Raman study of datolite CaBSiO$_4$(OH) at simultaneously high pressure and high temperature

S. V. Goryainov,[a]* A. S. Krylov,[b] A. N. Vtyurin[b] and Y. Pan[c]

Using an *in situ* method of Raman spectroscopy and resistance-heated diamond anvil cell, the system datolite CaBSiO$_4$(OH) – water has been investigated at simultaneously high pressure and temperature (up to P ~5 GPa and T ~250 °C). Two polymorphic transitions have been observed: (1) pressure-induced phase transition or the feature in pressure dependence of Raman band wavenumbers at $P = 2$ GPa and constant $T = 22$ °C and (2) heating-induced phase transition at T ~90 °C and P ~5 GPa. The number of Raman bands is retained at the first transition but changed at the second transition. The first transition is mainly distinguished by the changes in the slopes of pressure dependence of Raman peaks at 2 GPa. The second transition is characterized by several strong changes: the wavenumber jumps of major bands, the merging of strong doublets at 378 and 391 cm^{-1} (values for ambient conditions), the splitting of the intermediate-intensity band at 292 cm^{-1}, and the transformation of some low-wavenumber bands at 160–190 cm^{-1}. No spectral and visual signs of overhydration and amorphization have been observed. No noticeable dissolution of datolite in the water medium occurred at 5 GPa and 250 °C after 3 h, which corresponds to typical conditions of the 'cold' zones of slab subduction. Copyright © 2014 John Wiley & Sons, Ltd.

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Introduction

At experimental modeling of processes in 'cold' zones of lithospheric slabs at high P–T conditions in the typical ranges of P ~3–15 GPa and T ~300–600 °C, the state of silicate minerals containing hydroxyls in their lattices is usually emphasized. Several silicate minerals (serpentine, 10 Å, A, B, and E phases; lawsonite; talc; phengite; etc.) have been suggested as major transporters of water to subduction zones of submerging slabs. This water is extracted by dehydration and supports the major source of magmatism in these ranges.[1,2]

The borosilicate mineral datolite CaBSiO$_4$(OH), which is a common secondary mineral in mafic igneous rocks (e.g. associated with zeolites and carbonates in the vesicles of seafloor basalts[3,4]), can also participate in this process because of its high thermal and baric stability. In spite of comparably small abundance (i.e. relative to the more common tourmaline), datolite could contribute significantly to processes of water and boron transport and extraction of water in slab subduction zones.

The monoclinic $P2_1/c$ crystal structure of datolite consists of complex layers of corner-sharing SiO$_4$ and BiO$_3$(OH) tetrahedra, in which both the bridging O and OH are active.[5,6] The layer is built by four-membered and eight-membered rings formed with SiO$_4$ and BiO$_3$ (OH) tetrahedra. This complex layer of corner-sharing tetrahedra, disposed at different distances along the a-axis, could be considered as 2D framework. The Ca^{2+} ions are disposed in the interlayer space and are coordinated by six oxygen anions and two hydroxyls. These coordination neighbors 6O + 2(OH) form the twisted cube.

Calcium borosilicates, datolite CaBSiO$_4$(OH) and danburite CaB$_2$Si$_2$O$_8$, occur in a wide range of conditions of geological environments.[7] Datolite and danburite are stable with respect to other calcium borates in the system CaO–B$_2$O$_3$–SiO$_2$–H$_2$O at temperature 250 °C and pressure 0.1 GPa.[7,8] Several dominating phases are crystallized in this system: datolite, danburite, wollastonite (CaSiO$_3$), and quartz. At low temperature (<200 °C) and high activity of acid H$_3$BO$_3$, datolite reacts to form the borate mineral CaB$_6$O$_9$(OH)$_2$ · H$_2$O (nobleite type[9]) and quartz[8]: CaB$_6$O$_9$(OH)$_2$.

The dehydroxylation of datolite occurs at heating in air at approximately 770 °C, which is the maximum of Derivative Thermogravimetry (DTG).[10] At this thermal transformation, datolite CaBSiO$_4$(OH) breaks down to boron–melilite Ca$_2$B$_2$SiO$_7$ plus silica (quartz) and water:

$$2CaBSiO_4(OH) = Ca_2B_2SiO_7 + SiO_2 + H_2O$$
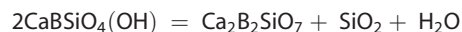
It is noteworthy that the behavior of datolite at P–T parameters corresponding to the 'cold' zones of lithospheric slabs had been studied only by *ex situ* methods and has not been investigated with *in situ* methods that could determine the existence of nonrecovered phases and states, including those with changing water and hydroxyl contents. Also, boron transportation or conservation may

* Correspondence to: Sergei V. Goryainov, V.S. Sobolev Institute of Geology and Mineralogy SB RAS, pr. Koptyug 3, Novosibirsk 630090, Russia.
   E-mails: svg@igm.nsc.ru, goryainov@ngs.ru

a V.S. Sobolev Institute of Geology and Mineralogy SB RAS, pr. Acad. Koptyug 3, Novosibirsk 630090, Russia

b L.V. Kirensky Institute of Physics SB RAS, Krasnoyarsk 660036, Russia

c Department of Geological Sciences, University of Saskatchewan, Saskatoon, SK, S7N 5E2, Canada

be defined on the basis of its preservation in the structures of borosilicates.

The main objective of the present work is to study with the *in situ* method of Raman spectroscopy the behavior of datolite $CaBSiO_4$ (OH), compressed in the water medium, at simultaneously high P–T conditions, corresponding to the 'cold' zones of slab subduction, and to elucidate the major trends in the change of both the structure and the vibrational bands.

Methods and samples

Raman spectra were excited with radiation of a 514.5-nm line (~1-W power) of Ar ion laser (Spectra-Physics) and recorded on a triple spectrometer T64000 (Horiba Jobin Yvon) with an Olympus BX41 microscope at the Institute of Physics, Krasnoyarsk. Back-scattered Raman spectra were registered at the range of 10–4000 cm^{-1} with spectral resolution of 2 cm^{-1}. Heated high-temperature diamond anvil cell (HT-DAC) device of membrane Diacell μScope DAC HT (G) type (EasyLab, UK) with diamond IIa anvils, electrical resistive heating, water-cooled casing, and Ar (with H_2 impurity) gas blowing was used for Raman study of processes at simultaneously high P and T (Fig. S1). Limit P–T parameters in the work volume of the given HT-DAC device are equal to 20 GPa and 500 °C. The maximal P–T values in the present experiments with datolite were set at 5.3 GPa and 250 °C. Lattice dynamical calculations were carried out with the program package LADY (CRYME[11] by M.B. Smirnov).

The chips of datolite crystals from the Bergen Hill locality (NJ, USA) were selected from the University of Saskatchewan reference mineral collection.[12] Chemical composition of the datolite crystals is close to the idealized formula $CaBSiO_4(OH)$.[12]

Results

Raman spectra of datolite are changed at the increase of P–T conditions (Figs 1 and S2). Wavenumbers of Raman bands of the borosilicate layer and Ca^{2+} in the interlayer space, registered in the range 150–1200 cm^{-1}, are increased with increasing P almost linearly with different slopes A_i in two ranges of pressure 0–2 and 2–3.5 GPa:

$$v_i(P) \sim v_{0i} + A_i P$$

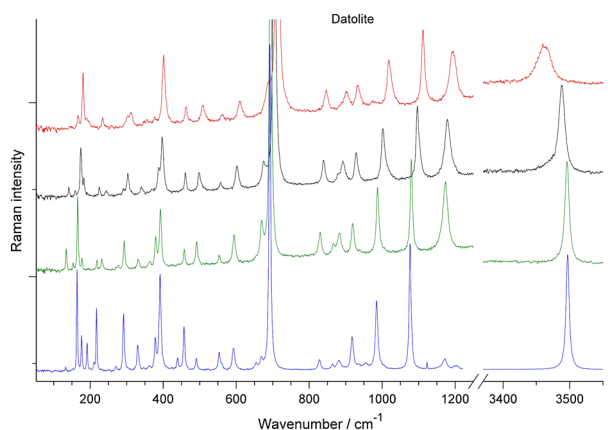where v_{0i} and A_i are constants, i is the mode number, the value of

Figure 1. *In situ* Raman spectra of datolite $CaBSiO_4(OH)$ at ambient conditions (1) and high P–T parameters: (2) 0.38 GPa, 22 °C; (3) 3 GPa, 22 °C; and (4) 5.08 GPa, 200 °C. Narrow weak bands below 120 cm^{-1} correspond to Raman spectra of air.

2 GPa is the transition pressure, and 3.5 GPa is the maximal pressure at a given run at fixed $T = 22$ °C (Fig. 2). Note that measurements at higher P up to 5.3 GPa have been made with simultaneously high T (Figs 3–5 and S2). Linear growing dependence $v_i(P)$ in the two pressure ranges is characteristic for the behavior of all wavenumbers of Raman bands of the borosilicate layer and the interlayer cation Ca^{2+}, whereas the wavenumber of the O–H stretching band decreases with P (Fig. 2). The dependence values $v(P)$ of the most representative bands are shown in this figure.

These bands of the 2D framework and Ca^{2+} cations are assigned to 2D-framework lattice vibrations presumably involving the libration of the four-membered rings (164 cm^{-1}), O–Si–O and O–B–O bending vibrations of the 'breathing' type in the four-membered rings (692 cm^{-1}), Fig. S3, and Si–O and B–O antisymmetric stretching vibrations (1075 cm^{-1}), according to assignment of vibration bands of similar tetrahedrally coordinated borates and silicates.[11,13–16] Lattice-dynamical calculations[11] showed that the most intensive Raman bands are the 'breathing' modes of the four-membered and other-membered rings, whereas the lower intensity, low-wavenumber bands are the external modes of tetrahedra, rings, and chains of silicate minerals. Note that the calculated form of vibrations at 692 cm^{-1} is associated with the 'breathing' vibrations of the four-membered borosilicate ring, having the main amplitudes in the layer *ZY*-plane of datolite, although the
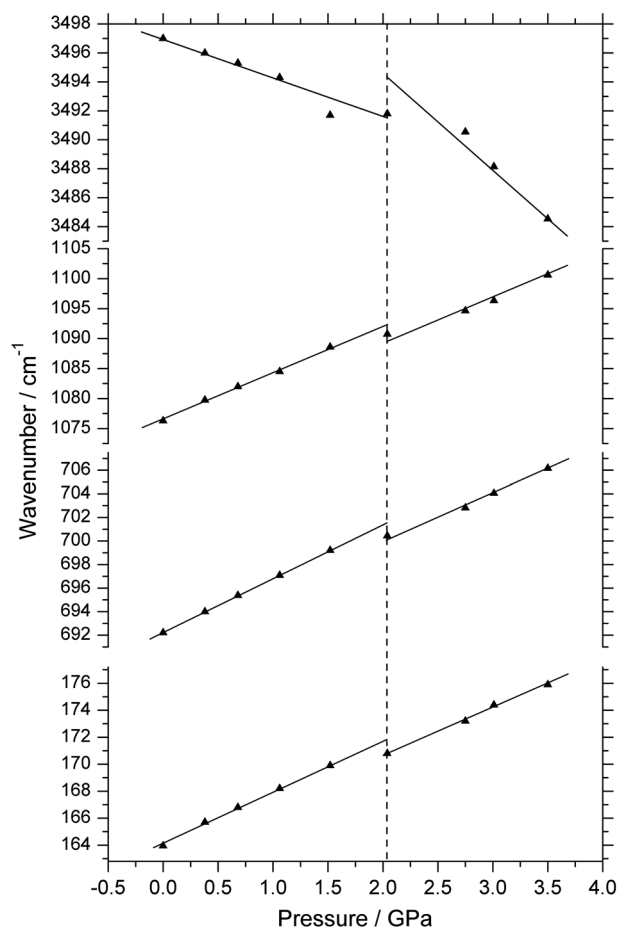

Figure 2. The dependence of the wavenumber of four datolite Raman bands (164, 692, 1075, and 3497 cm^{-1} at ambient conditions) on pressure at constant $T = 22$ °C. These four bands are assigned to 2D-framework lattice vibrations (164 cm^{-1}), O–Si–O and O–B–O bending 'breathing' vibrations (692 cm^{-1}), Si–O and B–O stretching vibrations (1075 cm^{-1}), and O–H stretching vibrations (3497 cm^{-1}), respectively.
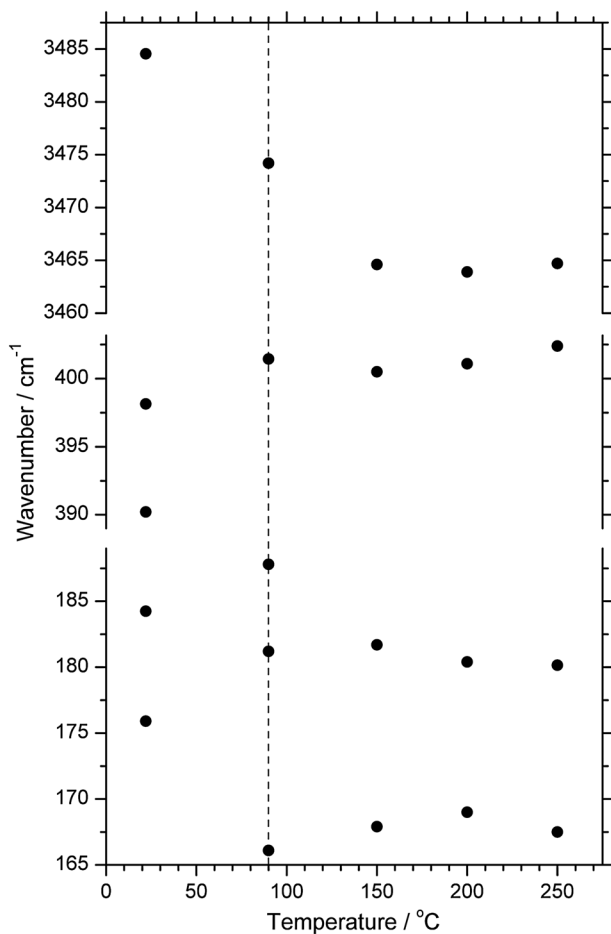
Figure 3. The dependence of the wavenumbers of selected Raman bands of datolite (166, 177, 184, 390, 398, and 3497 cm^{-1} at ambient conditions) on temperature at P ~3.5–5.3 GPa. These bands are assigned to 2D-framework lattice vibrations (164–184 cm^{-1}), O–Si–O and O–B–O bending vibrations (390–398 cm^{-1}), and O–H stretching vibrations (3497 cm^{-1}), respectively. Experimental points (circles) correspond to the T–P (°C, GPa) parameters: 22, 3.5; 90, 4.96; 150, 5.3; 200, 5.08; and 250, 5.05.
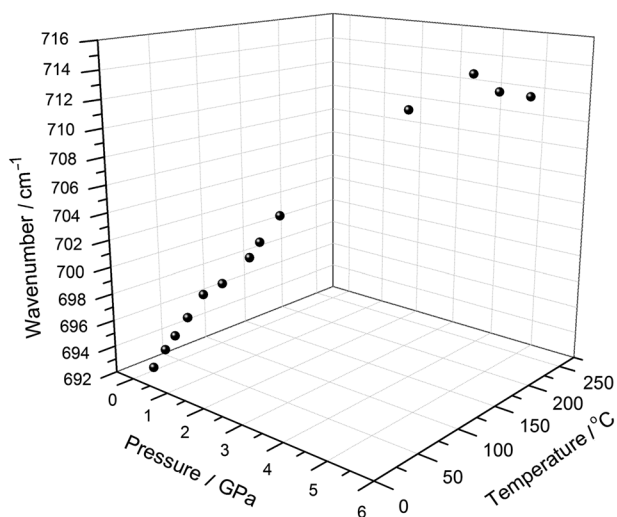

Figure 4. Dependence of the band wavenumber (692 cm^{-1} at ambient conditions) of the datolite 2D framework on pressure and temperature.
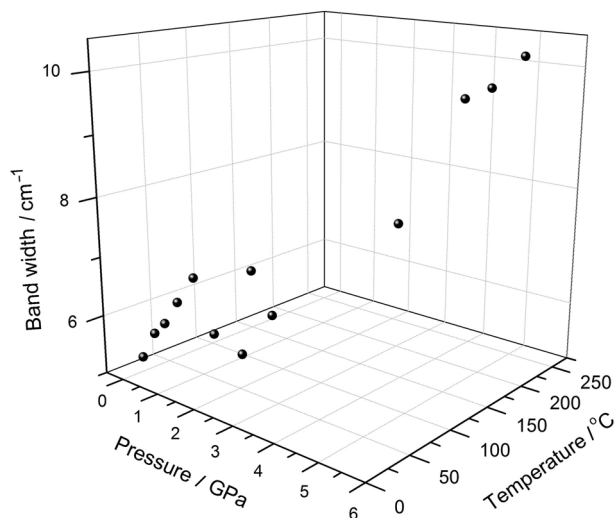

Figure 5. Dependence of the width of the 692-cm^{-1} band of the datolite 2D framework on pressure and temperature.

amplitude vectors of the ring oxygen atoms do not direct exactly to the ring center (Fig. S3).

Density functional theoretical calculations of datolite have been made to investigate the structural roles of the OH groups, but limited to the athermal condition of $T = -273$ °C (0 K).[12,17]

The apparent feature in the dependence values of Raman band wavenumbers $v_i(P)$ at ~2 GPa and constant $T = 22$ °C (Fig. 2) could prove some anomaly in the monotonous dependence of structural and spectroscopic parameters or a phase transition in datolite. The former interpretation is unlikely because the observed spectral changes are reproducible. We prefer the latter interpretation. The dependence values of Raman bands $v_i(P)$ with the change of slope and the small wavenumber jumps at $P = 2.04$ GPa are in accordance to this interpretation for the existence of a phase transition between two phases denoted I and II.

This pressure-induced phase transition or the feature in the P dependence of band positions in datolite has never been reported before now. Its nature including the structural changes is still unclear. One can suppose that this transition is polymorphic and is connected with the changes of the H bonds formed by protons of hydroxyls OH$^-$ because in the range of O–H vibrations, there are considerable anomalies in the dependence of v on P in the pressure range 2–2.75 GPa (Fig. 2), and this transition looks more lengthy than in the dependence of the 2D-framework bands on P (Figs 2 and 4). At this transition, no new bands of the O–H vibrations appeared, and one O–H stretching band is conserved. These spectral features suggest that the structural site of the OH groups in the unit cell remains to be single in both phases I and II.

It should be noted that the refined H sites in datolite[5] suggest a bifurcated hydrogen bonding with O5 as the donor and O4 and O2 as the acceptors, having the distances O5–H ~0.8 Å and (1) O5⋯O4 ~2.99 Å, H⋯O4 ~2.33 Å, and O5–H⋯O4 ~140° and (2) O5⋯O2 ~2.96 Å, H⋯O2 ~2.36 Å, and O5–H⋯O2 ~131°. X-ray diffraction measurements between +27 and −173 °C showed that the thermal expansion of datolite is mainly governed by the axial responses along the [100] and [010] axes, whereas the [001] length is almost unchanged.[5] Considering these irregularities in the dependence of the datolite structure on T and by analogy of the effects of compression and cooling on the structure, we can assume that the high-pressure transition is connected with the ordering of the bifurcated hydrogen bond as well.

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The decrease of the O–H band wavenumber with increasing P is a line of compelling evidence for a considerable enhancement of the H bond in both phases I and II. In the intermediate range of 1.5–2.75 GPa, however, an approximately constant wavenumber of this band is associated with the constancy of the H-bond energy and length that is described with the simplified models of the correlation for the H-bond length O–H…O and stretching O–H band wavenumber (for example, refer to ref.[18–23]). These models are developed for single linear H-bond X–H…Y, which nevertheless could be used for rough estimation of the H-bond length in datolite. Using the experimental[5] average distance O…O between O5···O4 and O5···O2, which is equal to $R = 2.975$ Å, and the relations,[23] our estimations of the average H-bond distance R with pressure are as follows: The 3497-cm^{-1} band corresponds to 2.975 Å at 1 bar and 22 °C, 3491.8–2.97 Å at 2.04 GPa and 22 °C, 3484.5–2.96 Å at 3.5 GPa and 22 °C, 3474.2–2.95 Å at 4.96 GPa and 90 °C, and 3464.2–~2.94 Å at 5.05 GPa and 250 °C, respectively.

The absence of any additional OH-stretching bands in the spectrum of the datolite phase II also suggests a lack of spasmodic overhydration, i.e. no entry of any excess amount of water into the structure from the medium. This observation is in direct contrast from those (i.e. existence of such processes) in zeolites[24–26] and cordierite[27,28] compressed in water medium. The crystal of datolite is not cracked at the transition I–II, and no long-time diffusive processes were observed. These characteristics of this transition suggest the polymorphic type. Additionally, we note that in our Raman spectra of datolite compressed in HT-DAC, no weak wide additional O–H bands were observed, which could appear at even weak overhydration as the H_2O molecules enter the defect sites.

Considerable changes in Raman spectra were found at the simultaneous increase of temperature from 22 to 90 °C and pressure from 3.5 to ~5 GPa (Figs 3 and S2). These changes could be evidence for a second phase transition between phases II–III. At this transition, the bands at 133, 176, and 232 cm^{-1} disappear; a new singlet band at ~300 cm^{-1} appears to accompany the band at 292 cm^{-1} to form a doublet of almost equal intensity. Also, a new middle-intensity band at about 166 cm^{-1} appears at the increase of T to 90 °C, which may be correlated with the disappearing weak band at 160.5 cm^{-1} (the value at $P = 3.5$ GPa, $T = 22$ °C). At the transition P–T parameters (P ~5 GPa, T ~90 °C), the doublet of bands at 390 and 398 cm^{-1}, corresponding to the doublet at 378 and 391 cm^{-1} at ambient conditions, merges into a singlet band at 401 cm^{-1}. At the transition, the intermediate-intensity band at 330 cm^{-1} disappears or dramatically decreases in intensity.

Changes in the range of the O–H stretching vibrations also occur (Figs 1, 3, and S2). The O–H stretching band shifts rather abruptly to the range of low wavenumbers, and its width increases considerably. At further increasing T from 150 to 250 °C, its width changes only slightly (Figs 3 and S2). We could assume that datolite crystal symmetry changes at the high-T transition, as evidenced by the changes in the number of observed Raman bands.

Comparison of the two observed transitions (increasing P to 2 GPa at constant $T = 22$ °C and increasing T to 90 °C and P to ~5 GPa) shows that the latter is characterized by more prominent changes in the Raman spectra and hence in the structure of the borosilicate 2D framework as well as in hydrogen bonds.

It should be additionally noted that datolite exhibits only one O–H stretching Raman band at the studied high P–T range including possible polymorphic transitions. Other layered structures such as brucite $Mg(OH)_2$ containing one OH site show the appearance of an additional weak O–H stretching band at the phase transition ($P = 4$ GPa and room T), forming the O–H doublet and retaining

the intensity ratio in this doublet up to 20 GPa.[29] Note that the O–H bonds in both structures, datolite and brucite, are oriented approximately normal to layers. Probably, the bifurcated H bonds, connected with oxygen atoms in the borosilicate layer of datolite, better stabilize the structure with respect to the formation of additional OH sites.

Figure 5 shows the typical dependence of the widths of the 2D-framework band (for example, the strongest band at 692 cm^{-1}). The bandwidths increase almost linearly with P in phase I, whereas in phase II, these bandwidths are scattered with increasing P: No apparent dependence is visible in Fig. 5.

At pressure P ~3.5–5.3 GPa, the bandwidths are strongly increased with increasing T at the beginning of heating from 22 to 150 °C in phases II and III. The bandwidths then increase slowly (or nearly steady) with T at the range 150–250 °C (Figs 1, S2, and 5). The latter feature can be attributed to the compensation of two contrasting trends: the usual homogeneous widening with increasing T and the decrease of inhomogeneous widening caused by high pressure. As a result of these two trends, the Raman bands, being initially nonhomogeneously widened as a result of compression to ~5 GPa at constant $T = 22$ °C, become more homogeneously widened because of heating in the range 150–250 °C at constant P ~5 GPa.

No noticeable dissolution of the datolite crystal in the water medium occurs for 3-h duration at the conditions of 5 GPa and 250 °C. Therefore, datolite is not dehydrated at these P–T conditions, which correspond to the 'cold' zones of slab subduction. The question of whether datolite decomposes to provide water and boron at substantially higher temperatures T ~700–800 °C, which correspond to the 'hot' zones of slab subduction,[8,10] requires further experiments.

The present experimental data on datolite are compared with published data on the behavior of talc and 10-Å phase at 'cold' subduction P–T conditions.[30] Datolite is proven to be stable at such high P–T conditions, taking into account their polymorphic transitions. Talc, on the other hand, transforms into a highly baric 10-Å phase at $P = 5$ GPa and $T = 500$ °C.

Conclusions

On the basis of *in situ* Raman study of datolite compressed in the water medium at simultaneously high pressure and temperature (up to 5.3 GPa and 250 °C), two polymorphic transitions have been observed for the first time: (1) pressure-induced phase transition I–II (or the feature in the P dependence of Raman band wavenumbers) at $P = 2$ GPa and constant room temperature, $T = 22$ °C, and (2) heating-induced phase transition II–III at T ~90 °C and $P \approx 5$ GPa. Emphasize that the second transition is observed at the simultaneous P–T run from 3.5 GPa and 22 °C to 4.96 GPa and 90 °C, induced by the heating the work volume in HT-DAC. The number of Raman bands is retained at the first transition but changed at the second transition (rather than decreasing number). The wavenumbers of datolite Raman bands are changed almost linearly with pressure at the corresponding phase ranges of P–T conditions. The second transition is characterized by several strong changes in different spectral ranges: the wavenumber jumps of the band majority, the merging of the strong doublet at 390 and 398 cm^{-1} (i.e. 378 and 391 cm^{-1} at ambient conditions in air), the splitting of the intermediate-intensity band at 305 cm^{-1} (292 cm^{-1} in air), and the transformation of the bands at low wavenumbers. The changes around the strong low-wavenumber band at 176 cm^{-1} (164 cm^{-1} at ambient conditions) at the heating-induced transition

(90 °C, 5 GPa) include the disappearance of the higher wavenumber satellite band at 184 cm^{-1} and the appearance of a new satellite band at 166 cm^{-1}. Note that the band wavenumber jumps measured at the transition are a joint result of proper band jumps and the effect of the step at increasing T and P.

These Raman data suggest that both transitions are most likely linked primarily to the change of the hydrogen bonds, which have been shown previously to be controlled by the bifurcation disorder.[5] No softening of low-wavenumber bands has been observed at an increase of P–T parameters. Simultaneous doubling of bands, which is characteristic of doubling of the unit cell, has not been detected at these transitions (or anomalies in P and T dependence of Raman bands) either. Moreover, neither overhydration nor amorphization of datolite compressed in the water medium has been observed at increasing P–T up to values corresponding to the 'cold' subduction zones of lithospheric slabs (at about P ~5 GPa and T ~250 °C).

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