



Raman investigation on the behavior of parasibirskite CaHBO_3 at high pressure



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ABSTRACT

Knowledge about the stability of hydrous borates and borosilicates at high pressures are of critical importance to our understanding on the boron geochemical cycle. Raman spectroscopic measurements of parasibirskite CaHBO_3 , containing the $[\text{BO}_2(\text{OH})]$ groups, have been made to pressures up to 5.4 GPa. The Raman data show that a progressive structural evolution from ambient pressure to 5.4 GPa can be accounted for by the same monoclinic phase $P2_1/m$, where the splitting of several Raman bands observed at some pressures is interpreted as the effect of the complex disordering in the H-bond network that has bifurcated H-bonds and $\frac{1}{2}$ -occupied H sites. There is no unambiguous evidence for phase transition to the ordered $P2_1$ monoclinic phase predicted by first-principles calculations at $T = 0$ K (W. Sun et al., Can. Miner., 2011). On the contrary, the disordering of parasibirskite, evidenced by the widening and attenuating Raman spectra, increases markedly at high pressures above 4.5 GPa that results in incipient amorphization.

Comparison of theoretical (lattice-dynamical) and experimental Raman spectra allows the reliable interpretation of almost all observed bands. The strongest symmetric B–O stretching band ν_1 at the wavenumber 908 cm^{-1} , which is split into a doublet at high pressures, exhibits a shift rate of $4.22\text{ cm}^{-1}/\text{GPa}$ for the main component.

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1. Introduction

The boron geochemical cycle has long been suggested to involve significant mantle degassing and transport in subduction zones [1–4]. For example, there is now a general consensus that boron, which is either adsorbed on hydrous silicates or incorporated in hydrous borates/borosilicates (e.g., tourmaline-group minerals, datolite, etc.) in hydrothermally altered oceanic crust, is transported to the mantle through deep subduction and returned to the surface via magmatism [1,3]. Therefore, knowledge about the stability and behavior of hydrous borates and borosilicates at high pressures is of critical importance to our understanding on the boron geochemical cycle [5–7].

We recently investigated the behavior of datolite $\text{CaBSiO}_4(\text{OH})$ [7], containing the tetrahedrally coordinated $[\text{BO}_3(\text{OH})]$ groups interconnected by bifurcated H-bonds [8], using in situ Raman spectroscopy measured in diamond anvil cells (DAC) at simultaneously high pressure and temperature (up to $P \sim 5$ GPa and $T \sim 250$ °C) corresponding to the “cold” subduction zones. We observed two polymorphic transitions: (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 $T \sim 90$ °C and $P \sim 5$ GPa. The number of Raman bands is retained at the first transition but changed at the second transition. In particular, the characteristic peaks of the $[\text{BO}_3(\text{OH})]$ groups in datolite were determined by lattice-dynamical calculations [7]. Similarly, Pereira et al. [6] reported in 2003 the Raman spectra of boric acid (H_3BO_3), containing the planar triangular $[\text{B}(\text{OH})_3]$ groups, from ambient pressure to 6.8 GPa at room temperature and observed pressure-induced amorphization associated with hindered decomposition through a mixture of H_2BO_3 and H_2O . Reliable interpretation of vibrations could help to elucidate the behavior of borate at high-pressure: the changes in structure and lattice dynamics, including those in the H-bond network. However, the interpretation of vibration modes in most previous Raman studies (e.g. olshanskyite [9], pinnoite [10], takedaite [11] and other borates [6,12–14]) are often uncertain and are commonly not supported by lattice-dynamical calculations.

Sibirskite and parasibirskite are diamorphs of CaHBO_3 and are both characterized by isolated $[\text{BO}_2(\text{OH})]$ groups [15–19]. For example, the crystal structure of parasibirskite, monoclinic $P2_1/m$ at ambient conditions, may be presented as sets of edge-sharing chains of $[\text{CaO}_7]$ polyhedra along axis c , linked in layer (100). These $[\text{CaO}_7]$ layers are bonded by the triangular $[\text{BO}_2(\text{OH})]$ groups to form the 3D crystal structure [18, 19]. The triangular $[\text{BO}_2(\text{OH})]$ group of parasibirskite possesses two

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short B–O bonds at 1.349 Å and one long B–OH bond at 1.417 Å, according to Sun et al. [19]. The H atom in the $P2_1/m$ structure is disordered over two equivalent sites (i.e., 50% occupancy each) and forms bifurcated H-bonds with two oxygen atoms O1–H...O2 and O1–H...O1. Therefore, parasibirskite represents an excellent model compound for investigating the behavior of hydrous borates at high pressures, especially those containing the $[\text{BO}_3]$ groups, for comparison with those containing the tetrahedrally-coordinated $[\text{BO}_4]$ groups. In particular, interpretation of vibrational modes on the basis of both theoretical calculations and comparison between experimental and theoretical spectra of parasibirskite is relevant for hydrous borates and borosilicates containing the triangular $[\text{BO}_3]$ groups and H-bonds.

It is also interesting to note that Sun et al. [19] observed that the distances of hydrogen bonds O–H...O are changed significantly when the monoclinic $P2_1/m$ structure of parasibirskite was cooled from room temperature to 173 K. On the basis of density functional theory (DFT) calculations at 0 K, these authors [19] predicted a displacive phase transition to the $P2_1$ space group below 173 K. However, experimental verification of this phase transition was not made. Often the loading of pressure has a similar effect on the crystal structure to the cooling, with respect to both the compression of the unit cell and the contraction of bond distances [20–24]. Therefore, a study of parasibirskite at high pressures may provide experimental verification for the theoretically predicted phase transition.

Accordingly we have measured in situ Raman spectra of parasibirskite CaHBO_3 from ambient pressure to 5.4 GPa to elucidate its stability and possible phase transformations into both crystalline and amorphous phases, including the possible ordering of the H atoms and the behavior of the bifurcated H-bonds. In particular, lattice-dynamical calculations of parasibirskite have been made to facilitate the interpretation of the Raman bands and their high-pressure behavior controlled by both the crystal structure and vibrational dynamics. The nature of high-pressure transitions and anomalies observed here are discussed in connection with earlier DFT calculations that predicted the $P2_1/m$ to $P2_1$ phase transition [19].

2. Materials and methods

2.1. Sample preparation and characterization

Parasibirskite investigated in this study was synthesized following the method described in the work [19]. Briefly, a mixture of 1.0 g $\text{LiOH}\cdot\text{H}_2\text{O}$ (23.83 mmol), 1.0 g H_3BO_3 (16.17 mmol) and 0.8 g $\text{Ca}(\text{OH})_2$ (10.8 mmol) with a molar proportion Li:B:Ca of 4.4:3:2 was prepared. After adding 15 mL deionized water, the mixture, with a pH value of ~14, was transferred into a 30 mL teflon-lined stainless-steel autoclave, heated to and held at 190 °C for three days, and finally cooled down to room temperature by turning off the furnace. Powder X-ray diffraction (PXRD) analyses showed that the solid product immediately after the synthesis experiment, obtained after filtering, washing with deionized water and drying in a desiccator, was pure parasibirskite. The composition of individual crystals of synthetic parasibirskite is close to that of the ideal formula [19]. However, Sun et al. [19] noted that parasibirskite left in the parental solution and exposed to the air transformed completely to calcite after only one week. PXRD analyses also showed that the sample of originally pure parasibirskite contains appreciable amounts of calcite after storage in air for a few months.

2.2. Raman experiments and lattice-dynamical calculations

Raman spectra of synthetic parasibirskite were recorded with a Horiba Jobin Yvon LabRam HR800 spectrometer equipped with a 1024-channel LN/CCD detector [25,26]. The sample of synthetic parasibirskite CaHBO_3 was compressed in an alcohol medium (methanol:ethanol 4:1). This powder sample was first pressed into a

tablet to obtain a dense material, which was then cracked into small pieces (<50 μm), appropriate for the working volume of DAC.

Spectra were excited with a 40-mW power neodymium-yttrium-aluminum garnet laser at the 532-nm line as double harmonic. Back-scattered spectra were collected from focal spot of diameter of 2 μm on the sample and recorded in the spectral region of 70 to 3800 cm^{-1} with 2.2 cm^{-1} resolution. An Olympus BX41 microscope with an Olympus 50× objective lens of long working distance (LWD) of 11 mm and 0.5-numerical aperture was used. The laser light that remained after scattering and data collection in the spectrometer, subsequently suppressed by an edge filter to the residual line at 0 cm^{-1} , was used for additional calibration correction of each recorded spectrum. High pressures up to 5.4 GPa at room temperature ($T = 22^\circ\text{C}$) were obtained in an apparatus with lever-arm-driven diamond anvils DAC [26].

The PeakFit program package was used for the deconvolution of Raman spectra into Voigt amplitude contours [27]. Lattice-dynamical calculations were carried out, using the program package LADY by Smirnov and Kazimirov [28]. The LADY package is based on the FORTRAN lattice-dynamical program CRYME written by M.B. Smirnov [29] and has been successfully applied for the simulations of various compounds [7,30,31].

3. Results

Raman spectra of parasibirskite with increasing and decreasing pressure (P) are illustrated in Figs. 1 and 2, where the representing spectra are plotted upwards in the sequence with increasing P from ~0 (in air) up to the maximal 5.35 GPa and then with decreasing pressure down to 0.08 GPa. These spectra change with increasing pressure: the wavenumbers of all bands are increased with one exception for the O-

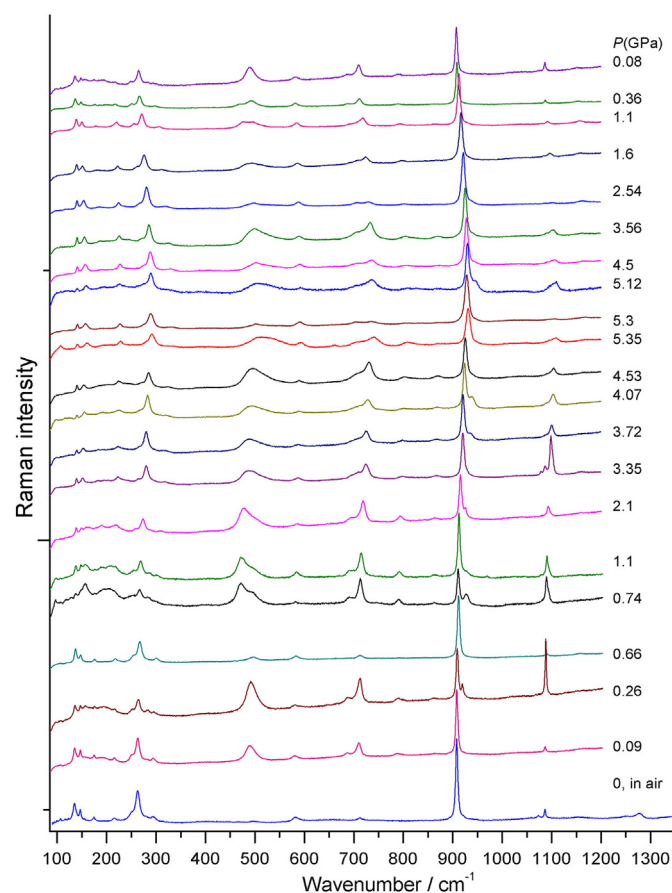


Fig. 1. Raman spectra of parasibirskite in the spectral range 80–1200 cm^{-1} at ambient conditions and high pressure.

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