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Contrasting high-pressure compression behaviors of $AlPO_4$-5 and SSZ-24 with the same AFI framework topology

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ABSTRACT

The high-pressure structures of $AlPO_4$-5 ($Al_{12}P_{12}O_{48}\bullet 9.9H_2O$) and SSZ-24 ($Si_{24}O_{48}$) with the same AFI framework topology were studied using synchrotron X-ray powder diffraction and a pore-penetrating (at a mixture of 16:3:1 by volume of methanol:ethanol:water) pressure medium. An analysis of the diffraction profiles of the $AlPO_4$-5 reveals that the *a*-axis length expands initially before it starts to contract, whereas the *c*-axis contracts steadily throughout the pressure range up to 5 GPa. As a result, the unit cell volume at 0.7(1) GPa appears larger by 3σ than that at ambient conditions, and the bulk modulus after this initial volume expansion is calculated to 50.5(7) GPa. In the SSZ-24, the unit cell contraction is monotonic with a steeper slope than that of $AlPO_4$-5 leading to a smaller bulk modulus of 21.7(3) GPa. The reason for the two contrasting compression behaviors of the AFI frameworks is suspected to be related to the difference in the hydrophobicity of the framework and hence the water distribution in the channel. To evaluate the effect of the pressure medium, the experiment on SSZ-24 was repeated using a non-penetrating silicone oil pressure medium and laboratory X-ray powder diffraction. The bulk modulus of SSZ-24 was found to the same low value of 21.7(3) GPa demonstrating that the measured compressibility of SSZ-24 is inherent to the AFI framework type.

1. Introduction

Zeolites are crystalline microporous materials which are commonly used as absorbents, ion-exchangers and catalysts [1]. Such useful properties stem from the relatively large surface area due to regularly spaced and molecular-sized cavities and channels throughout the crystalline structure. Thus far, nearly 201 unique zeolitic frameworks have been identified either from nature or via synthetic methods [2]. The term zeolite, meaning ‘boiling-stone’, was originally coined in 1756 by the Swedish mineralogist Axel Fredrik Cronstedt, who observed that upon the rapid heating of the aluminosilicate mineral stilbite, large amounts of steam were produced from water that had been adsorbed by the material [3]. The anhydrous zeolite becomes rehydrated when cooled down and exposed to the atmosphere. This temperature range is regarded as one of the major variables that alters the structure and chemistry of a given zeolite. The effect of pressure, however, has largely been underexplored despite the fact that it is another major thermodynamic variable and is applied in the synthesis and many application processes [4]. When pressure is applied, zeolitic pores and channels built from the polymerization of the primary tetrahedral building units (TO_4, T = Al, Si, Ga, Ge, P, etc.) are deformed and compressed through flexible T–O–T tetrahedral linkages. The pressure-driven structural responses of zeolites are, therefore, largely dictated by the arrangements of the pores and channels, in many cases leading to anisotropic compressions [5,6]. In addition, the contents of the non-framework species such as charge-balancing cations and adsorbed water molecules and their distributions within the pores and channels play an important role in modulating the compression behavior [7,8]. This is especially the case when pore-penetrating pressure-transmitting media are used [9]. An abrupt increase in channel water content and the resulting expansion of the unit cell volume reportedly occur in zeolite natrolite and its structural analogues under pore-penetrating hydrostatic conditions in the range of 0.6–1.5 GPa [10–12]. This phenomenon has been termed as pressure-induced hydration, demonstrating that pressure can be a useful means to alter both the structure and composition of zeolites in unprecedented ways compared to the temperature effects.

An important class of zeolitic materials includes the aluminophosphates ($AlPO_4$) molecular sieves, which represent the first family of non-silica open framework oxides [13]. This class of microporous materials has been studied extensively given that their structural and chemical properties are analogous to zeolites in the

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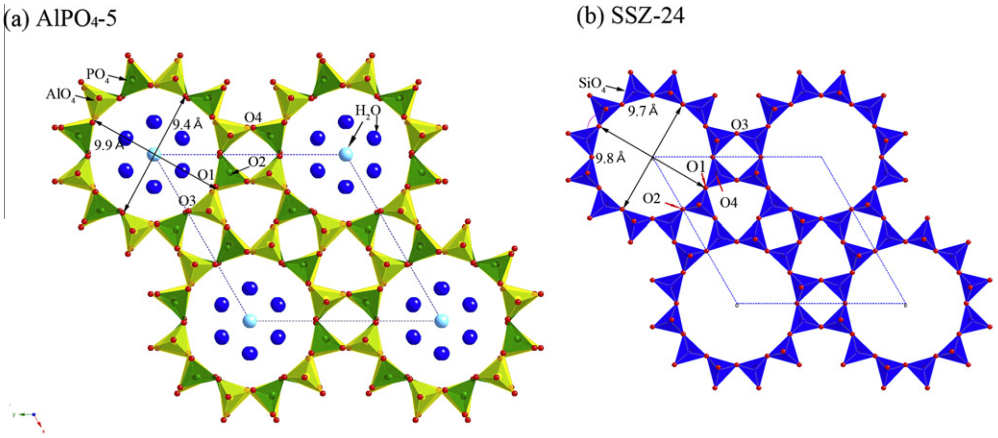

Fig. 1. Polyhedral representations of the structure models of (a) $AlPO_4$-5 and (b) SSZ-24 viewed along the *c*-axis. Two-tone color tetrahedra in $AlPO_4$-5 illustrate the alternation of AlO_4 and PO_4 throughout the AFI framework, while the single-color tetrahedra in SSZ-24 demonstrate the SiO_4 framework. Filled circles are water sites (site 1 at the center of the channel and site 2 near the wall). Dotted lines define the hexagonal unit cells. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

search for improved performance levels in adsorption and catalysis processes [14,15]. In fact, many $AlPO_4$ molecular sieves are isostructural with zeolites, while others possess unique framework topologies found only as different types of $AlPO_4$, e.g., DAF-1 and VPI-5 that defined DFO and VFI topologies, respectively [16,17]. The former case provides a unique opportunity to study the effect of the framework compositions on pressure- and/or temperature-induced structural changes. One such case is the AFI framework topology [18], which is adopted by $AlPO_4$-5 and SSZ-24, a pure-silica counterpart [19]. The structure of $AlPO_4$-5 is composed of corner-sharing alternation of AlO_4 and PO_4 tetrahedra such that AlO_4 and PO_4 tetrahedral sheets and circular 12-ring channels are stacked along the *c*-axis (Fig. 1a). The space group of $AlPO_4$-5 is *P*6*cc* with the origin at the center of the circular 12-ring channel. Alternatively, the structure of $AlPO_4$-5 can be described as hexagonal close packing of 12-ring channels perpendicular to the *c*-axis connected by the alternation of 4-ring and 6-ring windows. Within such a one-dimensional channel system with an access diameter of ca. 7.3 Å, structure-directing agents are occluded in synthesis conditions or water molecules in ambient conditions after calcinations [20–22]. By introducing different framework metal cations, $AlPO_4$-5 can be used as a recyclable catalyst for various oxidation reactions of alkanes, cycloalkanes or phenols [23]. $AlPO_4$-5 has also been used in nonlinear optics and as a nanoscale container to synthesize the smallest single-walled carbon nanotubes within its 12-ring channels [24]. In the case of SSZ-24, which possesses higher symmetry of *P*6/*mcc* due to the sole occupation by silicon in all of the tetrahedral sites, the framework is hydrophobic and the 12-ring channels are empty without any adsorbed water molecules under ambient conditions (Fig. 1b) [19].

We carried out comparative high-pressure structural studies on $AlPO_4$-5 and SSZ-24 to gain insight into the effect of the framework composition and hydrophobicity on the compression behavior using both pore-penetrating water and non-penetrating silicone oil pressure media.

2. Experimental section

2.1. Synthesis and thermogravimetric analysis

$AlPO_4$-5 zeolite was synthesized according to the procedure developed by Wilson et al. [25]. SSZ-24, a pure-silica version of $AlPO_4$-5, was prepared by a modification of examples in the Chevron patent [26]. As-made $AlPO_4$-5 and SSZ-24 were calcined under flowing air at 550 °C for 8 h to remove the occluded organic structure-directing agents. Thermogravimetric analysis (TGA) reveals that the $AlPO_4$-5 sample, calcined and subsequently exposed to ambient air for 3 days, is characterized by a weight loss of ca. 18.7 % up to 800 °C. However, the TGA curve of the similarly calcined and air-exposed SSZ-24 was found to give only a marginal weight loss of surface water up to 800 °C, indicating that its one-dimensional 12-ring channels are essentially free of water molecules.

2.2. High-pressure X-ray powder diffraction

High-pressure monochromatic synchrotron X-ray powder diffraction measurements were performed using a symmetric diamond-anvil cell (DAC) and an imaging plate detector at the 5A-HFMS beamline at the Pohang Accelerator Laboratory (PAL). The powdered $AlPO_4$-5 and SSZ-24 samples were each loaded into a 260 μm diameter–100 μm thick sample chamber in a pre-indented stainless steel gasket along with a few small ruby chips to function as a pressure standard. A mixture of 16:3:1 by volume of metha-

Table 1
Final refined atomic coordinates for $AlPO_4$-5 under hydrostatic pressure using the pore-penetrating pressure medium (16:3:1 medium).

	Ambient	0.7(1) GPa	1.4(1) GPa	2.1 GPa	3.1(1) GPa	4.1(1) GPa	5.2(1) GPa	Released
S. G.	*P*6*cc*	*P*6*cc*	*P*6*cc*	*P*6*cc*	*P*6*cc*	*P*6*cc*	*P*6*cc*	*P*6*cc*
$_wR_p$ (%)	0.97	1.14	0.75	0.9	0.82	0.76	0.79	0.86
R_{F2} (%)	2.80	2.15	1.40	1.05	1.39	1.27	1.29	2.04
χ^2	0.9277E-01	0.1177	0.9008E-01	0.1062	0.1148	0.1130	0.1277	0.7789E-01
H_2O/u.c.	9.9(2)	7.8(2)	7.6(2)	7.6(1)	7.8(2)	7.92(5)	6.6(4)	9.2
a (Å)	13.6316(9)	13.639(2)	13.609(2)	13.570(3)	13.477(4)	13.397(5)	13.310(6)	13.652(1)
c (Å)	8.3406(4)	8.338(1)	8.325(1)	8.304(1)	8.253(2)	8.217(2)	8.171(3)	8.3858(6)
V (Å^3)	1342.2(2)	1343.4(4)	1335.3(4)	1324.3(5)	1298.1(7)	1277.3(9)	1253(1)	1353.5(2)