

Raman spectroscopy of natural cordierite at high water pressure up to 5 GPa

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The high-pressure behaviour of cordierite, a widespread ring aluminosilicate with channels incorporating fluid compounds (H₂O, CO₂), is characterized by the absence of phase transitions up to 2.5 GPa. However, the distortion of the ring tetrahedra observed previously at 2.3 GPa is supposed to introduce a phase transition at higher pressure, which has not been checked so far. This work presents a high-pressure Raman spectroscopic study of natural cordierite compressed in water medium up to 4.7 GPa in a diamond anvil cell. At $P > 4$ GPa, a disordering of both the framework and intrachannel H₂O subsystem is apparent from significant broadening of Raman peaks and the evolution of short-range order parameters. This is followed by abrupt shifts of the framework and O–H stretching modes at about 4.5 GPa, indicating a first-order phase transition. Its reversibility is seen from the recovery of the initial spectrum at $P < 3$ GPa. The shift amplitudes of different framework modes indicate the predominance of distortion over contraction of the framework polyhedra upon this transition. The disordering of the H₂O subsystem in the high-pressure phase is likely a consequence of distortion of the channel-forming framework elements, which is supposed to be a driving force of this transition. Copyright © 2011 John Wiley & Sons, Ltd.

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Introduction

Cordierite, a ring framework aluminosilicate (Mg,Fe)₂[Al₄Si₅O₁₈]^{*n} (H₂O,CO₂), has attracted much interest because of its channel structure accessible for small molecules (predominantly H₂O and CO₂), and because of its stability in a wide P–T range covering a majority of metamorphic processes in the Earth's crust.^[1–5] The volume compressibility of cordierite measured up to 3 GPa was found to be intermediate between those of feldspars and ring silicates such as beryl.^[6,7] This reflects a 'mixed' character of the cordierite framework, built up of six-membered (Si,Al)O₄-tetrahedral rings and the layers of (Al,Si)O₄ tetrahedra and (Mg,Fe)O₆ octahedra.^[2,4,8] A relatively rigid structure determines a smooth character of the volume compression curve and the absence of phase transitions up to 3 GPa. Like zeolites,^[9] the cordierite structure is accessible for molecular compounds: the compressibility of 'empty' Mg-cordierite in water was found to decrease at $P > 2$ GPa because of the incorporation of H₂O molecules from the pressure-transmitting medium.^[10] At that, significant shrinking of ring tetrahedra is observed, which is supposed to introduce a phase transition at higher pressure. However, no information is available about the structure behaviour of cordierite at $P > 2.5$ GPa. The aim of this work is to characterize the evolution of intrachannel molecular H₂O and overall cordierite structure in the nearest pressure interval between 2–5 GPa by means of Raman spectroscopy, reproducing the compression conditions (penetrating water medium) of the previous experiment at 0–2.5 GPa.^[10]

Spectroscopic methods were widely used to study Si,Al-ordering and orientation of intrachannel compounds (H₂O, CO₂) in cordierite structure at ambient pressure and a wide temperature range.^[11–18] In particular, linear relations were found between splitting and width of some of the framework vibrational modes and the order parameters σ and Q_{od} characterizing the extent

of lattice distortion induced by Si,Al-ordering during high-temperature annealing of orthorhombic cordierite.^[14] Two main types of H₂O molecules are distinguished in cordierite channels: Class I H₂O has no contact with nonframework alkali cations and is aligned along the channel axis [001], whereas Class II H₂O molecules interact with alkali cations and lie perpendicularly to [001].^[15,16,19–22] Extremely weak hydrogen bonding of H₂O molecules with the framework is apparent from relatively high wavenumbers of the O–H stretching vibrations at ~ 3600 and 3575 cm⁻¹ for symmetric O–H vibrations (ν_1) for Class I and II, respectively.^[11,15,16,18,23,24] In the Raman spectra, the ν_1 modes are the most intense at room temperature.^[16] No spectroscopic studies on the high-pressure evolution of molecular water included in cordierite were performed so far, whereas it seems important because of petrological significance of this compound.

This work presents a high-pressure Raman spectroscopic study of natural hydrous (Mg,Fe)-cordierite compressed in water medium up to 4.7 GPa.

Experimental

We used homogenous, inclusion-free, transparent and uniformly coloured grains of natural cordierite from the Altai amphibolite

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complex, with the composition $\text{Na}_{0.07}(\text{Mg}_{1.57}\text{Fe}_{0.36}\text{Mn}_{0.07})[\text{Al}_{3.96}\text{Fe}_{0.06}\text{Si}_{4.98}\text{O}_{18}] \cdot 0.45\text{H}_2\text{O}$ (the average from seven microprobe analyses). The H_2O content was determined by gas chromatographic analysis with the accuracy of 0.08 wt%. According to X-ray diffraction (XRD) analysis, this cordierite is orthorhombic (space group $Cccm$), the distortion index $(\Delta=2\Theta_{131}-(2\Theta_{511}+2\Theta_{421})/2)^{[25]}$ is 0.254. The details of chemical and XRD analysis of this sample are described in Ref.^[24] A single crystal of about 50–100 μm in size was placed into the gasket hole of a diamond anvil cell (DAC) and compressed up to 5 GPa. Doubly-distilled water was used as penetrating pressure-transmitting medium. The DAC is based on a modified Mao–Bell design^[26] and employs two diamonds with 1 mm diameter culets. A Horiba Jobin Yvon T64000 spectrometer (HORIBA Scientific Service Engineer Fluorescence Division Jobin Yvon S.A.S., Villeneuve d'Ascq, France) equipped with a microscope and multichannel detector was used for microspectroscopic measurements. Raman spectra were collected using Ar^+ ion laser (514.5 nm excitation radiation) in the region between 150 and 3700 cm^{-1} comprising of framework modes and stretching modes of intrachannel molecular H_2O . Spectral resolution was 2 cm^{-1} . The pressure values were measured before and after Raman measurements from the R1 ruby fluorescence line^[27] with an accuracy of ± 0.05 GPa.

Results and discussion

Representative Raman spectra of natural cordierite collected at different water pressures in the framework and O–H stretching regions are shown in Figs 1 and 2, respectively. In the O–H stretching region the Raman spectrum shows a sharp band at 3600 cm^{-1} and another weak and broad band at around 3580 cm^{-1} , ascribed to symmetric O–H vibrations (ν_1) for Class I H_2O and Class II H_2O , respectively.^[16] The prevalence of nonbonded Class I H_2O because of a low content of the nonframework alkali cations in cordierite is seen from the intensity ratio for these two bands.

Upon increasing the pressure up to about 4.5 GPa, all the framework bands in the region of 400–1200 cm^{-1} show positive linear pressure dependence (Fig. 3(a)). The larger shift gradient of (Si,Al)–O stretching modes, as compared to that of bending and mixed vibrations in tetrahedral/octahedral (Si,Al) O_4 , (Mg,Fe) O_6 groups (Table 1), implies the prevalence of compression over deformation of the framework polyhedra. The bands at 150–300 cm^{-1} are apparently related to external translational

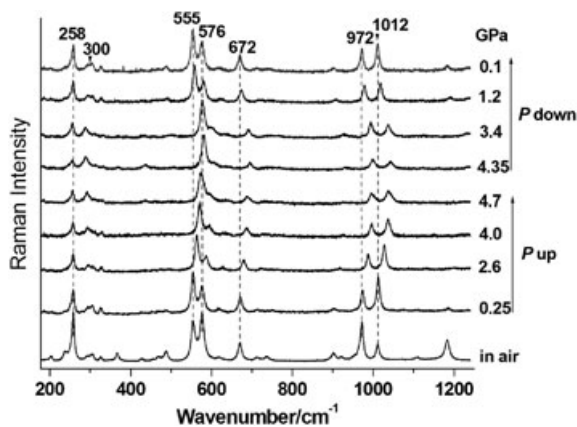


Figure 1. Selected Raman spectra of Altai cordierite under increasing (P up) and decreasing (P down) pressure in the region of framework vibrations.

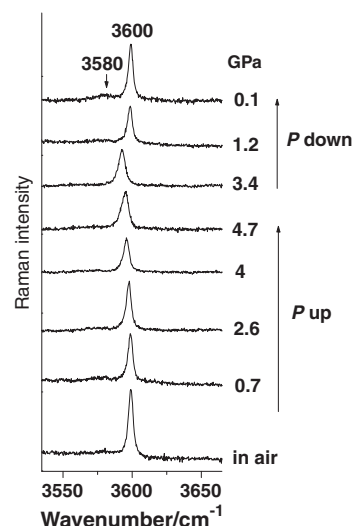


Figure 2. Selected Raman spectra of Altai cordierite under increasing (P up) and decreasing (P down) pressure in the region of stretching O–H vibrations.

and libration modes of larger framework groups, probably six-membered rings,^[28,29] and to the motions of Mg,Fe-cations and translational modes of H_2O .^[18] These bands are almost pressure independent or exhibit minor positive/negative $\nu(P)$ slopes (Fig. 3(a), Table 1). As a whole, these data are evidence for

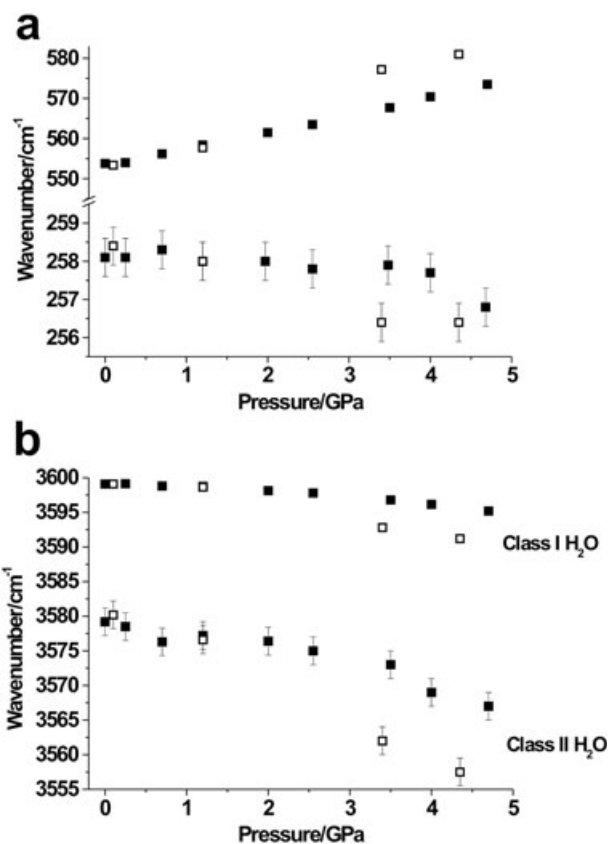


Figure 3. The $\nu(P)$ dependences for the framework vibrational modes (a) and O–H stretching modes for Class I H_2O and Class II H_2O (b) at the pressure increase (filled squares) and decrease (empty squares). A larger size of error brackets for the O–H mode at 3580 cm^{-1} (Class II H_2O) is due to weakness and large width of the corresponding band.

Table 1. The wavenumber shift of Raman bands of Altai cordierite with pressure

ν (cm^{-1})	$\delta\nu/\delta P$ ($\text{cm}^{-1}/\text{GPa}$)	Band assignment
156	-1.7(3)	
258	-0.2(2)	
294.5	-0.2(3)	
305.5	1.1(3)	
326.5	0.2(3)	
487.5	2.7(3)	Bending (Si–O–Al) and stretching
555	4.3(1)	(^{VI} Al–O), (Mg,Fe–O) vibrations of
576	4.0(1)	tetrahedral and octahedral
		groups ^[8]
618	3.4(3)	Bending and stretching vibrations of
672	4.1(2)	tetrahedral (Si,Al)O ₄ groups ^[8]
902	5.8(2)	
972	5.5(1)	
1012	6.1(1)	(Si,Al)–O stretching ^[8,38]
1183	9.3(2)	
3579	-2.3(3)	O–H stretching of Class II H ₂ O ^[16]
3560	-0.8(2)	O–H stretching of Class I H ₂ O ^[16]

To our knowledge, there are no further specific band assignments available in the literature.

a regular contraction and the absence of structural transformations in cordierite up to about 4.5 GPa. Such compressibility behaviour is similar to that of beryl, another important ring silicate with analogous structure, observed in the same pressure range of 0–5 GPa.^[30]

Start from 4 GPa, all the framework and O–H stretching bands appreciably broaden, and one of the doublet bands at 560 cm^{-1} sharply diminishes (Figs 1, 2 and 4). At about 4.5 GPa, noticeable shifts are observed for all the framework and O–H stretching modes (Fig. 3), indicating a phase transition. At that, the bands in the region of 400–1200 cm^{-1} shift to higher wavenumbers, whereas the bands in the region of 150–300 cm^{-1} and O–H stretching modes exhibit red shifts. In contrast to the pressure trends observed prior to this transition, the bands of mixed and bending vibrations show larger shifts ($\sim 8 \text{ cm}^{-1}$) as compared to those of (Si,Al)–O stretching modes ($\sim 4 \text{ cm}^{-1}$) (Fig. 3(a)). This indicates the prevalence of distortion over contraction of the framework polyhedra upon this transition. The initial wavenumbers and linewidths, as well as the intensity of the band at 576 cm^{-1} ,

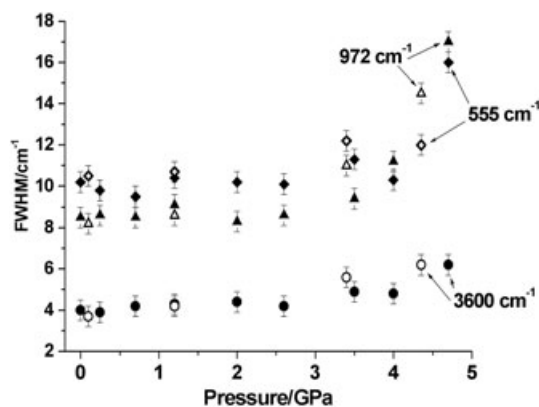


Figure 4. Pressure dependences of FWHM for selected framework and O–H stretching modes (with wavenumbers indicated in legend) at the pressure increase (filled symbols) and decrease (empty symbols).

are restored only at the pressure release down to 3 GPa (Fig. 1). It should be noted that, in fact, the transition associated with the bands shift develops at the beginning of pressure release down to 4.35 GPa, which is close to the maximum pressure of 4.7 GPa achieved in the experiment. Because upon further decompression down to $P < 3$ GPa we observe the reverse transition from the restoration of the initial spectrum, we can ascribe the spectrum recorded on decompression from 4.35 to 3.4 GPa to the high-pressure phase formed at nearly the maximum pressure of our experiment. The observed lateness of the formation of new phase at 4.35 GPa instead of 4.7 GPa is obviously related to a low-kinetics character of this transition, which is not unusual for the high-pressure displacive transitions in silicates.^[31–33]

It seems interesting to consider the high-pressure evolution of splitting of the 560 cm^{-1} doublet and the width of the 672 cm^{-1} mode. As mentioned above, these parameters are found to be a direct measure of the displacive order parameter Q_{od} and the short-range parameter σ , which characterize the extent of the lattice distortion because of Si,Al-ordering leading toward a perfectly ordered orthorhombic structure during high-temperature annealing of cordierite.^[14] Another parameter characterizing the ordering of cordierite structure is the distortion index Δ , which is a measure of deviation of the unit cell parameters from hexagonal metric of fully disordered cordierite.^[25] Although a strict correlation between Δ and Si,Al-ordering holds only for waterless, pure Mg-cordierites,^[5,25] it was shown to be roughly applicable also for natural Fe,Na,H₂O-bearing cordierites.^[34] The initial distortion index $\Delta = 0.254$ of our sample corresponds to highly ordered orthorhombic structure, which agrees with relatively small values of the 672 cm^{-1} width measured at the beginning of compression. Approximately the same values of the 672 cm^{-1} width are achieved at the progressive stage of the high-temperature Si,Al-ordering of Mg-cordierite.^[14] This means that, despite the difference in the chemical composition of these two cordierites, they demonstrate similar correlation between spectral characteristics and structure ordering. Therefore, we can roughly estimate the pressure-induced ordering/disordering of the cordierite structure based on the comparison between the change of spectral characteristics (splitting of the 560 cm^{-1} doublet and the width of the 672 cm^{-1} mode) in our high-pressure experiment and the high-temperature annealing^[14] (Fig. 5). Of course, in contrast to the high-temperature ordering caused by Si,Al migration, the pressure-induced ordering/disordering is mostly displacive in nature, i.e. it is related with slight displacements of all atoms leading to local distortion of the structure.^[35] From appreciable shifts of the 560 cm^{-1} splitting and the 672 cm^{-1} width at $P > 4$ GPa it is clearly seen that, prior to the transition, the cordierite structure becomes disordered, which agrees with the observed broadening of all the framework and O–H bands (Fig. 4). The transition point between 4.7–4.35 GPa is marked by abrupt shifts of both these parameters into opposite directions, which indicates some ordering of the cordierite structure, obviously related to the formation of the high-pressure phase.

Another important feature characterizing this transition is the change of the intensity ratio for the doublet bands at 555 and 576 cm^{-1} I_{555}/I_{576} (Figs 1 and 6). These bands are found to originate from one mode that splits on passing from hexagonal to orthorhombic cordierite.^[14] The abrupt increase of I_{555}/I_{576} between 4.7 and 4.35 GPa denotes a sensibility of this doublet mode to structural changes accompanying this transition. Such a behaviour of this mode implies a specific framework distortion characteristic of the high-pressure treatment, different from

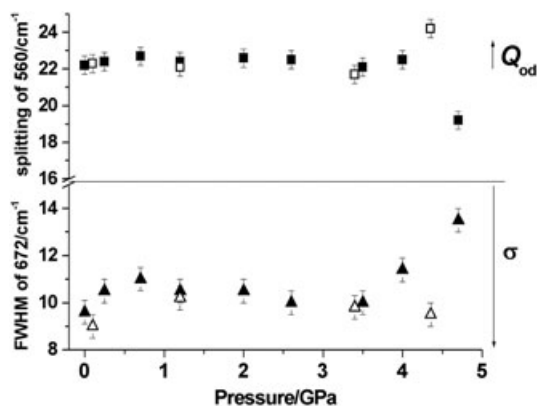


Figure 5. Pressure dependences of FWHM of the 672 cm^{-1} band (triangles) and splitting of the doublet at 560 cm^{-1} (squares) at the pressure increase (filled symbols) and decrease (empty symbols) in comparison with the trends of the displacive order parameter Q_{od} and the short-range parameter σ .^[14] Arrows indicate the direction of increase of Q_{od} and σ along with the progress of the lattice distortion and Si,Al-ordering during high-temperature annealing of cordierite. The arrow length corresponds to the range of the 672 cm^{-1} FWHM and 560 cm^{-1} splitting measured during the high-temperature annealing.

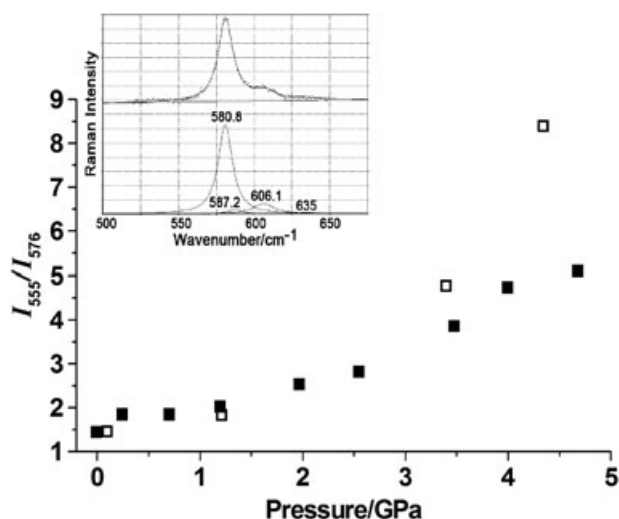


Figure 6. Pressure dependence of the intensity ratio for the doublet bands at 555 and 576 cm^{-1} , calculated with the PeakFit program (PeakFit 4.12 Systat Software Inc.(SSI), San Jose, California), at the pressure increase (filled squares) and decrease (empty squares). Small graph presents an example of the doublet bands fitting at the transition pressure of 4.35 GPa . The error bars are inside the symbols.

that observed at the high-temperature Si,Al-ordering, where no changes in relative intensities of these doublet bands were observed.^[14] Besides the bands shift, because the increase of I_{555}/I_{576} is the major change observed in the spectra upon the transition, we can suppose that this transition is driven by distortion of some framework elements.

The stretching O–H modes (ν_1) exhibit monotonic red shift with the pressure increase up to 4.7 GPa (Fig. 3(b)). Such a negative shift is known to be a clear indication that hydrogen bonds strengthen because of gradual contraction of structure cavities upon the pressure increase.^[18,36,37] The phase transition observed at about 4.5 GPa is accompanied by a further abrupt red shift of the O–H stretching modes that is more pronounced for Class II H_2O (Fig. 3(b)). Even after the transition the ν_1

wavenumbers for both types of H_2O molecules at 3557 and 3590 cm^{-1} still correspond to weak hydrogen bond.^[18] However, at ambient pressure, Class II H_2O is assumed to have no interactions with the framework because of unfavorable distances to the framework oxygen.^[16] Therefore, even weak hydrogen bonds require some deformation of channel-forming framework, which is apparently reflected in the observed shifts of the framework bands, and is probably related to the change of the intensities ratio I_{555}/I_{576} discussed above.

In contrast to the framework bands, the O–H stretching band of Class I H_2O remains as wide as before the transition (Fig. 4). The comparison of the pressure trends of the wavenumber shift and full width at half maximum (FWHM) for this band (Figs 3(b) and 4) indicates that the observed broadening is mainly influenced by some kind of displacive disordering, rather than by strengthening of hydrogen bonds. It seems reasonable to conclude that the disordered state of H_2O molecules in the new phase is related to the distortion of the framework building elements (presumably six-membered rings), which is supposed to be the driving force for this transition.

It should be noted that the disordering of cordierite structure observed at $P > 4\text{ GPa}$ is surely a proper characteristic of structure behaviour rather than a consequence of deviation from hydrostatic conditions at compression in ice. It is clearly seen from the pressure dependences of linewidths (Fig. 4): the rate of peak broadening is not increased after the formation of ice 6 at 0.9 GPa or ice 7 at 2 GPa .

Conclusions

The high-pressure Raman data indicate the existence of a reversible, low-kinetics phase transition in natural cordierite at about 4.5 GPa . The observed abrupt shifts of all the framework and O–H stretching modes indicate this transition to be of first order. It is preceded by a disordering of both the framework and intrachannel H_2O subsystem at $P > 4\text{ GPa}$. According to the evolution of the order parameters Q_{od} and σ , the transition leads to structure ordering comparable with that of the initial cordierite. The shift amplitudes of different framework modes indicate the predominance of distortion over contraction of the framework polyhedra upon this transition. The hydrogen bonds of the H_2O molecules with framework strengthen, though they remain relatively weak. The disordering of the H_2O subsystem in the high-pressure phase is likely a consequence of distortion of the framework building units (presumably six-membered rings), which is supposed to be a driving force of this transition. The phase transition first found in cordierite at 4.5 GPa apparently marks a lower pressure limit of the change of compressibility mechanism from predominant contraction to the distortion of the framework rigid elements in ring silicates.

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