Journal of Mineralogical and Petrological Sciences, Volume 114, page 214–218, 2019

LETTER

Raman spectra of tridymite modifications: MC, MX–1, and PO–10

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In order to facilitate identification of tridymite modifications using micro–Raman spectroscopy, the Raman spectra of synthetic and natural tridymite modifications (MC, MX–1, and PO–10) including low frequency region (v = 15–200 cm^{-1}) are measured. The Raman spectrum of MX–1 is reported for the first time. All modifications revealed the characteristic peaks below 150 cm^{-1}. Using the compiled Raman spectra, tridymite modifications of the reported Raman spectra from meteorites in the literature were identified. It revealed that not only MC, but PO–10 modification exists in the meteorites.

Keywords: SiO_2, Tridymite modification, Raman spectroscopy, Phase identification, Meteorite

INTRODUCTION

Tridymite has many modifications (e.g., Heaney, 1994). At ambient conditions, several modifications (MC, MX–1, and PO–*n*) are known. In this paper, the modifications are designated according to the nomenclature of Nukui et al. (1978) (also see Heaney, 1994). MC is a monoclinic modification commonly observed in synthetic samples, meteorites and lunar rocks (Dollase et al., 1971), but rare in terrestrial rocks (Kawai et al., 1978). MX–1 is another monoclinic modification with an incommensurate structure and can be produced by quenching high–temperature modifications, and by grinding or stressing the MC (Hoffmann et al., 1983). PO–*n* is the pseudo–orthorhombic group in which *n* represents the multiplicity of the *c* repeat relative to high temperature hexagonal modification (HP), and PO–*n* with *n* = 2, 5, 6, and 10 are known. However, only the crystal structure of PO–10 (Konnert and Appleman, 1978) is refined thus far.

Although the large number of studies on the tridymite modifications have been reported, there is little study on tridymite modifications by Raman spectroscopy. As a result, Raman spectra of tridymite modifications are not well established. This situation is unfavorable, as micro–Raman spectroscopy is convenient to identify mineral phases. Compared to other analytical techniques, micro–Raman spectroscopy has several advantages such as no need for sample preparation and its high spatial resolution. No sample preparation is especially advantageous as MC may transform to MX–1 during sample preparations.

Kingma and Hemley (1994) measured a natural tridymite sample (‘α–tridymite’). This tridymite is likely PO–10 as their sample came from the same locality of PO–10 studied by Konnert and Appleman (1978). Hirose et al. (2005) reported Raman spectrum of synthetic MC (from fired silica brick) in their in–situ high–temperature study. This is probably only Raman spectroscopic study of the synthetic MC. They also reported the Raman spectra of high–temperature modifications (OP, OC, and HP). Even some spectra of the modifications do exist, they are often presented in improper nomenclatures, creating difficulty for non–specialist. As far as we know, Raman spectra of MX–1 has not been reported. Since MX–1 is formed from MC by grinding and stressing, its identification is indispensable. Adding to those, it is important to measure low frequency region (below 200 cm^{-1}). The low frequency region contains rich information such as valuable structural information of tridymite modifications as suggested by Kihara et al. (2005), but the region is rarely reported. 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 system as demonstrated in our previous studies (Kanzaki, 2018, 2019). In this letter, Raman spectra of the room temperature modifications (MC, MX–1,

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doi:10.2465/jmps.190414

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and PO-10) from both synthetic and natural sources are reported including the low frequency region (ν = 15–200 cm^{-1}).

EXPERIMENTAL PROCEDURES

Synthetic tridymite was synthesized from a mixture of silica sand and 3 wt% K_2CO_3. The mixture was pressed into a pellet. The pellet was held at 1400 °C in a furnace for 8 h and was cooled down to room temperature by 1 h. This cooling rate was set to a temperature controller of the furnace, but actual cooling rate especially at low temperature region (<500 °C) was much slower than the nominal rate. The resultant product consists of mostly MC with minor cristobalite and MX-1, as detected by micro-Raman spectroscopy. Powder X-ray diffraction pattern of the powdered sample was measured using Rigaku's SmartLab diffractometer (CuKα_1) and is given in Figure 1. Figure 1 also shows simulated patterns of MX-1 and MC. Those patterns were calculated using RIETAN-FP software (Izumi and Momma, 2007), and crystal structures are taken from Graetsch and Topalović-Dierdorf (1996) and Hirose et al. (2005) for MX-1 (average structure) and MC, respectively. It is apparent from Figure 1 that the observed pattern can be well matched with the simulated pattern of MX-1. A peak near 22° is due to most intense peak of cristobalite, which was also observed by Raman spectroscopy. Two peaks at 24.5 and 32.3° cannot be indexed with the average structure of MX-1 or other phases. However, Graetsch and Flörke (1991) identified them as satellite reflections of MX-1. Therefore, the powdered sample now contains mostly MX-1 with minor cristobalite. MC is not clearly identified. Increased MX-1 in the powdered sample is most likely due to grinding as demonstrated by Hoffmann et al. (1983). Therefore, few fragments from the original pellet was used for the Raman measurement of synthetic MC.

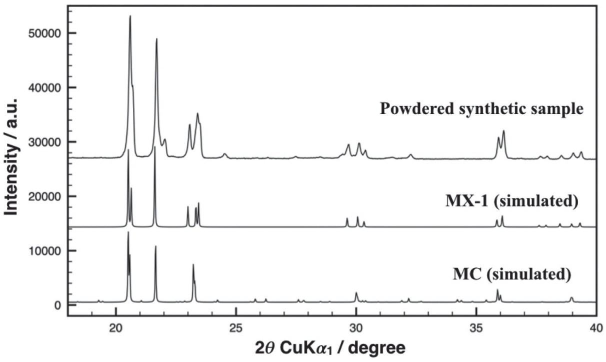

Figure 1. Powder X-ray diffraction pattern of the powdered synthetic 'MC sample'. Top, measured diffraction pattern; middle, simulated pattern of MX-1 (average structure); bottom., simulated pattern of MC. Each pattern is displaced vertically for clarity. A peak at around 22° is due to the most intense reflection of cristobalite, and two peaks at 24.5 and 32.3° are satellite reflections of MX-1 (Graetsch and Flörke, 1991).

For comparison, tridymite in Steinbach iron meteorite (IVA-an) was also measured. This meteorite contains silicate minerals, such as tridymite and orthopyroxene. Tridymite in this meteorite is MC and has been used in previous studies (e.g., De Dombal and Carpenter, 1993).

MX-1-rich sample was prepared using one of procedures given in Xiao et al. (1995). The synthetic MC sample (a large fragment) described above was heated at 400 °C for 1 h and then dropped into liquid nitrogen. The resultant sample contains both MX-1 and MC as identified by micro-Raman spectroscopy, and this result is consistent with that of Xiao et al. (1995).

For tridymite modification other than MC and MX-1, two natural samples of volcanic origin were measured. One is from Vechec, Vranov nad Topľou Co., Prešov Region, Slovakia. The crystals exhibit typical thin transparent hexagonal shapes of tridymite. For micro-Raman measurement, the single crystal fragments were measured. Several large crystals were ground, and the resultant powder sample was used for powder X-ray diffraction. Obtained powder X-ray diffraction pattern can be indexed as PO-10 modification (Graetsch and Flörke, 1991). Other tridymite is from Mt. Arci, Oristano Province, Sardinia, Italy. The tridymite crystals are rectangular in shape. The powder X-ray diffraction pattern of this sample is also well indexed as PO-10.

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 fixed to 80 mW, and the laser beam was focused to the samples using a long working distance 20× objective lens (Mitsutoyo M Plan NIR). Backscattered geometry was employed. In order to reject the Rayleigh scattering, two Ondax'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 as demonstrated in our previous studies (Kanzaki, 2018, 2019). The beam passed through the filters is introduced to a 500 mm monochromator (Acton Spectra Pro 500i) with 1200 g/mm grating, and the dispersed light was detected by a liquid nitrogen-cooled CCD detector (Princeton Instruments' PyLoN 400BR eXcelon). The reported spectra were typically obtained with one-minute exposure repeated for three times to have better S/N. Relative wavenumbers in reported spectra were calibrated against 10 Raman peaks of a synthetic coesite standard. The detailed calibration procedure is given in Kanzaki (2019). Reported peak positions are obtained by fitting Raman spectrum with Voigt profile

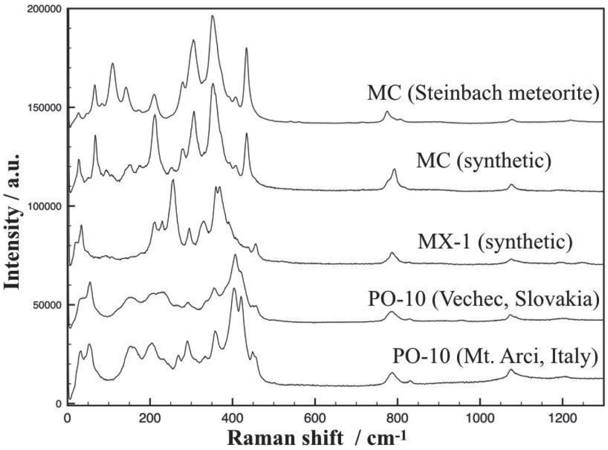

Figure 2. Unpolarized micro-Raman spectra of natural and synthetic tridymite modifications (MC, MX-1, and PO-10) at ambient conditions. Each spectrum is displaced vertically for clarity.

function using Fityk software (Wojdyr, 2010). Due to heavy overlaps, reported precision will be 1 cm^{-1}.

RESULTS AND DISCUSSION

Raman spectra of tridymite modifications

Unpolarized micro-Raman spectra of tridymite modifications are compiled in Figure 2. They represent typical spectrum for each sample. The spectrum of tridymite (MC) in Steinbach meteorite is shown in Figure 2 (top) and is essentially identical to that of our synthetic MC (original one, not powdered sample). Major Raman peak positions for both Steinbach meteorite and the synthetic MC are listed in Table 1. There are several additional small peaks in the synthetic MC as seen in Figure 2 (256 cm^{-1} for example), and they can be well explained by strong peaks of MX-1 (see below). Therefore, the synthetic MC contains small fraction of MX-1, but we could not observe isolated MX-1 grain, suggesting smaller grain size.

The peaks below 150 cm^{-1} are reported for the first time. The high frequency region ($\nu > 200$ cm^{-1}) of those spectra of MC is identical to the spectrum of MC reported by Hirose et al. (2005), confirming our identification. It should be noted that 213 Raman active modes are expected for MC from factor group analysis (Hirose et al., 2005). But observed Raman peaks are far less than that, apparently most peaks are heavily overlapped with others, and/or intensities are too low. Kihara et al. (2005) calculated vibrational Raman modes of MC using a valence force field model. No details were given for the low frequency modes of MC, but they showed the calculated Raman spectrum. There are three to four bands visible in the low frequency region of the calculated spectrum, but the correspondence with our spectrum is not apparent.

Table 1. Raman peak positions (cm^{-1}) of tridymite modifications at ambient conditions

MC synthetic	MC Steinbach	MX-1	PO-10 Vechec	PO-10 Mt. Arci
28	25	21	14	14
48	48	33		21
68	66	91	30	31
83	83	177	54	52
95		210	154	154
109	109	229	206	202
150	143	256	239	237
174	173	295	265	268
190	192	328	292	291
211	210	358		312
279	278	370	336	332
306	305	411	355	358
	331	438	407	403
352	351	456	421	422
361	368	788		448
394	393	828	455	458
408	408	1078		502
434	434	1197	787	788
	541	1248	828	829
	561		955	
	681		1073	1076
	714		1086	
778	774		1200	1200
787	787			
815	807			
1077	1077			
1220	1221			

Figure 2 also shows a Raman spectrum of MX-1 (quenched sample, not powdered MC). The peak positions of MX-1 are listed in Table 1. There are several unresolved peaks at around 425 cm^{-1} forming a higher frequency shoulder of the most intense band at around 370 cm^{-1}. We noted that one of strong peaks at 256 cm^{-1} is diagnostic feature for MX-1, as it does not overlap with the peaks of other phases.

We noted that two natural tridymite samples (PO-10) gave identical spectra. Two spectra are given in Figure 2. The spectrum at bottom (Mt. Arci) is typical Raman pattern for PO-10, commonly observed for two samples. In Figure 2, non-typical spectrum of Vechec is given to show possible variation of Raman spectrum for PO-10. The differences in the peak intensities between two spectra are due to difference in crystal orientation and are not due to the locality of the samples. The peak positions of those spectra are given in Table 1. Although the spectra look different for two spectra, peak positions are essentially same. We noted that the typical spectrum (bottom of Figure 2) is identical to that of ‘α-tridymite’ reported by Kingma and Hemley (1994). At moment, no Raman spectrum for PO-*n* with *n* other than 10 is known. We are currently trying to obtain other PO-*n* modifications to have Raman spectra of all tridymite modifications to further assist identification by Raman spectroscopy.

Identification of tridymite modifications from reported spectra in the literature

The Raman spectra of MC and supposed PO-10 were already reported by Hirose et al. (2005) and Kingma and Hemley (1994) as 'α-tridymite', respectively. Present study confirmed their identities. Additionally, the Raman spectrum of MX-1 is reported for the first time. Thus, now we can confidently identify tridymite modifications from the Raman spectra alone. In RRUFF database (Lafuente et al., 2015), three Raman spectra of tridymite are available (as of August 25, 2019). Two of them match well with our spectrum of MC. These tridymite samples (R090042 and R090063) are from Fukang pallasite and Mount Howe 88403 iron meteorite, respectively. Third Raman spectrum of tridymite (R040143) from Big Lue Mountain, Arizona matches well with our PO-10 spectra. This sample indeed has a pseudo-orthorhombic cell with c = 89.971 Å (n = 10), further confirming our identification. The low frequency region below 150 cm^{-1} is not available in the spectra of the RRUFF database for comparison.

Etchepare et al. (1978) reported a Raman spectrum of tridymite. No detail of the sample is given, but the spectrum resembles to that of our PO-10, suggesting their sample is PO-10. Their spectrum also has the low frequency region, and the peaks at 56, 100, and 152 cm^{-1} can be identified. Although the peaks corresponding to 56 and 152 cm^{-1} are also observed, the peak at 100 cm^{-1} is missing in our spectra.

Torre-Fdez et al. (2018) found tridymite from the Elephant Moraine (EET) 83227 polymict eucrite meteorite which is originated from 4 Vesta asteroid. Their observed Raman peaks (212, 307, 355, 435, and 793 cm^{-1}) match well with those of MC (Table 1). MC has been commonly detected in the meteorites but is rarely reported from terrestrial rocks (Kawai et al., 1978). Present study may help to readily identify previously unnoticed MC from terrestrial rocks.

We noticed that a Raman spectrum of tridymite from ALH84170 EH3 chondrite reported in Kimura (2002) is similar to our PO-10 spectrum (bottom spectrum of Fig. 2). Similar PO-10 identity was also noted for the Queen Alexandra Range (QUE) 93372 EH5 chondrite reported in Kimura et al. (2005). Recently 'orthorhombic tridymite' is also reported from Camel Donga eucrite (Oono et al., 2018). No Raman spectrum was reported. All known orthorhombic modifications of tridymite are high-temperature phases and are not quenchable to room temperature. But PO-n is metrically orthorhombic, so it is likely that 'orthorhombic tridymite' in Camel Dong eucrite could be PO-n, most likely PO-10. These findings are intriguing, because MC is exclusively reported for tridymite from the meteorites. Our compiled Raman spectra may help to find more PO-10 in meteorites in near future. The formation condition for PO-10 is not well understood. There are only a few reports which obtained PO-10 by heating natural MC (Kawai et al., 1978; Imamura and Matsumoto, 1980). The existence of PO-10 suggests that those meteorites experienced a specific thermal history, but apparently further experimental study is necessary.

An alternative interpretation for PO-10 in the meteorites will be a shock event. The density of PO-10 is slightly higher than those of MC and MX-1, so PO-10 might be stabilized at higher pressure. Yamaoka et al. (1979) and Nukui and Nakazawa (1980) observed a pressure-induced transition from MC to PO-10 at 0.5 GPa and room temperature. Therefore, PO-10 in those meteorites might be formed from original MC during a modest shock event. Apparently, further study is necessary to understand the formation conditions of PO-10 or PO-n in general. Although the identification of silica polymorphs (quartz, cristobalite, tridymite, and high-pressure polymorphs) in the meteorites has been used to infer their history (Kimura, 2002; Kimura et al., 2005), identification of 'tridymite modification' in the meteorites would provide further information of their thermal and pressure history.

Recently, tridymite was found in a drilled sample of laminated mudstone at Marias Pass in Gale crater, Mars by X-ray diffraction instrument onboard the Mars Science Laboratory (MSL) rover, 'Curiosity' (Morris et al., 2016). Observed powder X-ray diffraction pattern was refined using the Rietveld method, and monoclinic tridymite (= MC) is assumed along with other minerals. It is difficult to uniquely identify tridymite modification using the low-quality powder X-ray diffraction pattern. Even if it is indeed MC, the drilling likely resulted MX-1. If this tridymite was originally formed from a silicic volcanism like on the Earth as suggested by Morris et al. (2016), we would expect PO-n rather than MC. So, it is important to know which modification actually exists on Mars. A Mars rover mission with onboard Raman instrument would clarify this issue.

In summary, this study compiled the Raman spectra of three tridymite modifications (MC, MX-1, and PO-10) at ambient conditions. Although the Raman spectra of PO-10 and MC were already known, they are presented in different nomenclatures, which made identification by micro-Raman spectroscopy inconvenient. In this letter, in addition to two modifications, the Raman spectrum of MX-1 is presented for the first time. We hope that the compiled spectra with proper nomenclature are useful for identification of tridymite modifications for both synthetic materials and natural rocks, especially for the extraterrestrial rocks.

ACKNOWLEDGMENTS

The author thanks to two anonymous reviewers for constructive comments and suggestions. This study was supported by Grant-in-Aid for Scientific Research (No. JP16H04076) by JSPS and regular Operational Expenses Grant from Okayama University.

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Manuscript received April 14, 2019
Manuscript accepted August 22, 2019

Manuscript handled by Keiji Shinoda