Temperature-induced phase transition of AlPO_4 -moganite studied by in-situ Raman spectroscopy

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The moganite-form of AlPO_4 has recently been discovered from our high-pressure study. Similar to SiO_2 -moganite, a temperature-induced displacive phase transition is expected. In order to confirm the phase transition, high-temperature in-situ Raman spectroscopy study was conducted at ambient pressure up to 600 °C. One of the low-frequency Raman modes (74 cm^{-1} at room temperature) significantly softened with temperature, and disappeared at 420 °C. Its frequency versus temperature relation can be well fitted with an order parameter equation, and the mode is interpreted as a soft mode with a critical exponent of 0.232(8). According to this fitting, the transition temperature is determined as 415 °C. Some hard modes also revealed slight softening or hardening with temperature up to ~ 420 °C and reached nearly constant frequency at higher temperature. Vibrational mode calculations by the first-principles density functional theory (DFT) method showed that the soft mode corresponds to tetrahedral rotations, representing the pathway of the transformation.

Keywords: AlPO_4 , Moganite, Raman spectroscopy, Phase transition, Soft mode

INTRODUCTION

Recently, a moganite-type AlPO_4 phase was discovered from high-pressure experiments, and its crystal structure was reported (Kanzaki and Xue, 2012). Moganite (SiO_2) is a metastable phase (Heaney, 1994), whereas AlPO_4 -moganite is one of the stable high-pressure polymorphs of AlPO_4 . The structure of moganite is closely related to that of quartz and can be regarded as a periodic twinning according to the Brazil law on a unit-cell dimensional scale (Miehe and Graetsch, 1992). Since temperature-induced displacive phase transitions are common for the low-pressure phases of SiO_2 (cristobalite, tridymite, and quartz) and AlPO_4 , a similar phase transition is expected for moganite-like phases as well. Using natural SiO_2 -moganite, Heaney and Post (2001) observed an α - β ($I2/a$ to $Imab$) phase transition at about 570 K using synchrotron X-ray powder diffraction. Heaney et al. (2007) further studied this transition using hard mode Raman spectroscopy, and confirmed the phase transition. A soft mode is expected for this transition, but it has not been observed.

Good-quality SiO_2 -moganite samples are difficult to obtain, and natural samples are often intimate mixtures

of moganite, quartz and amorphous silica. Although there are several reports on synthesis of SiO_2 -moganite (Schäfer et al., 2006; Kyono et al., 2017), these synthetic samples also contain coexisting quartz. Since many Raman peaks of moganite overlap with those of quartz as a result of their structural similarity (Kingma and Hemley, 1994), it is difficult to study natural SiO_2 -moganite by Raman spectroscopy. Heaney et al. (2007) used a single peak (at 501 cm^{-1}) for their hard mode Raman study, which is intense and well separated from other Raman peaks of coexisting quartz. They revealed anomalous behavior across the transition for this phase. However, it is not clear whether this behavior is intrinsic to the phase transition or due to the nature of natural samples with complicated nanostructures. Also, a high background at lower angle was observed for natural samples in both X-ray and neutron diffraction patterns (Heaney and Post, 2001). The situation is far better for AlPO_4 -moganite, for which a pure synthetic phase is readily available (Kanzaki and Xue, 2012). Although AlPO_4 -moganite is not stable at ambient pressure, our preliminary heat treatment study at ambient pressure revealed that it can be heated up to 600 °C without transforming back to the stable phase (berlinite) at ambient pressure. Therefore, AlPO_4 -moganite could be used as an analogue of SiO_2 -moganite for a better understanding of the transition. Although their be-

haviors may not be identical, it should provide further insight into the phase transition, such as identifying the soft mode and comparing the anomalous behavior observed for SiO_2 -moganite.

In order to avoid confusion, the room-temperature phase of AlPO_4 -moganite will be designated as α - AlPO_4 -moganite, whereas the high-temperature phase will be designated as β - AlPO_4 -moganite, where the distinction is necessary.

Al and P replace Si in the SiO_2 -moganite structure in an ordered manner to form AlPO_4 -moganite, and the space group of α - AlPO_4 -moganite ($P2_1/a$) is different from that of α - SiO_2 -moganite ($I2/a$) (Kanzaki and Xue, 2012). It was also suggested that the expected β -form would have space group $Pmaa$ (Kanzaki and Xue, 2012). However, no crystal structural refinement of β - AlPO_4 -moganite has been conducted to date. In this study, the phase transition of α - AlPO_4 -moganite was explored by high-temperature in-situ micro-Raman spectroscopy. Although no soft mode was observed in SiO_2 -moganite by Heaney et al. (2007), they suggested the possibility that a soft mode is hidden in the low-frequency region, as their measurement below 100 cm^{-1} was highly attenuated by the Raman notch filter they used. In this study, newly available volume notch filters were employed to explore the low-frequency region down to $\sim 15\text{ cm}^{-1}$, where the soft mode is expected.

EXPERIMENTAL PROCEDURES

The α - AlPO_4 -moganite sample used in this study was from the same batch as that used in our previous crystal structure study (Kanzaki and Xue, 2012). In short, the sample was synthesized from dried reagent-grade AlPO_4 and was treated at 5 GPa and 1500°C for 1 h using a multi-anvil high pressure device installed at IPM. The recovered sample was a fine-grained (a few μm) sintered material, and our Rietveld refinement of the sample proved that the sample is mainly composed of α - AlPO_4 -moganite with trace corundum and an unknown phase (Kanzaki and Xue, 2012).

α - AlPO_4 -moganite is a high pressure phase and is not a stable phase at ambient pressure (Kanzaki and Xue, 2012; Wang and Kanzaki, 2015). However, our preliminary study revealed that AlPO_4 -moganite can be heated at ambient pressure up to near 800°C , and conversion to berlinite (the stable quartz-like phase at ambient pressure) was observed at around 800°C . In order to avoid complications due to the formation of berlinite, the present experiment was limited to below 600°C , and no berlinite was detected.

Unpolarized Raman spectra were acquired using a

home-built micro-Raman spectrometer with a 488 nm single-longitudinal-mode solid laser (Coherent Sapphire SF). It was noted that the frequency of the laser slightly depends on the operating power, so a fixed laser power (80 mW) was used for a series of in-situ runs, as well as during the wavenumber calibration. The laser beam was focused onto a fragment of the sintered sample with a long working distance $20\times$ objective lens (Mitsutoyo M Plan NIR), forming about $1\text{ }\mu\text{m}$ laser spot. Backscattered light was then focused to a pinhole (diameter of $200\text{ }\mu\text{m}$). The passed light was collimated, and passed through two Ondax's SureBlock Raman notch filters (Lebedkin et al., 2011) to reject Rayleigh scattering, and was focused to an entrance slit of the polychromator (Acton Spectra Pro 500i with focal length of 500 mm , and a grating of 1200 gr/mm). The dispersed light was detected by a liquid N_2 cooled CCD detector (Princeton Instruments, PyLoN 100BR eXcelon) with temperature set at -120°C . The present setup can measure Raman spectra down to $\sim 15\text{ cm}^{-1}$ including the anti-Stokes side.

For in-situ high-temperature Raman study, a wire-heater cell reported in our previous study (Kanzaki et al., 2012) was used. For heating, a digital DC power source (Kenwood PU8-90) was used. Temperature was calibrated against heating power of the DC power supply using the melting points (T_m) of the following materials: NH_4NO_3 (170°C), NaNO_3 (308°C), CsNO_3 (414°C), LiCl (605°C), and NaCl (801°C). The melting points of these materials were determined by visual observation under the microscope of the same micro-Raman system, and the required voltages and currents from the DC power supply were recorded. Then, a relation between the generated temperature and required heating power is fitted with a second order polynomial equation. This equation was used to estimate the heating power necessary for the desired temperature. The accuracy of the estimated temperature would be 10 – 20°C judging from reproducibility of the current and voltage and also repeated checks of the calibration materials, but the precision of relative temperature in a single heating experiment is much better within a few degrees.

A small sintered fragment of α - AlPO_4 -moganite was placed in the center of a hole in the heater (half-milled). For in-situ measurements, temperature was increased first in a step of 25°C in a few seconds and was then kept for 5 minutes to ensure thermal equilibrium before a Raman spectrum was acquired with a one-minute exposure time. This procedure was repeated up to 600°C . Near the transition temperature, additional measurements from 370 to 430°C with a 10°C -step were also conducted during both heating and cooling.

Relative wavenumbers in reported spectra were cali-

brated against the Raman shifts of a synthetic coesite sample using a third-order polynomial equation, which were precisely calibrated against Ar^+ plasma lines of a 488.123 nm Ar ion laser. A Voigt profile function was employed to fit the Raman peaks using the ‘fityk’ program (Wojdyr, 2010), resulting in a precision of 0.1 cm^{-1} for the Raman shift reported (for well-resolved peaks). There was no significant background increase due to thermal radiation up to 600°C , and no correction was applied for all the reported spectra except removal of cosmic-rays. When a sharp peak due to cosmic-ray overlapped with Raman peaks, the spectrum was discarded, and a new spectrum was acquired.

The first-principles density functional theory (DFT) calculation was performed using the QUANTUM ESPRESSO package (Giannozzi et al., 2017) similar to our previous studies of Mg-Zn olivine solid solution (Kanzaki and Xue, 2016) and hydrous forsterite (Xue et al., 2017). PAW-type potentials (Al.pbesol-n-kjpaw_psl.0.1.UPF, P.pbesol-n-kjpaw_psl.0.1.UPF, and O.pbesol-n-kjpaw_psl.0.1.UPF) from the PSLibrary (Dal Corso, 2014) were used. The initial crystal structure of $\alpha\text{-AlPO}_4$ -moganite ($P2_1/a$) taken from our Rietveld refinement (Kanzaki and Xue, 2012) was fully relaxed using the PWSCF program (ver. 6.1) at ambient pressure and 0 K. Then, this relaxed structure was used for phonon (vibrational mode) calculation with the PHONON program (ver. 6.1) in the package. Similar calculations were also conducted for the supposed $\beta\text{-AlPO}_4$ -moganite ($Pmaa$) structure. In this case, the structure of $\beta\text{-SiO}_2$ -moganite was used as a starting model with Si atoms replaced by Al and P alternatively, and optimization was conducted. The kinetic energy cutoffs for wave functions and charge density, and the scf energy convergence threshold for both phases were set to 60, 300, and 10^{-14} Ry, respectively. The Brillouin zone was sampled using the Monkhorst-Pack scheme with a $2 \times 4 \times 2$ grid.

RESULTS AND DISCUSSION

Raman spectrum of $\alpha\text{-AlPO}_4$ -moganite under ambient conditions

An unpolarized Raman spectrum of $\alpha\text{-AlPO}_4$ -moganite under ambient conditions is shown in Figure 1. We noted that there are two low-frequency modes at about 60 and 74 cm^{-1} . For our Raman spectrometer, these peaks are only detected with high intensities when the SureBlock filters are employed. Our single polychromator system now allows us to explore the low-frequency region down to $\sim 15 \text{ cm}^{-1}$ without employing an expensive double- or triple-monochromator system.

Figure 1. Unpolarized Raman spectrum of $\alpha\text{-AlPO}_4$ -moganite at 26°C and 1 bar. Vertical ticks at the bottom indicate predicted positions of 54 Raman modes by the DFT calculation with a scaling factor of 1.035 applied to the calculated frequencies in Table 1.

Factor group analysis of $\alpha\text{-AlPO}_4$ -moganite with space group $P2_1/a$ (C_{2h} point group) suggested that there are 54 Raman active modes ($26A_g + 28B_g$). Up to 33 peaks were detected from our Raman spectrum under ambient conditions and are listed in Table 1. The remaining 21 peaks were not observed possibly because of too low intensity or overlapping peaks. For $\beta\text{-AlPO}_4$ -moganite, if our predicted $Pmaa$ space group (D_{2h} point group) is assumed (see below), 54 Raman active modes ($14A_g + 16B_{1g} + 12B_{2g} + 12B_{3g}$) are expected. Unlike the case for the α - β quartz transition, there is no cell doubling for this transition. The total number of the Raman active modes are the same for both phases. This situation is identical to the α - β SiO_2 -moganite transition (Heaney et al., 2007), but there are more modes in AlPO_4 .

Raman shifts from the DFT phonon calculation of $\alpha\text{-AlPO}_4$ -moganite are listed in Table 1. The calculated Raman shifts are underestimated by 3–4% compared to the observed ones. This is a generally observed trend for DFT calculations with the GGA approximation. Therefore, a 3.5% correction for the calculated Raman shift positions are applied, and the results are shown in Figure 1 as vertical ticks. This correction is rather arbitrary, but it enables easier comparison with the observed spectrum as shown in Figure 1. Although some peaks apparently show larger deviations up to 10 cm^{-1} (Figure 1), most peaks show reasonable agreement. The positions of the two low-frequency modes at 60 and 74 cm^{-1} are well reproduced. Hereafter, these modes will be referred by their Raman shifts at room temperature (e.g., 74 cm^{-1} -mode).

Raman spectra of AlPO_4 -moganite at high-temperature

The compiled Raman spectra during heating are shown in

Table 1. Observed and calculated Raman shifts for α - AlPO_4 -moganite at 26 °C and 1 bar

Observed shift	Calculated shift	Representation
59.7	55.2	B_g
73.5	73.2	A_g
	92.0	B_g
97.4	96.8	A_g
	101.6	B_g
111.0	109.8	A_g
	122.3	B_g
126.2	123.7	B_g
132.9	134.2	A_g
153.7	143.3	B_g
178.9	172.2	A_g
190.6	181.4	B_g
	188.4	A_g
215.4	214.4	A_g
227.3	226.0	B_g
238.2	229.0	B_g
291.7	275.4	A_g
348.5	334.4	A_g
	343.2	B_g
362.4	344.5	A_g
383.0	364.5	B_g
390.7	377.1	B_g
	414.4	A_g
	415.6	B_g
432.8	421.3	A_g
444.7	423.6	B_g
	426.6	A_g
	455.6	A_g
474.9	457.3	B_g
485.4	465.9	A_g
495.4	474.0	B_g
	519.1	B_g
559.1	533.5	A_g
	631.3	A_g
648.7	631.6	B_g
	689.9	B_g
	696.9	A_g
	709.4	B_g
	718.4	A_g
710.5	729.1	A_g
734.7	729.3	B_g
747.1	744.5	B_g
	1059.9	B_g
	1064.6	A_g
	1075.5	A_g
	1076.2	B_g
	1081.1	B_g
	1083.6	A_g
1092.6	1086.1	A_g
1107.2	1092.2	B_g
1116.4	1104.7	A_g
1163.4	1106.7	B_g
1218.7	1180.5	B_g
1228.3	1192.5	A_g

Modes with similar frequencies between the observed and calculated are displayed in same line for convenience, but their correspondence are not all confirmed.

Figure 2. Raman spectra of AlPO_4 -moganite during heating up to 600 °C with a 25 °C-step. The bottom spectrum is at 26 °C, and top spectrum is at 600 °C. Spectra are displaced vertically for clarity. (a) Low-frequency region ($\leq 250 \text{ cm}^{-1}$). (b) High-frequency region ($\geq 250 \text{ cm}^{-1}$).

Figure 2 from 26 to 600 °C with a 25 °C-step. The Raman peak positions in these spectra were fitted, and the obtained Raman shifts are plotted against temperature in Figure 3. In the higher-frequency region ($\geq 250 \text{ cm}^{-1}$) given in Figure 2b, there is no significant change in the spectra during heating except small shifts and gradual broadening with temperature. It seems that the number of peaks decreases with temperature, but this is likely due to broadening and overlapping of the peaks. As mentioned above, no change in the number of Raman-active modes is expected across the transition. Figure 3 indicates that the intense peaks are continuously observed up to 600 °C without a discontinuity, but small changes in the slopes can be seen at around 400 °C.

The low-frequency region ($\leq 250 \text{ cm}^{-1}$) spectra are shown in Figure 2a. The 74 cm^{-1} -mode revealed significant softening, completely overlapping with the 60 cm^{-1} -peak at about 350 °C. The peak was still visible at 400 °C, but disappeared at 425 °C. In order to closely check the behavior of the 74 cm^{-1} -mode at around 420 °C, close-up views of the spectra near the transition with a 10 °C-step during the heating cycle are given in Figure 4. At 370 °C, the 74 cm^{-1} -mode was merely a shoulder of the 60 cm^{-1} -mode, but moved to lower frequency with temperature. At 410 °C, the 74 cm^{-1} -mode was still visible at around 20 cm^{-1} , but disappeared at 420 °C. A feature at around 10 – 15 cm^{-1} at 420 and 430 °C is due to the filters and is not a

Figure 3. Raman shifts of AlPO_4 -moganite versus temperature. The large scatterings are due to poor fitting of low-intensity peaks or heavily overlapped peaks.

Figure 4. Raman spectra of AlPO_4 -moganite in the low-frequency region during heating from 370 to 430 °C with a 10 °C-step. The anti-Stokes side (negative side) is also shown. Spectra are displaced vertically for clarity. Positions of the soft mode for α - AlPO_4 -moganite are indicated by triangles.

real Raman feature as it shows no change with temperature. The anti-Stokes side also shows identical behavior (with lower intensities), confirming that our observed softening of the 74 cm^{-1} -mode is not an instrumental artifact. The Raman spectra during the cooling process by a 10 °C-step (not shown) are very similar to those during the heating process. The 74 cm^{-1} -peak was not visible at 420 °C, but reappeared at 410 °C, suggesting little or very small ($<10\text{ °C}$) hysteresis for this transition. Heaney et al. (2007) observed a large hysteresis ($\sim 100\text{ K}$) for the α - β

Figure 5. Soft mode (74 cm^{-1} -mode) Raman shift of α - AlPO_4 -moganite versus temperature. Solid circles represent observed frequencies. The solid line represents curve fitted using an order parameter equation ($\omega_s = A|T_c - T|^\beta$), where ω_s is soft mode vibrational frequency, A is a constant, T_c is transition temperature, and β is critical exponent. Also shown are solid squares representing a low frequency mode in β - AlPO_4 -moganite.

SiO_2 -moganite transition, but no such large hysteresis was detected in the present study. Therefore, the hysteresis observed for the α - β SiO_2 -moganite transition is likely not intrinsic to the behavior of this transition, but originated from the complicated microstructures as already suggested by Heaney et al. (2007).

It was noted that a broad peak at around $15\text{--}20\text{ cm}^{-1}$ (see Figure 2a) became barely visible above 500 °C and apparently moved to higher frequency with temperature. The peak is broad, but peaks in the high-frequency region in the same spectra have comparable peak widths at those temperatures. This mode is likely a soft mode of β - AlPO_4 -moganite as discussed below.

The Raman shift of the 74 cm^{-1} -mode as a function of temperature is plotted in Figure 5. It is known that the soft mode vibrational frequency (ω_s) is an order parameter and can be correlated with $|T_c - T|^\beta$, where T_c is the transition temperature, and β is the critical exponent (e.g., Scott, 1974). In Figure 5, the observed soft mode vibrational frequencies were fitted by the non-linear least squares method with the following order parameter equation: $\omega_s = A|T_c - T|^\beta$, where A is a constant. As shown in Figure 5, the observed data can be reasonably fitted by the equation with $A = 18.7(9)$, $T_c = 415(1)$, and $\beta = 0.232(8)$. Therefore, the estimated transition temperature, where the soft mode vibrational frequency becomes zero, was 415 °C. This reasonable fit to the order parameter equation provides further support for the inference that the 74 cm^{-1} -mode is the soft mode of α - AlPO_4 -moganite.

The obtained critical exponent is 0.232(8). The critical exponent of the displacive phase transition generally falls within the range of 1/2 to 1/3. Theoretical studies

Figure 6. Two hard mode (362 cm^{-1} - and 559 cm^{-1} -modes) Raman shifts of AlPO_4 -moganite versus temperature. Solid symbols represent observed data. The solid line represents a curve fitted using an order parameter equation ($\omega_h = A|T_c - T|^\beta + \omega_c$), where ω_h is hard mode vibrational frequency, A is a constant, T_c is transition temperature, ω_c is a vibrational frequency at T_c , and β is critical exponent.

showed that $1/8$ for 2D Ising model, $1/2$ for the mean field model, 0.325 for 3D Ising model and 0.3646 for 3D Heisenberg model (e.g., Gebhardt and Krey, 1980). The reported critical exponent of the soft mode vibrational frequency for α -quartz is around 0.30 (Scott, 1974), although it is complicated due to Fermi resonance and other factors for quartz. Our critical exponent is much smaller than these numbers, except for 2D Ising model. The reason for smaller critical exponent is not clear at moment.

An analysis of hard modes can also offer insights into displacive phase transitions (e.g., Bismayer, 2000). Accordingly, the hard modes were also inspected. As examples, two of the hard modes (559 cm^{-1} - and 362 cm^{-1} -modes) in Figure 3 are shown in Figure 6 in expanded view. The 559 cm^{-1} -mode slightly softens with temperature up to $425\text{ }^\circ\text{C}$, but becomes almost constant above $425\text{ }^\circ\text{C}$. On the other hand, the 362 cm^{-1} -mode slightly hardens with temperature up to $425\text{ }^\circ\text{C}$, but becomes nearly constant above $425\text{ }^\circ\text{C}$. Therefore, the hard modes also indicated the existence of a displacive phase transition at around $425\text{ }^\circ\text{C}$. The behavior of the hard mode with temperature is in parallel to that of the soft mode, but with much smaller magnitude. As the frequency changes for these hard modes are large enough to be detected using Raman spectroscopy with modest resolution,

hard modes could be useful for studying phase transitions, especially when the soft mode is undetected (Bismayer, 2000).

Similar order parameter analysis was also conducted for the 559 cm^{-1} -mode, and a slightly modified equation was used; $\omega_h = A|T_c - T|^\beta + \omega_c$, where ω_h is hard mode vibrational frequency, and ω_c is a vibrational frequency at the transition. As shown in Figure 6, the observed data can be reasonably fitted by the equation with $A = 0.4(1)$, $T_c = 440(5)$, $\omega_c = 552.6(5)$, and $\beta = 0.47(4)$. The critical exponent for the 559 cm^{-1} -mode is apparently much higher than that of the soft mode, and the estimated transition temperature is $25\text{ }^\circ\text{C}$ higher than that from the soft mode analysis. Although the hard mode Raman peak is much easy to observe, small change in the vibrational frequency apparently resulted higher uncertainty. It will be interesting to explore further this peculiar behavior by other spectroscopy and diffraction methods.

Soft mode and vibrational mode calculations

Since the structure of moganite is closely related to that of quartz, the soft mode behavior of SiO_2 -quartz and AlPO_4 -berlinite is briefly compared with that of α - AlPO_4 -moganite. For SiO_2 -quartz and AlPO_4 -berlinite, a broad peak located at $\sim 220\text{ cm}^{-1}$ at room temperature is known as a soft mode. This 220 cm^{-1} -mode in SiO_2 -quartz shows complicated behavior due to Fermi resonance and interaction with another mode (Scott, 1974), and the mode did not reach 0 cm^{-1} at the transition. It is interesting to note that a corresponding broad $\sim 220\text{ cm}^{-1}$ -mode exists for SiO_2 -moganite as well (Kingma and Hemley, 1994). Again, this suggests a close structural relation between quartz and moganite. Therefore, it is not surprising to see a similar broad peak in the Raman spectrum of the α - AlPO_4 -moganite at 227 cm^{-1} in Figure 1. However, as was shown by Heaney et al. (2007), this mode is not a soft mode for SiO_2 -moganite. It is also evident for AlPO_4 -moganite from our present study. Therefore, in terms of soft mode behavior, there is no similarity between quartz and moganite.

There is no high-temperature diffraction study of AlPO_4 -moganite to date, but the DFT calculations of vibrational modes provide us insight for the mechanism of this phase transition. The optimized crystal structures of both phases are shown in Figures 7a and 7b drawn by the VESTA software (Momma and Izumi, 2011). The optimized structural parameters of α - AlPO_4 -moganite ($P2_1/a$) are given in Table 2, and they can compare well with those observed (Kanzaki and Xue, 2012). The optimized structural parameters of β - AlPO_4 -moganite are given in Table 3. In this case, atomic positional constraints were

Figure 7. Crystal structures of AlPO_4 -moganite phases optimized by the DFT calculations with vibrational directions (arrows) superimposed. Purple and blue tetrahedra represent PO_4 and AlO_4 , respectively. Small red spheres represent oxygen ions. (a) α - AlPO_4 -moganite with vibrational directions of soft mode (74 cm^{-1} -mode); (b) β - AlPO_4 -moganite with vibrational direction of an imaginary mode (-42 cm^{-1}). Drawn by the VESTA software (Momma and Izumi, 2011).

imposed according to special positions (see Table 3). The optimized structure belongs to space group $Pmaa$, and there is a supergroup-subgroup relation between the space groups of these two phases similar to the case of SiO_2 -moganite (Heaney et al., 2007). Although β - AlPO_4 -moganite is only stable at high temperature ($>415^\circ\text{C}$), our calculation was done at 0 K. Therefore, this structure is dynamically unstable relative to α - AlPO_4 -moganite at 0 K.

The calculated vibrational frequencies for α - AlPO_4 -

moganite is given in Table 1. Our particular interest is the 73.2 cm^{-1} (A_g) mode, which would correspond to the observed soft mode (the 74 cm^{-1} -mode). Vibrational directions (arrows) for this mode are superimposed on the crystal structure shown in Figure 7a. This mode rotates PO_4 - and AlO_4 -tetrahedra toward the realization of the β - AlPO_4 -moganite structure (Figure 7b). For SiO_2 -moganite, Heaney and Post (2001) found that a simple rotation of tetrahedra about $[010]$ functioned as a mechanism for the transition from their diffraction study. This is consis-

Table 2. Optimized crystal structure of α - AlPO_4 -moganite by the DFT calculation (1 bar and 0 K)

Wyckoff		x	y	z
Site	symbol			
P1	2e	1/4	0.9637	0
P2	4g	0.0151	0.2444	0.6671
Al1	2f	1/4	0.5362	1/2
Al2	4g	0.0152	0.2505	0.1659
O1	4g	0.0301	0.9461	0.7060
O2	4g	0.9737	0.4152	0.7804
O3	4g	0.1871	0.1461	0.1021
O4	4g	0.1680	0.3362	0.6142
O5	4g	0.8749	0.2205	0.0529
O6	4g	0.8898	0.2651	0.5693

$P2/a$ (No. 13), $a = 8.7802$, $b = 4.9087$, $c = 10.9191$ Å, $\beta = 90.33^\circ$.

Table 3. Optimized crystal structure of β - AlPO_4 -moganite by the DFT calculation (1 bar and 0 K)

Wyckoff		x	y	z
Site	symbol			
P1	2e	1/4	0	0
P2	4q	0	0.2385	0.6664
Al1	2h	1/4	1/2	1/2
Al2	4q	0	0.2545	0.1667
O1	4q	0	0.0667	0.3019
O2	4q	0	0.4028	0.7863
O3	8r	0.1552	0.1859	0.0801
O4	8r	0.8611	0.2989	0.5925

$Pmaa$ (No. 49), $a = 9.0682$, $b = 4.8904$, $c = 10.9793$ Å.

tent with the vibrational directions of the soft mode of α - AlPO_4 -moganite shown in Figure 7a, which represents a projection from the [010] direction.

The calculated vibrational frequencies for β - AlPO_4 -moganite gave one imaginary frequency mode (-42 cm^{-1}), which is a Raman-active B_{3g} mode. The imaginary vibrational frequency mode is expected as the structure at 0 K is dynamically unstable. The vibrational directions of this imaginary frequency mode are superimposed on the crystal structure of β - AlPO_4 -moganite in Figure 7b. It is clear from a comparison of Figures 7a and 7b that these vibrational directions match exactly with the transition pathway from the β - to α -phase. Therefore, this B_{3g} Raman-active mode should correspond to the soft mode of β - AlPO_4 -moganite in its stability field ($>415^\circ\text{C}$). The broad low-frequency peak visible at $\geq 500^\circ\text{C}$ in Figure 2a could correspond to this soft mode, and their shifts are plotted in Figure 5. However, the peak positions closer to the transition temperature are missing. Further detailed studies in the lower-frequency region are necessary to confirm this soft mode of β - AlPO_4 -moganite.

The present in-situ high-temperature Raman study revealed that α - AlPO_4 -moganite has a displacive phase transition at 415°C , and a soft mode was identified. A DFT calculation of the soft mode suggested that this transition involves cooperative rotations of the tetrahedra about [010]. The present study suggests that a similar soft mode would exist in α - SiO_2 -moganite. Our preliminary Raman study of α - SiO_2 -moganite revealed two partially overlapping peaks in the low-frequency region, but the obtained spectrum was of lower quality compared to that of α - AlPO_4 -moganite. Further structural studies by diffraction techniques for AlPO_4 -moganite, and by Raman spectroscopy for SiO_2 -moganite are useful to further confirm the transition mechanism and to gain more insight into the transition.

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REFERENCES

- Bismayer, U.B. (2000) Hard mode spectroscopy of phase transitions. In Transformation Processes in Mineral (Redfern, S.A.T. and Carpenter, M.A. Eds.). Review in Mineralogy and Geochemistry, 39, Mineralogical Society of America, Washington, D.C., 265-283.
- Dal Corso, A. (2014) Pseudopotentials periodic table: From H to Pu. Computational Materials Science, 95, 337-350.
- Gebhardt, W. and Krey, U. (1980) Phasenübergänge und kritische Phänomene: Eine Einführung für Physiker im Hauptstudium. pp. 246, Friedrich Vieweg & Sohn, Braunschweig/Wiesbaden.
- Giannozzi, P., Andreussi, O., Brumme, T., Bunau, O., Buongiorno Nardelli, O., Calandra, M., Car, R., Cavazzoni, C., Ceresoli, D., Cococcioni, M., Colonna, N., Carnimeo, L., Dal Corso, A., de Gironcoli, S., Delugas, P., DiStasio Jr, R.A., Ferretti, A., Floris, A., Fratesi, G., Fugallo, G., Gebauer, R., Gerstmann, U., Giustino, F., Gorni, T., Jia, J., Kawamura, M., Ko, H.-Y., Kokalj, A., Küçükbenli, E., Lazzeri, M., Marsili, M., Marzari, N., Mauri, F., Nguyen, N.L., Nguyen, H.-V., Otero-de-la-Roza, A., Paulatto, L., Poncé, S., Rocca, D., Sabatini, R., Santra, B., Schlipf, M., Seitsonen, A.P., Smogunov, A., Timrov, I., Thonhauser, T., Umari, P., Vast, N., Wu, X. and Baroni, S. (2017) Advanced capabilities for materials modelling with QUANTUM ESPRESSO. Journal of Physics: Condensed Matter 29, 465901.
- Heaney, P.J. (1994) Structure and chemistry of the low-pressure silica polymorphs. In Silica: physical behavior, geochemistry, and materials applications (Heaney, P.J., Prewitt, C.T. and Gibbs, G.V. Eds.). Reviews in Mineralogy 29, Mineralogical Society of America, Washington D.C., 1-40.
- Heaney, P.J. and Post, J.E. (2001) Evidence for an $I2/a$ to $Imab$

- phase transition in the silica polymorph moganite at ~570 K. *American Mineralogist*, 86, 1358–1366.
- Heaney, P.J., McKeown, D.A. and Post, J.E. (2007) Anomalous behavior at the *I2/a* to *Imab* phase transition in silica-moganite: An analysis using hard-mode Raman spectroscopy. *American Mineralogist*, 92, 631–639.
- Kanzaki, M. and Xue, X. (2012) Structural characterization of moganite-type AlPO_4 by NMR and powder X-ray diffraction. *Inorganic Chemistry*, 51, 6164–6172.
- Kanzaki, M., Xue, X., Amalberti, J. and Zhang, Q. (2012) Raman and NMR spectroscopic characterization of high-pressure K-cymrite ($\text{KAlSi}_3\text{O}_8 \cdot \text{H}_2\text{O}$) and its anhydrous form (kokchetavite). *Journal of Mineralogical and Petrological Sciences*, 107, 114–119.
- Kanzaki, M. and Xue, X. (2016) Cation distribution in Mg–Zn olivine solid solution: a ^{29}Si MAS NMR and first-principles calculation study. *Journal of Mineralogical and Petrological Sciences*, 111, 292–296.
- Kingma, K.J. and Hemley, R.J. (1994) Raman spectroscopic study of microcrystalline silica. *American Mineralogist*, 79, 269–273.
- Kyono, A., Yokooji, M., Chiba, T., Tamura, T. and Tsuji, A. (2017) Pressure-induced crystallization of biogenic hydrous amorphous silica. *Journal of Mineralogical and Petrological Sciences*, 112, 324–335.
- Lebedkin, S., Blum, C., Stürzl, N., Hennrich, F. and Kappes, M.M. (2011) A low-wavenumber-extended confocal Raman microscope with very high laser excitation line discrimination. *Review of Scientific Instruments*, 82, 0137055.
- Miehe, G. and Graetsch, H. (1992) Crystal structure of moganite: a new structure type of silica. *European Journal of Mineralogy*, 4, 693–706.
- Momma, K. and Izumi, F. (2011) VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, *Journal of Applied Crystallography*, 44, 1272–1276.
- Schäfer, O., Ghobarkar, H., Garnier, A., Vagner, C., Lindner, J.K.N., Hanss, J. and Reller, A. (2006) Synthesis of nanocrystalline low temperature silica polymorphs. *Solid State Sciences*, 8, 625–633.
- Scott, J.F. (1974) Soft-mode spectroscopy: Experimental studies of structural phase transitions. *Reviews of Modern Physics*, 46, 83–128.
- Wang, R. and Kanzaki, M. (2015) Phase diagram and thermodynamic properties of AlPO_4 based on first-principles calculations and the quasiharmonic approximation. *Physics and Chemistry of Minerals*, 42, 15–27.
- Wojdyr, M. (2010) Fityk: a general-purpose peak fitting program. *Journal of Applied Crystallography*, 43, 1126–1128.
- Xue, X., Kanzaki, M., Turner, D. and Lorocho, D. (2017) Hydrogen incorporation mechanisms in forsterite: New insights from ^1H and ^{29}Si NMR spectroscopy and first-principles calculation. *American Mineralogist*, 102, 519–536.

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