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Elastic behavior and high pressure-induced phase transition in chabazite: New data from a natural sample from Nova Scotia

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ABSTRACT

The high pressure behavior of a natural chabazite from Nova Scotia (Canada) $[(Ca_{1.32}K_{0.45}Na_{0.13}Sr_{0.10})[Si_{8.55}Al_{3.45}O_{24}]\cdot 11.30\ H_2O$, s.g. R-3m, $a = 9.38749(8)$ and $\alpha = 94.379(1)$] was investigated by means of *in situ* synchrotron X-ray powder diffraction and silicone oil as non-penetrating P-transmitting medium, in the P-range from P_{amb} to 7.2 GPa. Above 2.1 GPa, a phase transition from rhombohedral to triclinic (pseudo-rhombohedral) symmetry is observed. The phase transition is accompanied by an abrupt decrease of most of the cell parameters and of the cell volume. Above the transition – between 2.5 and 5.9 GPa – the triclinic/pseudo-rhombohedral cell parameters decrease regularly, with a compressibility decrease relative to the trend observed before the transition. A further increase in compressibility occurs in the highest P regime, between 5.9 and 7.2 GPa. Overall, the cell volume decrease in the investigated P-range is 12.6%. Notwithstanding the abrupt and marked cell volume decrease accompanying the phase transition, this is reversible upon decompression. The refined elastic parameters were $V_0 = 826(1)$ Å^3, $K_0 = 54(3)$ GPa and $V_0 = 784(2)$ Å^3, $K_0 = 91(5)$ GPa, for the rhombohedral and triclinic phase, respectively. The results of the complete structural refinements performed up to 1.1 GPa indicated that: (i) the double-six-membered ring present in chabazite framework undergoes flattening as a result of a HP-induced cooperative tetrahedral anti-rotation; (ii) the 8-membered rings, limiting the channel apertures, become more circular and their crystallographic free area decreases; (iii) the extraframework content does not exhibit relevant modifications under pressure – as concerns the site occupancies – while some significant changes are observed in the bond distances. The elastic behavior and deformation mechanism of chabazite from Nova Scotia are compared with those of another chabazite sample from Vallerano and with those of other porous materials belonging to the 6-ring zeolite family.

1. Introduction

The importance of framework and extraframework composition on the properties of microporous materials under both ambient and non-ambient conditions is well known. In particular, systematic investigations into the effects of these compositional parameters on the elastic behavior of microporous materials have been performed on fibrous [1] and MFI-type zeolites [2–4].

Recently, the high pressure (HP) behavior of a series of microporous materials with CHA framework topology [5] (natural chabazite from Vallerano [6], silicoaluminophosphate SAPO-34 [6], and aluminophosphate ALPO-34 [7]) has been studied by means of *in situ* synchrotron X-ray powder diffraction, in the context of a wider project aimed at understanding the role of the framework/extraframework content in the P-induced deformation mechanisms of natural and synthetic microporous materials with the same framework topology.

These studies, performed using silicone oil as non-penetrating P-transmitting medium, revealed that: (i) complete X-ray amorphization is not achieved up to the highest investigated pressure (from P_{amb} up to about 7 GPa); (ii) all observed peaks are consistent with the original space group, thus ruling out any P-induced change in the original symmetry; (iii) the patterns collected upon decompression down to room conditions demonstrate that the P-induced effects are almost completely reversible; (iv) natural chabazite is definitely less compressible than as synthesized SAPO-34, mainly due to the more complex and hindering extraframework content of the natural sample; (v) AlPO-34 is the most rigid material, due to the octahedral coordination of part of its

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framework aluminum, resulting in a more rigid framework compared to that of both chabazite and SAPO-34, which contain only tetrahedral aluminum.

Specifically, previous HP data on natural chabazite regarded a sample from Vallerano [6] ($(K_{1.36}Ca_{1.04}Sr_{0.40}Na_{0.28}Ba_{0.06}Mg_{0.02})[Si_{7.17}Al_{4.87}O_{24}]\cdot 13.16\ H_2O$) which is characterized by a low silicon/aluminum ratio (about 1.5) and by predominant K and Ca as extraframework cations. For this sample, the decreases in the unit cell parameters a, α and V were 3.7%, 1.3%, and 10.3%, respectively, and a clear discontinuity in the elastic evolution of the unit cell parameters between 1 and 1.4 GPa was observed. In particular, in the low-P regime, rhombohedral a and α parameters decrease much more than at higher pressure values. The bulk modulus values – obtained using a second-order BMEoS – were $V_0 = 842(2)$ Å^3 and $K_0 = 35(5)$ GPa, and $V_0 = 831(1)$ Å^3 and $K_0 = 62(1)$ GPa, for the low and high P-range, respectively.

Although the studies performed up to now on CHA-type materials provided important information on the baric stability, compressibility values, and reversibility of the HP-induced effects, they did not furnish a complete structural description of the response of these microporous phases to compression, since it was impossible to perform complete structural refinements. This paper is focused on a sample of natural chabazite from Nova Scotia (hereafter NS) characterized by a different chemical composition compared to the sample from Vallerano (hereafter VALL), and reports new data on a HP-induced phase transition not previously observed in VALL. Moreover, it describes, on the basis of a detailed structural study, the HP-induced deformation mechanism of this material before the symmetry change induced by compression.

2. Chabazite structure and sample studied

Chabazite framework can be described as an ABC sequence of double 6-rings (D6R) of tetrahedra linked together through single 4-rings [8–12]. The resulting framework (Fig. 1) is characterized by a three dimensional channel system confined by 8-membered rings (8MR) and by the so-called chabazite cage, hosting extraframework cations and water molecules. The topological symmetry is rhombohedral R-3m [8,9], but the real symmetry is reduced to R-3 (SAPO-34 [13], CoAPSO-34 [14]) or P-1 (willhendersonite [15], ALPO-34 [16], CoAPO-34 [17]). Also in some natural chabazites, a deviation from rhombohedral toward triclinic symmetry (P-1) is observed, due to some Si–Al ordering in the tetrahedra and to the extraframework cations distribution [11–13,18].

The chabazite studied here is from Wasson's Bluff, Two Islands (Nova Scotia, Canada) (hereafter NS). Its chemical composition and crystal structure ($(Ca_{1.32}K_{0.45}Na_{0.13}Sr_{0.10})[Si_{8.55}Al_{3.45}O_{24}]\cdot 11.30\ H_2O$, s.g. R-3m, $a = 9.38749(8)$ and $\alpha = 94.379(1)$) were determined by Gualtieri and Passaglia [19]. In this sample, the extraframework cations are distributed over three sites (C2, C3, C4), while the water molecules occupy the W1, W2, W3, W4, W5 and W6 positions (Fig. 1). In particular, C1 site, located at the center of the D6R and filled in some chabazite samples [20], is vacant. C2 site is located on the triad, outside the D6R, in a peripheral position within the chabazite cage and partially occupied by K^+ cations. It is closely coordinated to three oxygen atoms of the 6-ring (O4), loosely to the three others of the 6-ring (O3) and to W3 water molecule. Also C3 site is on the triad, but it resides nearly at the center of the chabazite cage. It is partially occupied by calcium and coordinated only by water molecules. C4 site – located in the large cage and partially occupied by calcium – is bonded to three framework oxygen atoms of the 8MR (O2 and O3) and to water molecules. For what concerns the water positions, W1 site is located exactly at the center of the 8MR. W2, W3, W4 and W5 reside inside the chabazite cage. W6 site is on the triad, too near to C2 site to allow their simultaneous presence.

3. Experimental methods

3.1. Synchrotron X-ray powder diffraction experiments

The HP X-ray powder diffraction (XRPD) experiments were performed at the SNBL1 (BM01a) beamline at the ESRF (European Synchrotron Radiation Facility) with a fixed wavelength of 0.7355 Å, using a modified Merril-Basset DAC [21] and silicone oil as the non-penetrating P-transmitting medium [22,23]. The pressure was measured using the ruby fluorescence method [24] on the non linear hydrostatic pressure scale [25]. The estimated error in the pressure values is 0.1 GPa. A MAR345 detector (pixel dimension 150 μm) was

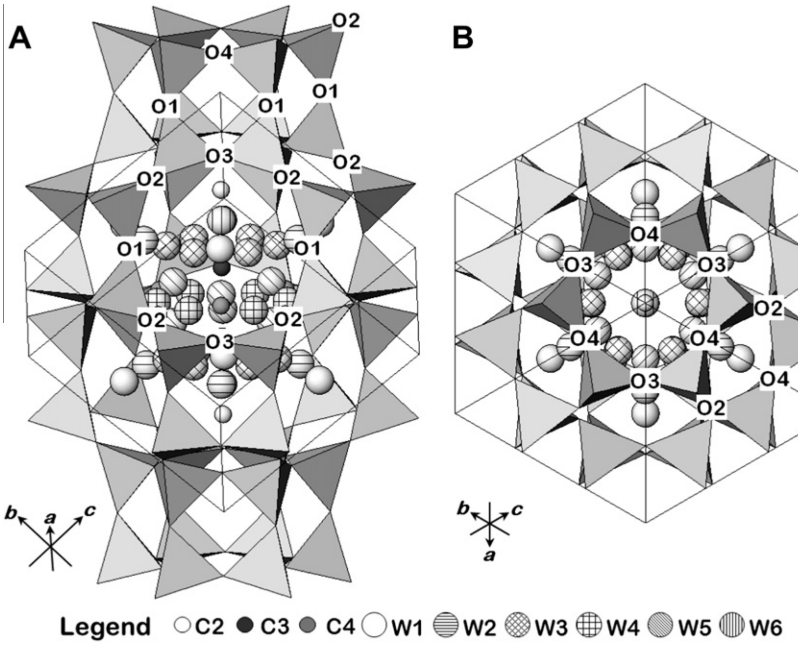

Fig. 1. Structure of Nova Scotia chabazite (NS) at P_{amb} (rhombohedral setting). (A) Chabazite cage; (B) projection along [1 1 1]. Labels refer to the tables discussed in the text.