Pressure-Induced Amorphization and Phase Transformations in β-LiAlSiO₄

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This work presents a comprehensive study on pressure-induced amorphization (PIA) in β-eucryptite (LiAlSiO₄) and on the equilibrium states of so-formed amorphous phase at elevated temperatures. Our results revealed that at 300 K β-LiAlSiO₄ underwent progressive amorphization at pressures above 4.5 GPa and became completely amorphous above 17.0 GPa. After release of pressure, β-LiAlSiO₄ that was partially amorphized at 7.5, 14.0, and 16.0 GPa reverted back to its original crystalline state. When subjected to a complete loss of long-range structural order, the system was recovered as an amorphous state and did not retain the so-called structural memory. Upon heating at high pressures, the partially or completely amorphous β-LiAlSiO₄ transformed into various crystalline phases at temperatures above 973 K: between 6.9 and 10.7 GPa it was decomposed into a mixture of LiAlSi₂O₆ and LiAlO₂; at 15.3 GPa the two phases recombined to form a new phase with a spinel structure; and at 22 GPa the spinel phase of LiAlSiO₄ was decomposed into its constituent oxides. The observed transformations are all of a reconstructive type and also involve profound changes in atomic coordination environments. A large activation energy barrier associated with coordination changes and a hindrance of atomic mobility at kinetically low temperatures are the primary factors that trigger the PIA.

Introduction

Pressure-induced amorphization (PIA), i.e., formation of an amorphous phase within a solid state by application of pressure, has been found to be a phenomenon of widespread occurrence among condensed matter, such as ice, silicates, phosphates, tungstates, hydroxides, and pure elements.[1–7] It is now widely believed that the pressure-induced amorphous state is a universal property of condensed matter.[8] The disordering process in PIA is distinct from thermally induced disorder such as melting and is of fundamental interest for understanding order–disorder phenomena in condensed matter and computational physics, including solid-state amorphization and stability of crystals.[8] The underlying mechanisms, however, remain one of the most fascinating open questions. Several possibilities, which are not neces-

sarily mutually exclusive, have been suggested as the driving forces for such solid-state amorphization. These include "thermodynamic melting" after a crystalline solid is compressed beyond its extrapolated or metastable melting curve,[1,2] mechanical instability when particular combinations of the elastic constants violate one of the Born stability conditions,[9] and kinetic hindrance of phase transformations to a thermodynamically stable high-pressure phase.[10,11] A few more structural factors such as polyhedral packing[12] and increases in the atomic coordination[9] have also been considered to contribute to PIA. To date, however, the final equilibrium state and/or structures of high-pressure phases in many systems undergoing PIA at 300 K remain unknown or speculative.

Among materials that have been found to undergo PIA, a relatively small family of framework tungstates, molybdates, and phosphates, composed of corner-sharing tetrahedra and octahedra and with negative thermal expansion,[3,4,13,14] has attracted special attention. This is in part due to recent computer simulations that suggested a possible connection between PIA and negative thermal expansion.[15] Furthermore,

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these materials become amorphous at pressures that are considerably lower than those observed in other crystalline solids exhibiting the PIA phenomenon. Similar to ZrW_2O_8, β-eucryptite (β-LiAlSiO$_4$), which also possesses a framework structure (though solely composed of tetrahedra) and is a stuffed derivative of β-quartz, exhibits unusual behaviors at elevated temperatures, with a negative linear expansion along the c axis and a near-zero volumetric thermal expansion over a wide temperature range of 300−1400 K.[16,17] These characteristics make β-LiAlSiO$_4$ especially useful for synthesizing composite materials with very low thermal expansion. To further investigate such a connection and to extend our understanding of the underlying mechanisms for PIA, we have in this work studied β-LiAlSiO$_4$ up to pressures of 24 GPa with a particular aim to elucidate the relationship between PIA and equilibrium phase transformations taking place at elevated temperatures.

Experimental Methods

The starting β-eucryptite sample was synthesized from Li$_2$CO$_3$, Al$_2$O$_3$, and SiO$_2\cdot n$H$_2$O powders with molar ratios of 1:1:2. The oxide mixture was first sintered at 1373 K for 15 h and, after regrinding, resintered at 1573 K for 24 h. The obtained sample was phase-pure and homogeneous, as indicated by transmission electron microscopy, electron microscope analysis, and synchrotron X-ray/neutron diffraction.[17−19] Ten experimental runs were performed using in-situ X-ray diffraction as well as quench techniques, with experimental pressure−temperature ($P-T$) paths shown in Figure 1. X-ray diffraction experiments were performed using a DIA-type[20] and a "T-cup" large-volume apparatus.[21] An energy-dispersive diffraction method was employed using synchrotron radiation from the superconducting wiggler magnet at beamline ×17B2 of the National Synchrotron Light Source, Brookhaven National Laboratory (BNL), and from the bending magnet at beamline 13-BM-D, Advanced Photon Source of Argonne National Laboratory. The incident X-ray beam was collimated to dimensions of 100 × 200 μm, and diffracted X-rays were collected by a solid-state Ge detector at fixed 2θ angles. The cell assemblies used in the DIA experiments were similar to those described by Weidner et al.[20] Briefly, a mixture of amorphous boron and epoxy resin was used as pressure-transmitting medium, and amorphous carbon was used as furnace material. The powdered samples of β-LiAlSiO$_4$ and NaCl were packed into a cylindrical container of boron nitride, 1 mm diameter and 2 mm length. In the "T-cup" experiments, the boron−epoxy octahedron was used as pressure-transmitting medium, and rhenium foils were used as heating material. The quench experiments were conducted at the high-pressure laboratory of Stony Brook using a USSA-2000 press and 14/8, 10/5, and 8/3 cell assemblies,[22] and the recovered samples were examined by
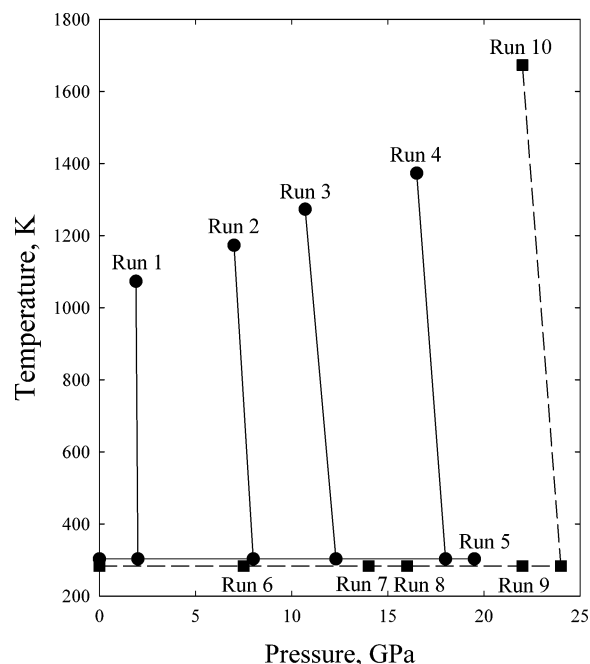

Figure 1. Simplified pressure−temperature paths for the experiments reported in this study. Solid circles and the connected lines denote $P-T$ paths for the in-situ X-ray diffraction experiments. Solids squares and dashed lines refer to the paths for quench experiments. The circle and square symbols with the run numbers next to them indicate the maximum pressure and temperature conditions reached in the experiments. Along $P-T$ paths in the X-ray diffraction experiments, diffraction patterns were collected during compression at 300 K, subsequent heating after reaching the desired pressures, and cooling to room temperature. In quench experiments (except for run 10), after staying at the target pressures for 10−15 min the samples were quenched and recovered to ambient conditions for synchrotron X-ray diffraction. The experimental results of run 1 have already been published in ref 24.

synchrotron X-ray diffraction at NSLS of BNL. For all the measurements at room temperature, a quasi-hydrostatic condition is expected as solid materials were used as pressure transmitting medium.

In both DIA and T-cup experiments, NaCl was used as an internal pressure standard. Pressures were calculated from Decker's equation of state for NaCl[23] using lattice parameters determined from X-ray diffraction profiles at each experimental condition. In these measurements the uncertainties in pressure are mainly due to statistical variation in the positions of diffraction lines and are less than 0.2 GPa in the pressure range of this study. Temperature was measured by a W/Re(25%)−W/Re(3%) thermocouple that was positioned at the center of the furnace and was in direct contact with the sample and NaCl layers. X-ray diffraction patterns were obtained for both sample and NaCl in close proximity to the thermocouple junction; errors in temperature measurements were estimated to be less than 10 K. In quench experiments, the pressures were determined by previous calibrations for 14/8, 10/5, and 8/3 cell assemblies.[22] No correction was applied for the effect of pressure on the thermocouple electromotive force (emf).

Results and Discussion

As observed in our previous study,[24] β-eucryptite underwent a phase transformation to ϵ-eucryptite between 1.0 and 1.5 GPa during room-temperature compression. The experi-

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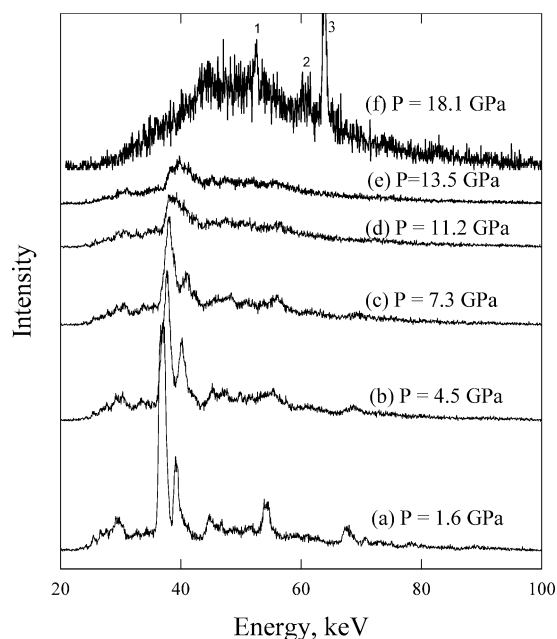
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Figure 2. Selected X-ray diffraction patterns under compression at 300 K. The diffraction peaks observed in pattern f at 18.1 GPa can be indexed as follows: (1) NaCl (200), (2) Re (002), and (3) Re (101), where NaCl and Re were used as pressure standard and heating material, respectively, in experimental run 5. In a different experiment (run 4), complete amorphization was observed at 17.0 GPa (see Figure 6a). Such a difference in pressure is partly due to the large pressure increments exercised in experimental run 5.

mental results obtained from two different runs at higher pressures (runs 4 and 5) are summarized in Figure 2. It can be seen that at 4.5 GPa all crystalline diffraction peaks began to broaden and lose their intensities, and with further increasing pressure the diffraction patterns were gradually replaced by a broad diffraction background characteristic of an amorphous material. In a large pressure range of 4.5−16.5 GPa, however, a remnant of some crystalline peaks was retained (Figure 2), indicating only partial amorphization under these pressure conditions. The most prominent changes occurred at a pressure of 17.0−18.1 GPa, where the sample lost all of its long-range ordering, as revealed by the disappearance of all diffraction lines in β-LiAlSiO₄ (e.g., Figure 2f). Evidently, at this pressure the sample had become completely amorphous. Note that the observations of this work on β-LiAlSiO₄ are similar to those on ZrW₂O₈,[4] in the sense that amorphization in both compounds are preceded by a phase transformation under room-temperature compression. Since nonhydrostatic conditions can strongly affect the PIA phenomenon by considerably lowering the amorphization pressure, as demonstrated in previous studies,[25] the pressures reported in this study are likely to provide lower bounds for both the onset and complete amorphization for β-LiAlSiO₄.

The diffraction peaks in Figure 2 show continuous broadening with increasing pressure. In particular, the observed increases in the peak widths are far beyond those expected from strain-induced broadening under nonhydrostatic conditions, which would ultimately be determined by the material strength and, as a first approximation, is

correlated to the materials incompressibility.[26] Since β-LiAlSiO₄ has a relatively small bulk modulus of 74 GPa,[27] the deviatoric stress built up during compression is expected to exceed the yield strength of β-LiAlSiO₄ at a certain relatively low pressure, as observed or expected in other weak materials. Above this pressure, the strain-induced broadening would no longer increase with increasing pressure. Therefore, some broadening in the diffraction peaks of β-LiAlSiO₄ is not likely to be strain-induced and, based on previous suggestion,[28] can be viewed as indirect evidence for occurrence of elastic shear instability under static compression. From this point of view, the mechanical instability or shear instability model[9] may be, at least partly, responsible for the observed pressure-induced amorphization in β-LiAlSiO₄. Obviously, this interpretation requires direct experimental confirmations of a phonon softening or of a decrease in elastic constants in the vicinity of PIA.

Molecular dynamics simulations and previous observations of high-pressure and high-strain-rate induced amorphization[29−31] have shown that collapse of crystal structure can take place along specific crystallographic orientations. In the case of β-LiAlSiO₄, the fact that a remnant of some diffraction peaks persists in a large pressure range (Figure 2) may indeed signify a likelihood of successive disordering of sublattices before ultimately leading to complete amorphization. This scenario is possible because the framework structure of β-LiAlSiO₄, a stuffed derivative of β-quartz (space group $P6_422$ or $P6_222$), is highly anisotropic.[17−19] Specifically, paired helical chains of [SiO₄] and [AlO₄] tetrahedra spiral in the same sense around 6_4 (or 6_2) screw axes parallel to c (Figure 3). The two helical chains are symmetrically related to each other by the 2-fold rotation within the 6-fold screw axes, and the intertwined chains produce open channels along c in which the charge-balancing Li resides. Moreover, the [SiO₄] and [AlO₄] tetrahedra alternate within (001) layers, and concomitantly Li is ordered within two distinct channels, as reflected by the doubled periodicities along both a and c axes relative to β-quartz. The structural anisotropy of β-LiAlSiO₄ results in its strong anisotropy in physical properties such as ionic conductivity, thermal expansion, and compressibility. In particular, linear isothermal compressibility (β) measurements indicate that β-LiAlSiO₄ is largely incompressible along the c axis ($\beta_c = -(1.13\pm 1) \times 10^{-13}$ cm²/dyn), whereas much more flexible parallel to the (001) plane ($\beta_a = +(22.4\pm 6) \times 10^{-13}$ cm²/dyn).[32] Thus, it is quite possible that, under nonhydrostatic loading, large anisotropic strains arise in β-LiAlSiO₄, and, further, they increase with increasing pressure, which would eventually lead to violation of the Born stability conditions for crystalline solids. Structurally, the progressive amor-

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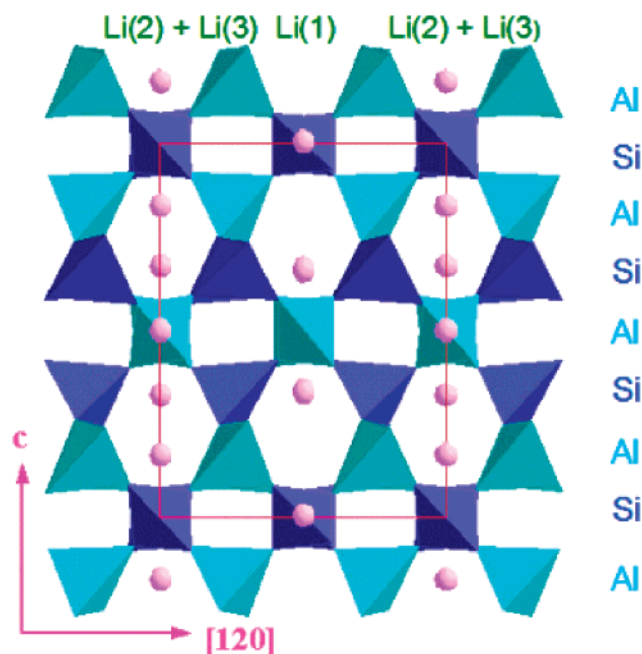(32) Hortal, M.; Villar, R.; Vieira, S.; Moya, J. S. *J. Am. Ceram. Soc.* **1975**, *58*, 262.

Figure 3. Structure of β-eucryptite projected down the *a* axis. Spheres represent Li ions; Si and Al tetrahedra are plotted in dark and light blue, respectively. Red lines outline the unit cell. Note that [AlO$_4$] and [SiO$_4$] tetrahedra alternate within layers normal to the *c* axis, while Li ions are ordered within two distinct channels along the *c* axis. The color variations of tetrahedra reflect the visual effects of graphic software.

phization may in turn involve a decrease in the Si(Al)−O−Si(Al) bond angle, distortion of Si/AlO$_4$ tetrahedra, shortening in the Si/Al−O distance, and finally possible increase in the Si/Al coordination. The revelation of the detailed structural mechanisms, however, would need diffraction data with higher resolution (such as single-crystal synchrotron XRD data) that allow determination of atomic positions as a function of pressure.

Previous observations have demonstrated that some materials exhibiting pressure-induced amorphization revert back to their original crystalline states (structure and orientation) when pressure is reduced or released.[8,33,34] This phenomenon is usually referred to as the structural memory of a material. In Figure 4, we show an X-ray diffraction pattern for one of the LiAlSiO$_4$ samples recovered from room-temperature compression to 14.0 GPa (run 7 in Figure 1). For comparison, we also present a pattern collected from an in-situ diffraction experiment at a similar pressure. The patterns for the recovered samples from 7.5 and 16.0 GPa are essentially the same as Figure 4b and therefore not presented here. These results suggest that β-LiAlSiO$_4$, when becomes only partially amorphous at 7.5, 14.0, and 16.0 GPa, returns to its initial crystalline structure. Following complete amorphization at 24 GPa, however, the system was recovered as a disordered phase that does not show any crystalline order, indicating that β-LiAlSiO$_4$ does not have structural memory when it becomes completely amorphous.

The fact that pressure-induced amorphization is reversible as long as a trace amount of remnant crystallinity is present indicates a close structural relationship between the ambient-
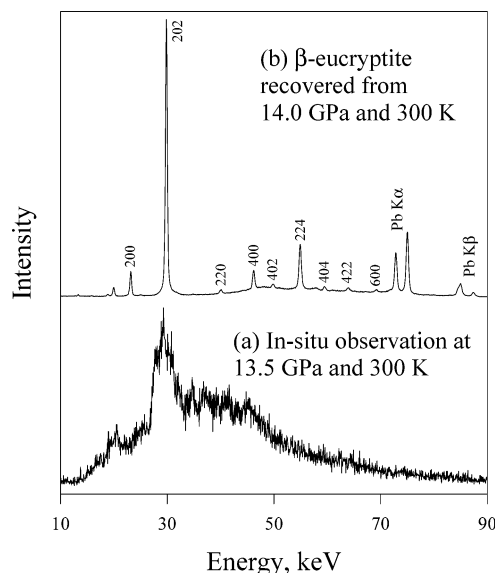

Figure 4. X-ray diffraction data (upper panel) for the eucryptite sample recovered from room-temperature compression to 14.0 GPa (run 7). The pattern collected from an in situ diffraction experiment at a similar pressure (lower panel) is shown for comparison. The diffraction patterns for the sample recovered from compression experiments at 7.5 and 16.0 GPa (runs 6 and 8) are essentially the same as pattern b and therefore not repeated here.

pressure crystalline state and the high-pressure disordered or amorphous state in LiAlSiO$_4$. This structural memory phenomenon is often discussed in terms of the presence of nondeformable units within the original structural framework.[35] While the exact mechanisms remain elusive, it has been suggested that these units can act as templates around which the original crystal structure can be regained upon release of pressure. In β-LiAlSiO$_4$, the [AlO$_4$] and [SiO$_4$] tetrahedra are linked by a three-dimensional framework via corner sharing (Figure 3). Since the Si−O bond is stronger than the Al−O bond, the more rigid [SiO$_4$] tetrahedra may act as the template units. Specifically, during compression to a certain pressure, the weaker [AlO$_4$] tetrahedra become gradually distorted, whereas the stronger [SiO$_4$] remain largely intact, resulting in a partially disordered state. Upon release of pressure, the nondeformable [SiO$_4$] units direct the transformed structure back to the ordered state through relaxation of Al and O atoms onto the original positions. The presence of Li ions in the structural channels (Figure 3) may also play a significant role in the relaxation, since it is energetically favorable to expand the structure, which effectively reduces the repulsion between Li and the aluminosilicate framework. However, when the pressure exceeds a certain threshold (e.g., $P \geq 17$ GPa for β-LiAlSiO$_4$), even the rigid [SiO$_4$] tetrahedra become deformable. Further, this process might involve breaking of tetrahedral Si/Al−O bonds and recombination of the bonds into polyhedra with higher coordination (such as octahedra), as demonstrated by previous studies on the amorphous−amorphous transitions that involve changes in coordination number.[36] It is thus conceivable that, upon release of pressure, this fully amorphous

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structure does not revert back to the original crystalline state, as that would require substantial structural reconstruction and large atomic movements. Note that a similar threshold pressure was also observed in a chemically complex system, $CaAl_2Si_2O_8$.[37] In this study, anorthite was observed to be fully amorphous at pressures above 16 GPa. However, only samples that were pressurized to $P > 22$ GPa can be recovered as amorphous phase upon decompression to ambient conditions.

For a given material that exhibits pressure-induced amorphization, previous studies have shown that the so-formed amorphous phase either reverts back to its original crystalline state or remains to be disordered upon release of pressure. For β-LiAlSiO₄, both phenomena are observed and the final, zero-pressure state of the amorphous phase depends on the compression history. Such characteristics make β-LiAlSiO₄ an ideal or a model material for elucidation of the underlying mechanisms of pressure-induced amorphization and the associated structural memory. Future studies of the disordered state using "local probe" techniques, such as neutron pair distribution function (PDF) and extended X-ray absorption fine structure (EXAFS) analyses, will allow us to gain detailed insights into such phenomena.

It is worthwhile to mention that the scale at which amorphization is observed is only for the long range. The observed amorphization in β-LiAlSiO₄ should be therefore termed X-ray amorphous, referring to the loss of long-range correlation within the crystal lattice. Since length scales giving rise to the X-ray diffraction indicate translational symmetry of the crystal on the order of 500−1000 Å,[38] the amorphization observed in this study is a result of the length scale of crystallinity reaching values less than the approximate threshold scale length of 500−1000 Å. One might tend to interpret the broadening and intensity reduction in diffraction peaks (e.g., Figure 2) to be a result of formation of nanocrystalline β-LiAlSiO₄ in the quasi-hydrostatic stress field. However, the ability of the samples to revert back to their initial crystalline state after decompression (Figure 4) argues against this possibility. Previous observations and theoretical calculations[39] have also revealed that nanostructured materials would preserve their crystalline ordering, even for crystallites that are less than 5 nm in size. Therefore, a complete loss of crystalline ordering in β-LiAlSiO₄ at pressures above 17 GPa (e.g., Figure 2f) cannot be attributed to the formation of nanocrystallites.

It is generally argued that pressure-induced amorphization is associated with kinetic hindrance of equilibrium-phase transformations.[10,11] The final state to which amorphous material would ultimately evolve at elevated temperatures, however, remains unknown or speculative in most systems. To explore the kinetics of amorphization and search for such final states, the partially or completely amorphous β-LiAlSiO₄ samples were heated at 8.1, 12.3, 17.0, and 22 GPa in four different experiments (Figure 1). With increasing
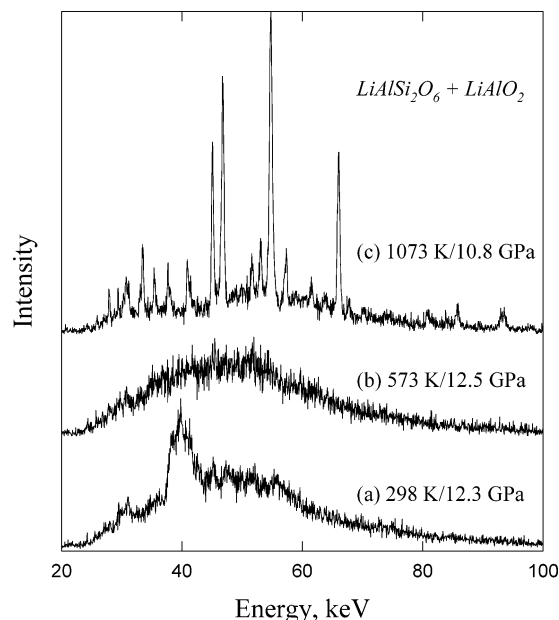

Figure 5. Selected X-ray diffraction patterns for β-LiAlSiO₄ during heating at 12.3 GPa. In another experiment where a partially amorphous sample was heated at 8.1 GPa (run 2 in Figure 1), the final equilibrium phases at 6.9 GPa and 1073 K are exactly the same as that shown in pattern c. At this lower pressure, unlike what has been observed in pattern b, the β-LiAlSiO₄ sample did not fully transform to an amorphous phase before it crystallized to the mixed phases.

temperature at 12.3 GPa, no significant changes were observed at temperatures below 523 K (Figure 5a). At 573 K, the remnant crystalline peaks quickly disappeared and the pattern is typical of an amorphous phase with broad background diffraction (Figure 5b), indicating that β-LiAlSiO₄ becomes completely amorphous at these conditions. Upon further heating to 1073 K, sharp diffraction peaks due to an amorphous-to-crystal transition appeared (Figure 5c). There was no change in diffraction patterns with increasing temperature up to 1273 K and then on slow cooling to room temperature. The pattern for the sample recovered at ambient conditions can be indexed as a mixture of spodumene $LiAlSi_2O_6$ and $LiAlO_2$ with a distorted rock salt structure. Similarly, a mixture of $LiAlSi_2O_6$ and $LiAlO_2$ phases was observed in a separate experiment when a partially amorphous β-LiAlSiO₄ was heated to 973 K at 6.9 GPa. However, we did not observe a transformation from a partial to complete amorphous phase before crystallization. A complete amorphization in β-LiAlSiO₄ is therefore pressure- and temperature-dependent. The results of this work confirm previous experimental results using α-eucryptite as starting material[40] and extend the stability field for the $LiAlSi_2O_6$ + $LiAlO_2$ assembly to at least 10.7 GPa.

In another high $P-T$ experiment (see $P-T$ paths for run 4 in Figure 1), we observed a transformation from a complete amorphous phase (Figure 6a) to a new, spinel-type polymorph at 15.3 GPa and 1273 K (Figure 6b). This finding is not surprising, and our results merely confirm previous observations at 12 GPa and 1273 K by the authors of ref 41, who yet again used α-eucryptite as starting material. Both

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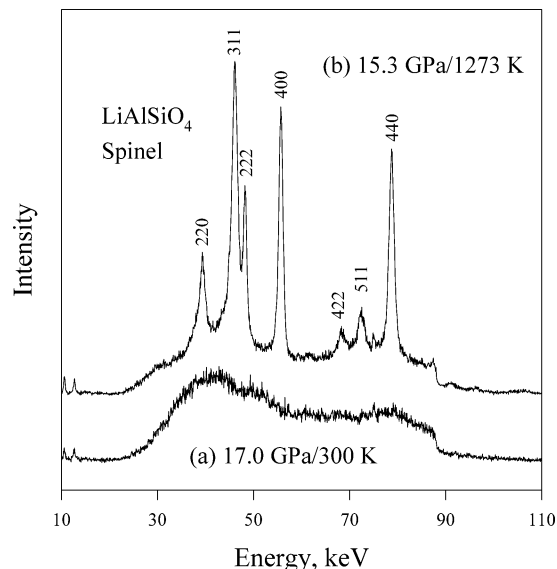
Figure 6. Selected X-ray diffraction patterns during heating at 17.0 GPa. Pattern a corresponds to the sample before heating. All diffraction lines in pattern b can be indexed as a spinel phase, which has previously been found in a quench experiment at 12 GPa and 1273 K.[41]
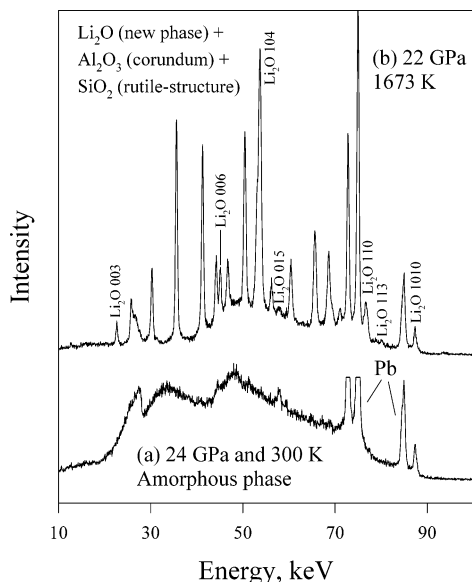

Figure 7. X-ray diffraction patterns showing the results of two quench experiments for the samples recovered from (a) 22 GPa/300 K and (b) 22 GPa/1673 K. All diffraction lines in pattern b can be indexed by Li_2O (Cs_2O_3 structure), Al_2O_3 (corundum), and SiO_2 (rutile-type).

studies demonstrate that $LiAlSi_2O_6$ and $LiAlO_2$ are recombined in the pressure range of ~12−15.3 GPa to form a spinel structure. The fact that the final equilibrium phases are independent of starting materials used in the experiments (i.e., β-eucryptite versus α-eucryptite) again indicates that pressure-induced amorphization is an intermediate state between the two thermodynamically stable states. In the fourth high $P-T$ experiment conducted at 22 GPa and 1673 K (run 10 in Figure 1), the recovered sample (Figure 7b) consisted of a crystalline mixture of Li_2O ($CdCl_2$ or C19 structure), Al_2O_3 (corundum), and SiO_2 (rutile-type), where C19 Li_2O is a new high-pressure polymorph of anti-fluorite-type Li_2O (see Table 1). Such observations indicate that the

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Table 1. X-ray Diffraction Data for a New High-Pressure Li_2O Phase[a]

d_{obs}, Å	d_{calc}, Å	$d_{obs} - d_{calc}$, Å	$h\,k\,l$
4.6730	4.6835	−0.0105	0 0 3
2.3370	2.3418	−0.0048	0 0 6
1.9619	1.9646	−0.0027	1 0 4
1.8100	1.8117	−0.0017	0 1 5
1.3700	1.3683	−0.0017	1 1 0
1.3121	1.3134	−0.0013	1 1 3
1.2100	1.2086	−0.0014	1 0 10

[a] Lattice constants for a hexagonal symmetry: $a = 2.737(2)$ Å; $c = 14.051(2)$ Å; $V = 91.13\,(2)$ Å^3. Note: The diffraction peaks listed here for the new Li_2O phase are those that are well-separated from diffractions of corundum (Al_2O_3) and rutile-type SiO_2. All these diffraction lines can be indexed by a hexagonal symmetry with a space group of $R\bar{3}m$, a C19 structure that has been observed in Cs_2O and $CdCl_2$.[47,48] For comparison, Li_2O at ambient conditions possesses an anti-fluorite structure. The present observations indicate an irreversible phase transformation for Li_2O between these two crystal structures.
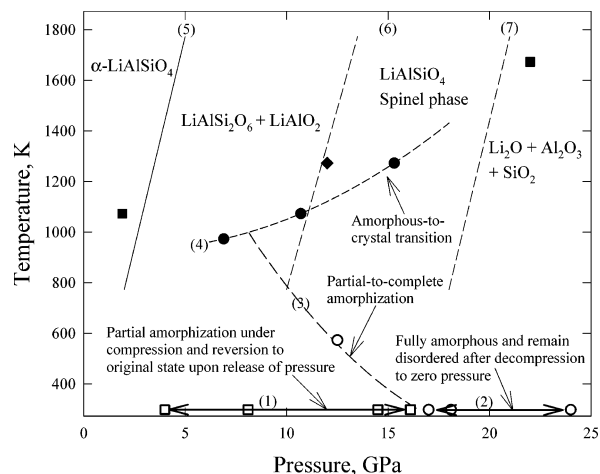

Figure 8. Summary of the experimental results in the $P-T$ space for illustration of pressure-induced amorphization (regions 1 and 2), its dependence on temperature (boundary 3), amorphous-to-crystal transformation (boundary 4), and tentative phase equilibrium boundaries for high-pressure transformation (boundaries 5−7) in $LiAlSiO_4$. The symbols indicate the conditions for the following key observations: open squares for progressive amorphization, open circles for complete disorder, solid circles for the onset temperatures of crystallization, and solid squares for the observations of runs 1 and 10. A solid diamond symbol refers to the $P-T$ conditions where a spinel phase of $LiAlSiO_4$ was observed in the study of ref 41. The decomposition boundary for α-eucryptite (line 5) is from ref 40.

spinel-type $LiAlSiO_4$ was decomposed into its constituent oxides at higher pressures. This decomposition reaction provides new information for the construction of a high-pressure phase diagram for $LiAlSiO_4$.

The key and representative observations discussed in the preceding paragraphs are summarized in Figure 8. In view of the limited experimental data points over a wide $P-T$ space, the exact locations of kinetic and equilibrium phase boundaries are far from being accurate and are shown with an aim to indicate a tentative phase diagram for $LiAlSiO_4$. Several conclusions, however, can be drawn on the basis of Figure 8. First, the pressures at which β-$LiAlSiO_4$ becomes completely amorphous decrease with increasing temperature (see curve 3 in Figure 8). Below the pressures defined by this kinetic boundary, the partially amorphous β-$LiAlSiO_4$ would not become completely amorphous even when subjected to elevated temperatures, at least within the time scale of the present experiments. Second, the temperatures for

nucleation and growth of crystalline phase(s) from the amorphous phase increase with increasing pressure, a consequence that may be associated with suppressed ionic mobility at higher pressures. Finally, all the equilibrium-phase transformations at elevated temperatures in the system $LiAlSiO_4$ are of a reconstructive type and characterized by a complex sequence of decomposition → recombination → decomposition with increasing pressure. Such observations support previous suggestions[42] that PIA could arise in many chemically complex systems when equilibrium decomposition to more densely packed daughter compounds is kinetically constrained.

Now that the final equilibrium phases and their crystal structures are known under a wide range of $P-T$ conditions, a brief review of the crystal chemistry of the phase transformations in the system $LiAlSiO_4$ could be elucidating. Both the Li and Al atoms are 6-fold coordinated in the spodumene and distorted rock salt structures,[41] as compared with both being 4-fold coordinated in the original β-$LiAlSiO_4$ structure. Hence, from the crystal-chemical point of view, the driving force for the breakdown of the β-$LiAlSiO_4$ framework at high pressures may be associated with the instability of the tetrahedral coordination around the Li and Al atoms. Following this argument, it can be speculated that the average coordination numbers for the Li and Al atoms would increase in the amorphous $LiAlSiO_4$ with increasing pressure. To take this argument one step further, even though there is no change involved in the polyhedral coordination for the Li, Al, and Si atoms in the recombination reaction $LiAlSi_2O_6 + LiAlO_2 \rightarrow LiAlSiO_4$ spinel,[41] the coordination number for Si changes from 4-fold in the $LiAlSiO_4$ spinel to 6-fold in the rutile-type SiO_2 when $LiAlSiO_4$ spinel breaks down into its constituent oxides at further high pressures. The observed phase transformations in $LiAlSiO_4$ thus involve profound changes in the atomic bonding configurations of high-pressure phases. Such changes are likely to reflect in the amorphous phase formed under different compression conditions, which upon confirmation would provide a firm support for the presumed correlation between pressure-induced amorphization and kinetically impeded phase transformations. The possibility that there may be a close structural relationship between the high $P-T$ crystalline state and the high-pressure disordered state may also explain the presence of a large pressure interval where a mixture of amorphous and crystalline $LiAlSiO_4$ phases coexists during room-temperature compression.

Since a large activation energy barrier is expected for changing the atomic coordination in oxygen-based compounds, phase transformations involving these changes are more likely to be kinetically inhibited, even at elevated temperatures.[43] Another factor that contributes to the sluggish kinetics arises from the fact that all the equilibrium phase transformations observed in $LiAlSiO_4$ (Figure 8) are not a polymorphic type and therefore diffusion-controlled. However, atomic diffusion, which is required for nucleation and growth of crystalline daughter phase(s) in a decomposition or recombination reaction, would be kinetically precluded in most systems at low temperatures. Indeed, the double sulfates such as $KHSO_4$ are the only known systems[42,44] that have exhibited pressure-induced decomposition at ambient temperature.

It can now be deduced that β-$LiAlSiO_4$ ends up in a disordered state under room-temperature compression primarily because the parent compound is metastable at the experimental conditions and because decomposition into denser daughter compounds or recombination of the daughter phases into a new high-pressure form is kinetically prohibited. A hindrance of atomic movement, as needed in the reconstructive phase transformations for $LiAlSiO_4$, is a primary factor that triggers pressure-induced amorphization at kinetically low temperatures. From this point of view, pressure-induced amorphization in β-$LiAlSiO_4$ and probably in most other systems can be viewed as one of the classic examples in which an intermediate or a metastable phase is often involved when transformation between the two thermodynamically stable states is kinetically hindered. Since the phase diagram of $LiAlSiO_4$ has not completely been determined in this study, it is difficult to determine if pressure-induced amorphization in this material can be of thermodynamic origin, i.e., directly connected to positions of phase boundaries for melting and solid-state transformation. However, based on the results of this work, pressure-induced amorphization does not appear to be necessarily connected either to such a thermodynamic origin. It must be emphasized that compression studies at 300 K are not sufficient for a comprehensive understanding of pressure-induced amorphization.

Since phase transformation is one of the focuses in this work, we would like to end this subject with a prediction that a mixture of Li_2O, Al_2O_3, and SiO_2 phases, observed at 22 GPa and 1673 K (Figure 7), will eventually recombine at higher pressures to form a new phase with a calcium ferrite ($CaFe_2O_4$) structure. Previous studies[40,45] have shown that $NaAlSiO_4$ (nepheline), a stuffed derivation of tridymite, was decomposed into a mixture of $NaAlSi_2O_6$ (Jadeite) + $NaAlO_2$ at 7−8 GPa and 1673 K, where $NaAlO_2$, like $LiAlO_2$, possesses a distorted rock salt structure. At higher pressures of 18−19 GPa, these two compounds recombine to form a new phase with a calcium ferrite structure. A more conclusive line of argument comes from high-pressure studies on $MgAl_2O_4$ spinel.[46] Like $LiAlSiO_4$ spinel, this compound breaks down to its constituent oxides of MgO and Al_2O_3 at pressures of ∼10 GPa, which yet again ends up in a calcium ferrite structure at pressures of 25−26 GPa. The presence of a calcium ferrite structure in $LiAlSiO_4$, if it can be proven, may serve as a good candidate for elucidation of the effect of crystal chemistry on the high-pressure phase transformations.

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Conclusions

We presented here another example that a state lacking long-range structural order can be created in β-LiAlSiO$_4$ under compression at 300 K. Upon release of pressure, the zero-pressure state of the so-produced amorphous phase depends on the compression history the sample has formerly experienced. As long as there is a trace amount of remnant crystallinity present at high pressures, the amorphous material is able to revert back to its original ordered structure, indicating a close structural relationship between the initial crystalline state and the high-pressure disordered state. When subjected to a complete amorphization at further high pressures, the LiAlSiO$_4$ sample was recovered as a fully disordered phase, thereby losing the so-called "structural memory".

For β-LiAlSiO$_4$, there is a large pressure interval where a mixture of amorphous and crystalline phases coexists during compression. In addition, the pressures at which β-LiAlSiO$_4$ becomes completely amorphous decrease with increasing temperature. These features indicate a kinetic origin for pressure-induced amorphization. The results of this work indicate that the mechanisms underlying such a kinetic origin arise from complicated phase equilibrium transformations at elevated temperatures, which are all of a reconstructive type and follow a complex sequence of decomposition $\rightarrow$ recombination $\rightarrow$ decomposition with increasing pressure. In particular, the observed phase transformations, which represent the final states that the amorphous material would ultimately attain at elevated temperatures, involve profound changes in the atomic coordination environments of high-pressure phases. Therefore, a large activation energy barrier associated with the changes in the atomic coordination and a hindrance of the associated atomic movement, as needed in the reconstructive transformations for LiAlSiO$_4$, are the primary factors that trigger pressure-induced amorphization at kinetically low temperatures. The present X-ray diffraction data, however, cannot provide any direct characterizations for the disordered state at high pressures, which warrants further studies utilizing "local probe" techniques such as PDF and EXAFS. The coordination changes observed for the Li, Al, and Si atoms in crystalline phases, for example, may also reflect in the amorphous phase formed under different compression conditions. This, if it can be proven, would indicate a close structural relationship between the high $P-T$ crystalline states and the high-pressure disordered state and therefore provide a firm support for the correlation between pressure-induced amorphization and kinetically impeded phase transformations.

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