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Direct Single Crystal to Amorphous Transformation and Memory Effect in $\text{AlPO}_4\text{-17}$.

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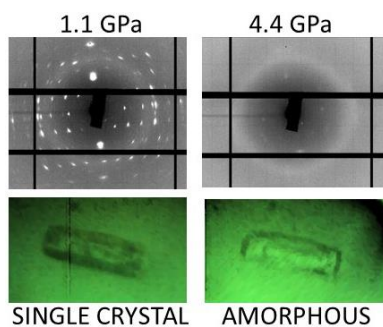
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ABSTRACT: Pressure induced amorphization provides a distinct route to prepare novel amorphous materials. Single crystals of the porous aluminophosphate $\text{AlPO}_4\text{-17}$ directly transform to an amorphous state beginning at 0.6 GPa, without fragmentation into polycrystalline material. Apart from a reduction in dimensions, the amorphous material retains the form of the initial single crystal. Remnant crystalline domains in the amorphous material also preserve the initial orientation of the single crystal. X-ray diffraction indicates the compression of the structure around the empty pores in the xy plane and such an amorphization mechanism is consistent with a direct structural relationship between the single crystal and amorphous forms. The collapse of the initial pore volume is almost complete at 2.5 GPa. A memory effect is observed in the amorphous form, which strongly expands on decompression. The present process opens the way for the synthesis of topologically-ordered amorphous materials approaching “perfect glasses” with improved mechanical properties.



The use of high pressure is a powerful tool to obtain new amorphous materials with distinct structural and physical properties with respect to standard glasses¹⁻³. In particular, pressure was found to produce a novel amorphous form of ice⁴. There was also considerable interest placed in the amorphization of quartz SiO_2 ⁵⁻⁷ and various minerals¹. Pressure-induced elastic softening has been identified in materials with the unusual property of negative thermal expansion⁸ followed in a large number of cases by amorphization such as in the case of zirconium tungstate ZrW_2O_8 ⁹⁻¹⁰. Both negative thermal expansion¹¹⁻¹³ and pressure-induced amorphization¹⁴⁻²¹ occur in a large number of porous materials, such as zeolites. Additionally, in the case of zeolites, slow compression opens the way for the synthesis of “perfect” or ordered

glasses¹⁶. Such “perfect glasses” exhibit a degree of structural order, low entropy and low fragility. The dense amorphous form obtained by the room temperature compression of the pure silica zeolite, silicalite-1, with the Mobil-five structure, was found to retain the framework topology of the starting zeolite, but is amorphous due to strong geometrical distortions¹⁷. This topologically ordered amorphous form exhibits permanent densification after compression at room temperature in contrast to silica glass²².

The aluminophosphate, $\text{AlPO}_4\text{-17}$, with the porous hexagonal erionite (ERI) structure (space group $P6_3/m$), is the zeolite-type material with the highest coefficient of negative thermal expansion²³ and exhibits an elastic instability and pressure-induced amorphization beginning near 1 GPa²⁰. In the present study, single crystals of this material are found to transform directly to the amorphous state retaining the form and orientation of the initial crystal. Single-crystal x-ray diffraction indicates a collapse of the pore network leading to amorphization.

Single crystals (110-160 μm maximum dimensions) of $\text{AlPO}_4\text{-17}$ (Figure 1a) were studied under hydrostatic pressure in DAPHNE 7474 oil²⁴ by single-crystal x-ray diffraction (XRD) in a diamond anvil cell at the Xpress beamline at the Elettra Sincrotrone Trieste. The ERI structure of $\text{AlPO}_4\text{-17}$ ²³ is built up of columns of alternating cancrinite (can) cages and double 6-membered ring (D6MR) secondary building units along the c direction with larger erionite (eri) cages between the columns (Figure 2a,b).

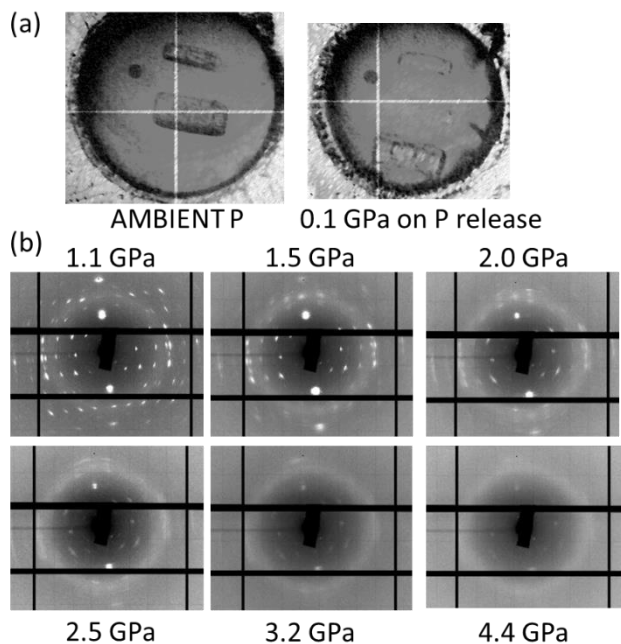


Figure 1. Optical images of investigated single crystal and amorphous $\text{AlPO}_4\text{-17}$ in the diamond anvil cell (a). X-ray rotation photographs ($\lambda=0.4956 \text{ \AA}$) of $\text{AlPO}_4\text{-17}$ at selected pressures (b).

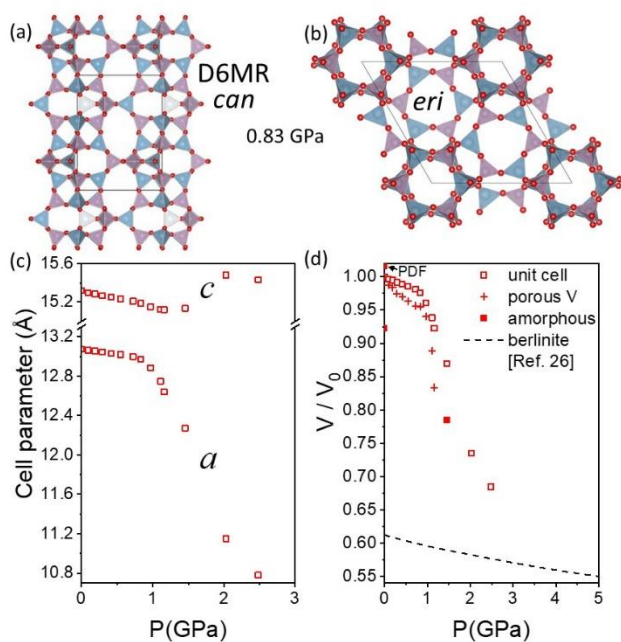


Figure 2. Projection of the polyhedral representation of the crystal structure of $\text{AlPO}_4\text{-17}$ along x (a) and z (b). Cell parameters of single-crystal $\text{AlPO}_4\text{-17}$ as a function of pressure (c). Relative unit cell volume and relative pore volume of $\text{AlPO}_4\text{-17}$ as a function of pressure (d). Data for the dense crystalline form of AlPO_4 , berlinite, from the literature are given for comparison²⁶.

The XRD data were of high quality with very good agreement factors for the structure refinements up to 0.6 GPa (Tables S1-S55). Up to this pressure, compression proceeded in a conventional manner (Figure 2c, S1) with similar compressibilities along the a ($0.0081(2) \text{ GPa}^{-1}$) and c ($0.0111(5) \text{ GPa}^{-1}$) directions and no direct evidence of elastic softening.

The pressure dependence of the unit cell volume (Figure 2d) can easily be fitted to a standard second-order Birch-Murnaghan²⁵ equation of state with a bulk modulus of 36(1) GPa and an implied first pressure derivative of 4 (Figure S2a). The Al-O-P angles most affected over this pressure range are the angles in the xy plane in the 4 membered rings (4MR) in the D6MR (Figure S3). The other angles remain quite stable. The main change is to the porous volume corresponding to the empty pores and cages (Figure 2d), which with a bulk modulus of 14(4) GPa (Figure 2b) decreases 2.6 times more rapidly than the unit cell volume and considering that the porous volume accounts for 38% of the unit cell volume, the compression mechanism correspond almost entirely to the collapse of the structure around the empty pores. At 0.55 GPa, for example, the reduction in pore volume of 32 \AA^3 corresponds exactly to the total reduction in unit cell volume.

Beginning above 0.7 GPa, elastic softening begins in the xy plane (Figure 2c) with decreases in the in-plane Al-O-P angles in the large *eri* cages (Figure S3). Concomitantly, a close to 30% decrease in intensity (Figure 3a) and broadening of the reflections of the single crystal are observed without the formation of polycrystalline material. At the same time, values of the agreement R-factors for the single crystal double (see supporting information). Another major decrease in intensity by more than a factor of two follows above 1.1 GPa. At this pressure, the diffuse signal of the amorphous form (Figure 1b) is clearly visible in x-ray rotation images, and based on its intensity, the majority of the material is already amorphous at this pressure. Additionally, in the remaining crystalline phase above 0.9 GPa a large number of superlattice *hkl* reflections (Figure S4) with half integer indices in h and k (i.e. $1/2$ 0 8 , $3/2$ 0 2 , $3/2$ $5/2$ 4 , etc.) with a maximum relative intensity of 4% appear indicating cell doubling along a and b as has also been found in oxygen filled $\text{AlPO}_4\text{-17}$ at much higher pressure²⁷. No clear distortion from a hexagonal unit cell metric is observed and any eventual lowering in symmetry could not be reliably determined due to the reduction in data quality at this pressure. Due to this reduced data quality, structure refinements were performed using the undoubled hexagonal sub-cell over the 0.9-1.2 GPa pressure interval, above which only the unit cell parameters could be refined. Cell doubling enables increased flexibility and subsequent rapid collapse of the decreasing amount of remnant crystalline material, which is progressively becoming amorphous with each further increase in pressure. Even though there is a decrease in crystal quality, the diffraction data continue to correspond to a single crystal albeit with a degree of strain corresponding the stress gradients experienced by the single crystal domains embedded in the amorphous material (Figure 1b). In addition, the orientation of the remnant crystal domains and the form of the macroscopic amorphous material are the same as that of the initial single crystal. These results are evidence for a direct relationship between the structure of the single crystal $\text{AlPO}_4\text{-17}$ and the collapsed network of the amorphous form around the empty pores, similar to the process in which the silicalite-1 structure collapses upon amorphization while retaining the structural topology of the crystalline phase¹⁷. The first stages of this collapse in $\text{AlPO}_4\text{-17}$ around the empty pores are clearly demonstrated by refined structures of the crystal up to 1.2 GPa (Figure 2d and Tables S2-S55).

The diffuse halo corresponding to the first sharp diffraction peak (FSDP) increases in intensity and shifts to higher Q values with increasing pressure (Figure 3b). The increase in FSDP is an indication of a modification of the intermediate range structure of the amorphous form and for higher pressures, the values are similar to those of silica glass²⁸. A large decrease in the FSDP occurs on pressure release with a value similar to that of recovered amorphous $\text{AlPO}_4\text{-17}$ ²⁰ (Figure S5). This decrease indicates that the changes in intermediate range structure are reversible. The relative volume and density of the amorphous form at ambient pressure, estimated by the reduction in single crystal dimensions upon transformation to the amorphous form (Figure 1a), are 0.92 and 1.7 g/cm^3 , respectively. An independent determination of the density based on the initial slope of the reduced pair distribution function $G(r)$ from a previously-obtained, recovered, amorphous powder sample (Figures S6 and S7) yields a density of close to 1.6 g/cm^3 . This is essentially the same as that of the initial crystal of $\text{AlPO}_4\text{-17}$ (1.607 g/cm^3). This low density is consistent with recovery of a significant degree of pore volume providing evidence for the retention of the initial structural topology in the amorphous form. The changes in intermediate range structure corresponding to the large decrease in the position of the FSDP in Q can be expected to arise from geometrical

changes (bond angles etc.) yielding voids in the structure. This recovered structure is not periodic and remains amorphous. This recovery of an amorphous material with a similar density to the initial crystalline phase is an indication of a memory effect at the level of the local and intermediate range order. It is distinct from the memory effect reported in crystalline, non-porous AlPO_4 berlinite, which was proposed to transform reversibly to an amorphous form under pressure²⁹. Later studies by Raman spectroscopy³⁰ and x-ray powder diffraction³¹ indicated that instead the high-pressure form was a poorly-crystallized phase with a CrVO_4 structure with Al in octahedral coordination, which retransformed to berlinite on decompression.

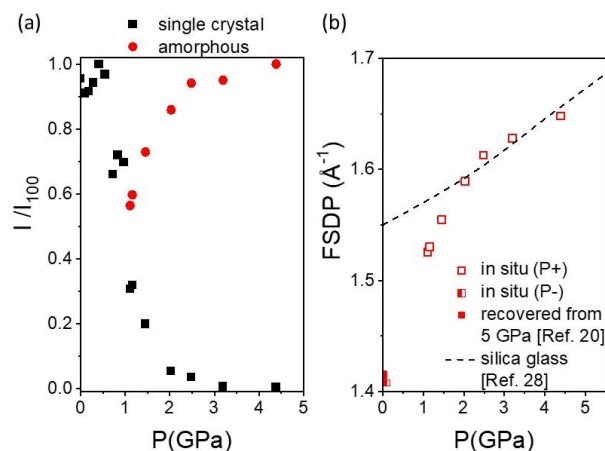


Figure 3. Normalized intensity of diffraction signals (with respect to maximum values for single crystal and amorphous) of AlPO_4 -17 as a function of pressure (a). Position of the FSDP in Q of AlPO_4 -17 as a function of pressure (b). Data for silica glass²⁸ are given for comparison.

Based on x-ray diffraction, the unit cell volume of the crystalline phase decreases by 32% between ambient pressure and 2.5 GPa. This can be compared with initial pore volume, which represents 38% of the total volume of the AlPO_4 -17 structure. The dimensions of the sample at 1.45 GPa, which was then predominantly amorphous, give a relative volume of 0.78 for the amorphous form. This is 8% lower than the remnant crystalline domains at the same pressure. Based on these results, the amorphous form can be expected to exhibit almost no porosity at 2.5 GPa. It can be noted that starting from this pressure, the position of the FSDP is similar to that of non-porous silica glass.

The present results provide a coherent overall picture of a direct transformation of a single crystal to an amorphous material. The retained shape of the crystal and the orientation of remnant crystal domains upon transformation are consistent with a direct transformation pathway. Single-crystal x-ray diffraction indicates the collapse of the structure around the empty pores. The estimation of the density of the amorphous form provides evidence that the pressure-induced volume changes are reversible. This collapse of the structure and the observation that the reversible volume change essentially corresponds to the initial porous volume of the crystal can be indirectly used to infer that the transformation mechanism corresponds to pore collapse while keeping the network topology of the AlPO_4 framework. A memory effect is observed in the amorphous form, which strongly expands on decompression returning to the density of the initial crystalline form without recovering long-range order. The amorphous form thus exhibits a very high degree of flexibility. Such a new topologically ordered amorphous phase could approach a low-entropy “perfect” glass with improved mechanical properties as compared to standard glasses.

ASSOCIATED CONTENT

Supporting Information

Experimental details, additional figures and tables of crystallographic data are supplied as Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Accession Codes

CSD 2323675-2323684 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Notes

The authors declare no competing financial interest.

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