Pressure-induced over-hydration of thomsonite: A synchrotron powder diffraction study

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Abstract

The structural behavior of thomsonite compressed in aqueous medium up to 3 GPa was studied by means of in situ synchrotron powder diffraction with a diamond anvil cell. In the range between 0.0001 and 2 GPa, the compressibility of thomsonite is markedly lower than that reported previously, where a non-penetrating medium (with only 6% H₂O) was used. This indicates a pressure-induced hydration (PIH), which results in the transition to an over-hydrated phase observed at 2 GPa. The structure of over-hydrated thomsonite contains an additional, half-occupied H₂O position, coordinated by the calcium at the Ca₂ site, with a scolecite-like coordination [CaO₃(H₂O)]. The appearance of new H₂O position causes a 4.5% volume expansion through the cooperative rotation of [T₂O₅]⁻ chains, leading to the enlargement of the cross-section of the main channels parallel to c axis. The observed deformation mechanism is similar to that found in high-hydrated and super-hydrated natrolite, although only half of the channels are affected by PIH. The present data indicate that the over-hydration effect in fibrous zeolites strongly depends on the partial water pressure in compressing medium.

Keywords: Zeolite, thomsonite, high pressure, compressibility, phase transition, crystal structure, over-hydration

Introduction

Recent structural studies of fibrous zeolite natrolite Na₂Al₅Si₆O₁₆·2H₂O and its related analogues compressed in aqueous medium (Lee et al. 2002, 2005, 2006; Colligan et al. 2005; Seryotkin et al. 2005) have created great interest in the over-hydration phenomenon, which is characterized by expansion of the framework due to formation of water molecules into the channels. This gives rise to a pressure-induced hydration (PIH) state of zeolite (Lee et al. 2004). Such an “anomalous” expansion is possible due to a high flexibility of the framework of fibrous zeolites provided by mutual rotation of the chains [(Al, Si)₅O₁₆]⁻ (Baur et al. 1990). The over-hydration and associated expansion of the channels may dramatically alter the ion-exchange and other sorption properties of zeolites, offering an enormous potential for their various industrial applications. Although this unique phenomenon has been known for a relatively long time (Kholdeev et al. 1987; Belitsky et al. 1992; Moroz et al. 2001), only recently has a detailed structural study of PIH in natrolite been reported (Lee et al. 2002, 2005; Colligan et al. 2005; Seryotkin et al. 2005). The transformation to high-hydrated phase at 1 GPa is related to the appearance of new water positions in the framework channels of natrolite. Thomsonite, NaCa₂Al₅Si₆O₁₆·6H₂O, is a widespread fibrous zeolite with the framework built up by [(Al, Si)₅O₁₆]⁻ chains, similar to those in natrolite but having a different connectivity.