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$AlPO_4$-5 zeolite at high pressure: Crystal–fluid interaction and elastic behavior

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ABSTRACT

The high-pressure behavior of the aluminophosphate zeolite $AlPO_4$-5 (AFI-topology) has been investigated by *in situ* single-crystal synchrotron X-ray diffraction with a diamond anvil cell, using the “non-penetrating” silicone oil and the “penetrating” 16:3:1 methanol:ethanol:water (*m.e.w.*) mixture as *P*-transmitting fluids. The crystals used in this study showed diffraction patterns typical of an incommensurate modulated structure, with modulation vector $q \approx 0.37\mathbf{c}^*$. Compression in silicone oil showed that $AlPO_4$-5 is one of the softest zeolites reported so far, being its refined bulk modulus ($K_{V0} = 1/\beta_V$) at ambient conditions only 13.2(11) GPa ($\beta_V = 0.076(6)$ GPa^{-1}), with an elastic anisotropy $K_a{:}K_c = 1.6$. The high-pressure experiment performed using *m.e.w.* showed a significantly lower compressibility of $AlPO_4$-5, if compared to the behavior in silicone oil, suggesting the occurrence of a *P*-induced intrusion of the fluid molecules into the zeolitic cavities. An indirect evidence for the molecules intrusion is provided by the comparative analysis of the structure deformation mechanisms at the atomic scale. When zeolite $AlPO_4$-5 is compressed in *m.e.w.*, a lower degree of distortion of the secondary building units is observed, with respect to the compression in silicone oil. Overall, this study suggests zeolite $AlPO_4$-5 as a promising microporous material for the pressure-mediated intrusion and hyper-confinement of molecules into the structural micropores.

1. Introduction

Aluminophosphate $(Al,P)_nO_{2n}$ compounds [1–2] are a group of microporous materials, which share with the most common $(Al,Si)_nO_{2n}$ zeolites a large diversity of structures [2–3], as well as applications as molecular sieves, catalysts, etc. [1]. An important member of this group is the aluminophosphate zeolite number 5 ($AlPO_4$-5, [4]), with the AFI-framework type [5]. As shown by the high number of very recent studies, spanning from synthesis methods (e.g. [6–7]) to structural characterization (e.g. [8]) or potential technological and industrial applications (e.g. [9–11]), $AlPO_4$-5 is an object of a growing research interest. The AFI-framework is characterized by very large channels made by 12-membered rings of tetrahedra (hereafter 12R-channels, Fig. 1a), which are an ideal host for several molecules and polymers, as single-walled carbon nanotubes [11–13], dye molecules [14–15] or 1D-arrays of iodine [16], nitrogen [17], etc.

The AFI-framework shows a $P6/mcc$ topological symmetry, with ideal cell parameters $a = 13.827$ and $c = 8.580$ Å [5]. The 12R-channels are parallel to the [001] direction and centered to the six-fold axis (Fig. 1a). Their largest free diameter (7.42 Å, [5]) is defined by the two symmetry-independent O1–O1 and O3–O3 (Fig. 1a) interatomic distances. The channels are connected to each other by “pseudo-cage” cavities that are confined in the (001) plane by single 6-membered rings of tetrahedra centered on the 3-fold axis (hereafter S6R[001], Fig. 1a). The access between the channels and these pseudo-cages is controlled by single 6-membered rings of tetrahedra, approximately parallel to the **c**-axis (hereafter S6R $[hk0]_1$, Fig. 2a,c). However, in order to diffuse from a channel to the neighboring ones, a molecule/ion needs to cross a second symmetry-independent single 6-membered ring of tetrahedra (S6R

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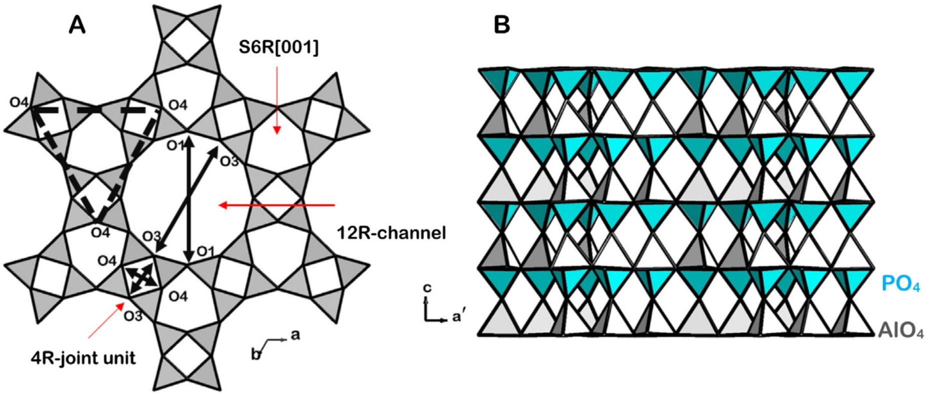

Fig. 1. (A). The AFI framework of the zeolite $AlPO_4$-5 viewed down the **c** crystallographic axis. The secondary building units and some relevant interatomic distances reported in Table 2 are shown. (B). The AFI framework viewed along the **b** crystallografic axis. The sheets made by upward AlO_4 and downward PO_4 tetrahedra are shown.

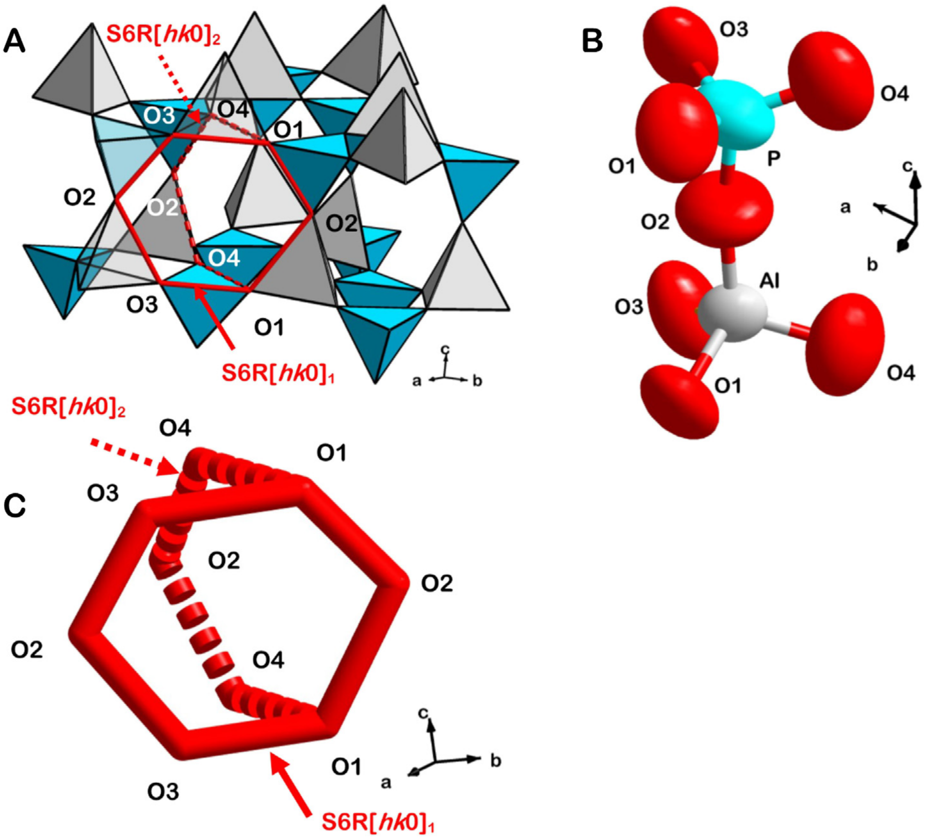

Fig. 2. (A) A view of the two symmetry-independent 6-membered rings "windows" of tetrahedra (S6R[*hk*0]$_{1,2}$) defining the access between neighboring 12R-channels. A schematic view of the two symmetry-independent S6R[*hk*0]$_{1,2}$ "windows" is also given in (C). (B) Upward AlO_4 and downward PO_4 tetrahedra, shown with the anisotropic displacement parameters and based on the structure refinement with the crystal in air of this study (displacement probability factor: 50%).

[*hk*0]$_2$, Fig. 2a,c). The diameters of these "windows" define the largest diameter of a sphere able to diffuse from a channel to another, reported to be 2.22 Å for the ideal AFI-framework [5].

The structure of $AlPO_4$-5 can also be described by the alternation, along the **c**-axis, of sheets made by isolated upward AlO_4 and downward PO_4 tetrahedra, respectively (Fig. 1b). The AlO_4 and PO_4 tetrahedra bases are linked through the O1, O3 and O4 sites, whereas the O2 site acts as a bridge between the tetrahedra pointing upward and downward, respectively (Fig. 2b). The observed distribution of Al and P between the tetrahedral sites reduces the symmetry of $AlPO_4$-5 from *P*6/*mcc* to *P*6*cc*. However, conflicting results are reported in the literature concerning the real symmetry of $AlPO_4$-5, as the space group *P*6*cc* leads to Al—O2—P interatomic angles close to 180°. A comprehensive overview is reported by Bordat et al. [18]. Several authors reported diffraction patterns being inconsistent with *P*6*cc*, and suggested the reduction of the $AlPO_4$-5 symmetry to a different hexagonal [19] or orthorhombic [20–22] subgroup of *P*6*cc*. Uncertainties concerning the real symmetry of $AlPO_4$-5 persist also if theoretical calculations are considered [18,23–24]. Therefore, a clear and unambiguous picture of the zeolite $AlPO_4$-5 crystal structure is still missing (see e.g.