Comparative compressional behavior of chabazite with Li⁺, Na⁺, Ag⁺, K⁺, Rb⁺, and Cs⁺ as extra-framework cations

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ABSTRACT

The high-pressure behavior of monovalent-cation-exchanged chabazites was investigated by means of in situ synchrotron X-ray powder diffraction with a diamond-anvil cell, and using water as penetrating pressure-transmitting medium, up to 5.5 GPa at room temperature. In all cases, except for Na-containing chabazites, a phase transition from the original rhombohedral (R₅m) to triclinic symmetry (likely P₁) was observed in the range between 3.0 GPa and 5.0 GPa. The phase transition is accompanied by an abrupt decrease of the unit-cell volume by up to 10%. Evidence of pressure-induced hydration (PIH), i.e., P-induced penetration of H₂O molecules through the zeolitic cavities, was observed, as reflected by the incompressibility of the cation-exchanged chabazites, which is governed by the distribution of the extra-framework cations. The reversibility of the PIH and P-induced phase transitions in the high-pressure behavior of the cation-exchanged chabazites are discussed in the context of the role played by the chemical nature and bonding configuration of the extra-framework cations, along with that of the H₂O content at room conditions.

Keywords: Chabazite, compressibility, high pressure, pressure-induced hydration, synchrotron diffraction; Microporous Materials: Crystal-Chemistry, Properties, and Utilizations

INTRODUCTION

There is a growing interest in understanding the behavior of microporous materials at non-ambient conditions and, in particular, at high pressure (e.g., Bish and Carey 2001; Alberti and Martucci 2005; Cruciani 2006; Gatta and Lee 2014; Gatta et al. 2017 and references therein). Pressure can cause important structural changes in microporous materials, modifying their physical-chemical properties and hence affecting their potential technological utilizations. Pressure-induced hydration (PIH) or pressure-induced insertion (PII), i.e., P-induced penetration of external molecules through the zeolitic sub-nanocavities at moderate pressure (≤1 GPa), is one of the most fascinating discoveries in materials science over the last decade. With potential technological and geological implications, it was recently reviewed by Gatta et al. (2017) and promotes new routes for creating hybrid host-guest composite materials or for understanding the stability of clathrates or the role played by zeolites as carrier of H₂O or CO₂ in subduction zones (e.g., Lee et al. 2011; Seoung et al. 2013, 2014, 2015; Im et al. 2015). Framework topology and extra-framework content are the key factors that govern the structural deformations at high pressure (e.g., Gatta et al. 2004; Gatta 2010; Danisi et al. 2015). Previous studies showed that the pressure-induced deformation of the tetrahedral framework in zeolites can be described in terms of tilting of quasi-rigid tetrahedra (e.g., Gatta 2008, 2010; Gatta and Lee 2014). There has not, however, been any systematic study on how the framework distortion in response to the applied pressure is influenced by the nature and distribution of the extra-framework cations. Only the “fibrous zeolites group,” which was extensively investigated at high pressure, provided a preliminary model to describe the effect of the extra-framework population on the elastic behavior of isotypic materials (e.g., Gatta 2005; Gatta et al. 2004; Seoung et al. 2013, 2015).

Chabazite (ideally [(Caₓ,K,Na)(H₂O)ₓ][AlₓSi₁₂₋ₓO₂₄₋ₓ]], with x = 2.4–5.0, see http://www.iza-online.org/natural/Datasheets/Chabazite/chabazite.htm) is one of the most widespread natural zeolites with excellent ion-exchange properties (e.g., Barrer et al. 1969; Shang et al. 2012). Its framework is built up by double 6-membered rings (D6R), stacked in an ABC sequence and linked together through single 4-membered rings (S4R) (e.g., Calligaris et al. 1982; Zena et al. 2008). As a result, the framework contains large ellipsoidal cavities (i.e., the CHA cage) with apertures of about 6.7 × 10 Å, which are accessible through single 8-rings (S8R) (Breck 1974). The largest opening of the S8R has a dimension of 3.8 × 3.8 Å and is located in the direction normal to the (001) crystal plane (Smith et al. 2001; Shang et al. 2012). Chabazites crystallizes with rhombohedral symmetry (space group R₅m), with only one independent tetrahedral framework site, populated by Al and Si with a statistically disordered distribution (Dent and Smith 1958). Exchangeable extra-framework cations and H₂O molecules are distributed over the D6R, S8R, and CHA cages with various occupancies (e.g., Fialips et al. 2005). A recent structural study of our group on various monovalent cation-exchanged chabazites revealed the systematic interplay...