Optical phonons, OH vibrations, and structural modifications of phlogopite at high temperatures: An in-situ infrared spectroscopic study

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ABSTRACT

The thermal behavior of optical phonons and OH vibrations of phlogopite (a trioctahedral mica) was examined at temperatures up to 1000 K using in situ infrared spectroscopy. The results showed that with increasing temperature, O–K bands in phlogopite exhibited a relatively strong variation in frequency in a manner similar to those in muscovite. The work revealed that different types of OH bands (fundamentals and combinations) have very different thermal behavior or temperature dependence, and their absorption coefficients are commonly not constant on heating. OH combination bands that are associated with summation processes of multi-phonon interactions commonly show a decrease in their intensities on heating, but in contrast combination bands due to difference processes generally exhibit an increase. This means that temperature dependencies of their absorption coefficients need to be considered when using the Beer-Lambert law to determine or estimate OH contents or hydrogen concentrations at high temperatures. The results showed a structural anomaly associated with a discontinuity in the temperature derivative of the wavenumber of Al–O and Si–O vibrations and O–H stretching near 600 K. However, framework-related phonon modes in the FIR and MIR regions do not suggest a break of the original monoclinic structural symmetry in the investigated temperature region. The complex changes are attributed to temperature-induced alteration of local configuration involving TO_4 tetrahedra and a possible change of the orientation of OH dipoles, in addition to a previously reported distortion of MO_6 octahedra. Increasing temperature to 1000 K also causes partial dehydroxylation, as evidenced by the disappearance of the OH band near 3623 cm^{-1} and the decrease in OH band height and area of other OH bands. The study did not record the formation of H_2O inside phlogopite as a result of partial dehydroxylation. The work offers new data and findings that have important implications in understanding the complex structural modifications and the behavior of phonon modes and the thermal stability of hydroxyls on approaching the dehydroxylation, as well as the way hydrogen is released from micas at high temperatures. Our data also show that phologpite becomes less transparent with increasing temperature suggesting a change of radiative properties and ability to transmit heat, which could be of interest for modeling thermal-transmission in crustal rocks.

Keywords: Phlogopite, infrared spectra, high temperature, phonon modes, OH, dehydroxylation, phase transition

INTRODUCTION

Micas, as common rock-forming phases, occur in various geological environments. They may be involved in many petrogenetic reactions occurring in fluid-absent melting processes and in mineral-fluid interactions and play important roles in the storage and release of water in the mantle through complex reactions (Virgo and Popp 2000). Phlogopite, with a typical chemical formula of $[KMg_3(AlSi_3)O_{10}(OH)_2]$, is a trioctahedral mica and has monoclinic C2/*m* symmetry. In natural phlogopite, an octahedral sheet (M = Mg, Fe, Mn, and Al) is sandwiched between two sheets of linked TO_4 (T = Si, Al) tetrahedra to form

a "1:2" layer. Interlayer cations, such as K, Na, Ca, and Ba, lie between these composite layers. In this trioctahedral mica, each octahedral site is similarly occupied and the O–H vector points along the [001] direction toward the interlayer cation. The OH ions in phlogopite can be replaced by F, Cl, etc., to form fluorphlogopite, chlorphlogopite, etc. Vacant positions (symbol: □) may occur in natural samples for charge balance (Vedder and Wilkins 1969; Rieder et al. 1998).

The present work is a continuation of our recent infrared (IR) studies on phyllosilicates (such as pyrophyllite, sericite, talc, and muscovite) (e.g., Wang et al. 2002, 2003; Zhang et al. 2005, 2006, 2010a, 2010b). The principle objectives are fourfold. First, we wish to gain better insights into the thermodynamic behavior of lattice vibrations and hydroxyls at high temperatures,

especially on approaching dehydroxylation. The importance and significance of such investigations in hydrous materials, hydrous layer silicates, and nominally anhydrous minerals have been well recognized and emphasized (e.g., Bell and Rossman 1992; Brigatti and Guggenherin 2002; Padron-Navarta et al. 2014). Gaining understanding of how water or hydrogen is released is of scientific significance. This type of work may help to identify the mechanisms by which phyllosilicates are altered through heating or weathering in the environment. There have been studies focusing on dynamics of hydrogen in silicates (Aines and Rossman 1985; Mookherjee et al. 2001; Tomlinson et al. 2007; Balan et al. 2010; Smrčok et al. 2011) and temperature dependencies of hydrogen species and their thermal stability (Keppler and Bagdassarov 1993; Su et al. 2008; Pawley and Jones 2011; Yang et al. 2011; Zhang and Moxon 2012). However, little is known about the thermodynamic behavior of phonon modes of phlogopite, and limited work has been carried out systematically, apart from some early investigations in the near infrared region (Vedder 1964; Fripiat et al. 1965). In the present study, we compare phlogopite with muscovite, a dioctahedral mica whose O–K motions and OH librations show strong variation at temperatures far below dehydroxylation (Zhang et al. 2010a) so as to gain better insights into the characteristics of phonon vibrations and OH absorption in micas on approaching dehydroxylation and the dehydroxylation mechanism. For phlogopite, it was proposed that dehydroxylation is associated with Fe oxidation (e.g., Vedder and Wilkins 1969; Zema et al. 2010). Second, the present study aims to investigate the possible formation and diffusion of H_2O during dehydroxylation, which has long been assumed or proposed as the mechanism of dehydroxylation in phyllosilicates (please see Zhang et al. 2010b for more details and reviews). However, recent direct measurements of hydrogen-related species in some typical layer silicates (e.g., muscovite, sericite, talc, and pyrophyllite) by IR spectroscopy did not record the characteristic bands of H_2O (Zhang et al. 2010b) in dehydroxylated samples. This finding raised a question as to whether H_2O is the principle diffusing species during dehydroxylation in phyllosilicates. Third, following the work of Zhang et al. (2007), we explore further the temperature-induced changes in absorption coefficients of OH species, which is of importance in determination or estimation of hydrogen contents at high or low temperatures using IR spectroscopy based on the Beer-Lambert Law. This is a poorly investigated field, especially for the behavior of OH bands associated with multi-phonon processes. Fourth, we look into the previously reported phase transitions or anomalous behavior of phlogopite at temperatures between 560–780 K. Due to its complex crystal structure and possible reactions, phlogopite has been reported to have structural variations at high temperatures. The physics behind the structural anomalies and what happens at the atomic level remains poorly understood. Anikin (1971) reported a second-order phase transition near 563 K. Egorov et al. (1972) suggested an increase in thermal conductivity in [001] direction in phlogopite at temperatures above 573 K (or 673 K for fluorphlogopite), and attributed the change to the expansion of Mg octahedra during heating and rotation of a tetrahedral grid from ditrigonal toward hexagonal. The X-ray diffraction work of Takeda and Morosin (1975) showed a clear break of temperature dependence for cell parameters a and b in a synthetic

fluorphlogopite near 673 K. Results from in situ neutron powder diffraction (Chon et al. 2006) showed that the expansion rate of unit-cell parameters for ferroan phlogopite varied discontinuously, with a break at a much higher temperature (773 K), which is considered to be due to a distortion of MO_6 octahedra, a decrease in mean <M-O> distance, and an increase in octahedral flattening angle. Chon et al. (2006) attribute these changes to Fe oxidation and dehydroxylation processes, however. The recent Raman study by Tutti and Lazor (2008) reported discontinuities in Raman frequencies as a function of temperature near 638 ± 15 K and suggested deformation and elongation of Mg octahedra along the crystallographic c-axis. The data of Tutti and Lazor (2008) appear to imply a "sharp" phase transition, in contrast to the previously proposed second-order transition by Anikin (1971). Why do the reported anomalies or phase transitions in different studies occur over such a relatively large temperature range (from about 560 to 780 K)? Is the reported change a real symmetry-related structural phase transition? What is the main driving force of the change? If the change is due to a structural phase transition, is it a second-order transition, as shown by most XRD data, or first order, as suggested by the Raman data of Tutti and Lazor (2008)? In the present work, we report new data for phlogopite from in situ high-temperature infrared spectroscopy up to 1000 K, which offers better insights into these issues.

SAMPLE AND EXPERIMENTAL METHODS

The sample (277) used in the present study was from the Sedgwick Museum (University of Cambridge, U.K.), and it is clear and optically transparent. Its chemical contents were determined by electron microprobe analysis (Table 1) as: $(K_{0.930}Na_{0.096})(Mg_{2.861}Fe_{0.027}Al_{0.266}Mn_{0.001}Ti_{0.005})(Si_{2.988}Al_{1.012})O_{10}[F_{0.613}OH_{1.387}]$. X-ray diffraction data showed that the sample is monoclinic. This was further supported by polarized infrared absorption measurements (between 50 and 1500 cm^{-1}) on oriented single single crystals, from which the A_u modes, and in-plane and out-plane B_u modes of phlogopite were recorded (the data will be published in a separated work). The X-ray diffraction measurements were carried out by single-crystal diffraction by using a Philips PW1100 four-circle diffractometer with point-counter detector. Operating conditions were 55 kV and 30 mA and graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). Horizontal and vertical apertures were 2.0° and 1.5°, respectively. Unit-cell parameters were derived from a least-squares procedure, based on a locally improved version of the Philips LAT routine, taking into account 50 to 60 d^*-spacing measured considering all the reflections in the range $3° < \theta < 25°$. The results showed $a = 5.311(5)$, $b = 9.189(24)$, $c = 10.249(18)$, and $\beta = 100.03(2)°$. Thin cleavage sheets or flakes with the (001) plane (it was difficult or impossible to cut thin sheets perpendicular to the layer plane, because of phlogopite's perfect cleavage with the base plane) and thickness ~3–310 μm were used for the IR measurements. The usage of different sample thicknesses is to ensure good recording of bands with different intensities.

The IR measurements from the far infrared (FIR) region to the near infrared (NIR) region were carried out under vacuum using a Bruker IFS 113v spectrometer. For in situ measurements (up to 1000 K), sample sheets or plates were supported with Pt foils with a hole of ~3–5 mm in diameter and loaded into a Pt-wired furnace that was located in the sample chamber of the spectrometer. The sample temperature was measured using a thermocouple that touched the sample and the heating rate was 10 K/min. The temperature uncertainty was less than 5 K at high temperatures. Data were also acquired on cooling. A mercury lamp, polyethylene-windowed DTGS detector, 3.5 and 6 μm Mylar beamsplitters were chosen for the measurements in the FIR region. The mid infrared (MIR) and NIR data were recorded using a MCT detector coupled with a Globar lamp and a KBr beamsplitter. Recording FIR absorption spectra in the region below 350 cm^{-1} at high temperatures up to 780 K was not straightforward, because the bands

TABLE 1. Chemical compositions of phlogopite sample (277) by electron microprobe analysis (dash = below 0.01)

Sample	SiO_2	Al_2O_3	KO_2	NaO_2	MgO	CaO	TiO_2	BaO	FeO	MnO	NiO	Cr_2O_3	F
277	41.33	14.99	10.08	0.69	26.54	–	0.11	0.07	0.45	0.01	–	–	2.68

of phlogopite in the FIR region are relatively weak compared with those in the MIR region. Also, the sample becomes less IR transparent on heating to higher temperatures. For good measurements in the FIR region, the techniques previously set up by Zhang et al. (2010a) were employed. They included using a stabilized power supply for the spectrometer, setting lab temperature to 18 °C, warming up the spectrometer for more than 8 h, and measuring samples at night to minimize the effect of possible mechanical vibrations from human activities in the building. The infrared spectra were obtained in absorbance, $A = -\log(I/I_0)$, where I_0 is the incident radiation energy at a given frequency or wavenumber, I is the transmitted energy. As the measurements were based on Fourier transform spectroscopy, the emission from the furnace at high temperatures is not expected to affect the recorded data because the emitted signals were not modulated and removed during the Fourier transformation process. Data analysis was carried out using software OPUS-IR. Peak positions were determined by curve fitting or the second derivative method. The band width (full-width at half maximum), band height (band linear intensity), and band areas (integrated band intensity) were obtained by fitting the data to Lorentzian function with a linear baseline.

RESULTS

Thermal behavior of lattice vibrations

In situ infrared spectra (between 50 and 1200 cm⁻¹) of the sample are shown in Figure 1. Main infrared bands are recorded at 89, 156, 161, 342, 375, 610, 656, 703, 729, 803, and 911 cm⁻¹. They are mainly in-plane vibrations as the sample is an (001) section. The assignments of most of these infrared bands can be found in the work of Jenkins (1989) and Beran (2002). Several intense bands occurred in the spectrum recorded in samples with different thickness at room temperature, and they give absorption maxima roughly around 450, 493, 510, 961, 1029, and 1079 cm⁻¹. They are expected to be due to Si–O–Si bending and Si–O stretching. These recorded bands are noisy and saturated the detector because of their strong absorption and the sample thickness, so their band positions might be affected somewhat. On heating, these absorptions were not clearly revealed due to a temperature-induced increase in background absorption and a decrease in transparency of the sample.

The phonon mode with the lowest wavenumber recorded in this study is located near 89 cm⁻¹. It is considered as K–O motion

and internal layer ion vibrations because it appears in K-micas (Prost and Laperche 1990; Zhang et al. 2006, 2010a). However, the bands may not be a pure K–O vibration, but involve other types of vibrations (Velde and Couty 1985; McKeown et al. 1999). The response of this band to heating is given with other bands in Figure 2. Among all measured fundamental phonon modes, this K–O vibration showed the largest relative change (6% in 300–750 K) in frequency (Fig. 2a). Its behavior is somewhat similar to that of the K–O vibration near 109 cm⁻¹ in muscovite, which exhibited a strong softening on heating (Zhang et al. 2010a). This finding suggests that K–O bond lengths increase on heating and that they have a thermal variation relatively greater than other bonds (Guggenheim et al. 1987; Mookherjee et al. 2001). The observation is consistent with the results of Russell and Guggenheim (1999) who investigated a hydroxyphlogopite crystal to 873 K by X-ray diffraction and found that the K–O bond distances increased with increasing temperature. The vibrational nature of the 156 and 161 cm⁻¹ modes remain unclear, although our polarized measurements (data will be published separately) showed that both modes purely vibrate within the sheet plane, with the former's dipole moment parallel to the a axis and the latter's parallel to the b axis. Based on their frequencies, they could be partially associated with the interlayer cations, because K–O bands commonly occur in this wavenumber region for other silicates (e.g., Zhang et al. 1996, 1997). The normal mode calculations by McKeown et al. (1999) also suggested the involvement of interlayer cations (K) as well as others (M, T, OH/F). Our data recorded at high temperatures show that increasing temperature has a weak effect on the bands near 156 and 161 cm⁻¹ (Figs. 2b and 2c). The relative frequency change of the 156 cm⁻¹ band is 2.6% from 300 to 750 K, whereas the 161 cm⁻¹ is nearly temperature independent (with a change as small as 0.3%). In fact, this 161 cm⁻¹ band had the weakest frequency change among the measured bands. It was also noted that the 156 cm⁻¹ mode showed an unusual increase in band height on heating (Fig. 3a), in strong contrast to the behavior of the other
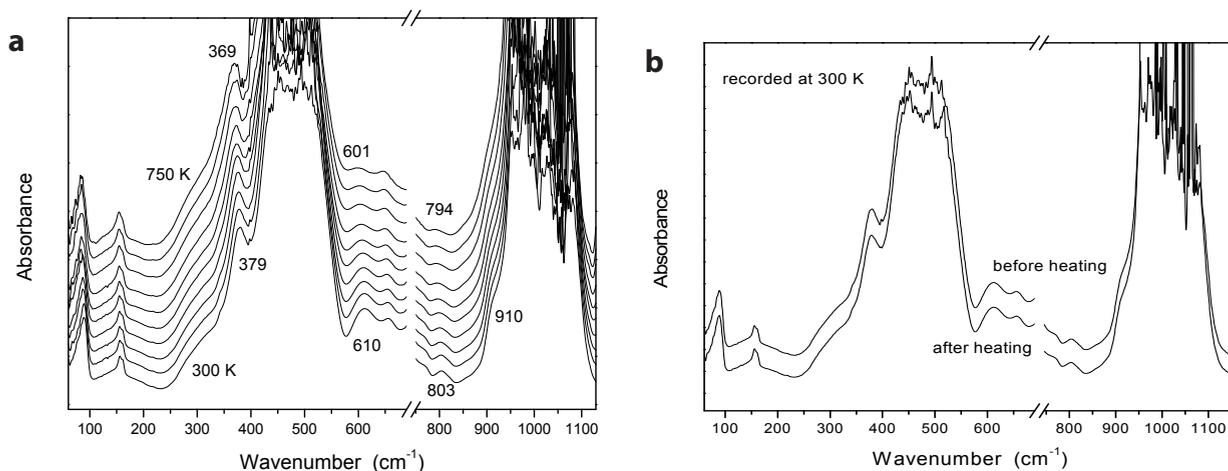

FIGURE 1. (**a**) Temperature evolution (in 300–750 K) of infrared spectra in the FIR and MIR regions (60–1130 cm⁻¹) on heating. The temperature interval is 50 K. The spectra are offset for clarity. (**b**) Comparison of FIR and MIR spectra recorded at 300 K before and after heating to 780 K. The spectral similarities before and after the heating indicate that the temperature of 780 K is not high enough to cause irreversible structural changes (such as dehydroxylation).
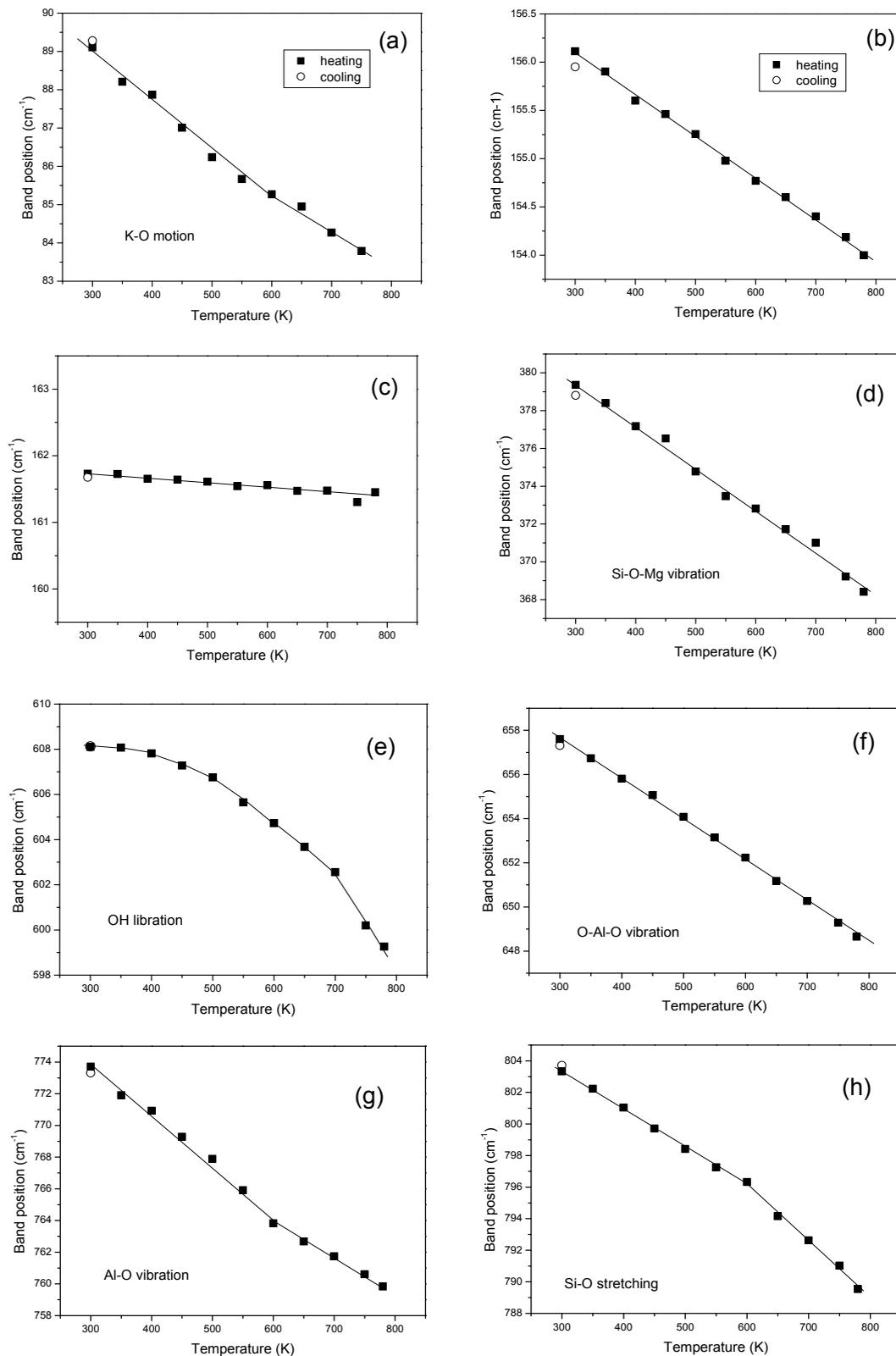
FIGURE 2. Temperature dependencies of band frequency for lattice phonon modes and OH libration. (**a**) K–O motion near 89 cm^{-1}, (**b**) K–O motion near 151 cm^{-1}, (**c**) band near 161 cm^{-1}, (**d**) the Si–O–Mg bending near 379 cm^{-1}, (**e**) OH libration near 610 cm^{-1}, (**f**) Al-O-Al band near 656 cm^{-1}, (**g**) Al-O vibration near 774 cm^{-1}, and (**h**) the Si–O stretching vibration near 803 cm^{-1}.

modes. It is interesting that muscovite also has a band (near 166 cm⁻¹) in the region showing an increase in band height with increasing temperature (Zhang et al. 2010a). The similar thermal behavior and close peak positions for the two bands appear to imply a similarity in terms of their vibrational nature, however, gaining the physics behind this requires further investigations.

IR data in higher-frequency regions show several vibrations with various temperature dependencies on heating (Figs. 2d–2h). There are modes at 379, 610, 656, 774, and 803 cm⁻¹ at 300 K. The 379 cm⁻¹ band is associated with Si–O–Mg vibration and its frequency dropped to 369 cm⁻¹ (with a relative change of 2.6%) at 750 K (Fig. 2d). The 656 cm⁻¹ band is due to a Al–O–Al vibration that exhibited a decrease to 646 cm⁻¹ (1.5%). There are two bands (near 774 and 803 cm⁻¹) in this frequency region that showed temperature behavior different from the others. The 774 cm⁻¹, which is associated with Al-O vibration, exhibited a change in temperature dependence near 600 K (Fig. 2g). On cooling to 300 K, its frequency essentially reversed to the values prior to heating. Although IR measurements on powdered phlogopite samples tended to show a weak band located within the range 822–830 cm⁻¹ (Stubican and Roy 1961; Farmer 1974; and Jenkins 1989), our measurements recorded only a band near 803 cm⁻¹ and this was also previously reported in clear phlogopite flakes by Vedder (1964) and Loh (1973). The vibrational nature of such bands is still not fully understood. Farmer and Russell (1964) have pointed out that for layer silicates band absorption in this region can increase with increasing aluminum content, indicating their connection with aluminum. A band in the above wavenumber region was attributed to an Al–O vibration by Jenkins (1989). In contrast, the normal mode calculations of McKeown et al. (1999) suggest that it is mainly due to M–O stretching. Although M–O stretching may occur, we consider it is likely to be related to Si–O stretching vibration, similar to the case of pyrophyllite. On heating, the 803 cm⁻¹ band shifted down to 794 cm⁻¹ (a change of 1.1%) at 750 K, accompanied by a clear break in the temperature dependence near 600 K (Fig. 2h). With cooling down from 750 K, the frequency of this Si–O stretching band shifted back to its original value before heating, similar to the Al–O band near 774 cm⁻¹. Considering the extremely low Fe content in our sample (Table 1), the break of temperature dependence in these phonon modes near 600 K (Fig. 2g) is not expected to have any connection with Fe oxidation, and the tem-

perature (600 K) is far too low compared to 900 K reported by Tutti et al. (2000) for Fe-related oxidation. It is interesting to note that the modes that showed a break in temperature dependence near 600 K are mainly bands associated with Al–O and Si–O stretching vibrations of TO_4 (T = Al, Si) tetrahedra (Figs. 2e and 2h). Our IR observations are consistent with previously reported structural anomalies around the same temperature region (e.g., Anikin 1971; Takeda and Morosin 1975; Tutti and Lazor 2008). More detailed discussions regarding the physics of our findings near 600 K will be given in a later section.

Thermal behavior of OH-related fundamental absorption bands

Phlogopite has a band near the 610 cm⁻¹ band (Fig. 1), which has also previously been reported by Stubican and Roy (1961) and is related to OH libration or bending (Farmer 1974; Jenkins 1989). Its frequency exhibits a non-linear decrease with increasing temperature (Fig. 2e). In contrast to other K–O and Si–O–Mg vibrations (near 89 and 379 cm⁻¹), the band height of this mode showed a relatively strong variation, decreasing by nearly 90% from 300 to 750 K (Fig. 3b). The observed change is much more significant than the OH libration or Al–OH bending in muscovite, where the linear intensity of the band dropped by about 50% at 750 K (Zhang et al. 2010a). The data in Figure 1b show the spectra recorded at 300 K before and after heating to 750 K, and the similarity of the spectra indicates that 750 K is not high enough to cause significant dehydroxylation and consequent structural modifications. This implies that the observed decrease in the OH libration near 610 cm⁻¹ on heating from 300 to 750 K (in Fig. 1a) is not due to loss of hydrogen or dehydroxylation, but a temperature-induced change in the absorption coefficient.

Absorption bands due to OH stretching were recorded near 3623, 3662, and 3707 cm⁻¹ (Figs. 4a and 4b). Similar OH bands of phlogopite were previously reported in other studies (e.g., Vedder 1964; Mookherjee et al. 2002; Wunder and Nelzer 2002). Based on the analysis of Vedder (1964), the 3707 cm⁻¹ band is due to the Mg_3-OH species. The 3662 cm⁻¹ band is associated with Al^{3+}-incorporation in the octahedral sheets replacing divalent cations (Robert and Kodama 1988), and is described as Mg_2Al-OH species. The 3623 cm⁻¹ is assigned to vacancies in the octahedral sheet (Vedder 1964). Mg_2Fe-OH bands were reported near 3641 cm⁻¹ (Robert and Kodama 1988), however,

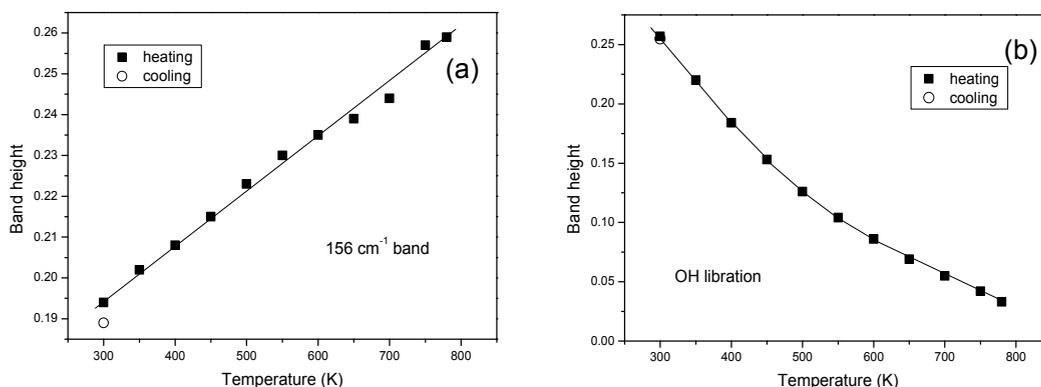**FIGURE 3.** Band height as a function of temperature: (**a**) K–O band near 156 cm⁻¹, and (**b**) OH libration near 610 cm⁻¹.

this absorption was not revealed in our sample probably due to very low Fe concentration of our sample. In phlogopite, the OH group is bonded to three octahedra cations are symmetrically arranged around the OH. The OH dipole directs away from the three M sites toward the interlayer cation and is believed to be perpendicular to the (001) plane (Scordari et al. 2006). Polarized spectroscopy done on the studied phlogopite (sample 277) showed that the O-H vector lies a few (~3) degrees off the [001] direction (the results will be published separately as an independent work).

Heating the sample to 1000 K led to partial dehydroxylation (Figs. 4–8). Our results show that OH groups in phlogopite have different responses to thermal treatments. The frequency and band height of the 3623 cm^{-1} component dropped dramatically starting at 750–800 K, and became undetectable at 900–950 K (Figs. 4b and 6). The band did not return after cooling, indicative
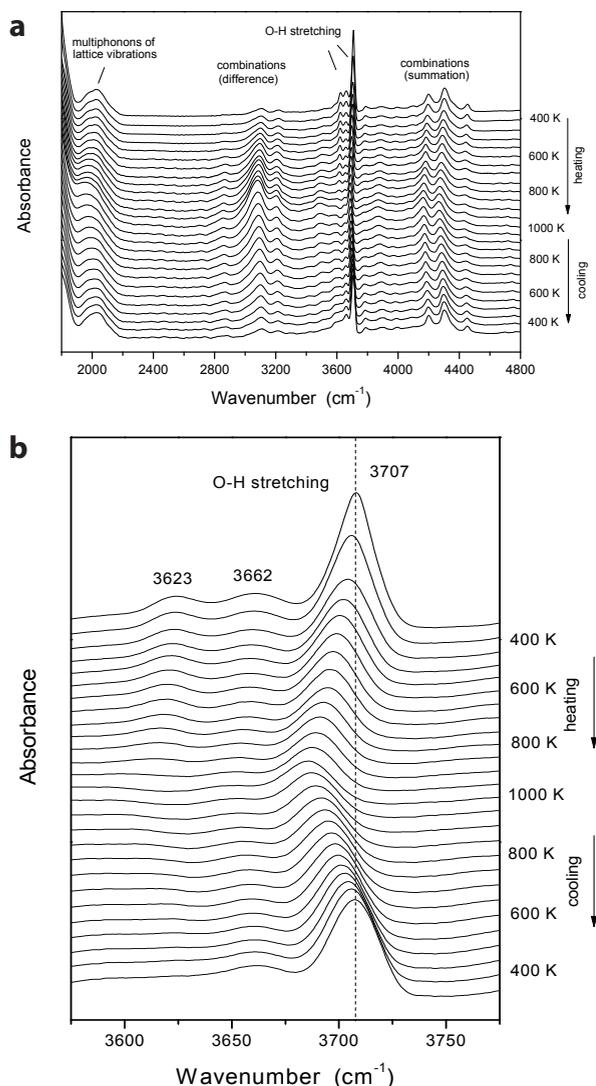

FIGURE 4. Temperature evolution of NIR spectra on heating and cooling (**a**) in the range 1800–4800 cm^{-1} and (**b**) enlarged section of the OH stretching region (in the range 3575–3775 cm^{-1}). The spectra are offset for clarity.

of dehydroxylation (Fig. 5). The 3662 cm^{-1} Mg$_2$Al-OH band, however, exhibited a break in temperature dependence near 650 K in its band height and frequency (Fig. 7), likely indicative of local arrangements related to Al^{3+}-incorporation in the octahedral sheets. The 3707 cm^{-1} band, associated with Mg$_3$–OH environments, showed a dramatic and non-linear decease in band height on heating (Fig. 8b). On cooling, its band frequency recovered in a reversible process. However, its height was lower than the value before heating as a result of partial dehydroxylation. The observation suggests that different OH groups have different thermal stability. OH bands with lower frequencies are commonly considered to have stronger hydrogen bonds and one expects they would be more stable on heating. However, the vacancy-related OH band near 3623 cm^{-1} behaves in an opposite way. This is likely due to thermally induced changes in the environments or the state of the related vacancies. The direct implication of the observation is that heating to 1000 K appears to lead to an alteration of vacancies. The results also indicate a net loss of hydrogen during the heating. Based on the change in integrated band area (integrated absorbance) (Fig. 5), the net loss of hydrogen caused by heating to 1000 K is about 20% (i.e., 0.56 wt% in terms of H$_2$O for sample 277). Our data also show that on heating, the sample became less transparent. The background absorbance at 4600 cm^{-1} increased by 0.51 in absorbance from room temperature to 1000 K. The increase took place in two stages (at 550 and 750 K), which is somehow similar to the case of muscovite (at 650 and 850 K) (Zhang et al. 2010a). The background change is not the thermal emission from the furnace at high temperatures. As explained in an earlier section, our measurements were based on Fourier transform spectroscopy, and the emitted thermal signals from the furnace were not modulated and should not affect our results. The change is likely related to alteration of refractive index, optical conductivity/resistance, surface quality, oxidation states of impurities, and electronic defects. This information might be of interest for those modeling thermal-transmission in crustal rocks.

The experiments did not record additional absorption bands, which could be due to the formation of H$_2$O in the bulk of the sample during dehydroxylation. For dehydroxylation of phyllosilicates, a general picture (see Zhang et al. 2010b for reviews) can be summarized as follows: first, the two most adjacent OH ions condense into a H$_2$O molecule and leave a residual oxygen atom. The water molecule then diffuses though the sample. However, evidence for this model was not from direct observations of dehydroxylation-induced H$_2$O in the *bulk*, but mostly from weight loss and structural analyses of partially dehydroxylated materials and dehydroxylation-induced changes in coordination of some cations (Zhang et al. 2010b). Although the principal species released from sample surfaces during dehydroxylation was identified as H$_2$O (e.g., Kristóf et al. 1985), for some phyllosilicates (e.g., kaolinite, halloysite, and sepiolite), the release of H$_2$O was observed by mass spectrometry to be accompanied by H$_2$ (e.g., Heller-Kallai et al. 1989). In fact, releases of H$_2$O may or may not fully relate to the condensation and diffusion of H$_2$O in bulk, because hydrogen can diffuse in different forms or speciations, e.g., H$_2$O, OH, and H$^+$ and also because the released H$_2$O might simply form near the sample surface. For hydrous minerals such as micas, they contain high concentrations of

hydrogen or hydroxyls (about 3–4 wt% in terms of H_2O). In our present study, although the net loss of H_2O in the phologpite crystal heated to 1000 K would be about 0.56 wt% (which is huge for the sensitivity of IR), we did not record detectable H_2O. The lack of detectable H_2O bands during dehydroxylation suggests that no H_2O is formed during heating because infrared spectroscopy is extremely sensitive and able to detect H_2O at

the the parts per million scale. Therefore, this study suggests that the possible formation of H_2O in the bulk of the partially dehydroxylated sample is the detection limit of the infrared experiments, indicative of the fact that H_2O does not form during the heating experiments and further supportive of the results of Zhang et al. (2010a, 2010b).

Thermal behavior of OH-related absorptions associated with multi phonon processes

Phlogopite has a large number of weak absorption bands in the regions of 2600–3400 and 3800–4500 cm^{-1} (Fig. 4), due to combination bands related to two-phonon processes ($\nu_1 \pm \nu_2$). Because of experimental difficulties in recording multi-phonon bands, they have not often been investigated. They involve the interaction of OH stretching with (1) OH libration or bending, or with (2) vibrations of the framework or lattice phonon modes. According to the nature of these two-phonon processes, the combinations can be further grouped into two types. Those with wavenumbers above the OH stretching bands are associated with summation processes ($\nu_1 + \nu_2$) [i.e., OH stretching + OH bending ($\nu_{OH} + \delta_{Lib}$) or OH stretching + phonons/lattice vibrations ($\nu_{OH} + \nu_{Phonon}$)], whereas those with frequencies lower than the OH stretching bands are due to difference processes ($\nu_1 - \nu_2$) [($\nu_{OH} - \delta_{Lib}$) or ($\nu_{OH} - \nu_{Phonon}$)]. The behavior of this type of OH-related combinations or multi-phonon processes remains poorly investi-
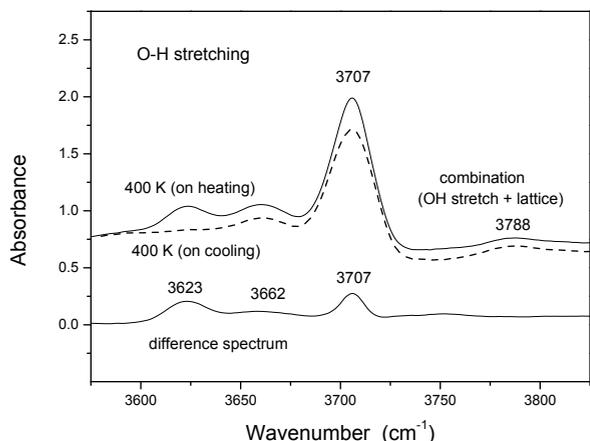
FIGURE 5. Difference spectrum between OH stretching bands recorded at 400 K before and after heating to 1000 K. The difference spectrum reveals the 3623 cm^{-1} band disappeared due to heating, whereas partial dehydroxylation occurred for the main Mg_3-OH species that produced the stretching band near 3707 cm^{-1}.
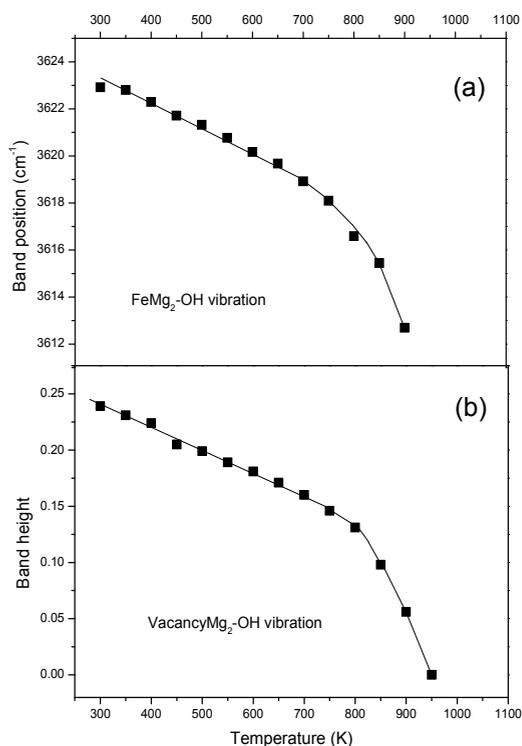
FIGURE 6. (**a**) Band frequency and (**b**) area of the 3623 cm^{-1} OH stretching vibration as a function of temperature.
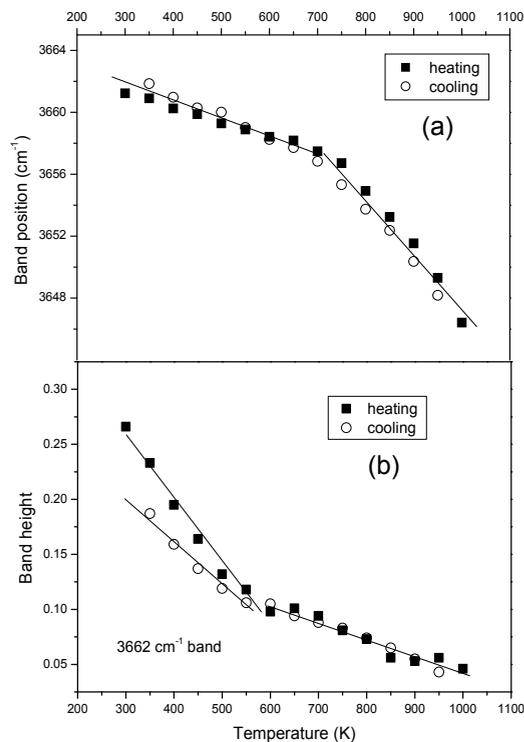
FIGURE 7. (**a**) Band frequency and (**b**) band area of the 3656 cm^{-1} OH stretching vibration as a function of temperature. In **b**, a discontinuity in the temperature derivative of the band height occurred near 600 K on cooling, but its slope was not fully recovered. This is due to a partial loss of OH that causes the bands to have smaller band height on cooling.

gated and understood, and little work has been done to explore their thermal behavior (Zhang et al. 2007 for review). As shown in Figures 4a and 9, changing temperature does not seem to cause significant variations in the combination bands associated with summation processes in the range 3800–4500 cm⁻¹. However, the difference bands in the range 2600–3400 cm⁻¹ clearly become more and more intense on heating (Fig. 9). Their absorption change with temperature may not only be due to the concentration of hydrogen, but also to phonon interactions and change in absorption coefficients (Zhang et al. 2007), and more details will be addressed in the following section. One important result from the present study is that different types of OH absorption bands (i.e., libration, stretching, and combination due to summation and difference processes) commonly show different thermal behavior. Figure 10 summarizes their detailed change in band height (with respect to that at 300 K) as a function of temperature. The data also indicate that when IR absorption or intensities of different types of OH bands recorded at high temperatures are used to estimate hydrogen concentration, the type of band and its temperature dependence need to be considered.

DISCUSSION

The key issue of interpreting IR absorption data and the band behavior depends on a good understanding of the changes of spectra at high temperatures and possible causes. So far, most in situ IR studies on silicates seem to indicate: (1) individual fundamental bands have different thermal behavior or different temperature dependencies; (2) on heating, band height and integrated intensity (band area) of fundamentals decrease in

most cases (this is common for solids with positive thermal expansion coefficients, but some modes may behavior differently, e.g., the band near 156 cm⁻¹ in Fig. 3a); (3) most OH stretching bands show a general decrease in frequency on heating (although some exceptions exist, e.g., OH in quartz reported by Yamagishi et al. 1997); and (4) OH bands become broad on heating. Our data show that with increasing temperature, OH modes in phlogopite exhibit the most significant changes, indicating that their structural variations and phonon anomalies on heating are mainly associated or even driven by changes of OH bonds. This might be related to the weakening of the K–O bonds or an increase in the bond lengths, as shown by the
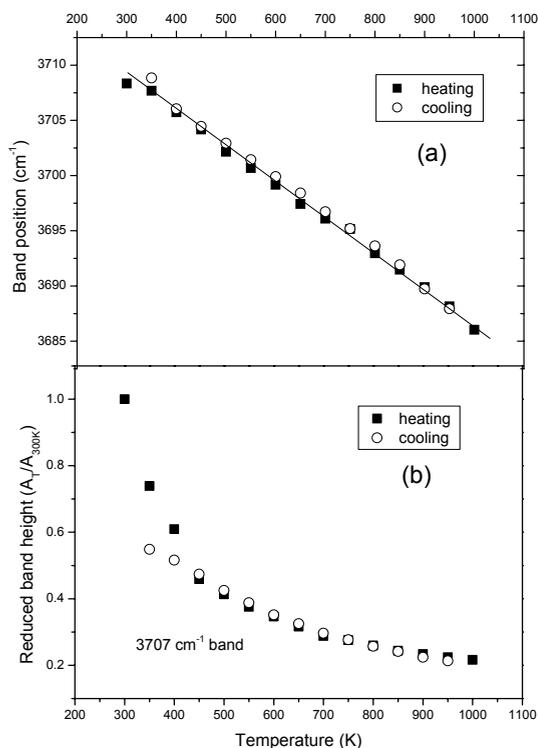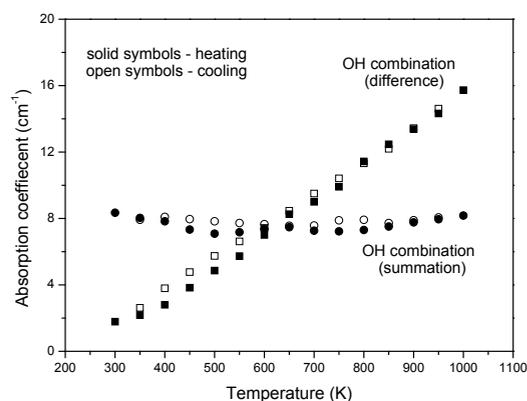
FIGURE 9. Absorption coefficients (calculated by absorbance over thickness in centimeters) for the combination band (summation) near 3402 cm⁻¹ and combination (difference) near 3102 cm⁻¹. The solid symbols indicate data from heating whereas the open symbols are data on cooling. The results indicate that different types of combination bands of OH can have very different changes in band heights on heating.
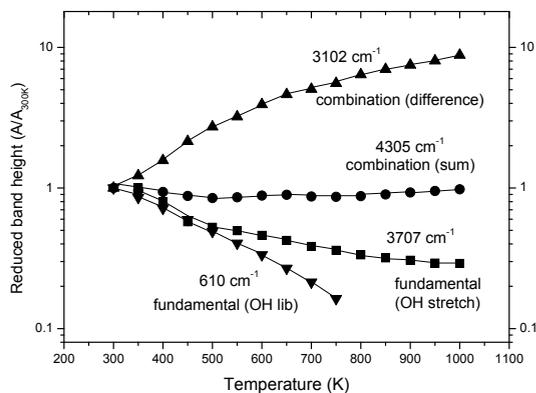
FIGURE 8. (**a**) Band frequency and (**b**) area of the 3707 cm⁻¹ OH stretching vibration as a function of temperature.

FIGURE 10. Temperature dependencies of band heights (as compared with that 300 K) for fundamental bands (OH libration near 610 cm⁻¹ and OH stretching near 3707 cm⁻¹) and combination bands (summation near 4302 cm⁻¹ and difference near 3102 cm⁻¹) on heating. Although fundamental bands of OH species tend to show a decrease in band height with increasing temperature, combination bands may behave very differently and even give opposite variations. The dispersions shown by different types of vibrations are very significant and different in order of magnitude, as the y axis is in log10 rather than a linear scale.

K–O modes near 89 cm^{-1} (Fig. 2a), because in phlogopite, O-H dipole is perpendicular to the (001) plane resulting maximum K$^+$–H$^+$ repulsion and the proton position may affect the K-O bonding strength (Guggenheim et al. 1987). This observation is consistent with the single-crystal X-ray diffraction work of Russell and Guggenheim (1999), which showed that heating a natural phlogopite-1M crystal (near-OH end-member) to 873 K resulted in an increase in the K–O bond distances.

Several factors may contribute to the absorption or band height variation, and experimental data are commonly associated with their combined effects. The first is a purely temperature-induced change in absorption coefficients of OH species. This issue was systematically examined and discussed by Zhang et al. (2007), who pointed out that, at high temperatures, the use of a temperature-independent Beer-Lambert Law needs to be reconsidered. Several works have further addressed the effect of temperature on the change in OH bands (e.g., Balan et al. 2010; Yang et al. 2011) and CO$_2$ absorption (Radica et al. 2016). The change of absorption coefficient is expected to be responsible mainly for the variation in the relatively low-temperature region where other factors (e.g., delocalization of hydrogen and conversion between OH and H$_2$O, etc.) do not take place or have little impact. The change related to pure temperature dependence of the coefficient is commonly reversible on cooling. In the case of phlogopite, this is partially responsible for the variation of OH absorption below 800 K (Fig. 6b), although additional factors may also be involved. Second, dehydroxylation may play an important role in the decrease of absorption of OH species. In this case, the band linear intensity change is due to delocalization of hydrogen from its structural sites, which is caused purely by weakening or breaking of bonds, and is also associated with hydrogen diffusing out of the material. Delocalization of hydrogen was mostly discussed in some early studies, and it was considered as the main cause for the decrease of OH band height at high temperatures. However, it appears that the issue was overstated, because in some cases, the delocalization was even considered to take place at temperatures as low as just above room temperature (e.g., Shishelova et al. 1974), which is highly unlikely for phlogopite. At what temperature hydrogen delocalization starts to take place and how hydrogen leaves from its original site (as well as how hydrogen diffuses in solids like layer silicates) remains unclear or under investigation (see Zhang et al. 2010b for details).

There are several ways in which hydrogen can be delocalized. A common consideration is due to thermal-expansion-induced increase in the bond length and weakening of the bonding to an extent that the bond is broken. Changes in oxidation states of cations (such as oxidation of Fe^{2+} to Fe^{3+}) may, in principle, lead to variation of local charge balance, resulting in release of hydrogen from its structural site, however, this is not a big issue for our sample that contains limited Fe. As a result, the related absorption may be affected. The dramatic drop of absorption of the 3623 cm^{-1} band between 800 and 950 K is indicative of delocalization of hydrogen from its site and the loss of OH from the crystal. The other important fact that may affect the measured absorption of OH is the change of the orientation of the OH dipole during heating. For the case

of anisotropic crystals, OH band intensities commonly exhibit strong orientational dependencies. On heating, the OH dipole may alter its orientation to some degree from perpendicular to the (001) plane. Thermally induced changes of OH dipole orientation may result in a change in the recorded absorption projected on the (001) plane. Changes in orientations of OH dipoles were reported in 2M_1-phengite (a dioctahedral mica) on heating (Mookherjee et al. 2001). Neutron diffraction data reported by Chon et al. (2006) showed that the angle between the OH vector and the (001) plane in phlogopite started to decease (i.e., OH dipole turned away from the [001] direction) in a nonlinear manner from about 600–700 K. As a result of the change in OH dipole orientation, its project on the (001) plane may change and this affects the measured absorption. This may also account for the abnormal temperature dependence of the OH libration and stretching bands (Figs. 2e, 3b, 7, and 8b) in the same temperature range. The alteration of the OH orientations is also understandable, because it would be difficult to imagine they would remain unchanged while there are local structural variations related to TO$_4$ tetrahedra and the shape of MO$_6$ octahedra. These factors have different impact on the linear band intensity of OH bands. The absorption variations caused by a purely temperature-induced change in absorption coefficients and orientations of OH dipoles are commonly reversible on heating and cooling, while the intensity change caused by oxidation and dehydroxylation is irreversible on cooling (although this is not a major issue for our case). Such differences can be helpful for identifying the cause of the changes. Finally, thermal healing of defective or disordered lattice or changes in crystallinity may lead to an increase in absorption (e.g., heated metamict zircon as reported by Zhang et al. 2010c), but this may not be the case for our samples.

Our IR data on OH fundamental bands (libration and stretching) (Figs. 3b, 6b, 7b, and 8b) show a decrease of the band intensities even below 600 K. This is mainly due to temperature-induced changes in absorption coefficients. However, the non-linear change in the interval 600–700 K (Figs. 2e, 7b, and 8b) is not caused by pure changes in absorption coefficients, but instead is more likely due to the orientation of OH dipoles, which turns away from the (001) direction. As a result, the absorption projected on the sheet layer increases, and the total effect is that the band height shows a weaker decrease in relation to the value below 600 K. Our data are basically consistent with the observations by the neutron diffraction work of Chon et al. (2006), which showed an alteration of OH orientation of phlogopite on heating. The results also show that the environments around the proton (H$^+$) as well as OH bonds are more affected by heating as compared to other phonons.

Our IR data do not support any symmetry-breaking phase transition in the temperature interval 600–700 K. From the temperature dependencies of lattice phonons (in the range 90–1500 cm^{-1}) (Fig. 2), the phonon bands are all active at high temperatures and no additional modes were formed. The original monoclinic symmetry remains up to 750 K. Although the K–O band at 89 cm^{-1} showed a relatively large frequency drop (as high as 6%), the phonon modes all exhibited gradual changes (Fig. 2). Our data do not support a first-order phase transition. Among the measured phonon modes of phlogopite,

Al–O and Si–O stretching vibrations showed a discontinuity in the temperature derivative of the wavenumber near 600 K (Figs. 2g and 2h), together with a nonlinear change of OH bands (Figs. 2e, 3b, and 8b). This appears to suggest that in addition to a distortion of MO_6 octahedra, TO_4 (T = Si, Al) tetrahedra and OH modes are also responsible for, or involved in, the previously reported local structural change (e.g., Chon et al. 2006; Tutti and Lazor 2008). Considering the change in OH bonds and the lattice vibrations of the framework, we believe that there is a connection between structural change or so-called phase transition near 600 K and the change of OH dipole orientation, which both occurred near 600–700 K. What is more, it is the OH-related bands that showed significant abnormality (Fig. 2), in contrast to the behavior of lattice phonons for the framework. The structural variations in the interval 600–700 K could be driven or triggered by the alteration in OH environments.

IMPLICATIONS

Significant amounts of water on the Earth are believed to be stored in minerals and rocks underneath the crust's surface. The behavior and concentrations of these hydrogen-related species at high temperatures as well as the dehydroxylation mechanisms are of importance for understanding of their state and how hydrogen is released from minerals at high temperatures. IR spectroscopy has been a key tool for analysis of these hydrogen-related species, but understanding of how IR absorption of OH species changes at high temperatures and the physics behind the change are essential for understanding the behavior of OH-bearing minerals with depth in the Earth. The present study shows that phonon modes and different types of OH bands have complex responses to heating. Multi-phonon bands of OH species may have very different thermal behavior. The combination modes and multi-phonon modes of OH species that are due to difference processes exhibit an increase in absorption on heating that is in contrast to the modes associated with summation processes. More interestingly, for phlogopite, heating may lead to a change of OH dipole orientation. The results from the present IR study have shown that on heating phlogopite to high temperatures, the 89 cm^{-1} mode of O–K motion exhibited the largest relative decrease in frequency (6% in 300–750 K), somewhat like the behavior of muscovite. All the recorded phonon modes of phlogopite remain consistent with monoclinic symmetry at 780 K. Our analysis also indicates that the orientation of its OH dipoles start to tilt away from the (001) direction near 600 K, where a break of temperature dependencies for the band heights of the 3662 and 3707 cm^{-1} OH bands was recorded. The orientation change is considered to be the cause of the previously reported structural modifications that show phase-transition-like behavior in the same temperature region. Our data do not support a first-order phase transition near 600 K. The results reveal the local structural changes on heating to the dehydroxylation and the findings may be useful for interpretations of IR data on OH species recorded at high temperatures. Our experimental results also show that phologpite becomes less transparent with increasing temperature implying a variation of radiative properties and ability to transmit heat. This finding could be of interest for studying thermal-transmission in crustal rocks.

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