

Raman spectroscopic study of microcrystalline silica

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ABSTRACT

Samples of microcrystalline silica have been examined with Raman spectroscopy to investigate the vibrational and structural characteristics of the component phases, including their spatial distribution. Using microspectroscopic techniques, we found variable amounts of a novel silica polymorph (“moganite”) in samples of chalcedony, chert, and flint and have obtained the Raman spectrum of the pure phase. We identified 19 of the 27 Raman-active vibrational modes predicted by factor group analysis assuming the monoclinic structure previously reported for “moganite.” Notably, a strong band is found at 501 cm^{-1} , which may be correlated with the four-membered rings of SiO_4 tetrahedra in the refined structure. Comparison with Raman spectra of other tetrahedrally coordinated minerals confirmed that this new phase is a structurally distinct polymorph of silica.

INTRODUCTION

Microcrystalline quartz has traditionally been divided into two main types on the basis of crystallite habit, as determined by light optical microscopy (Klein and Hurlbut, 1985). Granular varieties include chert and flint, whereas fibrous varieties of microcrystalline quartz are collectively called chalcedony. Chalcedony typically is length-fast with the *c* axis perpendicular to the long axis of the fibers. Although most chalcedony grows in this orientation, reports of length-slow chalcedony are numerous (e.g., Folk and Pittman, 1971). The term “quartzine” was used for this peculiar chalcedony if the *c* axis was found to be parallel with the fibers, and “lutecite” was the name given to the samples with *c* at an angle of approximately 30° to the long axis of the fibers (Michel-Lévy and Munier-Chalmas, 1890, 1892).

In 1976, Flörke et al. found that the X-ray diffraction patterns produced by some specimens of length-slow chalcedony could not be indexed as quartz, revealing the presence of a new silica polymorph. Flörke et al. (1984a) proposed the name “moganite,” and Miehe et al. (1984) suggested a structure of alternating (101) slabs of right- and left-handed α quartz, twinned periodically at the unit-cell scale according to the Brazil law. This structure was later confirmed by neutron and X-ray diffraction, and it was refined using space group $I2/a$ (Miehe et al., 1984; Miehe and Graetsch, 1992). Recent X-ray studies have shown that length-slow varieties of microcrystalline quartz, previously labeled “lutecite,” actually contain high concentrations of “moganite” (Godovikov et al., 1991a; Heaney and Post, 1992). In their X-ray diffraction and electron microscopy study of 150 samples of microcrystalline silica from around the world (including both fi-

brous and granular varieties), Heaney and Post (1992) surprisingly detected at least some “moganite” in virtually every sample. At this time, the new phase has not been accepted by the Commission on New Minerals and Mineral Names of the International Mineralogical Association as a distinct mineral species (see *American Mineralogist* New Mineral Names abstracts: Flörke et al., 1976b, 1984b; Miehe et al., 1988b; and Godovikov et al., 1991b). For the purpose of our discussions, however, we will refer to this monoclinic polymorph of microcrystalline silica as moganite.

Micro-Raman spectroscopy provides a unique method for characterizing the crystal chemical properties of heterogeneous samples. The spatial resolution and ease of data collection of this technique are particularly useful for rapid identification of minerals in thin section (Mao et al., 1987). Because of the sensitivity of vibrational frequencies and scattering intensities to slight differences in crystal structures (e.g., bond angles, site symmetries, lattice vibrations), such vibrational spectroscopic methods are also well suited for distinguishing among mineral polymorphs. In this paper, we report the Raman spectrum of pure moganite and demonstrate that it is distinct from spectra of other tetrahedrally coordinated silica polymorphs.

EXPERIMENTAL

All Raman spectra were measured with a Dilor XY spectrograph equipped with a conventional optical microscope, as described elsewhere (Hemley, 1987). The 514.5-nm line from a Spectra-Physics 165 Ar ion laser was directed at an angle of 135° relative to the axis of the microscope, thus eliminating strong spurious scattering

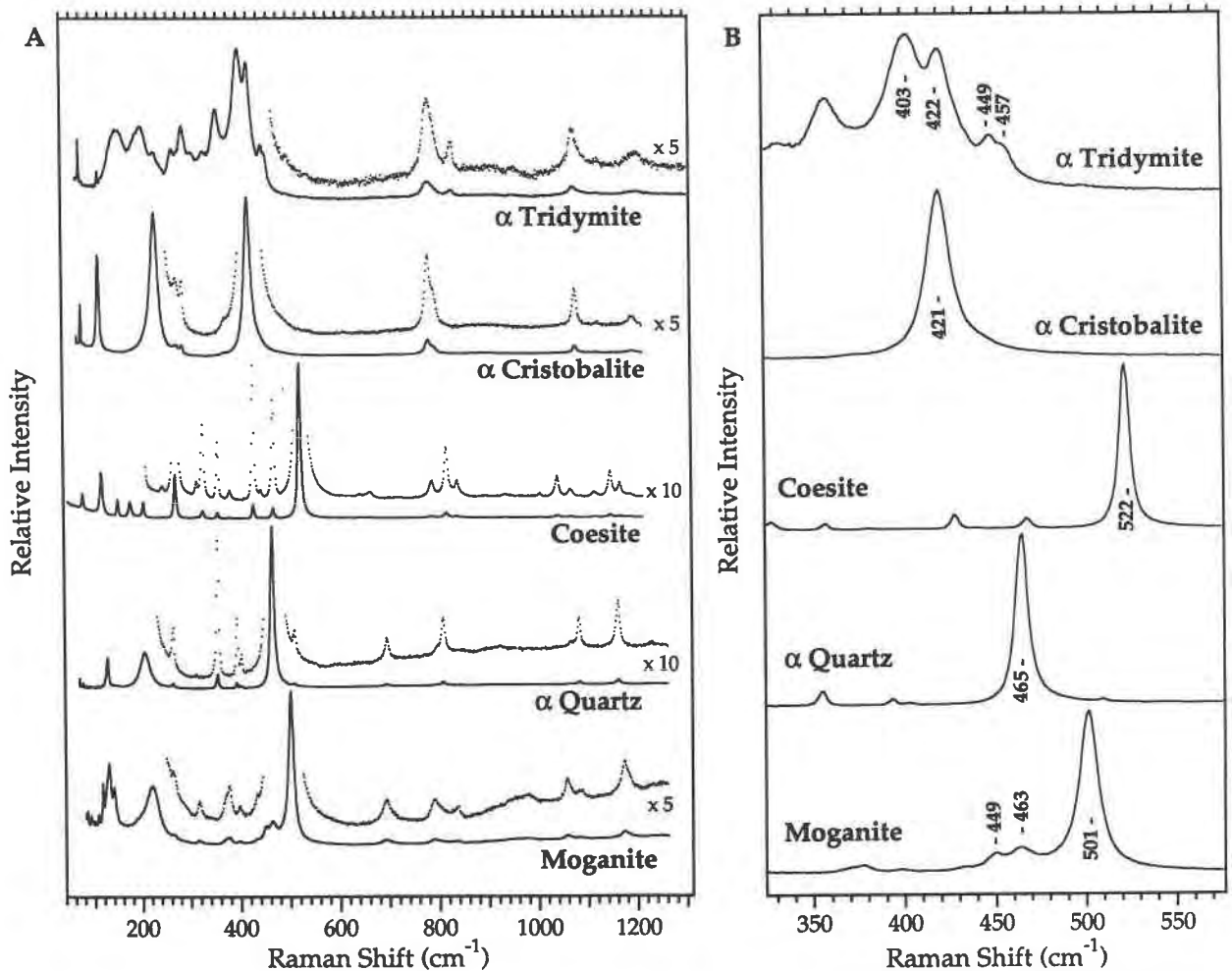


Fig. 1. (A) Raman spectra of tetrahedrally coordinated silica polymorphs. (B) Raman peaks in the range 380–550 cm^{-1} . The labeled peaks correspond to the symmetric Si-O-Si stretching-bending modes.

at low frequencies. Spectra were measured with an EG & G CCD (charged-coupled device) detector. With this system, sample areas as small as $\sim 1 \mu\text{m}$ can be analyzed. All measurements were taken at room temperature ($297 \pm 3 \text{ K}$).

The reference moganite sample is from the type locality on Gran Canaria. These samples are nodular and vary in character from a massive gray chert at the center to a white powdery material at the edges. This white powder has been reported to have high concentrations of moganite, on the basis of bulk diffraction and infrared measurements (Heaney and Post, 1992; Miede and Graetsch, 1992). Raman spectra of other silica polymorphs were measured for comparison with that of moganite. These included natural samples of α tridymite and α quartz (single-crystal and microcrystalline), as well as synthetic samples of α cristobalite and coesite.

RESULTS AND DISCUSSION

Moganite spectrum

The Raman spectrum of moganite, measured from selected areas of the white powder of the Gran Canaria

sample, is shown in Figures 1 and 2. Micro-Raman measurements in the range of 50–1250 cm^{-1} reveal sharp bands with frequencies and relative intensities that are reproducible throughout the entire sample. The most intense peaks are centered at 501, 220, and 129 cm^{-1} , whereas groups of less intense bands are found in the ranges 250–480, 650–850, and 1040–1210 cm^{-1} . The asymmetric shapes of the less intense bands and of the 220- cm^{-1} peak probably arise from overlap of modes. The region at 850–1040 cm^{-1} of the moganite spectrum is characterized by broad features resembling the spectral characteristics of a glassy material. Fitting the asymmetric bands as single peaks, we identified 19 distinct bands in the moganite spectrum. The positions of these peaks and the two broad bands between 850 and 1040 cm^{-1} are listed in Table 1.

Raman spectra of other silica polymorphs are shown with the spectrum of moganite in Figure 1A. These spectra share common features that can be correlated to similar motions of Si and O atoms within the framework structures of these tetrahedrally coordinated phases (Etchepare et al., 1974; McMillan and Hess, 1990). Weak

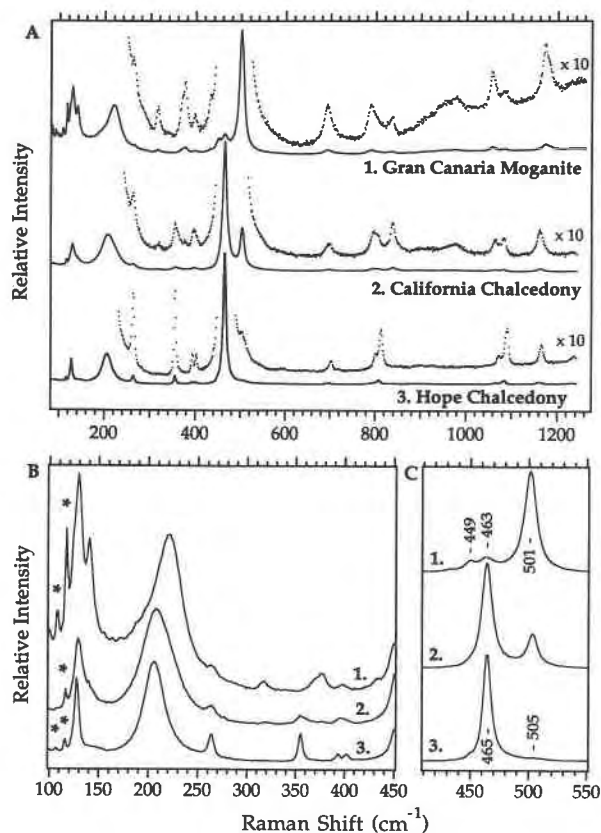


Fig. 2. Raman spectra of three representative microcrystalline silica samples, including (1) moganite from Gran Canaria (NMNH no. 168357), (2) a mixed-phase chalcedony from near Johannesburg, California (NMNH no. 79546), and (3) pure quartz chalcedony from Hope, Arizona (NMNH no. 113103). Low- and mid-frequency ranges of A are expanded in B and C. Peaks labeled with asterisks are from the laser excitation of air vibrations or laser plasma lines and do not correspond to moganite or quartz modes.

peaks above 600 cm^{-1} are correlated to Si-O stretching modes, whereas peaks below about 400 cm^{-1} originate from torsional vibrations and O-Si-O bending modes. The strongest bands in these spectra, which occur in the range of $400\text{--}530\text{ cm}^{-1}$ (Fig. 1B), involve motions of O in Si-O-Si symmetric stretching-bending modes. The Raman frequencies of these modes are found to correlate with the number of tetrahedra that form rings within framework silicate structures (Table 2) (e.g., Sharma et al., 1981). For example, it has been demonstrated that structures with four-membered SiO_4 rings (such as coesite and feldspars) have $\nu_s(\text{T-O-T})$ modes above 500 cm^{-1} , whereas structures with six-membered rings (such as quartz, cristobalite, tridymite, and nepheline) have $\nu_s(\text{T-O-T})$ between 380 and 480 cm^{-1} (Matson et al., 1986). These observations have been important for assigning spectral features associated with the distribution of rings in silicate glasses (e.g., McMillan et al., 1984; Sharma et al., 1984; Hemley et al., 1986). The position of the 501-cm^{-1} mode in the moganite spectrum is consistent with this proposed model, since the structure of moganite consists

TABLE 1. Raman-active phonon frequencies of moganite and α quartz

Moganite*	α quartz	
ν_i (cm^{-1})	ν_i (cm^{-1})**	Mode symmetry
129	128	$E_{(\text{LO}+\text{TO})}$
141		
220	206	A_1
265	265	$E_{(\text{LO}+\text{TO})}$
317		
	355	A_1
370		
377		
398	394	$E_{(\text{TO})}$
	401	$E_{(\text{LO})}$
432		
449	450	$E_{(\text{TO})}$
463	464	A_1
501		
	511	$E_{(\text{LO})}$
693	696	$E_{(\text{LO}+\text{TO})}$
792		
	796	$E_{(\text{TO})}$
	808	$E_{(\text{LO})}$
833		
(950)		
(978)		
1058		
	1069	$E_{(\text{TO})}$
1084	1085	A_1
1171	1162	$E_{(\text{LO}+\text{TO})}$
1177		
	1230	$E_{(\text{LO})}$

* Moganite from Gran Canaria (U.S. National Museum of Natural History no. 168357); spectrum in Figs. 1 and 2.

** Minor frequency differences ($1\text{--}2\text{ cm}^{-1}$) between these values (Hemley, 1987) and peak positions for some of the bands in Figs. 1 and 2 reflect small temperature differences in the measurements.

of four-membered rings of corner-sharing SiO_4 tetrahedra. In addition to the strong peak at 501 cm^{-1} , there are also weaker peaks in the moganite Raman spectrum at 463 and 449 cm^{-1} , which may be loosely correlated to the additional six- and eight-membered rings also present in the moganite structure.

The irreducible representation for the optical modes of moganite can be calculated by factor group analysis (Fateley et al., 1972), if one assumes the monoclinic structure with space group $I2/a$ ($=C2/c$) (Miehe et al., 1988a): $\Gamma_{\text{op}} = 13A_g + 12A_u + 14B_g + 12B_u$ where the A_g and B_g modes are Raman active, and the A_u and B_u modes are infrared active. Of the Raman-active modes, 12 ($6A_g + 6B_g$) originate from Si-O stretching within the two unique SiO_4 tetrahedra (Si at 4e and 8f Wyckoff sites) of the structure proposed by Miehe et al. (1988a). Our observation of 19 bands in the Raman spectrum (Table 1), of which seven of the identified peaks are in the region where the stretching modes are expected ($600\text{--}1200\text{ cm}^{-1}$), is consistent with the reported structure. If the proposed structure is correct and the observed bands represent fundamental transitions (i.e., $\nu = 1 \rightarrow 0$), eight modes are not yet identified. The failure to observe all the moganite Raman-active modes may be the result of overlapping peaks or weak scattering.

It is well known that twinning is very common in microcrystalline quartz. The structure of moganite can be

TABLE 2. Correlation of Raman Si-O-Si symmetric stretching-bending modes with silicate ring structures

SiO ₂ polymorph	$\nu_s(\text{Si-O-Si})$ (cm ⁻¹) ^A	No. of SiO ₄ in rings ^B	Density (g/cm ³)
α tridymite ^C	403, 422, 449, 457	6	2.281 ^C
α cristobalite ^D	421	6	2.335
Moganite	449, 463, 501	8, 6, 4	2.55 ^E
α quartz ^F	465	6	2.655
Coesite ^G	522	4	2.912

^A Frequencies from spectra in Fig. 1.

^B Zoltai (1960).

^C Single crystals in rhyolite from Plumas County, California (NMNH no. 121899); density calculated from refined structural parameters (Konert and Appleman, 1978).

^D Sample synthesized by B.O. Mysen; frequencies consistent with previously measured values (Bates, 1972).

^E Miehe and Graetsch (1992).

^F Single-crystal quartz from Hot Springs, Arkansas (NMNH no. R17701).

^G Sample synthesized by Y. Fei; frequencies consistent with other Raman studies (Sharma et al., 1981; Hemley, 1987).

derived from the structure of the (101) composition plane of Brazil twins (McLaren and Pitkethly, 1982). In a sample having a high concentration of Brazil twins, vibrations from these defect areas may be detected by spectroscopic methods. A random distribution of defects would give rise to general broadening of bands; the shape of the spectrum would approach the vibrational density of states because of the breakdown of $k = 0$ selection rules for the perfect crystal (e.g., Cardona, 1983). In addition, broadening could also arise from local strains associated with the twin-boundary defects. We find that the microcrystalline quartz samples that were previously demonstrated by X-ray diffraction to contain the new phase (moganite) have sharp peaks in their Raman spectra, with characteristic frequencies that do not correspond to quartz modes. These observations indicate that the distinct non-quartz Raman vibrations originate from a well-crystallized phase; the spectrum is not that expected for microcrystalline quartz containing a high density of random defects (e.g., broadened bands at quartz positions). Our results support previous diffraction studies (Miehe et al., 1988a; Miehe and Graetsch, 1992), which indicate that moganite is a unique structural polymorph of SiO₂.

Comparison with quartz spectrum

Because α quartz and moganite share many of the same structural elements, it is not surprising that the moganite vibrational spectrum most closely resembles that of α quartz, compared with the other silica polymorphs tested (Fig. 1A; see also Miehe and Graetsch, 1992). Quartz is seen to have a broad low-frequency Raman band at 206 cm⁻¹, which is not apparent in coesite, tridymite, or cristobalite. The broadness of this band, which is also observed in the Raman spectrum of α berlinite (AlPO₄, isostructural with α quartz), has been attributed to the anharmonic coupling of an *A*₁ phonon with a two-phonon (acoustic) mode (Jayaraman et al., 1987). Moganite has a broad peak at 220 cm⁻¹ that probably has a similar

origin. The asymmetry of this peak may arise from overlap with an additional lower frequency mode in the spectrum.

Despite the similarity in the character of the quartz and moganite vibrational spectra, there exists a significant variation in the positions of the similarly shaped peaks for the two phases (Table 1). The most striking difference between the Raman spectra of quartz and moganite is the position of the strongest peak, which differs by 36 cm⁻¹. The 463-cm⁻¹ peak in the moganite spectrum is very close to the strong quartz *A*₁ peak at 465 cm⁻¹ (Fig. 1B). If this band originates from a minor amount of quartz in the probed sample area, other quartz peaks should appear in the Gran Canaria spectrum. Because of the notable absence of additional quartz peaks (especially the sharp quartz *A*₁ mode at 355 cm⁻¹) in this spectrum, however, we conclude that the 463-cm⁻¹ peak originates from moganite and not from quartz. Thus, the ratio of quartz to moganite within a single probe area can be qualitatively estimated from the relative intensities of the strong quartz (465-cm⁻¹) and moganite (501-cm⁻¹) peaks in the Raman spectrum. It would be useful to calibrate the relative intensities of these strong quartz and moganite Raman peaks to the moganite concentration as determined by the refinement of diffraction patterns (as in Heaney and Post, 1992).

Moganite distribution in microcrystalline silica

A variety of microcrystalline quartz samples (including chert, flint, chalcedony, and "lutecite") from around the world were selected for Raman characterization. These measurements revealed that there is no difference in the position or width of quartz vibrational modes in macrocrystalline and microcrystalline samples. In agreement with the results of the exhaustive X-ray study of Heaney and Post (1992), we found evidence of moganite in portions of all microcrystalline varieties. We compare the Raman spectra from three of our microcrystalline samples in Figure 2. Whereas the Gran Canaria moganite and Hope chalcedony spectra represent the end-member cases (i.e., pure moganite and pure quartz), the spectrum measured from the chalcedony from California is representative of the majority of the analyzed microcrystalline samples. These spectra show evidence for the intergrowth of two silica polymorphs. Utilizing the microprobing characteristic of the present Raman technique, we found that polished or freshly broken surfaces of most chert, flint, and massive chalcedony samples are homogeneous (on a probe scale at 1 μ m) with respect to their moganite concentrations. However, the quartz to moganite ratio varies among these individual specimens. In samples showing macroscopic variations in color or texture, such as agates or banded cherts, this ratio can vary significantly across a single specimen. For example, the sample from Hope, Arizona, varied from a white opaque chalcedony (probe area of the pure quartz spectrum in Fig. 2) to a gray translucent variety having a Raman spectrum very similar to that shown in Figure 2 for the California

chalcedony. Similarly, we found a high variability in moganite concentration between the massive chert core and the white powder rind of the Gran Canaria sample. Whereas this white material was found by Rietveld refinement from X-ray powder diffraction patterns to consist of approximately 80% moganite (Heaney and Post, 1992), we were able to find regions of the powder rind that yielded a pure moganite spectrum using the micro-Raman technique. Such in-situ information about sample heterogeneity, unattainable with conventional optical microscopy or X-ray diffraction techniques, may be useful for interpretation of the conditions and mechanism of moganite formation.

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