Raman Investigation of Fibrous Zeolites of the Natrolite Group at High Pressures of an Aqueous Medium

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Abstract—The intermediate phases preceding overhydration are observed by Raman spectroscopy both in scolecite $Ca[Al_2Si_3O_{10}] \cdot 3H_2O$ and in thomsonite $NaCa_2[Al_5Si_5O_{20}] \cdot 6H_2O$ upon compression in an aqueous medium. The first intermediate phase of scolecite is attributed to a phase precursor revealed earlier using XRD at pressure of ~1 GPa. The widening of the Raman bands of O–H vibrations caused by the disordering of H_2O, which appears after additional water molecules are embedded in the zeolite channels, is typical of this intermediate phase. It is assumed on the basis of the Raman spectroscopy data that scolecite contains second overhydrated and second intermediate phases.

INTRODUCTION

The overhydration of zeolites under high pressures, when excess water is incorporated in the channels of an aluminosilicate framework, has been actively studied as of late [1–5]. Overhydrated zeolites exhibit a number of anomalous properties, including an increase in diffusion and ionic conduction in their channels and pores under the pressure of an aqueous medium [5, 6]. Structural studies of the overhydration of the fibrous zeolites scolecite $Ca_8[(AlO_2)_{16}(SiO_2)_{24}] \cdot 24H_2O$ and thomsonite $Na_4Ca_8[(AlO_2)_{20}(SiO_2)_{20}] \cdot 24H_2O$ [1, 2] point to the formation of new water positions in their channels, resulting in a jump in volume due to the widening of the channels. In the case of scolecite, a low-population defective water position, emerging as a precursor to overhydration prior to the transition to the overhydrated phase, was detected at 1.06 GPa (Fig. 1). The stability of the initial phase at pressures below 5 GPa upon compression in nonpenetrating media has been confirmed in Raman studies of scolecite [4]. Meanwhile, compression in water results in the emergence of an overhydrated phase at 1 GPa [3]. Raman studies of thomsonite under high pressures have not yet to be conducted.

The aim of this work is to study the evolution of hydrogen bonds in zeolites upon overhydration (including its precursor) using the Raman spectra of O–H. A diamond anvil cell (DAC) was used to study fibrous zeolites of the NAT group of natrolite (scolecite and thomsonite) under high pressures of an aqueous medium (up to 4 GPa) by means of Raman spectroscopy.

EXPERIMENTAL

The Raman spectra were excited with the radiation (514.5 nm) of an argon laser and recorded on a Horiba Jobin Yvon T64000 spectrometer in the ranges of 16–1200 and 3000–3700 cm^{-1}. Crystals with sizes of $\sim 60 \times 40 \times 40~\mu m^3$, consisting of scolecite and thomsonite with the composition described in [1, 2]), were placed under a single load in the DAC unit into an aqueous medium. The pressure, which was equal for both crystals, was determined from the shift of ruby luminescence band R_1 with an accuracy of ±0.03 GPa. The Raman spectra of aqueous media under high pressures were also recorded. The contribution from the signal of the surrounding environment was monitored as the zeolite spectrum was recorded. The signal from the environment remained low due to the considerable thickness of the crystal and the limited depth of light acquisition by an OLYMPUS-LM Plan FL 50× lens (WD = 11 mm).

RESULTS AND DISCUSSION

We observed differences in the Raman spectra of scolecite when passing from air to an aqueous medium (the spectra at 0 and 0.004 GPa in Fig. 1) with small shifts of the band frequencies $\nu(P)$ (Fig. 2). We attribute the weak widening of the bands and the presence of a spectral pedestal to the small amount of additional water contained in the scolecite channels in the form of structural defects at pressures of the liquid aqueous medium as low as 1 atm. According to NMR [5] and Raman [7] data, water is capable of penetrating into the channels of NAT zeolites at the onset of compres-
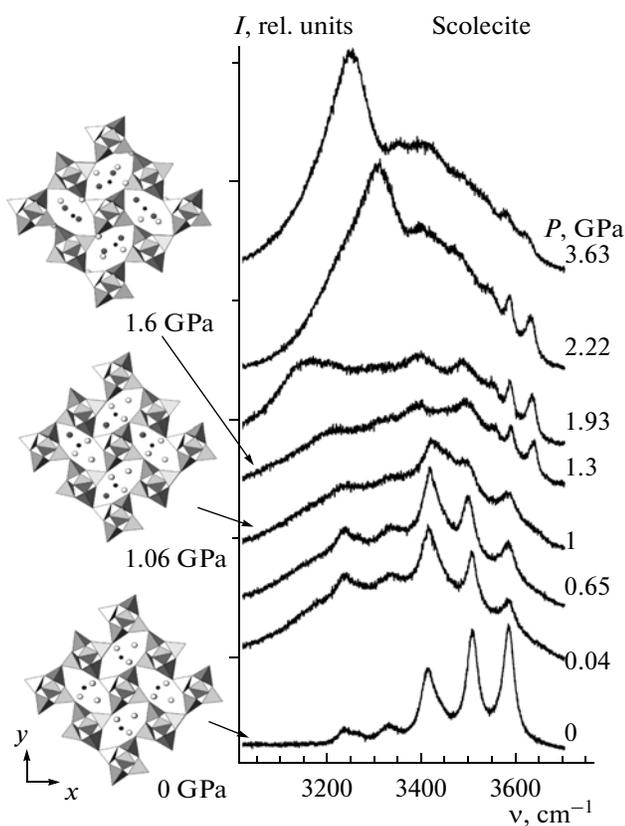
Fig. 1. Raman spectra of scolecite at different pressures. The crystalline structure of scolecite is shown for the initial phase at ~0 GPa, the overhydration precursor at 1.06 GPa, and the overhydrated phase at 1.6 GPa [1]. The arrows indicate the correspondence of the structures to the Raman spectra at the closest pressures.

Fig. 2. Pressure dependence of the frequencies of the Raman bands of scolecite: at 1 atm (white circles), in the major phases (black circles), and in the two intermediate phases (asterisks).

sion at $P \sim (0-1)$ GPa, thereby sharply increasing the diffusion of H_2O molecules in the channels.

The changes in the spectra of O–H vibrations of scolecite attest to changes in the H_2O positions at pressures of 1–1.3 GPa. The O–H spectrum at 1 GPa appears as a spread spectrum of the initial phase. This intermediate state was identified as a precursor to overhydration, and its structure was determined from the XRD data [1] at 1.06 GPa. This state is notable for the filling of the 0.1 defect H_2O position O70 (Fig. 1). Based on the Raman data, we may state the majority of positions of atoms O in water remain unchanged, while the proton positions are spread under 1 GPa. In other words, the incorporation of additional H_2O molecules into the channels results in orientational disorder in the existing H_2O positions.

The appearance of the spectrum of O–H vibrations in scolecite remains constant in the range of $1 < P < 1.9$ GPa. At 1.93 GPa, the spectrum changes abruptly: a strong wide band at 3166 cm^{-1} emerges, while the second most intense band experiences a jump in frequency to 3394 cm^{-1}. The other three high-frequency bands are weakly sensitive to this transition to the second inter-
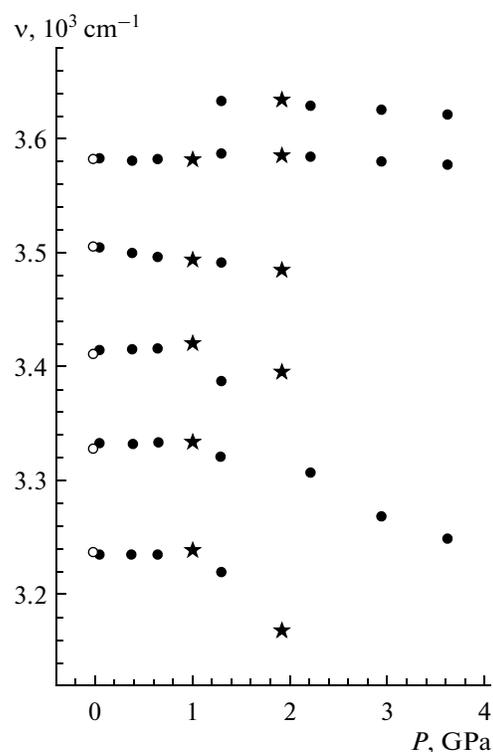
mediate phase at 1.93 GPa (Fig. 1). We believe that the introduction of additional H_2O molecules into the defect positions corresponding to the band at 3166 cm^{-1} has virtually no effect on the existing H_2O positions with weak hydrogen bonds, which yield high-frequency bands.

Raising the pressure to $P = 2.22$ GPa and the assumed increase in H_2O content in the channels result in considerable rearrangement of their positions and the emergence of an O–H spectrum containing a very strong ice-like band at ~3307 cm^{-1}, plus a group of strong bands at 3394–3462 cm^{-1}. It is noteworthy that virtually none of the other H_2O positions experience this change, and the two narrow high-frequency bands remain unaltered. They only begin to widen and grow weak with a subsequent increase in P. Note that the frequency of the ice-like band corresponding to scolecite at ~3307 cm^{-1} (and at ~3302 cm^{-1} for thomsonite) is shifted considerably from the major band of ice VII, is wider than the band of ice, and has a weak low-frequency shoulder at ~3235 cm^{-1}.

Jumps in band frequencies and changes in the slopes of the $d\nu/dP$ dependences were also observed in the vibrational spectrum of the scolecite structure.

The first intermediate phase in scolecite was observed earlier by XRD [1] (Fig. 1); however, no second intermediate and the second overhydrated phases
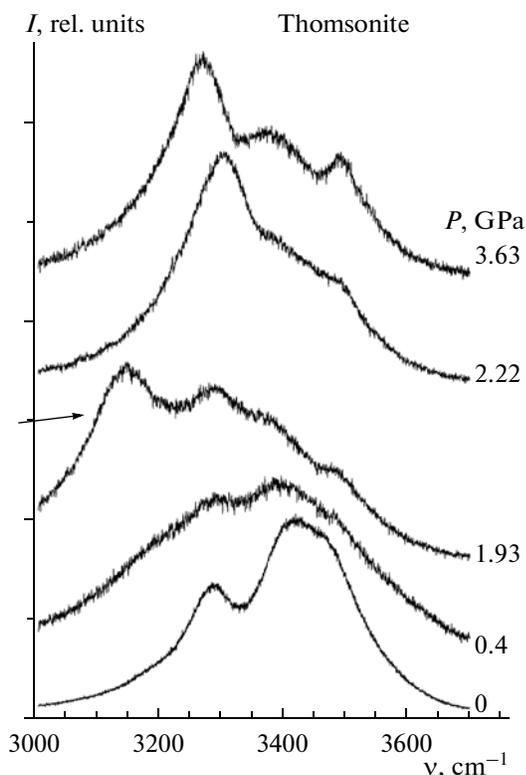
Fig. 3. Raman spectra of thomsonite at different pressures. The arrow indicates the Raman spectrum of the intermediate phase at 1.93 GPa.

Fig. 4. Pressure dependence of the frequencies of the Raman bands of thomsonite: at 1 atm (white circles), in the major phases (black circles), and in the intermediate phase (asterisks). Linear interpolations of the dependences were performed for the initial (without point $P \sim 0$ GPa) and overhydrated phases.

were detected. This is associated with the attenuation of the diffraction reflections upon amorphization, which progresses more quickly in the powder sample and makes it impossible to determine the coordinates of atoms at high pressures ($P > 2$ GPa). A jump at $P \sim 2$ GPa can be seen in the pressure dependence of the scolecite unit cell volume [1], indicating a transition to a second overhydrated phase.

In our experiments, scolecite retained its crystallinity, as was confirmed by its Raman spectra of O−H (Fig. 1) and framework bands, which did not undergo widening or attenuation up to ~4 GPa. The second overhydrated phase manifested itself in the Raman spectra through the emergence of the strong O−H band at 3307 cm^{-1} and the lattice band of medium intensity at 190 cm^{-1}, and by kinks in pressure dependences of a number O−H and skeletal bands.

The Raman spectra of thomsonite are changed upon transfer from air to the aqueous medium in DAC unit, although both spectra remained similar at 0 and 0.4 GPa (Figs. 3 and 4). These changes, which resulted in spectral blurring, can be attributed to the incorporation of a small amount of water into the channels.

According to the structural data in [2], the thomsonite lattice structure widens slightly even at water pressure $P \sim 0$ GPa, supporting our belief that water is
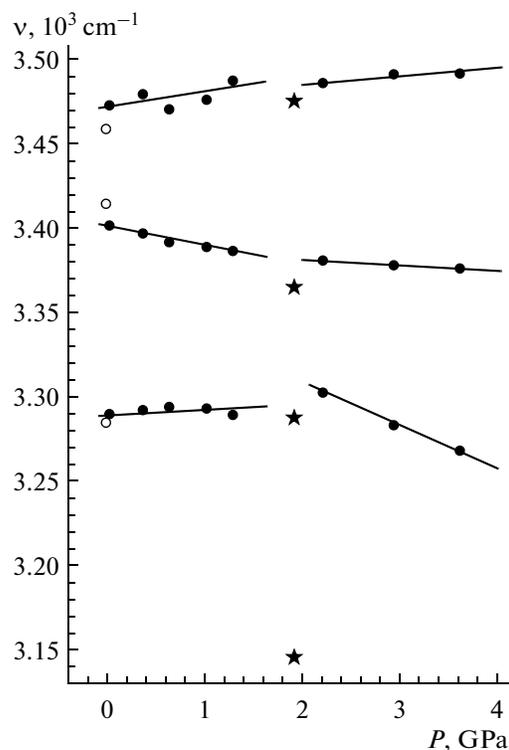
incorporated into the channels. This phase of zeolite when submerged in water is characterized (with a very small amount of excess water) by the same symmetry as the phase in air at 1 atm; we shall refer to it below as the initial phase. The Raman spectra of the initial phase of thomsonite undergo negligible changes upon compression in an aqueous medium in the pressure range ~0−1.3 GPa.

The Raman spectrum of thomsonite subsequently changed abruptly at $P = 1.93$ GPa, yielding two strong O−H bands at ~3144 and 3287 cm^{-1}; we attribute this to the emergence of an intermediate overhydrated phase (i.e., an overhydration precursor) that precedes the phase transition to the overhydrated phase saturated with water at $P = 2.22$ GPa.

According to [2], a jumpwise increase in the amount of water in the channels and a change in the thomsonite unit cell parameters are observed when the pressure is increased to ~2 GPa. A very strong ice-like band at ~3302 cm^{-1} and a strong high-frequency shoulder corresponding to this band emerge in the Raman spectrum of thomsonite at 2.22 GPa. The Raman spectra thus change considerably upon transition to the supersaturated state at $P \sim 2$ GPa. Jumps in the band frequencies and a change in the slope of dependences $d\nu/dP$ were also observed in the vibra-

tional spectrum of the thomsonite framework structure upon transition to the overhydrated state. Note that the water band at ~3490 cm^{-1} grows appreciably when the pressure rises to 3.63 GPa.

CONCLUSIONS

The appearance of intermediate phases preceding overhydration both in scolecite and thomsonite was observed by means of Raman spectroscopy. A widening of the O−H bands is typical for the first intermediate overhydrated scolecite phase (at 1 GPa; Fig. 1). According to the XRD data, this phase should be classified as an overhydration precursor at 1.06 GPa [1]. No phase of this type has yet been detected in thomsonite by means of X-ray diffraction [2].

It should be added that the emergence of a second intermediate phase (at 1.93 GPa) and a second overhydrated phase (at ~2.2 GPa) was observed in scolecite by means of Raman spectroscopy. The emergence of strong bands (3166 and 3144 cm^{-1}, respectively) corresponding to H_2O molecules with short hydrogen bonds resulting from the compaction of channel stuffing is typical of the intermediate overhydrated phase observed at 1.93 GPa in both scolecite and thomsonite.

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