Raman spectroscopic study of pressure-induced phase transitions in tridymite modifications

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Pressure-induced phase transitions of tridymite modifications (MC, MX–1, and PO–10) were investigated by in-situ Raman spectroscopy. Starting from MC, a transition to PO–10 was observed at 0.4 GPa. At about 1.6 GPa, new Raman peaks appeared and were observed up to 8.7 GPa. This revealed a new phase, and it reverted to PO–10 at around 0.4 GPa during decompression. Contrary to previous study, PO–10 was recovered to ambient pressure. MX–1 also transformed to PO–10, and PO–10 was recovered. Starting from PO–10, the transition to the new phase was also observed but was gradual and the phase reverted to PO–10 during decompression. Present study revealed a new route to form PO–10 from MC and suggests rare PO–10 found in meteorites could be formed through this route.

Keywords: SiO2, Tridymite, Raman spectroscopy, High-pressure phase, Phase transition

INTRODUCTION

Tridymite exhibits many modifications (e.g., Heaney, 1994). In this paper, the modifications of tridymite are represented based on the nomenclature proposed by Nukui et al. (1978) and Nukui and Nakazawa (1980). In the temperature range of 867 and 1470 °C, HP (Hexagonal Primitive) modification is the only thermodynamically stable modification, while OC, OS, and OP modifications appear as the temperature decreases (Kanzaki, 2020). However, these modifications cannot be quenched, and three modifications are commonly reported at room temperature: MC, PO–n, and MX–1. MC is observed exclusively in extraterrestrial samples, including a Martian rock (Morris et al., 2016), as well as in synthetic products. On the other hand, MC is rare in terrestrial volcanic rocks and only a few have been reported (Kawai et al., 1978). As for PO–n (n = 1, 2, 5, and 10), PO–10 seems to be dominant in natural samples such as volcanic rocks on Earth, but it can also be found in synthetic samples. The reasons for the differences in the natural and synthetic occurrence of MC and PO–n are still not well understood. Recently an ‘orthorhombic tridymite’ (most likely PO–10, judging from the reported Raman spectrum) was reported from a cumulate eucrite (Ono et al., 2019). Kanzaki (2019) suggested the possible presence of PO–10 in an enstatite chondrite judging from the reported Raman spectrum in the literature (Kimura et al., 2005). MX–1 is formed when a high-temperature phase is quenched, or MC is stressed (Heaney, 1994). No natural MX–1 has been reported thus far.

Although pressure-induced phase transitions in other silica polymorphs such as quartz, cristobalite, coesite, and stishovite have been extensively studied (Hemley, 1987; Hemley et al., 1994; Palmer et al., 1994), tridymite modifications have not been examined well. Nukui et al. (1980) reported a transition from MC to PO–10 at 0.5 GPa, both visually and by single-crystal X-ray diffraction. This transition was reversible. Natural PO–5 single crystal was also examined, but no structural change up to 3 GPa was detected (Nukui et al., 1980). Cohen and Klein (1980) studied the phase transitions of tridymite by DTA and determined the two transition temperatures seen at ambient pressure to 0.6 GPa. Prakapenka et al. (2004) studied the polymorphs of SiO2 and GeO2 under very high pressure. However, they have not studied the transition of tridymite at low pressure (<10 GPa).

Kanzaki (2019) suggested that PO–10 in meteorites may have been formed from MC by shock events based on the study of Nukui et al. (1980). However, if the phase transition is completely reversible, no evidence of the MC to PO–10 transition would be detected in shocked
meteorites. The objectives of this study are to confirm the reversible phase transition between MC and PO–10 observed previously, to study other modifications (PO–10 and MX–1) as well, and to extend the pressure range. For this purpose, in-situ Raman spectroscopy was used. Recently, Kanzaki (2019) clarified the Raman spectra of MC, PO–10, and MX–1, allowing us to identify those tridymite modifications and other silica polymorphs based on Raman spectra alone.

**EXPERIMENTAL PROCEDURES**

MC, MX–1, and PO–10 modifications were investigated. For PO–10, natural PO–10 single crystals from Vechec, Vranov nad Topľou Co., Prešov Region, Slovakia (obtained from N’s Mineral Co.) were used. The transparent platy crystals were coarsely crushed, and small fragments less than 100 µm were used. Raman spectra of the crushed fragments are identical to that of PO–10 reported by Kanzaki (2019). Two synthetic samples were used for MC. The first is the same sample used in Kanzaki (2019) and was synthesized from a mixture of silica sand and K2CO3 (3 wt%) heated to 1400 °C and 8 h. The second one was synthesized by heating silica glass plus Na2WO4 as flux at 1400 °C for 3 days. Tridymite crystals were precipitated from the evaporated flux. The crystals obtained from the flux growth method were identified by Raman spectroscopy as MC only. Larger crystals were obtained by this method. A single crystal with dimension of 120 × 100 × 30 µm was used. Preliminary experiment was also carried out on MX–1, and the same sample obtained from powdered synthetic MC reported in Kanzaki (2019) was used.

A symmetric diamond anvil cell (DAC) was used for the in-situ high-pressure Raman studies. The culet size of the low-fluorescence diamond anvils was 500 µm. A stainless-steel gasket (SUS301H) with a thickness of 250 µm was pre-indentend to about 100 µm, and then a hole with a diameter of 250 µm was made using an electric discharge device. The sample was introduced into the hole in the gasket along with several ruby chips. A 4:1 mixture of methanol and ethanol was used as the pressure medium. All measurements were carried out at 24 °C. The pressure was increased in steps, and each step took about 10 min for the pressure and Raman measurements.

Unpolarized Raman spectroscopic measurements were conducted using a home-built micro-Raman spectrometer equipped with a 488 nm solid state laser (80 mW). The laser beam was focused on the sample piece in the diamond anvil cell by a 20× or 50× long working distance objective (Mitsutoyo M Plan Apo). The backscattered light was then focused onto a pinhole (200 µm in diameter), and the light passing through it was collimated, passed through a long wavelength pass filter ‘RazorEdge’ (Semrock Inc.), and further focused on the entrance slit of the imaging monochromator (Acton Spectra Pro 500i with a grating of 1200 gr/mm). The dispersed light was detected by a CCD detector (Princeton Instruments, PyLoN 400BR eXcelon) cooled with liquid nitrogen. The exposure time required to take single spectrum was typically 60 s. Due to a problem with the CCD detector, some of the spectra show small depressions of 5–10 cm−1 width (their positions are shown in the spectra by triangles), but the important Raman features remain unchanged. The pressure was measured using the same spectrometer with the ruby fluorescence technique (Piermarini et al., 1975).

The relative frequencies of the reported spectra are calibrated against the ten Raman shift positions of synthetic coesite. A Ne lamp (Sato Parts Co. Ltd., BNS701–1–R) was used for the ruby R1 peak region (centered at 6100 cm−1 relative to 488 nm). Since this lamp contains a small amount of Ar gas, emission lines from Ar were also observed. This allowed us to increase the numbers of calibration points in addition to the initial 4 Ne lines (7 in total). The ‘fit’ program (Wojdyr, 2010) was used to fit the Raman peaks and the ruby fluorescence peaks using the Voigt profile function. The accuracy of the reported pressures is 0.02 GPa.

**RESULTS AND DISCUSSION**

**MC and MX–1 modifications**

MC modification was compressed to about 8.7 GPa. The Raman spectra during compression and decompression are shown in Figure 1, and the Raman peak positions as a function of pressure were given in Figure 2. These spectra were obtained from the single crystal grown from the flux. Similar results were obtained from another MC sample synthesized from silica sand and K2CO3, suggesting that the difference in synthesis method had little effect on the results. Up to 0.16 GPa, five prominent peaks of MC were observed at 212, 308, 350, 360, and 435 cm−1, but they disappeared at 0.35 GPa, and a new broad band appeared between 400 to 450 cm−1. The other two new broad peaks at about 150 and 200 cm−1 were also observed. These spectral features are unique to PO–10 (Kanzaki, 2019). Thus, MC to PO–10 transition was detected. This observation is consistent with the previous observation of the MC to PO–10 transition at 0.5 GPa from single crystal X-ray diffraction by Nukui et al. (1980). The observed transition pressure (0.35 GPa) seems lower than that of Nukui et al. (1980), but the accuracy they reported was ±0.15 GPa. Since PO–10 is slightly denser than MC, this transition is reasonable. Microscopically, there were
no obvious changes in the crystal during this transition.

At 1.6 GPa, a new sharp peak at 450 cm$^{-1}$ overlapping with the main band of PO–10 appeared and became the strongest peak. Several cracks were noted in the single crystal at this pressure. At the same time, many small new peaks appeared in the region of 100–400 cm$^{-1}$. The Raman spectra above 1.6 GPa cannot be explained by tridymite modifications nor by other silica polymorphs.

The Raman spectrum of cristobalite II, which transformed from cristobalite at 1.2 GPa (Palmer et al., 1994), has some similarity with this new spectrum, but the low frequency peaks do not match. The peak around 450 cm$^{-1}$ shifts significantly to higher frequencies with increasing pressure. This new spectrum was observed up to 8.7 GPa, which is the highest pressure for this sample.

In this paper, we tentatively refer to this new phase as ‘tridymite II’. It is possible that tridymite II is one of PO–n or some structural variants of PO–n, but it cannot be identified only from the Raman spectrum at this time.

As can be seen from Figure 1 (and others below), the overall Raman intensity increased with increasing pressure, especially above 1 GPa. This increase in intensity is due to a decrease in the refractive index contrast between the sample and the pressure medium. At 4 GPa, the boundary between the sample and the pressure medium has been obscured. Similar phenomenon was also observed during compression of other low-pressure silica polymorphs (e.g., Palmer et al., 1994).

During decompression, Raman spectra of tridymite II were observed down to 0.6 GPa but were not clear at 0.4 GPa. At 0.13 GPa, Raman spectra typical of PO–10
were observed, but no transition to MC was observed. The sample recovered to ambient pressure was PO–10. Several cracks occurred at 1.6 GPa during compression, but all other parts of the recovered crystal remained clear and transparent. Nukui et al. (1980) observed that a single crystal MC reversibly transformed to PO–10 without destroying the crystal at 0.5 GPa. Our recovered crystal suggests that the transition from PO–10 to tridymite II does not involve reconstructive structural change.

We also performed a preliminary experiment on MX–1 up to 0.98 GPa, and the spectra are shown in Figure 3. This MX–1 was made by pulverizing the original MC sample, therefore the crystal size was small, and some MC still remained. Bottom spectrum of Figure 3 is showing a mixture of MX–1 and MC before compression. MX–1 transformed to PO–10 at 0.19 GPa whereas MC was still observed (third spectrum from the bottom). At 0.98 GPa, MC also disappeared and only PO–10 was observed. During decompression, PO–10 was recovered. Hence, just like MC, MX–1 transformed to PO–10 and cannot be recovered to ambient pressure. MC was not recovered at this time either.

The mechanism of transition from MC to PO–10 was discussed by Nukui et al. (1980). PO–10 is composed entirely of six-membered SiO₄ rings of the ‘oval’ type, whereas MC is composed of one-third oval and two-thirds ‘ditrigonal’ type rings. The oval rings are slightly compact compared to ditrigonal rings. The transition can be achieved by slight rotations of the SiO₄ tetrahedra without any major reconstruction. This explanation can also be applied to the transition from MX–1 to PO–10 as well. MX–1 is composed of ditrigonal type rings only (Graetsch and Topalovic–Dierdorf, 1996), therefore even less dense compared to MC. Therefore, PO–10 is again favored at high pressures. We might expect MX–1 to PO–10 transition at lower pressure than MC to PO–10. Our preliminary result shown in Figure 3 suggested that MX–1 transformed at lower pressure than MC, but further in–depth study is needed.

The recovery of PO–10 to ambient pressure contrasts with the observations of Nukui et al. (1980), who reported the reversible transition between MC and PO–10. Both studies used the methanol–ethanol mixture as the pressure medium and were hydrostatic condition in the pressure range studied. There seem to be two differences between the study of Nukui et al. (1980) and the present study. Nukui et al. (1980) used hydrothermally synthesized tridymite crystal. In my study, I used two different MC samples, but the results were same. Another difference is that my MC was compressed to 7–9 GPa, much higher than Nukui et al. (1980). However, MC observed in the MX–1 run was compressed up to 0.98 GPa, while PO–10 was still recovered. Apparently, the recovery of PO–10 is not related to the maximum pressure reached. Further studies are needed to clarify this discrepancy.

**PO–10 modification**

In the experiments with MC and MX–1, it was found that they transformed to PO–10 at relatively low pressure, and then PO–10 transformed to tridymite II. Therefore, starting from PO–10, a direct transition from PO–10 to tridymite II would be expected to be observed. Two experiments were performed, but the results were essentially the same. Therefore, the second run is presented here. A natural PO–10 single crystal was compressed up to 7.0 GPa (8.2 GPa in the first run). The Raman spectra during compression and decompression are shown in Figure 4, and the Raman peak positions as a function of pressure were given in Figure 5. At 0.29 GPa, the existing peak was superimposed by a new peak near 420 cm⁻¹, and it became the strongest peak at 0.48 GPa. This behavior is similar to that observed for MC at 1.6 GPa. However, in contrast to the MC case, a gradual change with increasing pressure was observed below 400 cm⁻¹.

The transition pressure cannot clearly be defined, but it took place between 1.4 and 3.0 GPa. The reason for the difference is not clear thus far, and in–situ X-ray diffrac-
tion experiments are needed to clarify this. Nukui et al. (1980) compressed PO–5 to 3 GPa and did not observe any transition. Although the structure of PO–5 is not the same as that of PO–10, structural similarity may exist. The reason why no transition was observed in Nukui et al. (1980) may be that the transition was gradual extending to near 3 GPa, as in PO–10. Alternatively, I cannot rule out the possibility that tridymite II is PO–5. Unfortunately, the crystal structure of PO–5 is not clarified yet, and no Raman spectrum has been reported thus far.

At decompression, the Raman spectra became almost the same as at compression when compared at similar pressures and they returned to that of PO–10 at ambient pressure. In this case too, the Raman spectra changed gradually, and the transition pressure ranged from 1.4 to 3.0 GPa. The observation of the recovered single crystal under the optical microscope showed no obvious changes compared to the initial state before pressurization.

The dominant peaks of PO–10 (and the corresponding peaks of tridymite II) locating at about 410 cm$^{-1}$ at ambient pressure, rapidly moved to higher frequencies with increasing pressure and exceeded 500 cm$^{-1}$ at 5 GPa (Figs. 1 and 4). Similar behavior was observed in quartz and cristobalite. In quartz, the main peak at 464 cm$^{-1}$ at ambient pressure reached 500 cm$^{-1}$ at about 5 GPa (Hemley, 1987). In cristobalite (and cristobalite II), the major peak at 420 cm$^{-1}$ at ambient pressure reached to 500 cm$^{-1}$ at about 5 GPa (Palmer et al., 1994). These peaks originate from the Si–O–Si bending modes. The relationship between the frequency of the bending mode and the Si–O–Si angle is well known. The average Si–
O-Si angle of the bending mode at 500 cm\(^{-1}\) is about 135° based on the known structural correlations established for quartz and cristobalite (Palmer et al., 1994). The average Si-O-Si angle is 148.3° in PO-10 at ambient pressure (Konnerth and Appleman, 1978). Therefore, the main compression mechanism of tridymite seems to be the pressure-induced decrease of the Si-O-Si angle, like other low-pressure silica polymorphs. However, in-situ single-crystal X-ray diffraction studies are needed to determine the details of the pressure-induced structural changes of tridymite modifications.

Possible occurrence of PO-10 in shocked meteorites

This study reveals a new route for the formation of PO-10 from MC. Of course, PO-10 is commonly found in the voids of volcanic rocks on Earth, and no high pressure is necessary to explain the formation of PO-10 in those rocks. However, in the case of shocked meteorites, the story is different. Tridymite MC is the most common silica polymorphs observed in meteorites, and if a meteorite containing MC is subjected to a light impact (\(p \geq 0.35\) GPa), PO-10 could form and be preserved. Recently, PO-10 has been discovered in meteorites as mentioned before. Those PO-10 may have been formed by shock events. However, our study is based on static high-pressure experiments at room temperature, and the pressure loading time is very long compared to the shock events. Therefore, it is not clear whether it is directly applicable to impacted meteorites. Further studies considering the transition kinetics are needed to explore this interesting transition. In any case, clarifying the modification of tridymite and establishing the conditions for its formation will provide a new opportunity to elucidate the thermal and impact history of tridymite-bearing meteorites.

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