

Amorphization, insertion and reactions in microporous $\text{AlPO}_4\text{-54}$ at high pressure

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Microporous materials, such as zeolites and aluminophosphates exhibit low-density, porous structures built up of corner-sharing tetrahedra (SiO_4 , AlO_4 , PO_4) and are extensively used in important technological applications as molecular sieves and catalysts. Pressure-induced amorphization (PIA) is commonly observed in such open framework structures and has been linked to the effect of pressure on low-energy vibrations, such as rigid-unit modes. Incorporation of guest species [1,2] and PIA [2-4] may confer useful properties in these materials for new potential applications, related to their high porosity, in the field of the absorption of mechanical shocks. $\text{AlPO}_4\text{-54}$ is a hydrated aluminophosphate with the hexagonal VFI structure (space group $P6_3$) [5] with $a=18.9678(13)\text{\AA}$ and $c=8.0997(4)\text{\AA}$, $Z=18$ [6]. This material exhibits among the largest pores known for zeolites and aluminophosphates, with a diameter of 12\AA . The framework is built up of 4, 6 and 18-membered rings of alternating AlO_6 octahedra or AlO_4 tetrahedra and PO_4 tetrahedra. One third of the aluminum cations are octahedrally coordinated due to the presence of two water molecules in the coordination sphere. The effect of superhydration on the compressibility of zeolites has been investigated [7,8]; however, its effect on PIA is not yet clear. Based on x-ray powder diffraction and Raman spectroscopy, $\text{AlPO}_4\text{-54}$ was found to begin to amorphize near 2 GPa using either a non-penetrating pressure transmitting medium (PTM), silicone oil, or no PTM. When H_2O is used as a pressure-transmitting medium, amorphization begins at a lower pressure of 0.9 GPa. In this case superhydration effects are observed and no decrease in the unit cell volume is observed up to the beginning of PIA, due to insertion of the H_2O molecules in the pores. The incorporation of certain guest species (Ar , CO_2) has been found to strongly increase the PIA pressure in the pure SiO_2 zeolite, silicalite [4]. The opposite effect in the present case may be due to interactions between the water molecules and the remaining Al cations in 4-fold coordination, which may increase to 6 providing a possible mechanism for PIA.

The goal of the present experiment was to obtain direct structural information (bond distances and angles, Al coordination numbers, positions of the oxygen atoms from the water molecules) on $\text{AlPO}_4\text{-54}$ at high pressure in silicone oil and H_2O using single-crystal x-ray diffraction in a diamond anvil cell on the F1 beam line. These results will be used to determine the compression mechanism in this material and the study the superhydration process (changes in position and occupancy of the water oxygen sites, changes in coordination of aluminum). These measurements and the differences in behavior with the two pressure-transmitting media are thus expected to provide an insight on the PIA mechanism in this material.

Single crystals of $\text{AlPO}_4\text{-54}$ with dimensions of $25\mu\text{m}\times 25\mu\text{m}\times 220\mu\text{m}$ were studied in Merrill-Bassett diamond anvil cells (DAC) at high pressure on the 4-circle diffractometer equipped with a MarCCD 165 detector on the F1 beamline ($\lambda=0.5000\text{\AA}$). Phi-scans were performed at a series of pressures in the DAC (0.2 and 0.5 GPa in H_2O and 0.4, 0.7 and 1.2 GPa in DAPHNE 7474 oil, which is hydrostatic up to 4 GPa and does not enter the pores). Pressure was measured using the ruby fluorescence method. The higher values obtained for the unit cell parameters in H_2O as compared to silicone oil using the present data confirm the superhydration effect in this material. The unit cell volume at 0.5 GPa in H_2O is 2491\AA^3 , whereas it is almost 2% lower at 0.7 GPa in DAPHNE 7474, 2447\AA^3 . The data obtained are of high quality (Figure 1). At 1.2 GPa, 2466 unique

reflections were measured of which 1497 were greater than 2σ . Structure refinements have been successfully performed in the $P6_3$ space group with an R-factor of 6.6% and the distances in the AlO_6 octahedra, AlO_4 tetrahedra and PO_4 tetrahedra are found to vary little with pressure. The detailed analysis of the positions of the oxygen atoms in the H_2O molecules is in progress and can be expected to provide a detailed understanding of the compression mechanism in this material.

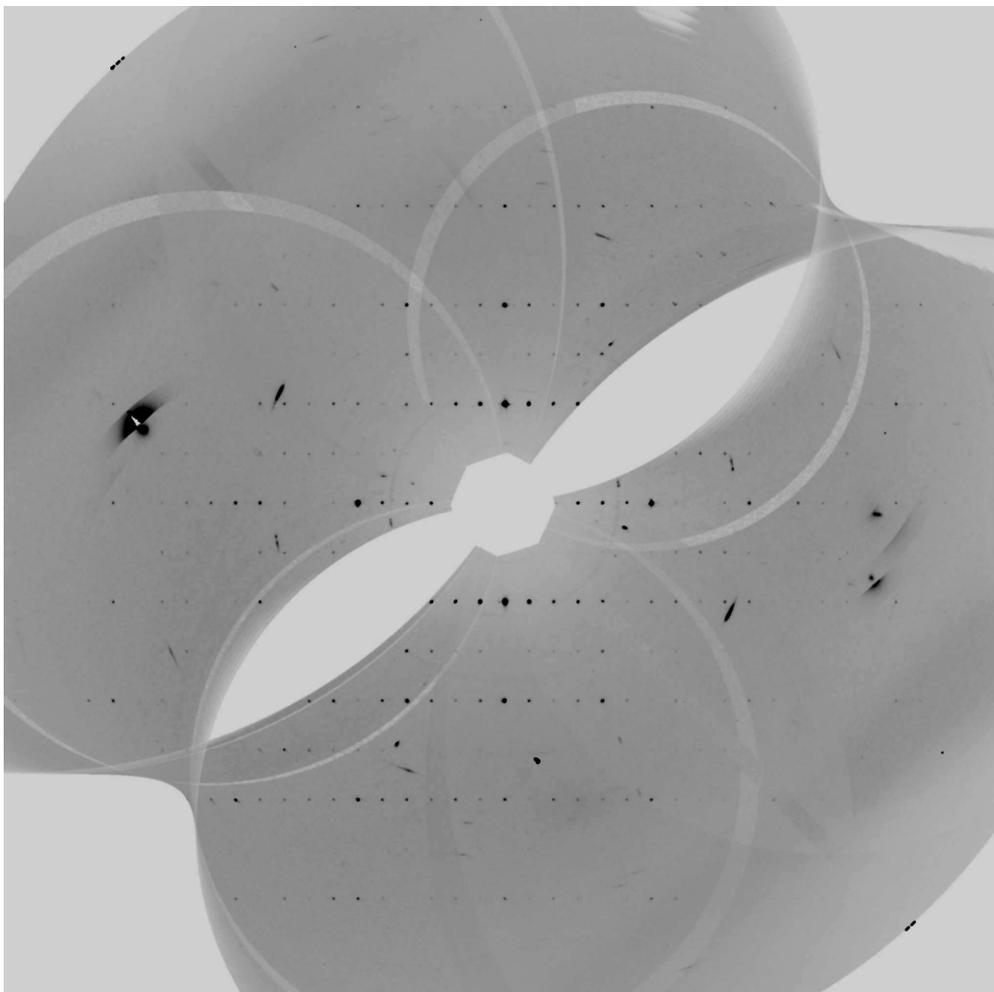


Figure 1: 0kl Reciprocal space reconstruction from $\text{AlPO}_4\text{-54}$ at 0.5 GPa in H_2O .

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