Phase transitions of tridymite MC: 
A low frequency Raman spectroscopic study

Masami KANZAKI
Institute for Planetary Materials, Okayama University, Misasa, Tottori 682-0193, Japan

In-situ high-temperature Raman spectra of tridymite starting from MC modification were measured up to 500 °C. Low frequency Raman spectra (ν = 15–100 cm⁻¹) of the high-temperature modifications (OP, OS, OC, and HP) were reported for the first time. It was noted that there are significant changes in the low frequency region upon the transitions, and those transition temperatures are consistent with those reported in previous studies except OC/HP transition. The OC/HP transition was detected at around 470 °C. This temperature is about 70 °C higher than the transition temperature determined by previous X-ray diffraction studies. The disagreement on the transition temperature is discussed.

Keywords: SiO₂, Tridymite, Low frequency Raman spectroscopy, Phase transition

INTRODUCTION

Temperature-induced phase transitions of tridymite have been studied by many researchers (e.g., Nukui et al., 1978; Nukui and Nakazawa, 1980; Graetsch and Flörke, 1991; Xiao et al., 1993; Kihara, 1995). In this paper, tridymite modifications are expressed according to the nomenclature proposed by Nukui et al. (1978) and Nukui and Nakazawa (1980). At high temperature (>400 °C), a modification with hexagonal structure (HP) is stable, and this structure is regard as ideal tridymite structure. This HP structure (P6₃/mmc) is made of sheets which in turn consist of six-membered rings of SiO₄ tetrahedra, and those sheets are stacked vertical to c-axis (Heaney, 1994). Within the sheet, all next neighbor tetrahedra are pointing opposite side against to the central tetrahedron. Each ring is stacked on directly-overlie one another, creating continuous tunnels vertical to the sheets. Two adjacent sheets are symmetrically related by a mirror plane. In this ideal hexagonal structure, Si–O–Si bond angle is 180°, which is not energetically stable configuration (Gibbs et al., 1994). Based on X-ray diffraction study of HP at 460 °C (Kihara et al., 1986b), the probability density function of electron by oxygen is circular about ideal oxygen position with radius of about 0.4 Å. This effectively reduces actual instantaneous bond angle to 149° in the HP structure.

A transition sequence of tridymite modification starting from MC to HP is given in Figure 1. Upon cooling some of dynamically disordered distributions of oxygens freeze, and an orthorhombic modification (OC) is formed at around 380 °C (Nukui et al., 1978). At lower temperature (about 190 °C), an incommensurately modulated modification (OS) with a modulation wavevector in a-axis direction in which the wavelength depends on temperature is formed from OC. OS then transformed to an orthorhombic modification (OP) with triple a lattice parameter at around 150 °C. Finally, OP transforms to MC at 110 °C. MC is one of stable modifications at room temperature and is often found in synthetic samples and meteorites. In addition to MC, PO–10 and MX–1 are also known to appear at room temperature. Natural tridymite from volcanic rocks are mostly PO–10, whereas MX–1 is

![Figure 1. Transition sequence of tridymite modifications starting from MC to HP (after Nukui and Nakazawa, 1980).](image-url)
experimentally produced by rapidly quenching high-temperature modifications or by grinding/stressing MC (Hoffmann et al., 1983). The transition sequence starting from MC is most well established as shown in Figure 1, and we examine this sequence using Raman spectroscopy in this paper.

Although the large number of studies have been conducted, there are still unresolved issues for the transitions of tridymite modifications. For example, the existence of LHP modification (Cellai et al., 1995) is not well confirmed. Raman-active soft mode is predicted for OC phase (Kihara, 1995), but none investigated experimentally. In order to study the transition behaviors, Raman spectroscopic study is necessary to complement X-ray diffraction and IR studies. The X-ray diffraction study provides us time- and space-averaged structure, but it is difficult to distinguish static disorder and dynamic disorder. Spectroscopic study may provide us local structure and dynamical aspect of the transitions, but without exact information of atomic positions in the cells. Therefore, it is apparent that comprehensive diffraction and spectroscopic studies are needed. However, not much spectroscopic studies have been conducted for tridymite thus far. Xiao et al. (1993, 1995) studied the temperature–induced transitions of tridymite MC and MX–1 using 29Si MAS NMR spectroscopy. Although NMR provides unique information not obtainable from the diffraction and vibrational spectroscopy, it provided less structural information above 300 °C as original multiple Si site peaks at low temperature merged into single peak at high temperature. De Dombal and Carpenter (1993) and Cellai et al. (1995) studied the transitions of tridymite MC taken from Steinbach meteorite and a synthetic one using in-situ infrared (IR) spectroscopy. From their analysis of hard-mode IR peaks, they proposed that an intermediate phase (LHP) exists between OC and HP. Compared to IR, Raman has several advantages such as easy access to low frequency region and no sample preparation necessary. Hirose et al. (2005) studied MC up to 500 °C using in-situ Raman spectroscopy, X-ray diffraction, and DTA. They reported Raman spectra of MC, OP, OC, and HP for the first time. This is only in-situ high-temperature Raman spectroscopic study of tridymite reported thus far.

Low frequency region of vibrational spectroscopy potentially provides us valuable information, such as soft mode. Kihara (1995) suggested existence of soft mode (Raman active) in OC toward OC/HP transition. Kihara et al. (2005) simulated Raman spectra of MC, OP, and OC modifications using a valence field force model and revealed that low frequency Raman modes below 100 cm−1 exist for those phases. He also suggested a relation between the low frequency vibrational modes and a pattern of anisotropic displacement factors for oxygens obtained from single X-ray diffraction study. Although Hirose et al. (2005) reported the Raman spectra of tridymite modifications at high temperatures, they could not observe Raman peaks below 100 cm−1 because of the instrumental limitation. Also, they used a rather special sample which does not exhibit OS phase. As most of samples in previous studies at high temperature confirmed OS phase, the transitions regarding OS phase (i.e., OP/OS and OS/OC) should be studied. New generation Raman notch filter (Lebedkin et al., 2011) now allows us to measure the lower frequency region even using a conventional single monochromator-based Raman system as demonstrated in our previous studies (Kanzaki, 2018; Kanzaki, 2019a). Recently, Raman spectra of tridymite modifications (MC, MX–1, and PO–10) stable at room temperature including the low frequency region were reported (Kanzaki, 2019b), and the low frequency peaks were found for all phases studied. In this paper, a preliminary result of in-situ high-temperature low frequency Raman spectroscopic observation of tridymite MC is reported.

EXPERIMENTAL PROCEDURES

A synthetic tridymite used in this study is same sample reported in our previous study (Kanzaki, 2019b) and was synthesized from a mixture of silica sand and 3 wt% K2CO3 at 1400 °C. The sample consists of mostly MC with minor cristobalite and MX–1, as detected by micro-Raman spectroscopy.

Unpolarized Raman spectra were acquired using a home-built micro-Raman spectrometer with a 488 nm solid laser (Coherent Sapphire 488 SF). The laser power was 80 mW, and the laser beam was focused to sample using a long working distance 20× objective lens (Mitsutoyo M Plan NIR). Backscattered geometry was employed. In order to reject the Rayleigh scattering, two Onix’s SureBlock Raman notch filters (Lebedkin et al., 2011) were used, and the present configuration can measure Raman spectrum down to ~ 15 cm−1 including the anti-Stokes side. See Kanzaki (2019b) for further details of the Raman spectrometer used.

For in-situ high-temperature Raman study, a wire-heater cell reported in our previous study (Kanzaki et al., 2012) was used. The experimental details are reported in Kanzaki (2018). In this study, temperature was calibrated against heating power of the DC power supply using the melting points (Tm) of the following materials: NH4NO3 (170 °C), NaNO3 (308 °C), CsNO3 (414 °C), and LiCl (605 °C). The accuracy of the estimated temperature would be within 10 °C judging from reproducibility of
the current and voltage, and from frequently repeated calibrations.

A polycrystalline fragment of synthetic tridymite MC was loaded in the center of a hole in the heater (half-milled). For in-situ measurements, temperature was increased to desired temperature within a few seconds and was then kept for 5 minutes to ensure thermal equilibrium before the Raman spectrum was acquired. One-minute exposure was repeated the same time to improve signal/noise ratio of the spectrum. This procedure was repeated up to 500 °C, and then measurements during cooling were also conducted. Despite movement of the sample under the microscope due to thermal expansion of the heater wire, we tried to measure same position of the sample within a few μm by manually adjusting an XYZ stage. Relative wavenumbers in reported spectra were calibrated against 10 Raman peaks of a synthetic coesite sample using a third-order polynomial equation. Detailed calibration procedure is given in Kanzaki (2019a). There was no significant background increase due to thermal radiation up to 500 °C, and no correction including background subtraction was applied for all the reported spectra. The spectra given in this paper will be deposited to Raman Open Database (ROD).

RESULTS AND DISCUSSION

Raman spectra of tridymite MC at high temperature

For convenience of description below, a frequency range below 100 cm⁻¹ will be designated as the low frequency (LF) region, and higher than 100 cm⁻¹ will be designated as the high frequency (HF) region on the following pages. For the in-situ study, the polycrystalline fragment from the coarsely crushed MC sample was used. The Raman spectra during heating to 500 °C are shown in Figure 2, whereas those during cooling to 60 °C are shown in Figure 3. In Figure 4, the LF regions of Figures 2 and 3 are expanded including the anti-Stokes side. It should be noted that the Raman notch filters were adjusted asymmetrical against 0 cm⁻¹. As a result, the anti-Stokes side (<0 cm⁻¹) provides us less distorted peak shapes near 0 cm⁻¹ (see Fig. 4).

The spectrum measured at room temperature before heating is given in the bottom of Figure 2. We noted that most major peaks can be assigned to those of MC, but there are additional peaks. There is a peak at 256 cm⁻¹, which is diagnostic for MX–1 (Kanzaki, 2019b). Other strong peaks of MX–1 also exist. Therefore, the sample contains minor MX–1.

At 60 °C, the peaks originated from MX–1 disappeared (Fig. 2), and remaining peaks in the HF region can be compared well with those of MC (Hirose et al., 2005). Hoffmann et al. (1983) reported that if sample is an inter-growth of MC and MX–1, it became single MC phase when heated above 70 °C. This observation is consistent with present observation. It should be noted that if single MX–1 phase is heated, it transformed to an orthorhombic
phase at 65 °C (Graetsch, 1998; Xiao et al., 1995). Except for those peaks originating from MX-1 below 60 °C, temperature-induced changes in the Raman spectra in the HF region up to 500 °C (Fig. 2) are essentially identical to those of Hirose et al. (2005). Therefore, we will mostly focus to the LF region in the following description and discussion.

Between 100 and 120 °C, there are significant changes in both LF and HF regions which would correspond to MC/OP transition. Hirose et al. (2005) detected this transition at 115 °C in their Raman study. Our observed transition temperature is within 10 °C of previous reported ones for MC/OP transition (e.g., Shahid and Glasser, 1970; Nukui et al., 1978; Thompson and Wennemer, 1979).

The Raman spectrum of OP in the HF region is identical to that of Hirose et al. (2005). At the LF region, two major peaks of OP at 32 and 100 cm$^{-1}$ are observed for the first time. Kihara et al. (2005) calculated the Raman vibrational modes of OP and OC using the valence force field model which was adjusted to reproduce the Raman spectrum of MC. They noted good agreement between the calculated and observed Raman spectrum in the HF region for OP, but not so good agreement for OC. The calculated Raman modes of 15.7 ($A_1$), 22.8 ($B_1$), 18.1 ($B_2$), 24.7 ($B_3$), and 74.9 ($B_3$) cm$^{-1}$ for OP were reported. Kihara et al. (2005) pointed out that displacement directions of the 74.9 cm$^{-1}$ ($B_3$) vibrational mode can be well correlated to the observed directions of the principal axes of the thermal anisotropic displacement ellipsoids of O atoms in OP. The calculated mode of 74.9 cm$^{-1}$ might correspond to the peak at 100 cm$^{-1}$ in the observed spectrum of OP. Less satisfactory agreement is likely due to the empirical force field model and the averaged structure used for the calculation.

From 120 to 240 °C, there is no discernable change in the HF region of the spectra, except gradual broadening of the peaks. However, there are clear changes in the LF range at 180 °C. The peak of OP at 100 cm$^{-1}$ disappeared, and the peak at 32 cm$^{-1}$ reduced its intensity. Also, a sharp peak appeared at around 17 cm$^{-1}$ (Fig. 4). These changes already started at 160 °C as demonstrated by a shoulder at around 17 cm$^{-1}$. This would correspond to OP/OS transition as the transition is reported to start at 150 to 160 °C (Shahid and Glasser, 1970; Nukui et al., 1978; Graetsch and Flörke, 1991).

From 200 to 240 °C, there is gradually intensity reduction of a peak at 30 cm$^{-1}$ (a shoulder) with temperature. Simultaneously, the sharp peak at about 17 cm$^{-1}$ is replaced with a broader peak at 220 °C. This change is better represented in the spectra of 250 and 200 °C at the cooling stage (Fig. 3). This temperature is close to observed OS/OC transition temperature of 190 to 220 °C in previous studies (Nukui et al., 1978; Graetsch and Flörke, 1991). Therefore, OS phase is identified in our sample using the LF Raman spectroscopy.

From 240 to 400 °C, the spectrum of OC at the HF region does not change much, except apparent reduction
of intensities of the peaks at 290 and 450 cm\(^{-1}\). For the LF region, the apparent peak observed below 15 cm\(^{-1}\) above 400 °C could be artificial due to the absorption by the filters (Fig. 4). Nevertheless, there is a relatively sharp component exists below 15 cm\(^{-1}\) and is apparently moving to lower frequency with temperature. Quantification of the peak position was difficult due to the complicated spectra close to 0 cm\(^{-1}\). From lattice dynamical calculations, Kihara (1995) predicted the Raman-active soft mode for OC. If soft mode does exist, a peak with significant softening with increasing temperature is expected. However, no such peak was observed in both heating and cooling stage. This could be due to low intensity or very wide peak width of soft mode or both. Further detailed Raman spectroscopic study is necessary. Kihara et al. (2005) simulated Raman vibrational bands of OC using ordered structure model. They noted that the simulated Raman spectrum for OC was not so satisfactory as compared to the observed spectrum in the HF region. For the LF region, a very strong Raman mode at about 100 cm\(^{-1}\) was predicted, but no such peak is observed in the present study. This again is likely due to the empirical force model adjusted for MC and the structure model used, and revised calculations using present spectra are necessary.

At 480 °C, the peak near 15 cm\(^{-1}\) completely disappeared, and the background slope below 100 cm\(^{-1}\) apparently changed. This change was also observed between 480 and 460 °C in the cooling stage (Fig. 4). This change is interpreted as OC/HP transition. In a re-heating run (not shown), this change was also reproduced between 460 and 480 °C. Therefore, OC/HP transition was observed at around 470 °C. At 480 and 500 °C, there is a very broad peak with a tail extending to 100 cm\(^{-1}\). This peak should be a vibrational mode of HP phase.

During the cooling stage (Figs. 3 and 4), the transitions of HP/OC, OC/OS, and OS/OP are also observed at similar temperatures compared to those of the heating stage. However, the transition of OP/MC has large hysteresis, and even at 60 °C in the cooling stage, OP phase was still dominant (Fig. 3). This hysteresis for MC/OP was also reported in previous studies (e.g., Shahid and Glasser, 1970; Graetsch and Flörke, 1991; Hirose et al., 2005). In summary, the transition temperatures observed in our study are fully consistent with those of previous studies, except the transition at 470 °C, which will be discussed in next section.

**Interpretation of a transition at 470 °C**

We interpreted that the change observed at 470 °C could be due to OC/HP transition. However, the transition temperature for OC/HP has been generally reported at 380 to 420 °C in previous studies which are based on X-ray diffraction and thermal analysis (e.g., Nukui et al., 1978; Kihara, 1978; Thompson and Wennemer, 1979; Graetsch and Flörke, 1991). On the other hand, this temperature can compare well with that of LHP/HP transition from hard-mode IR bands proposed by Cseh et al. (1995). These authors detected two transitions at 380 °C and 473 °C and suggested an intermediate phase (LHP) between OC and HP. Therefore, the change at 380 °C corresponds to OC/LHP, and that of 473 °C corresponds to LHP/HP based on their interpretation. The latter transition temperature matches well with our observation. If the LHP/HP transition does occur at 473 °C, we would expect OC/LHP transition at around 380 °C. However, no discernable change was detected in the Raman spectra in our study. Therefore, our study does not support the existence of LHP.

It is intriguing to note that both Raman and IR spectroscopy detected certain change near 470 °C. Vibrational spectroscopy monitors local vibrational motions of short time scale, whereas diffraction provides us time and space averaged structure. Therefore, vibrational spectroscopy is more sensitive to local symmetry of phase at high temperature, and this could be the reason for higher transition temperature observed in our Raman study. There are some supporting observations for this interpretation. Nukui et al. (1978) reported that weak diffraction spots of OC were still observed at around 400 °C and gradually faded away at around 450 °C. Kihara et al. (1986a) noted that the structure of OC at 420 °C can be refined with ideal hexagonal cell, but with an orthorhombic cell as well. Kihara (2001) suggested that y position of O2 site in OC can be regarded as an order parameter for OC toward OC/HP transition. Based on his analysis, the estimated transition temperature is 513 °C. Those observations suggest that ‘true’ OC/HP transition temperature could be much higher than previously thought. Apparently further study is necessary to resolve this issue by combining diffraction and spectroscopy techniques.

In summary, this study observed the low frequency Raman spectra of tridymite OP, OS, OC, and HP phases for the first time. The transitions between those phases were detected from changes in the low frequency region of the Raman spectra. This study demonstrated the importance of the low frequency region for study of the phase transitions of tridymite.

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