

Temperature dependence of Raman shifts and line widths for Q⁰ and Q² crystals of silicates, phosphates, and sulfates

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ABSTRACT

The temperature dependence of Raman shifts and line widths (full-width at half maxima or FWHM) for the A₁ symmetric stretch of TO₄ (T = Si, P, S) have been analyzed for nine alkali and alkaline earth silicates, phosphates, and sulfates. In crystalline silicates, the Q⁰ and Q² species Raman shifts decrease with temperature, whereas FWHM increase. The strikingly similar behavior of Q⁰ and Q² in silicates and Q⁰ in phosphates makes it possible to estimate to within ± 4 cm⁻¹ Raman shifts up to ~ 1000 K. Similarly systematic increases in FWHM with temperature can be estimated to within ± 5 cm⁻¹ up to ~ 1400 K. The type of element centering TO₄ (i.e., Si, P, or S) has no appreciable effect on the temperature dependence of Raman shifts or line widths; the local environment of the Q⁰ and Q² tetrahedra is the primary determinant of the temperature dependence. The type of cation in the first coordination sphere of the tetrahedron may have a secondary effect by affecting Heisenberg lifetimes of Raman virtual states.

Previous theoretical considerations have been modified to include the effect of the Heisenberg (or natural) lifetime on Raman FWHM. This contribution is required to explain the anomalous FWHM of Li₂SiO₃ relative to the FWHM of isostructural Na₂SiO₃ and the large Li₂SO₄ and Li₃PO₄ FWHM (relative to Ba and Sr phosphates). The theoretically based expressions dictate a necessary, simple relationship among temperature, Raman shift, and FWHM. The relationship is developed and it allows, with one measurement of Raman shift and FWHM (e.g., measured at 298 K), prediction of Raman shifts and FWHM of Q⁰ and Q² crystals to within 5 cm⁻¹ up to ~ 1500 K. The properties of the TO₄ moiety (T = Si, P, S) are mostly responsible for the striking regularity of Raman shifts and FWHM, although alkali and alkaline earth cations affect to varying extent Heisenberg lifetimes, hence FWHM.

Keywords: Raman shifts in crystals, Raman line widths in crystals, temperature dependence of Raman shifts, temperature dependence of Raman line widths

INTRODUCTION

The Raman spectra of crystals in the region 800–1200 cm⁻¹ (i.e., the A₁ TO₄ symmetric stretching mode) commonly display a prominent, narrow Lorentzian peak with a well-defined position at room temperature. The best documented data on crystalline silicate Raman shifts and line widths are provided by Richet et al. (1996, 1998), who present data for Li₂SiO₃, Na₂SiO₃, CaSiO₃, and Ca_{0.5}Mg_{0.5}SiO₃ metasilicate crystals from 298 K to their melting points. These crystals have different structures but all consist of Si tetrahedra where each Si center is bonded to two bridging oxygen atoms (BO or Si-O-Si) and two non-bridging oxygen atoms (NBO or e.g., Si-O-Na). These are referred to as Q² species (Q indicates a Si center and the superscript indicates the number of BO atoms per tetrahedron). In addition, numerous papers provide reasonably well-characterized data (in graphical form) on Raman shifts and line widths for crystals containing Q⁰ species, including silicates, phosphates, and sulfates (Cazzanelli and Frech 1984; Popovic et al. 2003; Kolesev and Geiger 2004;

Zhai et al. 2011, 2014). These data have been inspected and where feasible Raman shifts and line widths have been evaluated. After studying the data we arrive at two major questions concerning the spectra of crystals. First, do Raman shifts and FWHM of the Q species describe similar trends as a function of temperature or do they describe unique trends in temperature, each trend being dependent on crystal structure and composition? Second, can the temperature dependence of the Raman shifts and FWHM be explained using existing theories? Our goals are to answer these questions. There has been no comprehensive study relating these two temperature-dependent spectral properties for silicates, phosphates or sulfates and few on other materials (e.g., Klemens 1966; Liu et al. 2000). Our most important observation is that the temperature dependence of Raman shifts and FWHM predicted from theory is observed for experimental data. Moreover, Raman shifts or FWHM can be reasonably estimated at high temperature provided the temperature dependence of the other is known.

Richet et al. (1996, 1998) demonstrated that the Raman line widths and peak shapes change within the premelting regions of the Q² crystals Na₂SiO₃, Li₂SiO₃, and CaSiO₃, and Nesbitt et al. (2017a) interpreted the changes in these spectra to result from

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introduction of a Q^3 band to the Raman spectra. The interpretation would have been tenuous had not Richet et al. (1998, 1996) demonstrated that the Raman shift and line widths of the Q^2 band changed systematically with temperature. These systematics now can be calculated by theoretical means here outlined allowing prediction of Raman shifts and line widths at temperatures where experimental studies are difficult. An important aspect of the theory is the quantification of “constants” of the equations utilized. These constants relate to fundamental properties of crystals, glasses, and melts, such as thermal expansion, the Grüneisen parameter (McMillan and Wolfe 1995), and the relative importance of harmonic and anharmonic contributions to Raman shifts and line widths. Thus Raman spectral measurements can be related directly to other fundamental properties of crystals, glasses, and melts.

Theoretical aspects developed by Balkanski et al. (1983) relate directly to the temperature dependence of Raman shifts and line widths. The line widths of some crystals are appreciably broader than others at ambient temperature, and the line widths of glasses are still broader than those of crystals for equivalent composition (Richet et al. 1996, 1998). As proposed here, broad Raman bands are the result of short Heisenberg lifetimes of Raman virtual states (see also Bancroft et al. 2018). The theory of Balkanski et al. (1983) has been expanded to include Heisenberg lifetimes. In addition, Raman shifts are dependent on thermal expansion and the Grüneisen parameter (McMillan and Wolfe 1995), and the theory may be used to gain insight into these parameters for crystals, glasses, and melts over a wide range of temperature. An understanding of these aspects begins with a reasonable theory such as that of Balkanski et al. (1983). Here we demonstrate that their theory, modified to include Heisenberg (natural) lifetimes, may be used to address these aspects.

SUMMARY OF THEORY

Several papers discuss theoretical aspects of temperature dependences of Raman shifts and FWHM of elemental solids such as silicon and diamond, and of alloys (e.g., Klemens 1966; Hart et al. 1970; Balkanski et al. 1983; Menéndez and Cardona 1984; Burke and Herman 1993; McMillan and Wolfe 1995; Cui et al. 1998; Liu et al. 2000). Theoretical considerations of temperature dependence begin with the classical anharmonic oscillator where the potential energy (V_s) is described by an expansion in “ x ”, which is the displacement of the oscillator from its equilibrium position (e.g., Hart et al. 1970):

$$V_s = ex^2 + fx^3 + gx^4 \quad (1)$$

where e , f , and g are constants. The quadratic term represents the potential energy associated with a harmonic oscillator. The cubic term gives rise to thermal expansion and is partially responsible for the temperature dependence of Raman shifts and FWHM of Raman spectra (e.g., Hart et al. 1970; Balkanski et al. 1983). The quartic term reflects large amplitude vibrational weakening. In the anharmonic approximation, the fundamental Raman shift (ω^*) or alternatively the zone-center unperturbed frequency (Liu et al. 2000) consists of a real and an imaginary part. Both parts are temperature dependent with the real part, the Raman shift, decreasing in frequency with temperature and

the imaginary part, the line width, increasing (Liu et al. 2000).

The equations that follow relate to zone centers of a crystal (Balkanski et al. 1983; Nishidate and Sato 1992; Burke and Herman 1993; Sato and Asari 1995; Cui et al. 1998; Liu et al. 1999, 2000; Moura et al. 2016). From the treatment of Balkanski et al. (1983) the equation for the temperature dependence of the Raman shift at temperature $[\Omega(T)]$ is:

$$\Omega(T) = \omega^* + C[1 + 2/(e^x - 1)] + D[1 + 3/(e^y - 1) + 3/(e^y - 1)^2] \quad (2)$$

C and D are constants and include the coefficient of thermal expansion and the Grüneisen parameter (McMillan and Wolfe 1995). The constant ω^* is the fundamental (or Einstein) frequency of the Raman oscillator at absolute zero. Also, $x = \hbar\omega^*/2kT$ and $y = \hbar\omega^*/3kT$, where h is Planck's constant, k is Boltzmann constant, and $\hbar\omega^*/k$ is the Einstein temperature (θ_E) for the Raman oscillator. The terms $2/(e^x - 1)$ and $3/(e^y - 1)$ are closely related to the average energy of the Raman oscillator (ϵ_R) at thermal equilibrium [i.e., $\epsilon_R = \hbar\omega^*/(e^{\hbar\omega^*/kT} - 1)$, Omar 1975, p. 76–77]. Expansion of Equation 2 and collection of constants yields:

$$\Omega(T) = \Omega^* + C[2/(e^x - 1)] + D[3/(e^y - 1) + 3/(e^y - 1)^2] \quad (3)$$

where Ω^* is the Raman shift at absolute zero and is equal to $\omega^* + C + D$; it is the Raman shift in the “harmonic limit” (i.e., arises from the quadratic term of Eq. 1). As shown subsequently, the numerical values for C and D are less than 10, whereas values for ω^* are very large so that $\Omega^* \sim \omega^*$ (e.g., $\omega^* \sim 950\text{--}1000\text{ cm}^{-1}$ for the Q^2 symmetric stretch in chain silicates). The second and third terms on the right-hand side of Equation 3 are the cubic and quartic contributions that give rise to the non-linear temperature dependence of Raman shifts (Ω). Balkanski et al. (1983) also provided an equation for the temperature dependence of FWHM:

$$\text{FWHM}(T) = A[1 + 2/(e^x - 1)] + B[1 + 3/(e^y - 1) + 3/(e^y - 1)^2] \quad (4)$$

where $\text{FWHM}(T)$ is the line width at temperature T and A and B are constants. Other terms are as for Equation 2. Expansion of the equation and collection of the constants yields:

$$\text{FWHM}(T) = \text{FWHM}^* + A[2/(e^x - 1)] + B[3/(e^y - 1) + 3/(e^y - 1)^2] \quad (5)$$

where FWHM^* is the line width at absolute zero and is equal to $A + B$ (e.g., Liu et al. 2000, their Eq. 3). Balkanski et al. (1983) did not consider the lifetime effect of the Raman virtual state (excited or intermediate state) and it must be included if their treatment is to apply to phases whose natural (or Heisenberg) lifetimes are short. The Heisenberg lifetime (FWHM^H) is given by the Heisenberg uncertainty principle (e.g., Adamson 1973, p. 742):

$$\text{FWHM}^H = k/t_{1/2} \quad (6)$$

where k is a constant and $t_{1/2}$ is the half-life of the Raman virtual state. The shorter the lifetime of the virtual state (i.e., the smaller

the value of $t_{1/2}$) the greater the FWHM of the Raman line. Virtual states with long lifetimes yield effectively a constant, minimum line width (FWHM*). For short lifetimes $\text{FWHM}^H > \text{FWHM}^*$ so that:

$$\text{FWHM}^H = \text{FWHM}^* + \Delta\text{FWHM}^H \quad (7)$$

where ΔFWHM^H is the difference between FWHM^H and FWHM^* . The corrected form of Equation 5 is:

$$\text{FWHM}(T) = \text{FWHM}^H + A[2/(e^x - 1)] + B[3/(e^y - 1) + 3/(e^y - 1)^2] \quad (8a)$$

or

$$\text{FWHM}(T) = \text{FWHM}^* + \Delta\text{FWHM}^H + A[2/(e^x - 1)] + B[3/(e^y - 1) + 3/(e^y - 1)^2] \quad (8b)$$

where FWHM^* and ΔFWHM^H are constants for a given crystal. With our present state of understanding, the constants ω^* , A, B, C, and D must be evaluated from experimental data, although ω^* can be reasonably well estimated from the Raman shift of a Q species. The constants are treated subsequently as fit parameters and their numerical values are evaluated by fitting Equations 2 and 8a to data over appropriate temperature ranges.

Only Liu et al. (2000) report a direct relationship between Raman shifts and FWHM (for diamond) as a function of temperature. The circumstance is surprising because the cubic and quartic terms of Equations 2, 4, or 8 are the same (coefficients excepted). The data collected here provide an opportunity to test Equations 2, 4, or 8, and to investigate the relationship between Raman shift and FWHM as a function of temperature. Our findings also allow assessment of the effects of crystallographic properties and long-range electrostatic (cation-SiO₄) interactions on the numeric values of constants incorporated into the equations.

Our approach is useful because the temperature dependence of the FWHM and Raman shifts generally have been unsuccessful where evaluated from first principles by calculating the phonon dispersion curves across the Brillouin zone of crystals, using site potential energies that include cubic and quartic terms (MgF₂ = Nishidate and Sato 1992; α -GaPO₄ = Nakamura et al. 1990; SnO₂ = Sato and Asari 1995; PbMoO₄ = Sinagawa et al. 2000; PbWO₄ = Suda et al. 2014; β -(AlGa)₂O₃ thin films = Wang et al. 2016; β -Ag₅MoO₄ = Moura et al. 2016). The calculated phonon dispersion curves give an estimate of FWHM at a given temperature but as shown for the symmetric Mg-F stretch of MgF₂, good agreement with the experimental FWHM generally cannot be obtained (e.g., Nishidate and Sato 1992). The exception is PbMoO₄ (Sinagawa et al. 2000) where the temperature dependence of the shifts and FWHM were successfully calculated from first principles.

DATA SOURCES AND ERRORS

Raman shifts and FWHM from the literature

All Raman shifts and FWHM in this paper come from previously published spectra. Richet et al. (1996, 1998) tabulate values for crystalline Na₂SiO₃, Li₂SiO₃, CaSiO₃, and Ca_{0.5}Mg_{0.5}SiO₃; associated errors probably are less than $\pm 2 \text{ cm}^{-1}$ for Raman shifts

and FWHM. We rely heavily on these data. Some results are derived from Raman shifts and FWHM of published, large-scale figures and the data have been accurately extracted by scanning and digitizing the plots (Kolesev and Geiger 2004; Popovic et al. 2003; Cazzanelli and Frech 1984). Raman shifts or FWHM from these plots have associated errors of about $\pm 2 \text{ cm}^{-1}$. For the phosphate crystals, Sr₃(PO₄)₂ and Ba₃(PO₄)₂ (Zhai et al. 2014), the FWHM have been extracted with an accuracy of about $\pm 1 \text{ cm}^{-1}$. Unfortunately, Raman shifts for the two crystals cannot be utilized because they could not be accurately extracted from the small-scale plots. In a few cases, Raman shifts and FWHM at 298 and 1200 K were estimated from the published spectra (Voronko et al. 2015; You et al. 2001; Sadykov 2004), and associated errors are ± 3 – 5 cm^{-1} .

FWHM: Instrumental limits

Some crystals yield very narrow FWHM. For calcite (CaCO₃), the A_{1g} symmetric CO₃ stretch at 1086 cm⁻¹ has a FWHM of $\sim 0.5 \text{ cm}^{-1}$ at $< 50 \text{ K}$ and $\sim 1.5 \text{ cm}^{-1}$ at 300 K (Park 1967). Similarly, the FWHM of crystalline SiF₄ is $\sim 1 \text{ cm}^{-1}$ at 77 K (Bernstein and Meredith 1977) and is much narrower than any of the TO₄ symmetric stretches at 298 K. Raman spectroscopy therefore is capable of exceptionally high resolution and it must be concluded that FWHM of the TO₄ symmetric stretch observed for silicates, phosphates and sulfates are *not* instrumental in origin; the instrumental line width in all of these studies is less than 2 cm^{-1} .

INTERPRETATION OF RESULTS

Line shape and line widths of silicates

Individual Raman bands display fully Lorentzian lineshapes in the absence of other contributions (Loudon 1963; Efimov 1999). The major band of an α -cristobalite spectrum (Fig. 1a) and other SiO₂ polymorphs, (Fig. 1b) are narrow near the band maximum but are distinctly flared toward the band extremities. These are properties characteristic of Lorentzian peaks. A 98% Gaussian Voigt peak (2% Lorentzian) has been fit to the upper portion of the low-frequency side of the band in Figure 1a. Although the upper portion of the peak is well fit, the flared extremity on the low-frequency side is poorly fit. A second, 98% Lorentzian Voigt peak (2% Gaussian) was fit in precisely the same manner. The major difference in the two fits is that the (mostly) Lorentzian peak fits well the flared portion of the band between ~ 410 – 350 cm^{-1} ; the α -cristobalite band is mostly Lorentzian in shape. There is, however, an additional contribution to the band that leads to asymmetry on the high-frequency side of the band.

Raman shifts and FWHM for numerous crystalline silicates are summarized in Table 1. The silicate spectra usually consist of a prominent, narrow Lorentzian band with FWHM between ~ 4 – 13 cm^{-1} at 298 K (Richet et al. 1996, 1998). The bands arise from the A₁ symmetric SiO₄ stretch in all cases, although a small site symmetry splitting of the symmetric stretch is evident in four minerals of Table 1 (e.g., Kolesev and Geiger 2004; Zucker and Shim 2009). Each Q species here addressed is restricted to a narrow frequency range regardless of alkali or alkaline earth present (Table 1; see also Nesbitt et al. 2017b). From Table 1, FWHM ~ 9 (± 4) cm⁻¹ at 298 K and ~ 25 (± 5) cm⁻¹ at $\sim 1200 \text{ K}$. Apparently, the FWHM for crystalline silicates are similar at

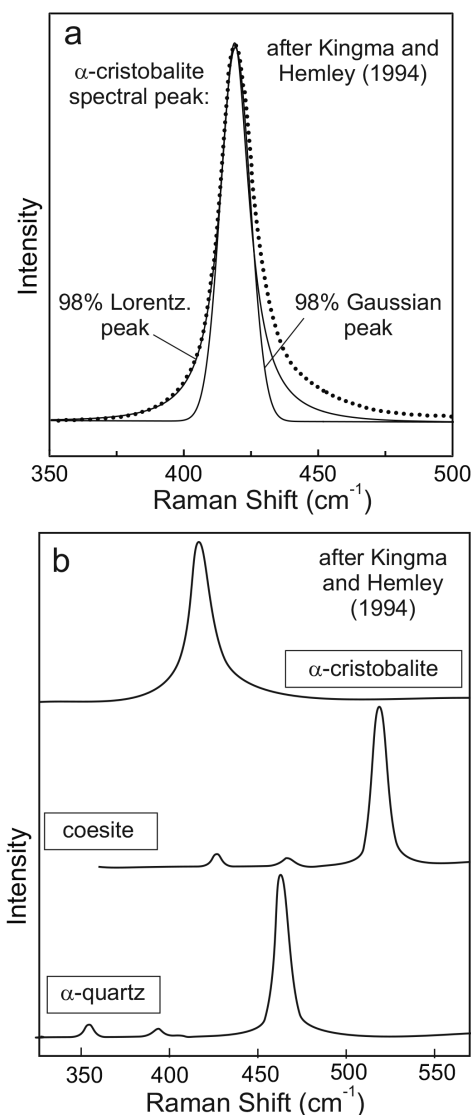


FIGURE 1. The dominant bands of numerous polymorphs of crystalline SiO₂. (a) The dominant band of α-cristobalite (dots) with a Gaussian and a Lorentzian peak fitted to the upper portion of the low-frequency side of the band. (b) The major band of other SiO₂ polymorphs. The figure is redrawn after Kingma and Hemley (1994).

a given temperature regardless of chemical composition or structure of the crystal.

Metasilicate crystals

Q² Raman shifts. The most intense Raman bands of the Q² crystalline silicates, Na₂SiO₃, Li₂SiO₃, CaSiO₃, and Ca_{0.5}Mg_{0.5}SiO₃, range from ~950–1000 cm⁻¹ at 298 K (Richet et al. 1996, 1998; Nesbitt et al. 2017b) and their Raman shifts decrease systematically with temperature (Figs. 2a and 2b). With the Raman shifts standardized to the value at 298 K (Fig. 2c), the similarity in temperature dependence becomes obvious and although the Raman shifts of the crystals diverge somewhat with temperature, all remain within ~5 cm⁻¹ at 1500 K. Equation 2 was used to fit the Raman shifts and the fit coefficients are listed in

TABLE 1. Raman shifts and FWHM for the SiO₄ symmetric stretch of crystals

Crystal	Species	T = 298 K		T ~ 1200 K		Reference
		Shift (cm ⁻¹)	FWHM (cm ⁻¹)	Shift (cm ⁻¹)	FWHM (cm ⁻¹)	
Mg ₂ SiO ₄	Q ⁰	856	8	824	23	Kolosev and Geiger (2004)
	Q ⁰	856	<10	826		McKeon et al. (2010)
	Q ⁰	855		830	20	Voronko et al. (2006)
CaMgSiO ₄	Q ⁰	850	10	816		Mohanen et al. (1993)
Gd ₂ Si ₂ O ₇	Q ¹	915	<10	902	~30	Voronko et al. (2015)
MgSiO ₃	Q ²	1036	12	1014	22	Zucker and Shim (2009)
Na ₂ SiO ₃	Q ²	965	6	950	27	Richet et al. (1996)
Li ₂ SiO ₃	Q ²	975	13	960	26	Richet et al. (1996)
Ca _{0.5} Mg _{0.5} SiO ₃	Q ²	1008	10	988	24	Richet et al. (1998)
	Q ²	1014	7			Swamy et al. (1997)
CaSiO ₃	Q ²	981	10	967	26	Richet et al. (1998)
Na ₂ Si ₂ O ₅	Q ³	1072	~5			You et al. (2001)

the figures. The solid curves represent best fits, the dashed curve the contribution of the C[1 + 2/(e^x - 1)] term of Equation 2. The difference between the dashed and solid curves represents the contribution of the last term of Equation 2. Both terms contribute significantly to the Raman shifts at high temperature.

Equation 3 can be used to obtain the Raman shift at absolute zero (Ω*) using the fit coefficients listed in Figures 2a and 2b (i.e., Ω* = ω* + C + D). This value may be used in turn to test the applicability of the Balkanski et al. (1983) theory to the metasilicate crystals. The Ω* value calculated for Li₂SiO₃ is 977 cm⁻¹, Na₂SiO₃ is 966 cm⁻¹, CaSiO₃ is 982 cm⁻¹, and Ca_{0.5}Mg_{0.5}SiO₃ is 1010 cm⁻¹. The Balkanski et al. (1983) theory predicts that Ω* is similar to but a few wavenumbers less than the Raman shifts at 298 K (Table 1), as shown in Figure 2 by the near-flat trends of solid curves between 0 and 298 K. The theory and observation are consistent.

Li₂SiO₃ and Na₂SiO₃ are isostructural, having orthorhombic symmetry and consisting of Si₂O₆ chains with two BO per SiO₄ tetrahedron (Richet et al. 1996). Diopside, Ca_{0.5}Mg_{0.5}SiO₃, has monoclinic symmetry and is made up of Si₂O₆ chains, whereas pseudowollastonite, CaSiO₃, is triclinic and consists of Si₂O₉ rings (Richet et al. 1998). Although the structures of these metasilicate crystals are different, the standardized Raman shifts (Fig. 2c) are similar indicating that Raman shifts do not depend substantially on the crystal structure or composition. This leaves the properties of the TO₄ tetrahedral bonds and the associated site potentials as the major factors controlling the temperature dependence of Raman shifts for Q² crystals.

Q² FWHM. As shown in Figures 3a and 3b, the FWHM of Na₂SiO₃, CaSiO₃, and Ca_{0.5}Mg_{0.5}SiO₃ increase systematically with temperature. Equation 8a was used to fit these data and the fits are illustrated by the solid curves (Figs. 3a and 3b). These fits employed ω* values derived from the fits to the Raman shift data (Fig. 2). The contributions from the second term, i.e., A[1 + 2/(e^x - 1)] of Equation 8a are illustrated by dashed curves of Figure 3a and the difference between the dashed and solid curves represents the FWHM contribution from the anharmonic (last) term of Equation 8a.

The line width of Li₂SiO₃ at 298 K is anomalously large compared with the FWHM (at 298 K) of isostructural Na₂SiO₃ (Fig. 3a). Equation 4 yields a poor fit to the FWHM of Li₂SiO₃ with FWHM (298 K) = 3.4 cm⁻¹ and with the “B” coefficient being negative producing a sigmoid fit and a maximum in FWHM

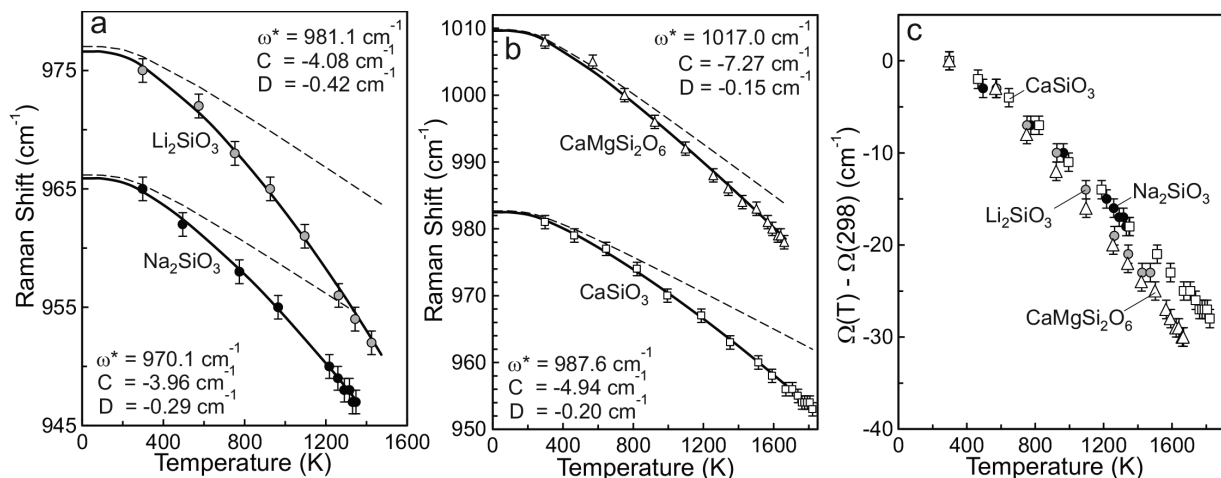


FIGURE 2. Temperature dependence of the Raman peak shifts (cm⁻¹) for the SiO₄ symmetric stretch peak in the four metasilicate minerals containing the Q² species (Richet et al. 1996, 1998). (a) Li₂SiO₃ (shaded circles) and Na₂SiO₃ (solid black circles); (b) Ca_{0.5}Mg_{0.5}SiO₃ (open triangles), and CaSiO₃ (open squares); (c) Raman shifts for all four silicates standardized to the value at 298 K. The errors bars are all ±1 cm⁻¹. Best fits using Equation 2 are shown with solid black lines, with the dashed lines showing the contribution from the second term (i.e., C term) to the Raman shift. The best fit values for the constants ω*, C, and D for the four minerals are shown in the figures.

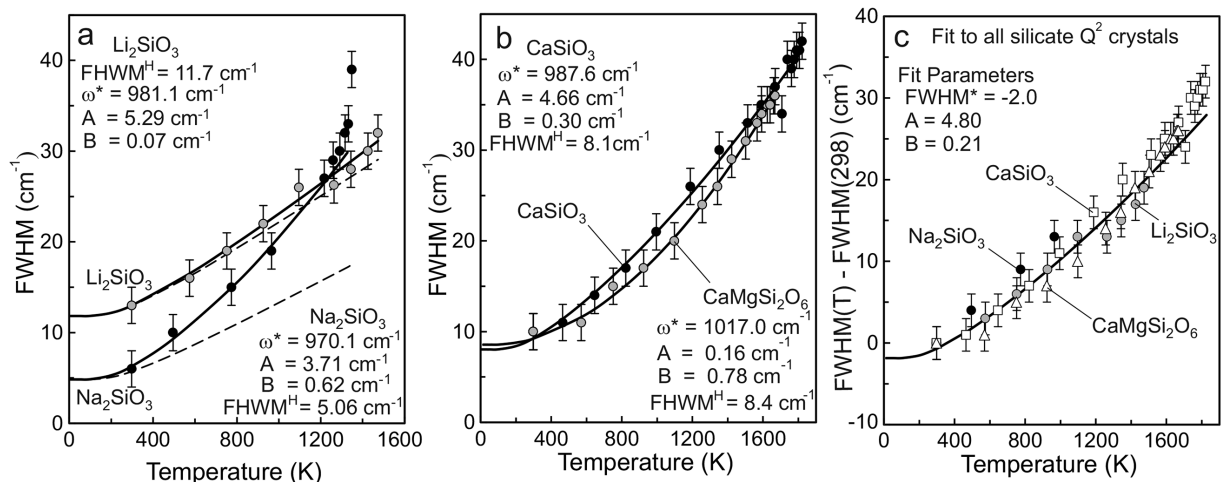


FIGURE 3. Temperature dependence of the FWHM (full-width at half maximum, in cm⁻¹) for the SiO₄ symmetric stretch peak of same Q² crystals as in Figure 2. (a) Li₂SiO₃ (shaded circles) and Na₂SiO₃ (solid black circles). Dashed curves illustrate the contribution of the quadratic term (i.e., A[2/(e^x - 1)]) of Equation 8a to temperature dependence. (b) CaSiO₃ (solid black circles) and Ca_{0.5}Mg_{0.5}SiO₃ (shaded circles). (c) Line widths for the above four silicates standardized to the Raman line width at 298 K set to 0 cm⁻¹. Error bars are all ±2 cm⁻¹. The solid curve is the best fit to all plotted data using Equation 8a. The best fit values for the constants FWHM*, A, and B are provided in the figures.

(which has no physical meaning). The poor fit emphasizes the inadequacy of Equation 4, which lacks a Heisenberg lifetime contribution. Equation 8a was used to fit successfully the Li₂SiO₃ FWHM data. The best fit, using ω* = 981.1 (Fig. 2a), is illustrated in Figure 3a (fit coefficients listed in the figure). With FWHM^H = 11.72 cm⁻¹ and FWHM* = A + B = 5.36 cm⁻¹ then ΔFWHM^H = 6.36 cm⁻¹. We suggest that the virtual state of Li₂SiO₃ has a short natural lifetime leading to an elevated FWHM at 298 K relative to the FWHM of isostructural Na₂SiO₃ at 298 K (Fig. 3a).

The FWHM of the Q² silicate crystals were standardized to the value at 298 K (i.e., FWHM at *T* minus FWHM at 298 K) and the standardized FWHM have been plotted in Figure 3c. The

FWHM values of Na₂SiO₃ above 1200 K (Fig. 2a) are affected by premelting (Richet et al. 1996; Nesbitt et al. 2017a) and have not been plotted. The standardized FWHM for the four crystals fall within ±3 cm⁻¹ at any given temperature (Fig. 3c). The data has been fit as a group using Equation 5 and the solid curve of Figure 3c is the result. The FWHM*, A, and B fit parameters are given in the figure. The fit reproduces remarkably well the standardized FWHM up to ~1500 K. Beyond this temperature, the Q² crystals containing Ca undergo Ca disordering and are subject to premelting phenomena (Dimanov and Ingrin 1995; Richet et al. 1998; Dimanov and Jaoul 1998; Bouhfid et al. 2002; Nesbitt et al. 2018).

The similarity of the standardized FWHM values (Fig. 3c) is taken as evidence that different crystal structures and different alkali and alkaline earth elements have only minor effects on FWHM of the Q^2 silicate crystals. As with Raman shifts, the temperature dependence of the Q^2 FWHM are controlled primarily by the properties of the TO_4 tetrahedra and associated site potentials; hence the Balkanski et al. (1983) formalism with a natural lifetime included successfully reproduces the FWHM temperature trends. There is a strong negative correlation between the temperature dependence of the standardized Raman shift (Fig. 2c) and FWHM (Fig. 3c). The standardized shift decreases by about 30 cm^{-1} from 298 to 1600 K, whereas the standardized FWHM increases by about 30 cm^{-1} over the same temperature range. The negative correlation has not been observed or explained before, and it is addressed subsequently.

Orthosilicate crystals

Forsterite Q^0 Raman shift. The temperature dependence of the Q^0 Raman shift for Mg_2SiO_4 (Kolesov and Geiger 2004) is illustrated in Figure 4a. The shifts decrease linearly with temperature indicating that the “D” coefficient of Equation 2 is effectively 0.0 so that the quadratic term of Equation 1 dominates the Raman shifts of forsterite. The standardized Q^0 Raman shift of forsterite, the Q^2 shift of $CaSiO_3$ and Li_3PO_4 (Popovic et al. 2003, discussed subsequently), are plotted in Figure 4b. All decrease at a similar rate between 298 and ~ 1000 K and they differ by about 3 cm^{-1} at 1200 K. Although not shown, the standardized Q^0 Raman shift of Mg_2SiO_4 is also similar to the Q^2 Raman shifts of the other metasilicates up to ~ 1000 K. Apparently, the temperature dependence of Q^0 and Q^2 Raman shifts of crystals are influenced by a property common to all Q^2 and Q^0 crystals, the TO_4

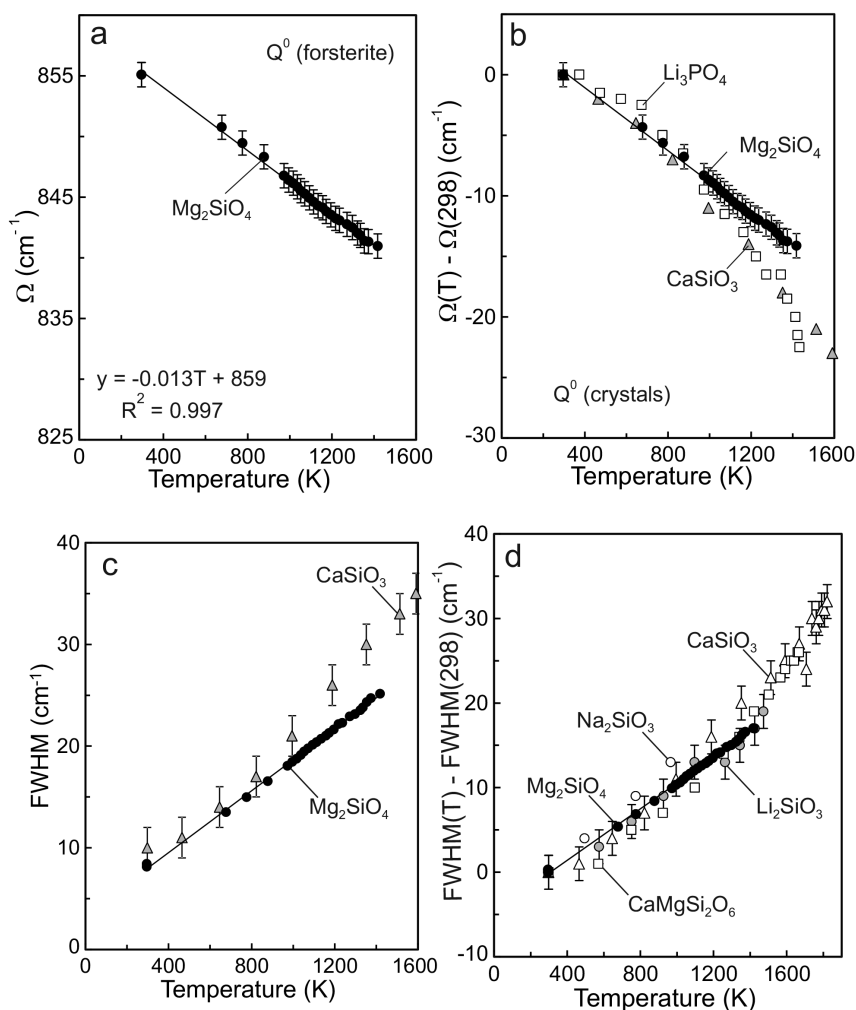


FIGURE 4. Temperature dependence of the Raman shift and FWHM for the SiO_4 symmetric stretch peak in the Q^0 species Mg_2SiO_4 (Kolesov and Geiger 2004) compared to the shifts and FWHM for other Q^0 and Q^2 species. (a) The Raman shifts for Mg_2SiO_4 (black circles) along with best least-squares linear fit to the data. (b) The standardized shifts [$\Omega(T) - \Omega(298)$] for Mg_2SiO_4 compared to the standardized shifts for the Q^0 species Li_3PO_4 (open squares), and the Q^2 species $CaSiO_3$ (shaded triangles). The errors bars are all $\pm 1\text{ cm}^{-1}$. (c) The FWHM for Mg_2SiO_4 compared to the FWHM for $CaSiO_3$, and the best least squares linear fit for Mg_2SiO_4 are shown. The errors bars are all $\pm 2\text{ cm}^{-1}$ in c. (d) The FWHM standardized to the line width at 298 K at 0 cm^{-1} for Mg_2SiO_4 compared to those for the four metasilicates shown earlier in Figure 2c. In d, the FWHM for Na_2SiO_3 for five values in the premelting region (1259–1348 K cm^{-1}) are again omitted—see text.

tetrahedra of the crystals. Composition and structure apparently have little influence on Raman shift temperature dependence of the Q^0 crystals. The linear temperature dependence above 298 K for the forsterite Q^0 Raman shift implies that harmonic oscillator properties alone affect the Raman shift. Anharmonic contributions produce a non-linear response in temperature and these apparently are minimal (i.e., “D” of Eq. 3 is ~ 0). Higher temperature measurements are required to test the conclusion.

Forsterite Q^0 FWHM. The FWHM of the Q^0 band for Mg_2SiO_4 increases linearly with temperature (Fig. 4c). The linear behavior indicates that the B coefficient of Equations 4 and 8a is effectively zero and that the quadratic term (i.e., $A[2/(e^x - 1)]$) controls temperature dependence and as indicated by the dashed curves of Figure 3a this term is linear in T above 298 K. The FWHM of the Q^0 band for Mg_2SiO_4 and the Q^2 band for $CaSiO_3$ are similar up to ~ 1000 K (Fig. 4c) but they diverge at higher temperatures. Figure 4d illustrates FWHM values standardized to the value at 298 K [i.e., $FWHM(T) - FWHM(298)$] for the Q^0 band of forsterite and the Q^2 bands of the four metasilicates. All respond similarly to temperature up to ~ 1400 K. Apparently the controls on the temperature dependence of Q^0 and Q^2 FWHM are effectively the same to high temperature. Clearly the temperature dependence of these Q species line widths do not reflect crystal composition or structure. Moreover, the molecular symmetry of the two tetrahedra (Q^0 and Q^2) differs as do site symmetries in the respective crystals. Apparently, the temperature dependence of FWHM of the Q species of the crystals is controlled primarily by the essential SiO_4 tetrahedral properties and little else.

Q^0 of sulfates and phosphates. The low-temperature space groups for Li_2SO_4 , Li_3PO_4 , $Sr_3(PO_4)_2$, and $Ba_3(PO_4)_2$ are $P2_1/b$, $Pmn2_1$, $R\bar{3}m$, and $R\bar{3}m$, respectively, with Li_2SO_4 and Li_3PO_4 undergoing phase transitions at higher temperatures. The phosphate and sulfate spectra contain only one symmetric Lorentzian

peak, which arises from the symmetric TO_4 ($T = P, S$) stretch (Table 2). The Q^0 Raman shift of Li_2SO_4 decreases systematically with temperature to ~ 840 K (Fig. 5a), where a monoclinic-fcc phase transition occurs (Cazzanelli and Frech 1984). The monoclinic and fcc trends display similar slopes and these are almost coincident with the slope of the Q^2 Raman shift vs. temperature trend of Li_2SiO_3 (Fig. 5a). Apparently, neither crystal structure nor composition (Si or S of tetrahedra) affects appreciably the temperature dependence of the Raman shifts of the sulfate.

The Q^0 Raman shift vs. temperature trend for Li_3PO_4 (Popovic et al. 2003) is illustrated in Figure 5b. Equation 3 was used to fit the data and the three fit parameters are listed in the figure. Although the fit is good, it is not robust, primarily because the lowest temperature datum point is at ~ 350 K and the trend of the 6 highest temperature points is offset from the trend of the lower temperature data. Nevertheless, the Li_3PO_4 Q^0 Raman shift dependence on temperature is similar to the Q^2 trend for Li_2SiO_3 up to ~ 1300 K. The standardized Raman shifts for Mg_2SiO_4 , Li_3PO_4 , Li_2SO_4 , and Li_2SiO_3 (Fig. 5c) behave similarly and are within ± 2 cm^{-1} up to ~ 850 K (the temperature

TABLE 2. Raman shifts and FWHM for symmetric stretch of P and S crystals

Crystal	Species	$T = 298$ K		T (K)	FWHM (cm^{-1})	Reference
		Shift (cm^{-1})	FWHM (cm^{-1})			
Li_2SO_4	Q^0	1012	~ 9.5	~ 900	20	Cazzanelli and Frech (1984)
$Ca_3(PO_4)_2$	Q^0	980	~ 9	~ 1200	21	Zhai et al. (2011)
$Sr_3(PO_4)_2$	Q^0	1080	6	~ 1200	19	Zhai et al. (2014)
$Ba_3(PO_4)_2$	Q^0	1045	5	~ 1200	18	Zhai et al. (2014)
$CaSr_2(PO_4)_2$	Q^0	961	~ 10			Xue et al. (2012)
$Li_3PO_4(\beta, \gamma)$	Q^0	980	6	~ 1420	30	Voronko et al. (2005)
$Li_3PO_4(\beta, \gamma)$	Q^0	950	11	~ 1370	34	Popovic et al. (2003)
$Li_4P_2O_7$	Q^1	1050	6	~ 1200	25	Voronko et al. (2005)
$NaPO_3$	Q^2	1180	6	~ 850	20	Voronko et al. (2005)
	Q^2	1180	6	~ 785	20	Sadykov (2004)

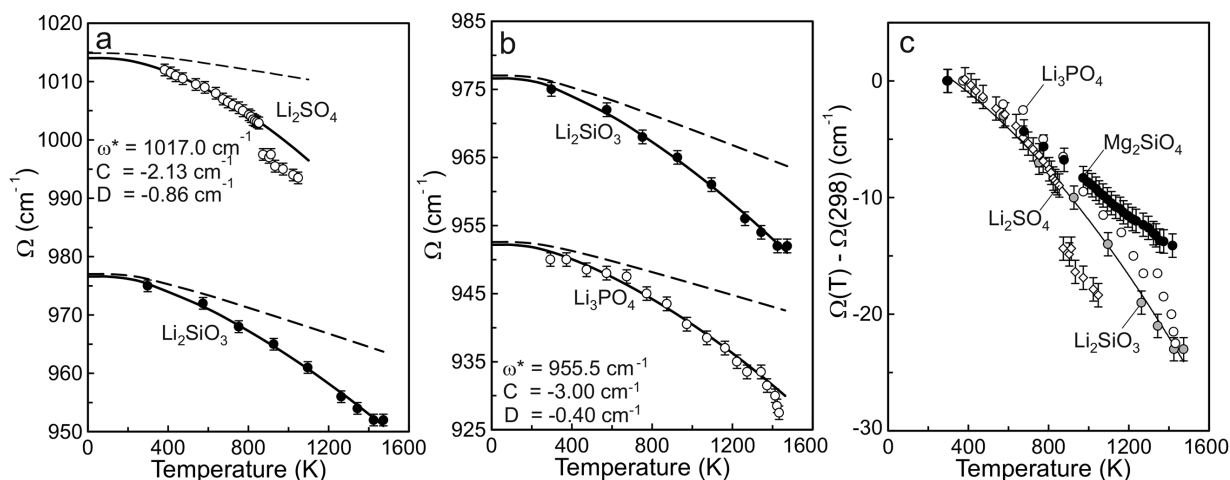


FIGURE 5. Temperature dependence of the Raman peak position (cm^{-1}) for the TO_4 ($T = Si, P, S$) symmetric stretch peak for Q^0 species in Li_2SO_4 (Cazzanelli and Frech 1984), Li_3PO_4 (Popovic et al. 2003), and Mg_2SiO_4 (Kolesev and Geiger 2004) compared to Li_2SiO_3 (with Q^2 species) previously shown in Figure 1a. (a) Li_2SO_4 (open circles), and Li_2SiO_3 (solid black circles); (b) Li_3PO_4 (open circles) and Li_2SiO_3 (solid black circles); (c) positions for all the three crystalline compounds and the positions for Mg_2SiO_4 (black circles) from Figure 4a standardized to the peak position at 298 K [$\Omega(T) - \Omega(298)$]. The error bars are ± 1 cm^{-1} . The best fits in a and b using Equation 2 and the best-fit values for the constants ω^* , C, and D are shown with solid black lines, with the dashed lines showing the contribution from the second term to the Raman shift. The solid line in c is from a quadratic fit just to guide the eye.

at which Li_2SO_4 changes structure). These data demonstrate that the temperature dependence of the Q^0 Raman shifts are largely independent of composition and structure of the crystal and dependent primarily on the properties of the tetrahedron, whether SiO_4 , PO_4 , or SO_4 .

The FWHM-temperature trends of Li_2SO_4 , Li_3PO_4 , $\text{Sr}_3(\text{PO}_4)_2$, and $\text{Ba}_3(\text{PO}_4)_2$ are compared with that of Mg_2SiO_4 in Figure 6a. All incorporate Q^0 species and where standardized to the value at 298 K (Fig. 6b), they display remarkably consistent trends with respect to temperature. As shown in Figure 6c, their trends are also similar to CaSiO_3 , which contains Q^2 species. Agreement between standardized Q^0 and Q^2 slopes is within $\sim 2 \text{ cm}^{-1}$ up to $\sim 1400 \text{ K}$, indicating a common control on the temperature dependence of the two Q species FWHM for these crystals. The common response can be explained only if the TO_4 tetrahedron is the only major control on the temperature dependence of FWHM for Q^0 crystals.

Figure 6a illustrates that the crystals containing Ba and Sr plot lower on Figure 6a than do those containing the lighter elements, Li and Mg. Apparently, the metal in the first coordination sphere of the TO_4 tetrahedra ($T = \text{Si}, \text{P}, \text{S}$) influences the absolute values of FWHM, although they do not affect temperature dependences (Fig. 6b). A mass effect (via Hooke's Law) might be expected to affect Raman shifts but it is not certain how it would affect FWHM as shown in Figure 6a. Perhaps the cation affects the Heisenberg (natural) lifetime (FWHMⁿ of Eq. 8a) as proposed for Li_2SiO_3 (Fig. 3a), with the lighter elements decreasing the lifetime of the virtual state thereby increasing FWHM. The possibility requires exploration. Also, the temperature dependence of the Q^0 and Q^2 species FWHM is independent both of the type of cation coordinated to the tetrahedron and of the nature of the central element of the tetrahedron. The crystal structures have little effect on Q^0 and Q^2 line widths. There remains, however, ambiguity as to how cations in the first coordination spheres of tetrahedra affect FWHM.

RELATIONSHIP BETWEEN RAMAN SHIFT AND FWHM

Theoretical aspects

The second and third terms of the right-hand side of Equation 2 and the first and second terms of Equations 4 and 8a are identical, although the coefficients of these terms differ. Rearrangement of Equation 2 to isolate the last term yields:

$$[1 + 3/(e^y - 1) + 3/(e^y - 1)^2] = \{\Omega(T) - \omega^* - C[1 + 2/(e^x - 1)]\}/D \quad (9)$$

Its substitution into Equations 4 or 8a, rearrangement and collection of terms gives:

$$\text{FWHM}(T) = Q[\Omega(T)] + R[2/(e^x - 1)] + S \quad (10)$$

where Q , R , and S are constants with $Q = B/D$, $R = (A - BC/D)$ and $S = [A - (B/D)\omega^* - BC/D]$. Equation 10 relates the FWHM of a Raman band to its Raman shift. The second term (i.e., $R[2/(e^x - 1)]$) represents the thermal effect on FWHM arising from the potential energy associated with the symmetric stretch of TO_4 . As apparent from Figures 2, 3, and 5 (dashed curves) the slope of the second term of Equations 3–5 and 8 is zero at $T = 0.0 \text{ K}$. At higher temperature where the energy of the oscillator is greater than kT ($\sim 300 \text{ K}$), the second term contributes linearly to the Raman shift and to FWHM. A consequence is that FWHM plotted against Raman shift should produce a linear trend provided temperatures are greater than about 298 K . The relationship between $\text{FWHM}(T)$ and $\Omega(T)$ for the four Q^2 silicates and the Q^0 silicate (Mg_2SiO_4) is illustrated in Figure 7. Straight lines of slope -1.0 are superimposed on each trend and they reproduce reasonably well the experimental data regardless of composition or type of Q species (note that the Mg_2SiO_4 data are shifted to fit on the diagram). The straight line relationship predicted from Equation 10 thus is realized at temperatures

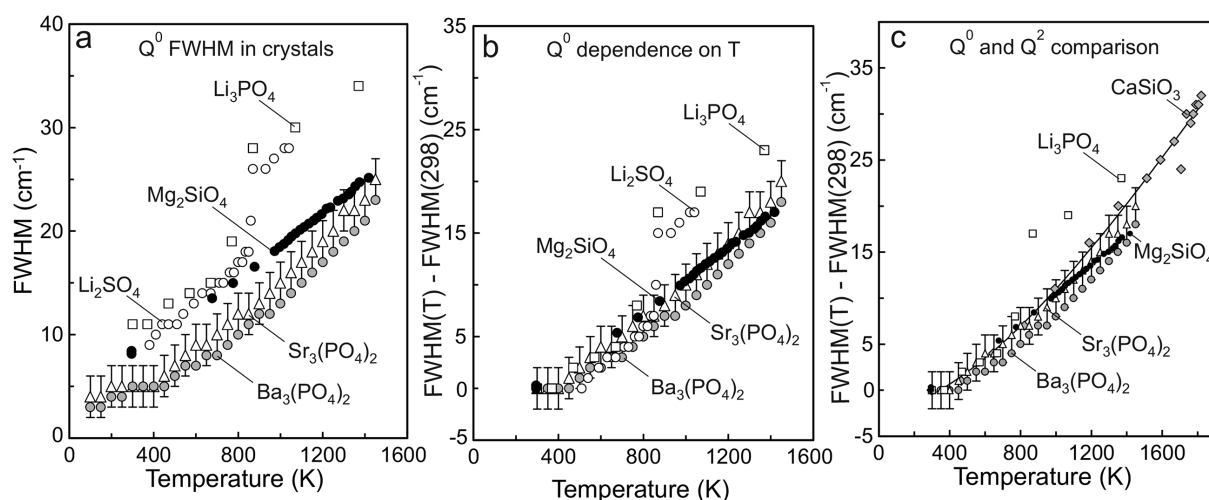


FIGURE 6. Temperature dependence of the FWHM for the TO_4 ($T = \text{Si}, \text{P}, \text{S}$) symmetric stretch peak for Q^0 species in Li_2SO_4 (Cazzanelli and Frech 1984), Li_3PO_4 (Popovic et al. 2003), $\text{Ba}_3(\text{PO}_4)_2$ and $\text{Sr}_3(\text{PO}_4)_2$ (Zhai et al. 2014), and Mg_2SiO_4 (Kolesev and Geiger 2004). (a) Li_2SO_4 (open circles), Li_3PO_4 (open squares), $\text{Ba}_3(\text{PO}_4)_2$ (shaded circles), and $\text{Sr}_3(\text{PO}_4)_2$ (open triangles), and Mg_2SiO_4 (solid black circles). (b) FWHM for the five Q^0 compounds standardized to the Raman line width at 298 K taken as 0 cm^{-1} . The error bars are $\pm 2 \text{ cm}^{-1}$. (c) Standardized FWHM for the phosphates and Mg_2SiO_4 compared to the standardized FWHM for CaSiO_3 (shaded diamonds).

above ~ 298 K. The relationship allows for reasonably accurate estimates of FWHM at high temperature provided the Raman shift and FWHM are known at one temperature. Using CaSiO_3 as example, consider the 298 K datum point (Fig. 7). With this point and a straight line of slope -1.0 , the relationship between Raman shift and FWHM is accurately estimated. To obtain an estimate of FWHM of, for example, CaSiO_3 at 1100 K, turn to Figure 2b. At 1100 K, the Raman shift of CaSiO_3 is ~ 969 cm^{-1} . In Figure 7, a Raman shift of 969 cm^{-1} corresponds to a FWHM of ~ 23 cm^{-1} , which is the FWHM forecast for 1100 K. Inspection of Figure 7 indicates slight (concave-upward) curvature to the experimental data of diopside, CaSiO_3 , and Mg_2SiO_4 (forsterite). The curvature suggests a small additional contribution to the site potential energy (Eq. 1).

Relationships to other properties and phases

From Figure 6a, the cation in the first coordination sphere of TO_4 apparently affects the FWHM of Q species bands, with lighter cations producing broader Q^0 bands. This is attributed to increased lifetime broadening induced by the lighter cations. The data of Figure 6a, when standardized to FWHM value at 298 K (Fig. 6b), yield a common trend demonstrating that the temperature dependences of these FWHM are independent of the mass of first coordination sphere cations and are controlled solely by properties of TO_4 ($\text{T} = \text{Si}, \text{P}, \text{S}$). An implication is that all Raman FWHM associated with the symmetric stretch in crystals are con-

trolled by temperature dependences of the properties of individual tetrahedra of the unit cell, thus FWHM of glasses and melts may be calculated considering only the array of distinct tetrahedra in these states of matter.

Several papers from crystal structures of silicates and sulfates support the control of the “local TO_4 environment” interpretation (e.g., Gibbs 1982; Downs et al. 1992; Bartelmehs et al. 1995; Jacobsen et al. 1998; Antao 2012). These studies show that for many silicates and sulfates, similar vibrational T-O motion is expected regardless of composition of the crystal or its overall structure. Indeed, the Si-O and S-O bond lengths vary little with composition, structure, or temperature and many of the TO_4 tetrahedra display rigid body thermal motion, with the O-T-O librational angles (θ_L) controlling the size of the thermal ellipsoids. The θ_L at 300 K for different structures (e.g., the Q^0 species in olivine, the Q^2 species in pyroxenes, and the Q^3 species in talc), is similar at $2.8\text{--}3.5^\circ$, $3.0\text{--}3.6^\circ$ (with the exception of $\text{LiFeSi}_2\text{O}_6$ at 5.0° ; perhaps the reason why Li_2SiO_3 has a larger FWHM than for other silicates), and 4.0° , respectively (Bartelmehs et al. 1995). In addition, θ_L increases greatly with temperature (Fig. 2, Bartelmehs et al. 1995; Armbruster and Geiger 1993), for the same reason that Raman FWHM increase with temperature.

The larger θ_L values for quartz and feldspars of >5 at 300 K (Bartelmehs et al. 1995) are consistent with the large increase in FWHM with temperature, resulting from the A_1 symmetric stretch of quartz. The FWHM of the 464 and 1084 cm^{-1} A_1 bands in quartz at 300 K $\leq$ are 7–8 cm^{-1} (Dean et al. 1982; Schmidt and Ziemann 2000; Ranieri et al. 2009), and these are similar to the FWHM at 300 K for the TO_4 species here addressed (Table 1; Figs. 1a and 1b). However at high temperatures, these quartz FWHM increase nonlinearly to ~ 35 cm^{-1} at ~ 900 K (Schmidt and Ziemann 2000) and ~ 40 cm^{-1} at ~ 1100 K (Ranieri et al. 2009), compared to ≤ 20 cm^{-1} at 1200 K for the TO_4 compounds with Na and Ca cations (Figs. 1a and 1b). Thus, there is good evidence that the libration of the TO_4 tetrahedron alone is a major factor for determining the temperature dependence of the FWHM.

A few other qualitative observations are worth mentioning. The FWHM at 300 K for the high-energy symmetric A_{1g} or A_g M-X stretch ($\text{M} = \text{Mg}, \text{Sn}, \text{P}, \text{Mo}$; $\text{X} = \text{F}, \text{O}$) for MgF_2 , SnO_2 , $\alpha\text{-GaPO}_4$, and PbMoO_4 are 4, 10, ~ 10 , and 13 cm^{-1} , respectively, compared to the ~ 10 cm^{-1} for most of the silicates, phosphates, and sulfates compiled here (Table 1, Fig. 1). More importantly, the temperature dependence of these FWHM are often similar to ours (e.g., Figs. 3c and 6c). For example, MgF_2 yields a FWHM of 23 cm^{-1} at 900 K, compared to the average of ~ 18 cm^{-1} from the data of Figure 2c. We emphasize, however, that we have focused on Q^0 and Q^2 A_1 stretching modes. Other vibrational modes can yield very different FWHM and different temperature dependences of the FWHM. Three different vibrational Raman bands of quartz (Dean et al. 1982), for example, produce FWHM that differ by a factor of three and greater, both at 100 and 300 K. Finally, the temperature dependences of Raman shifts and FWHM of some TO_4 species do not behave as described here. The temperature dependence of the Raman shift of the symmetric MoO_4 stretch from ~ 100 to 450 K is large at $+20$ cm^{-1} for PbMoO_4 (Sinagawa et al. 2000), whereas the change in FWHM over the same temperature range is about -11 cm^{-1} . Clearly the temperature dependences of Raman shift and FWHM are different than shown in Figure 7.

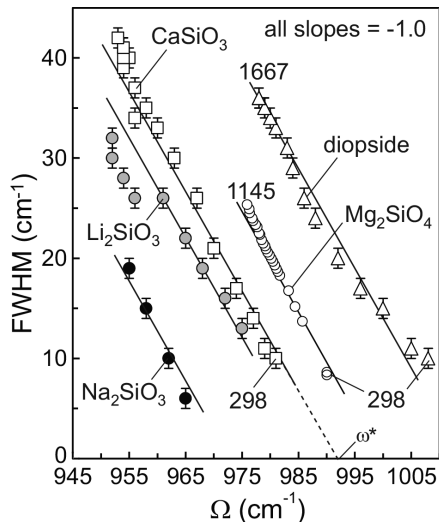


FIGURE 7. Plots of FWHM vs. Raman shift (Ω) for the five silicates—four Q^2 species (Li_2SiO_3 , Na_2SiO_3 , CaSiO_3 , $\text{Ca}_{0.5}\text{Mg}_{0.5}\text{SiO}_3$) and one Q^0 species (Mg_2SiO_4). The five lines (all with a slope of -1) are drawn to guide the eye so that most of the data is close to the line for a given crystal. Note that the Mg_2SiO_4 trend is offset by 135 cm^{-1} to greater $\Omega(T)$ values to include the trend on this plot. The temperature increases from the far bottom right to the far upper left for each of the five crystals, as is indicated by the 298 K for $\text{Ca}_{0.5}\text{Mg}_{0.5}\text{SiO}_3$ and Mg_2SiO_4 (bottom right) to the highest temperatures (1667 K for $\text{Ca}_{0.5}\text{Mg}_{0.5}\text{SiO}_3$ and 1145 K for Mg_2SiO_4). Note the ω^* value (992 cm^{-1}) for CaSiO_3 , obtained from the extrapolation of the line to 0 FWHM. This is slightly higher than the ω^* value obtained in Figure 1b (987.6 cm^{-1}).

IMPLICATIONS AND CONCLUSIONS

These results answer the questions posed in the Introduction. Line shapes of crystals are mostly 100% Lorentzian (e.g., Balkanski et al. 1983; Richet et al. 1996) and their Raman shifts describe unique temperature trends (Figs. 2, 4, and 5) primarily because Einstein frequencies (ω^*) differ for the A_1 vibrational mode of each Q species. They vary between ~ 970 – 1017 cm^{-1} for the Q^2 crystals studied and ω^* is $\sim 859\text{ cm}^{-1}$ for forsterite (Q^0 crystal). The full-width at half maxima (FWHM) also describe unique temperature trends (Figs. 3, 4, and 6) due mostly to different Heisenberg lifetimes of the virtual states (FWHM^H); apparently the lighter cations cause virtual state lifetimes to decrease, thus increasing FWHM.

Standardized Raman shifts display a common trend with respect to temperature (Figs. 2c, 4b, and 5c) as do standardized FWHM (Figs. 3c, 4d, and 6c). The explanation for both trends lies in the origin of the temperature dependence. The harmonic and anharmonic contributions of TO_4 common to all crystals studied apparently are similar and effectively independent of either the nature of the element centering the tetrahedron (Si, P, or S) or of the nature of the cation in the first coordination sphere of the tetrahedron (Li, Na, Mg, Ca, Sr, or Ba). The Balkanski formalism (Balkanski et al. 1983) provides the insight and the explanation for Raman shifts and FWHM temperature trends; they are dependent primarily on the properties of the tetrahedron and virtual (excited) state. Specifically, the temperature dependence of the standardized Raman shifts and FWHM are similar for the seven crystals here considered. The crystals are of different composition and structure, with the only common feature being the TO_4 moiety. The similarities in Raman shift and FWHM displayed by these crystals must arise primarily from the properties of this moiety. The shifts and FWHM for all crystals show a strong negative correlation in that the shifts decrease by $\sim 30\text{ cm}^{-1}$, whereas the FWHM increase by about 30 cm^{-1} FWHM from 298 to $\sim 1600\text{ K}$, illustrating the influence of the TO_4 moiety on temperature dependence of Raman shifts and FWHM. This observation is entirely consistent with the theory of Balkanski et al. (1983) modified to include Heisenberg lifetimes (Eq. 8). It is now possible to predict the shift or line width for any TO_4 symmetric stretch to within $\pm 5\text{ cm}^{-1}$ up to $\sim 1600\text{ K}$ provided the Raman shift and FWHM are known at 298 K. This remarkable regularity of Raman shifts, FWHM, and their temperature dependences, regardless of composition or crystal structure, makes it very likely that local TO_4 tetrahedra and their associated first coordination sphere of cations are the major controls on Q species Raman bands in crystals.

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