure induced transformations involve small movements in positions of atoms and in that sense they are by and large displacive. In fact from the mechanism point of view, it is possible to classify these transformations in terms of a well defined symmetry classification [29, 30]. Many transformations proceed through multistage steps of symmetry ascent and descent. In this multistage process any arbitrary initial phase can descend to the lowest symmetry amorphous phase. We have shown that recently observed phase transformations in sulphur [31] demonstrate this point of view elegantly [32]. In this the ambient orthorhombic phase transforms to a monoclinic phase at 5 GPa which becomes amorphous at ≈ 25 GPa. At 78 GPa, the amorphous phase ascends to a low symmetry crystalline structure which becomes base centred orthorhombic at 83 GPa. At 162 GPa sulphur reaches the highest symmetry in rhombohedral $\beta\text{-Po}$ type phase. In LiKSO_4 , LiCsSO_4 and LiRbSO_4 also one notes the symmetry descent prior to amorphization [33-37]. Similar symmetry lowering transformations have also been noted in C_{60} as well as C_{70} ([38,39]). In this context,

the symmetry descent observed in α -quartz by Kingma *et al*, interpreted by us from P3₁21 to a monoclinic phase, confirms this picture. So it could have been acceptable to see lower symmetry phase preceding the amorphous phase in GeO₂ and AlPO₄ also. Only way these opposing results could be understood is that in these systems the kinetics of the lower symmetry phases is such that these exist as a transient. It may be noted that in our MD results the monoclinic phase evolves systematically as a transient structure as stated above. It is probable that under some appropriate stresses, temperatures, defects or impurity conditions this transient structure gets stabilized. It is known that the HREM images of sample decompressed from 20 GPa show lattice plane spacings that could not be indexed to either the quartz or the rutile phases [13]. This and the observation of additional diffraction lines in the retrieved samples of shock loaded GeO₂ ([14]) may provide material for speculation as to whether these are related to the transient structures.

In conclusion, we report careful EDXRD studies on α -GeO₂ and α -AlPO₄, close to amorphization pressures. No new diffraction lines were observed in either of the two materials in spite of the close structural relationship with α -quartz, in which a precursor phase transition, prior to amorphization under pressure, was observed. In contrast with the HREM studies and shock results on decompressed samples of α -GeO₂, no new diffraction lines were observed when decompressed from pressures as high as ≈ 9 GPa. Changes in diffraction patterns of α -GeO₂ are reversible up to ≈ 9 GPa, although substantial broadening of diffraction peaks sets in above 7 GPa. Time dependence is noted in both the evolution of amorphous phase as well as the reverse transition on pressure release.

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