LETTER

Raman and NMR spectroscopic characterization of high-pressure K-cymrite (KAlSi$_3$O$_8$·H$_2$O) and its anhydrous form (kokchetavite)

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To facilitate identification of high-pressure K-cymrite (KAlSi$_3$O$_8$·H$_2$O) phase and its anhydrous form (kokchetavite) in natural rocks, we have synthesized both phases and have characterized them by micro-Raman and NMR spectroscopy. K-cymrite was synthesized at 5 GPa and 800 °C. Kokchetavite was obtained by dehydrating K-cymrite at ambient pressure and 550 °C. The $^1$H MAS and $^1$H–$^29$Si CP MAS NMR spectra of K-cymrite are consistent with the reported crystal structure that contains H$_2$O molecules and has a disordered Si–Al distribution. The Raman spectra obtained under ambient conditions for K-cymrite (and kokchetavite) contain major peaks at 114.0 (109.1), 380.2 (390.0) and 832.5 (835.8) cm$^{-1}$. For K-cymrite, OH stretching vibration is also observed at 3541 cm$^{-1}$ with a shoulder at 3623 cm$^{-1}$. The Raman spectrum for kokchetavite is consistent with that previously reported for a natural sample found as inclusions in clinopyroxenes and garnets in a garnet-pyroxene rock. However, the data for K-cymrite are inconsistent with the Raman features of a previously reported “relict K-cymrite in K-feldspar” from an eclogite. Pressure– and temperature–dependencies of the Raman shifts for the strongest peak of both phases are also reported.

Keywords: K-cymrite, Kokchetavite, Raman, NMR, High pressure, KAlSi$_3$O$_8$·H$_2$O

INTRODUCTION

K-cymrite (KAlSi$_3$O$_8$·H$_2$O) was first discovered experimentally at >2 GPa by Seki and Kennedy (1964). It is isostructural with natural cymrite (BaAl$_2$Si$_2$O$_8$·H$_2$O). Both phases have a unique crystal structure consisting of double-layers of Si(Al)O$_4$ tetrahedra that are linked together by large cations (K or Ba), with water molecules occupying cages within the double-layers (Fasshauer et al., 1997). When heated at ambient pressure, K-cymrite dehydrates to a metastable anhydrous hexagonal KAlSi$_3$O$_8$ phase while retaining its original structure (Thompson et al., 1998). The latter is isostructural with hexacelsian (BaAl$_2$Si$_2$O$_8$) (Takéuchi, 1958), although with a different space group.

K-cymrite could be a potential reservoir of water and large alkali ions in ultrahigh-pressure (UHP) rocks. Until recently, no natural K-cymrite had been reported, although K-feldspar pseudomorph after K-cymrite had been suggested for natural UHP metamorphic rocks (e.g., Harlow and Davis, 2004). Hwang et al. (2004) first reported a natural occurrence of the anhydrous form of K-cymrite (named kokchetavite) as micrometer-sized inclusions in clinopyroxenes and garnet in a garnet-pyroxene rock from the Kokchetav UHP terrane. Kokchetavite was identified by TEM, and its Raman spectrum was also reported. More recently, Zhang et al. (2009) reported K-feldspar after K-cymrite from a Dulan eclogite in the Qaidam UHP terrane, western China. They observed a Raman peak at 390–395 cm$^{-1}$ in addition to peaks characteristic of K-feldspar, and interpreted the former as resulting from relict K-cymrite that survived the transformation to K-feldspar. However, the peak assignment relied on
comparison with the corresponding Raman peak for cymrite (396 cm$^{-1}$) (Graham et al., 1992) and kokchetavite (390–391 cm$^{-1}$), because no Raman data for K-cymrite were available at the time. This renders the assignment unreliable.

Micro–Raman spectroscopy is increasingly recognized as a useful tool for identifying trace amounts of high-pressure phases in inclusions of UHP rocks such as coesite and diamond. In order to unambiguously identify K-cymrite and its anhydrous form with natural UHP rocks by means of micro–Raman spectroscopy, their Raman spectroscopic features need first to be established. In this study, we have synthesized K-cymrite and kokchetavite, and have characterized them by Raman spectroscopy both under ambient conditions and as a function of pressure and temperature. In addition, $^1$H and $^{29}$Si nuclear magnetic resonance (NMR) spectroscopy was also applied to K-cymrite to provide complementary local structure information.

**EXPERIMENTAL**

Two K-cymrite samples were synthesized as follows. A hydrous KAlSi$_3$O$_8$ glass with 2.3 wt% water as described in Xue and Kanzaki (2006) was used as starting material. The glass powder was loaded along with de-ionized water (to give a nominal total water content of 6.1 wt% as required for K-cymrite) and sealed into a platinum tube with 3.0-mm outer diameter. K-cymrite was then synthesized at 5 GPa and 800 °C for 2 hrs using a Kawai-type multi-anvil press. The procedure for the high-pressure and high-temperature experiments is identical to that reported in Kanzaki et al. (2011). The anhydrous form (kokchetavite) was produced at ambient pressure by heating K-cymrite at 550 °C for 1 hr. This temperature was determined on the basis of results from in-situ heating experiment described below.

The recovered samples were first examined with an optical microscope and a micro-focused X-ray diffractometer (RINT Rapid II, Rigaku Co.) for phase identification. The samples were then coarsely crushed for NMR measurements, and finally further ground to a fine powder for closer inspection with a powder X-ray diffractometer (SmartLab, Rigaku Co.).

$^1$H and $^{29}$Si NMR spectra have been obtained for both (natural isotopic abundance) K-cymrite samples using a Varian Unity–Inova 400 MHz spectrometer and a Varian 2.5 mm T3 MAS probe, at a resonance frequency of 400.4 and 79.5 MHz, respectively. $^1$H and $^{29}$Si chemical shifts are referenced externally to tetramethylsilane (TMS).

$^1$H magic-angle spinning (MAS) NMR spectra were obtained with the DEPTH sequence that consists of three back-to-back pulses ($\pi/2$–$\pi$–$\pi$) with a phase cycle of 16 (Cory and Ritchey, 1988) to suppress the probe background. A small residual probe background signal (as measured on the empty rotor) has been subtracted from the reported spectra. The $^1$H–$^{29}$Si cross-polarization (CP) MAS NMR spectra were acquired for both K-cymrite samples with a ramped power for the $^{29}$Si channel (with a RF field range of about 6 kHz), a recycle delay of 12 s or 15 s, and a range of contact times from 4 to 20 ms. $^{29}$Si MAS NMR spectra were acquired with a $\pi/6$ (1.1 μs) pulse and recycle delay times of 200 s and 600 s (with about 460 and 1600 transients averaged respectively) for one of the K-cymrite sample. No proton decoupling was applied during acquisition for both types of $^{29}$Si NMR experiments.

Unpolarized Raman spectra were acquired using a home-built micro–Raman spectrometer with an Ar$^+$ ion laser (wavelength 488 nm and 60 mW) in backscattering geometry. The laser beam was focused onto the sample with a 50x objective lens (NA 0.55), resulting in about 1-μm beam size. The light scattered from laser spot on the sample was focused onto a pinhole (diameter of 200 μm), before entering a polychromator with a focal length of 500 mm and a grating of 1200 gr/mm, and detected by a liquid nitrogen cooled CCD detector. Rayleigh scattering was rejected using a RazorEdge long–wave pass filter (Semrock Inc.). A Voigt function was used to fit the Raman peak using the peak fitting program fityk (Wojdyr, 2010), resulting in a precision of 0.1 cm$^{-1}$ for the Raman shifts reported below.

For in-situ high-temperature Raman measurement, a wire-heating cell described by Mysen and Frantz (1992) was used, with the heating system and temperature calibration procedures based on those of Richet et al. (1993). A Pt87%Rh13% wire of 1.0 mm in diameter was used as a heater. The central part of the wire was flattened to 0.5 mm thickness, and a 1 mm diameter, 0.25 mm deep blind hole was made. The sample was placed in the center of this hole. Temperature was calibrated using the relationship of melting points of NH$_4$NO$_3$, NaNO$_3$, CsNO$_3$, LiCl and NaCl versus heating currents (or power) of the DC power supply necessary to melt these compounds. The melting point of each compound was determined by visual observation under the microscope of the micro–Raman system. Precision of the estimated temperature is better than 20 °C. For in-situ high-temperature Raman measurements, temperature was increased in steps of about 50 °C in a few minutes, and then Raman spectrum was measured for 1 min at the end of each step. Due to thermal
expansion of the heater wire, beam position and focus at the sample were adjusted at each temperature.

For in-situ high-pressure Raman measurement, a Merrill-Bassett type diamond anvil cell (DAC) was used. The cullet size of the low fluorescence diamonds was 600 μm. Gaskets made of SUS301H steel were pre-indent to about 100-μm thickness. Then a 300-μm diameter hole was made using a home-build electric discharge machine. Small fragments of K-cymrte or kokchetavite were placed along with ruby chips in the gasket hole. The pressure medium was a 4:1 methanol-ethanol mixture. The exposure time was 1 min, and the spectrum was stacked up to 5 times. Pressure was determined by the ruby fluorescence method (Piermarini et al., 1975) using the same spectrometer. Precision of the estimated pressure is 0.3 GPa.

RESULTS AND DISCUSSION

The two recovered samples synthesized at 5 GPa and 800 °C both consist of K-cymrte plus sanidine, as identified by powder X-ray diffraction and Raman spectroscopy. The occurrence of sanidine suggests that some of the added water may have been lost during synthesis.

The 1H MAS NMR spectra for both samples are similar. Typical 1H MAS NMR spectra acquired at spinning rates of 5 kHz and 25 kHz with a recycle delay of 60 s are shown in Figure 1. The spectra contain a single peak near 3.0 ppm with a full-width-at-half-maximum (FWHM) of 1.2 ppm (25 kHz MAS) ~ 1.9 ppm (5 kHz MAS) in the central band region, and a set of spinning sidebands spanning a frequency range of ~ 100 kHz. The wide frequency range for spinning sidebands is as expected for relatively rigid H2O molecules. The 1H chemical shift of 3.0 ppm indicates relatively weak hydrogen-bonding [with an O-H···O distance around 3.0 Å according to the correlation of Xue and Kanzaki (2009)], consistent with the reported crystal structure for K-cymrte (Fasshauer et al., 1997).

The 1H-29Si CP MAS NMR spectra acquired with contact times of 4 to 20 ms at a spinning rate of 20 kHz for both samples are similar. All contain six peaks at ~108.7, ~104.4, ~102.4, ~100.2, ~98.1, and ~94.0 ppm with FWHM of 1.15, 1.23, 1.93, 1.30, 1.66 and 1.71 ppm, respectively (see Fig. 2 for a spectrum with a contact time of 20 ms). The absolute intensities for all the peaks increase continuously with contact time up to 20 ms, whereas their relative intensities show only minor changes. Additional two-dimensional 29Si J-coupling mediated NMR experiments on a separate 29Si-enriched K-cymrte sample has confirmed that all six peaks belong to the same phase (K-cymrte) and may be attributed to Si of nSi and (4-n)Al next-nearest neighbors, with n=4,3,2,2,1 toward less negative chemical shifts (X. Xue and M. Kanzaki, unpublished data, 2012). Because there is only a single crystallographically unique tetrahedral site in K-cymrte (Fasshauer et al., 1997), the presence of multiple Si local structures with different Si-Al

Figure 1. 1H MAS NMR spectra of a K-cymrte sample acquired at spinning rates of 5 kHz (top) and 25 kHz (bottom). Also shown in the inset is the enlarged central band region of the latter. No line broadening has been applied.

Figure 2. 29Si MAS NMR spectrum acquired with a π/6 pulse and a recycle delay time of 200 s (top), and 1H-29Si CP MAS NMR spectrum acquired with a contact time of 20 ms (bottom), both at a spinning rate of 20 kHz for a K-cymrte sample. A 40-Hz Gaussian line broadening has been applied to both. Also labelled are the numbers of next nearest neighbor Si for peaks of K-cymrte.
next-nearest neighbors indicates disordered Si–Al distribution. The presence of two peaks each for \( n = 3 \) and 2, despite of a single tetrahedral site, is unique, and has been confirmed to be attributable to different permutations of Si/Al in the four neighboring tetrahedral (T) sites that have two distinct T–O–T angles (139° within each layer, 180° across the double-layer; Fasshauer et al., 1997)(X. Xue and M. Kanzaki, unpublished data, 2012).

The \(^{29}\)Si MAS NMR spectra acquired with a π/6 pulse and recycle delay times of 200 s and 600 s are similar in relative intensities (see Fig. 2 for the former). In addition to the six peaks of K-cymrite described above, there is also a broad component underneath. The latter may be attributed to the coexisting anhydrous sanidine phase, which has been reported to give broad, poorly resolved peaks with maxima near −97 ppm and −101 ppm (Kirkpatrick et al., 1985).

The Raman spectrum of the K-cymrite sample is shown in Figure 3 (top). Except for a few weak peaks that are attributable to coexisting sanidine (as marked in Fig. 3), the spectrum resembles that of cymrite (BaAl\(_2\)Si\(_2\)O\(_8\)·H\(_2\)O), and may be attributed to vibrations of K-cymrite. There are two intense peaks of K-cymrite at 114.0 cm\(^{-1}\) and 380.2 cm\(^{-1}\), which may be correlated with the two prominent Raman peaks of cymrite at 104 cm\(^{-1}\) and 396 cm\(^{-1}\) (Graham et al., 1992). A peak at 832.5 cm\(^{-1}\) with intermediate intensity is also assigned to K-cymrite. The corresponding peak of cymrite appears at 800 cm\(^{-1}\) (Graham et al., 1992). In addition, three weak and broad peaks at 1003, 1060 and 1107 cm\(^{-1}\) are also present. A weak peak at around 1605 cm\(^{-1}\), attributable to H–O–H bending mode is also visible, confirming the presence of molecular H\(_2\)O (Fig. 3, left inset). Within the OH stretching region, an intense peak at 3541 cm\(^{-1}\) with a shoulder at 3623 cm\(^{-1}\) is observed (Fig. 3, right inset). These are consistent with the observed OH stretching modes of K-cymrite at 3530 cm\(^{-1}\) and 3620 cm\(^{-1}\) by infrared spectroscopy (Thompson et al., 1998). The corresponding Raman peaks for cymrite appear at 3500 cm\(^{-1}\) and 3557 cm\(^{-1}\) (Graham et al., 1992). These two peaks may be attributed to the symmetric and antisymmetric stretching vibrations of molecular H\(_2\)O, respectively.

The Raman spectrum of dehydrated K-cymrite (kokchetavite) is also shown in Figure 3 (bottom). The spectrum in general resembles that of K-cymrite with subtle but significant differences. The two strongest peaks are shifted from 114.0 cm\(^{-1}\) to 109.1 cm\(^{-1}\) and from 380.2 cm\(^{-1}\) to 390.0 cm\(^{-1}\) by dehydration. The next most intense peak appears at 835.8 cm\(^{-1}\) and is narrower than the corresponding peak of K-cymrite. No detectable OH stretching mode was observed (not shown).

In-situ high-temperature Raman measurements revealed that the intensity of the OH stretching peak decreases gradually above 300 °C, and completely disappears at 500 °C (not shown). The Raman shift of the strongest peak (~ 380 cm\(^{-1}\)) of K-cymrite from high-temperature measurement is shown in Figure 4. The peak shifts to higher wave number with increasing temperature up to 500 °C. The larger change from 300 °C to 500 °C can be attributed to dehydration. The dehydration temperature range observed by the Raman modes is consistent with the thermogravimetric analyses of Thompson et al. (1998). The curve in Figure 4 likely reflects kinetic behavior of the dehydration process, and does not represent the equilibrium state. A time dependent study is necessary to further constrain the kinetics of dehydration. Kokcheta-
vite shows an opposite temperature dependency as is apparent from the curve above 500 °C.

The pressure dependencies of the strongest peak for K-cymrite and kokchetavite are shown in Figure 5. Both of them exhibit similar positive pressure dependency. Above 10 GPa, the shift levels off for K-cymrite (Fig. 5), possibly due to solidification of the pressure medium. A linear regression gives a slope of 5.1(1) cm⁻¹/GPa for K-cymrite (excluding the points above 10 GPa), and 5.3(1) cm⁻¹/GPa for kokchetavite.

Peak positions of the corresponding Raman modes are clearly shifted between K-cymrite and kokchetavite (Figs. 3 and 4). The shift is the largest (about 10 cm⁻¹) for the strongest peak near 380 cm⁻¹, rendering it a useful parameter for distinguishing the two phases. Hwang et al. (2004) observed two Raman peaks at 108.3 cm⁻¹ and 390.0 cm⁻¹ and no detectable OH stretching vibration peak for a natural kokchetavite. These are consistent with our observed Raman peaks at 109.1 cm⁻¹ and 390.0 cm⁻¹ for synthetic kokchetavite, confirming their assignment.

Zhang et al. (2009) suggested possible residual K-cymrite in K-feldspar based on the occurrence of peaks at 390-396 cm⁻¹ and 669 cm⁻¹. However, no peaks near 669 cm⁻¹ were observed in our study of K-cymrite or kokchetavite, and thus this peak is likely due to other coexisting phase. The peak at 390-395 cm⁻¹ is closer to that of kokchetavite (390.0 cm⁻¹) than K-cymrite (380.2 cm⁻¹) at ambient condition from the present study. Therefore, the K-cymrite speculated by Zhang et al. (2009) could well be kokchetavite instead. Nevertheless, the existence of the latter could still suggest that K-cymrite once existed in the eclogite before uplift. An alternative possibility is that the peak could be due to K-cymrite inclusion that is still under residual pressure. This possibility may be assessed using our observed pressure dependency on the Raman shift of K-cymrite. From Figure 5, it is clear that about 2-3 GPa of residual pressure would be necessary in order to explain the observed Raman shift at 390-395 cm⁻¹ as K-cymrite. Zhang et al. (2009) neither reported Raman spectra in the OH stretching region nor provided evidence by other techniques to support their identification of K-cymrite. Raman measurement in the OH stretching region should clearly resolve this issue.

Our study was performed on the end-member KAISi₄O₆·H₂O and KAISi₃O₉ compositions, whereas natural K-cymrite and kokchetavite samples contain a small albite component (Hwang et al., 2004; Zhang et al., 2009), which could potentially affect the Raman shifts. Nevertheless, Raman peaks at higher wave numbers (>300 cm⁻¹) are due to vibrational modes related to the (Si,Al)O₄ double-layers, rather than the potassium ion layer where sodium ions are incorporated. Therefore, Raman shifts of all peaks except for that at about 110 cm⁻¹ are likely largely unaffected by solid solution of a small albite component. Si-Al ordering is another factor that could potentially affect the Raman shifts. Our ²⁹Si NMR study revealed that the Si-Al distribution in the tetrahedral sites of K-cymrite is disordered, consistent with the crystal structural study of a synthetic sample by Fasshauer et al. (1997). Although the states of Si-Al ordering for natural samples are unknown, close agreement of the peak positions for the two most intense Raman peaks between natural and synthetic kokchetavite suggests that this effect is also likely insignificant.

Finally, our study demonstrated that in order to identify K-cymrite and kokchetavite from natural UHP rocks using micro-Raman spectroscopy, it is necessary to observe the three main Raman peaks at around 109-114, 380-390 and 832-836 cm⁻¹. To distinguish between the two phases, precise measurement of the Raman shift of the strongest peak near 380-390 cm⁻¹ and observation of the OH stretching region are essential.

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