

Behavior of Natrolite Zeolite and Fluorapatite at High Pressures in a Water Medium

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Abstract—The hysteresises (–0.3–0.4 GPa) of two transitions in natrolite at 0.9 and 1.45 GPa, considerable changes in the Raman spectra, and the appearance of very intense low–frequency mode at 75 cm^{-1} in the overhydrated phase of high pressure of water medium up to 6.2 GPa are observed for the first time. The dependences of the band frequencies of this phase are nonlinear, due clearly to changes in the positions of H₂O in the channels. According to Raman data, fluorapatite placed together with natrolite in a water medium in a diamond anvil cell exhibits no transitions up to 6.2 GPa and displays linear pressure dependences of the band frequencies.

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INTRODUCTION

Under compression in a water medium, many zeolites transition to overhydrated states that contain excessive amounts of water, relative to their initial phase at 1 atm. [1–4]. Overhydrated zeolites exhibit several anomalous properties, including a rise in the diffusion of intrachannel cations and molecules [5, 6]. X-ray investigations show that this ability of zeolites is associated either with the presence of additional positions for H₂O molecules that were vacant in the initial phase and can be filled at high pressures, or with an increase in the occupation of available positions. Some zeolites (type A [1]) gradually transition to overhydrated states with structures of the same symmetry when the water content rises in zeolite channels and the water pressure increases; other zeolites (NAT-type natrolites [2–4]) change their state as soon as new overhydrated phases appear. Natrolite $\text{Na}_2[\text{Al}_2\text{Si}_3\text{O}_{10}] \cdot 2\text{H}_2\text{O}$ exhibits phase transitions (PTs) accompanied by the appearance of two phases with excessive water content: phase II at ~1 GPa and phase III at ~1.5 GPa [4]. In structure and water content, phase II is similar to paranatrolite, a special representative of the NAT group with a chaotically arranged framework of Si–Al cations in the equivalent natrolite framework and an increased water content.

These transitions in natrolite were discovered in 1987 using the Raman method [2] and then were studied via X-ray and neutron diffraction [3, 4]. During the first transition, the W2 positions that were vacant at 1 atm were occupied; upon the second transition, the water positions change, H₂O molecules filled new positions similar to those in scolecite channels [4]. Note that the positions became more occupied and

the total amount of water grew in the elementary cell during both PTs.

In this work, our primary task was to investigate natrolite over a wider range of pressures in a water medium, and to establish features of the above PTs, the changes in spectra upon a rise in P , and the emergence of these transitions in the domain of low frequencies. We also decided to perform calculations by means of lattice dynamics [7] and to analyze whether the above PTs can have soft modes when their composition changes.

Another subject of our investigations was apatite, the general formula of which is $\text{Ca}_5[\text{PO}_4]_3(\text{F}, \text{Cl}, \text{OH})$. It is a widespread mineral of major practical importance. Being a typical component of the bones and teeth of animals, biogenic apatite carbonate usually contains hydroxyl and great amounts of CO_3^- . Its composition is $\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl}, \text{CO}_3)$. According to [8, 9], apatite is stable at moderate pressures in different media, including water media. According to [8], under different P – T conditions of synthesis, there is a phase transition of the A1 → A2 type with a change in the orientation of carbonate ions at pressures of 2–4 GPa, depending on the composition.

In this work, we also chose to study the baric behavior of fluorapatite (which undergoes no transitions) by means of Raman spectroscopy in order to compare it to the behavior of natrolite subjected to overhydration in the form of two transitions at high pressures of a water medium.

EXPERIMENTAL

The minerals natrolite (Khibiny, Kola Peninsula; composition presented in [4]) and apatite (natural flu-

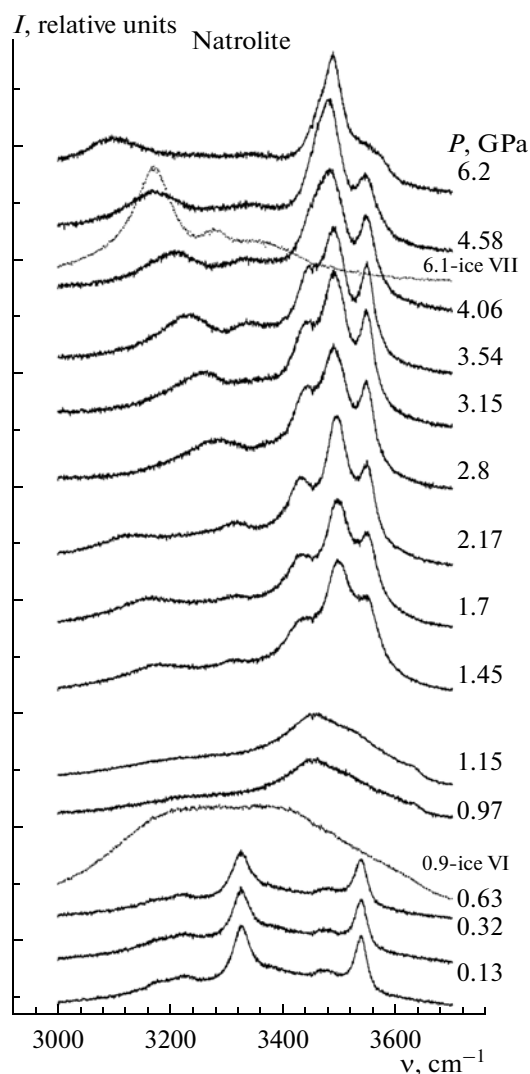


Fig. 1. Raman spectra in the domain of valent O–H oscillations of natrolite at different pressures. The dashed lines represent the medium spectra.

orapatite, Slyudyanka, Baikal region) were studied via Raman spectroscopy in a diamond anvil cell (DAC) at high pressures of a water medium (up to 6.2 GPa). The Raman spectra were recorded using a Horiba Jobin Yvon T64000 spectrometer. Both crystals $\sim 50 \times 40 \times 40 \mu\text{m}^3$ in size were placed in the DAC in a water medium. The pressure that was equal for the two crystals was determined from the displacement of the ruby luminescence R_1 line with an accuracy of ± 0.03 GPa. The lattice dynamics was calculated using the LADY program (M.B. Smirnov, 2001) [7].

RESULTS AND DISCUSSION

To study the lattice dynamics of natrolite and apatite, we recorded their unpolarized Raman spectra in the range of 11–3700 cm^{-1} at high pressures of a water medium. According to the Raman data (Figs. 1–3), as

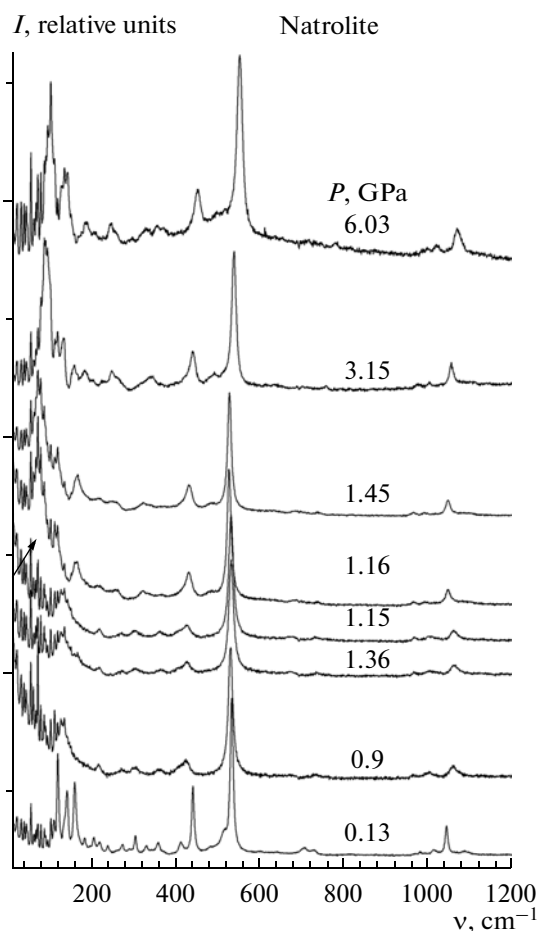


Fig. 2. Raman spectra of natrolite at different pressures in the average and low-frequency domains. The arrow marks the strong band at 75 cm^{-1} in phase III. The narrow lines in the domain of less than 140 cm^{-1} are the parasitic Raman spectrum of air in the spectrometer.

the pressure grows, natrolite transits from initial phase I to the first overhydrated phase II at 0.9 GPa, and then passes to the second overhydrated phase III at 1.45 GPa.

Both transitions displayed hysteresises in their Raman spectra. When the pressure fell, the III \rightarrow II transition occurred at 1.15 GPa (hysteresis, ~ 0.3 GPa) and the II \rightarrow I transition was observed at 0.5 GPa (hysteresis, ~ 0.4 GPa). Hysteresises were observed for all bands that were active above or below each transition. Figure 3 presents examples of hysteresis for the band frequencies 122, 442, and 534 cm^{-1} . The low-frequency band at 75 cm^{-1} appears only in phase III.

The Raman spectra in Fig. 1 show the marked evolution of the O–H valent bands of natrolite with pressure, which could indicate changes in the positions of the H_2O molecules and their occupation. The experimental points of frequencies (ν) of bands for phase III do not lie on a single linear dependence; more likely, we can plot three linear dependences (Fig. 3) or one nonlinear dependence for each band using these data.

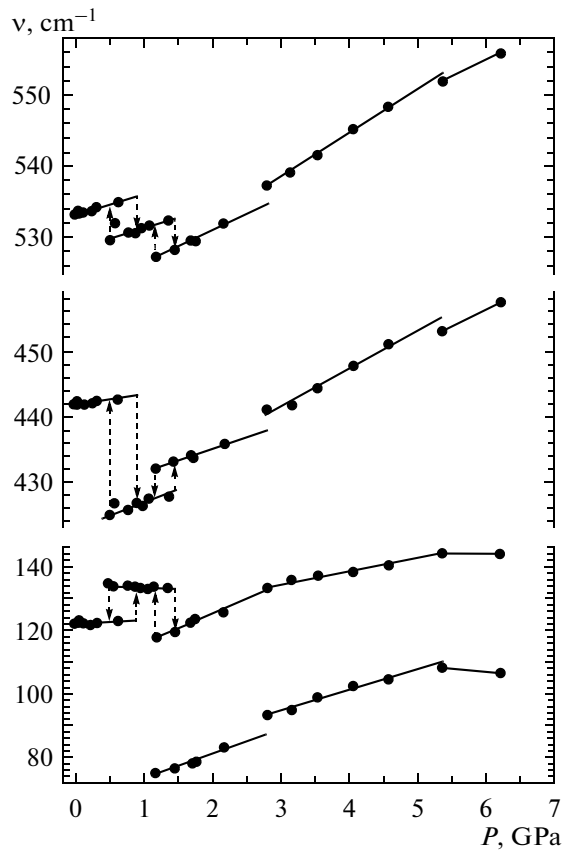


Fig. 3. Pressure dependence of the frequencies of the most intense Raman bands at 442 and 534 cm^{-1} and the low-frequency bands of natrolite.

Since the Raman spectrum remains similar for all three regions, we believe that phase III remains in the 1.5–6.2 GPa range of pressures.

The band at $\sim 3550 \text{ cm}^{-1}$ drops in intensity and widens at pressures of about 6 GPa. There is a considerable reduction in band frequency to about 3100 cm^{-1} . This band is attributed to the water medium penetrating into the microcracks that appear during the two transitions to the overhydrated phases.

Figure 2 shows the appearance of a rather intense low-frequency mode at 75 cm^{-1} . According to our lattice dynamics calculations, this anomalously strong band is associated with the oscillation of a channel-forming ring that changes its radius, controlling the diffusion of $\text{Na}^+ - \text{H}_2\text{O}$ along the fibers (the c axis). Our lattice dynamics calculations allow us to interpret the modes and stability of each natrolite phase, and to associate the transitions with features of the lattice dynamics and channel filling.

The comparative behavior of natrolite zeolite and fluorapatite was studied as they were simultaneously compressed in a water medium. According to [9], the Raman band frequencies of apatite, which undergoes no transitions, must conform to the linear depen-

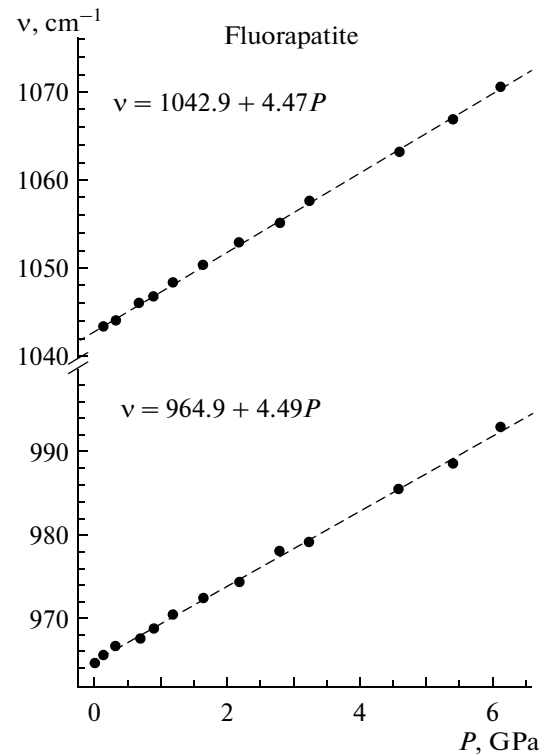


Fig. 4. Pressure dependence of the frequencies of fluorapatite Raman bands at 965 and 1043 cm^{-1} .

dences $\nu(P)$ under hydrostatic compression up to moderate pressures. Fluorapatite exhibits linear pressure dependences for the frequencies $\nu(P)$ of all bands (Figure 4 shows the baric dependence of the most intense band at 965 cm^{-1} and the band at 1043 cm^{-1}). This indicates there are no transitions in fluorapatite, along with the negligible effect of deviations from hydrostatics upon compression in quasi-hydrostatic media, e.g., ices VI and VII. Note that thomsonite and scolecite compressed in a water medium exhibit linear pressure dependences for the band frequencies in both the initial and overhydrated phases of high pressure [10].

When compressed in a methanol–ethanol medium, natrolite almost always displays linear pressure dependences for the band frequencies in the initial and high baric phases [11, 12]. The linear dependences $\nu(P)$ of the Raman bands in the phases I and II of natrolite compressed in water (Fig. 3) are thus associated with the consistency of water composition and the positions of $\text{Na}^+ - \text{H}_2\text{O}$, as was shown by the X-ray data [3, 4]. In contrast, nonlinear dependences $\nu(P)$ can appear in phase III of natrolite (Fig. 3) due to unusual behavior upon a change in the positions of exchange cations and water, along with a hypothetical change in H_2O composition as P increases.

CONCLUSIONS

Raman spectroscopy was used to study in detail the overhydration of natrolite zeolite under compression in a water medium. Relative to [2], the range of pressures doubled (from 3 to 6.2 GPa), and the spectral range extended toward the low frequencies (11–100 cm^{-1}). Hysteresises occurring during the two transitions to overhydrated phases II and III were observed. The lattice dynamics of high baric phases II and III of natrolite was calculated for high pressures on the basis of the X-ray results [3, 4].

The two phase transitions of natrolite exhibited no soft modes. A low-frequency mode of considerable intensity manifested itself at 75 cm^{-1} (Fig. 2). Lattice dynamics calculations allowed us interpret this anomalous mode as an oscillation at a channel entrance that modulates and grows in size for the diffusion of cations and H_2O molecules along the c axis.

Nonlinear pressure dependences of the Raman frequencies of bands were observed in overhydrated natrolite III, due possibly to changes in the positions of water molecules and cations, or to a change in the water composition of zeolite as P rises.

The behavior of natrolite zeolite (which undergoes two transitions) and the behavior of fluorapatite (which undergoes no transitions) were comparatively studied during their simultaneous compression in a water medium. The linear pressure dependences were recorded for the Raman frequencies of the fluorapatite bands associated with the permanent composition and symmetry of the crystal phase and the subtle influence of hydrostatic deviations under compression in ice. Analysis of the fluorapatite Raman spectra confirms

there were no phase transitions in the range of water pressures up to ~6 GPa.

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