

Vibrational Spectroscopy of Beryllium Aluminosilicates: Heat Capacity Calculations from Band Assignments

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Abstract. Far-infrared, mid-IR, and Raman powder spectra were measured on six phases (bromellite, chrysoberyl, phenakite, bertrandite, beryl, and euclase) in the system $\text{BeO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. A single-crystal absorption spectrum of IR fundamentals in beryl is also presented, which more closely resembles the powder absorption spectrum than it does absorption spectra calculated from single-crystal reflection data.

Assignments of the SiO_4 and BeO_4 internal vibrations are made in accordance with each mineral's symmetry and composition and by comparison to structural analogs. Heat capacities C_V calculated for these partial band assignments agree with C_V derived from experimental C_P for all six phases, provided that Kieffer's (1979c) model is slightly modified to correctly enumerate both Si–O and Be–O stretching modes in the high frequency region ($>750\text{ cm}^{-1}$). Si–O stretching bands were found to out-number Be–O stretching modes in the high-energy region of the vibrational spectra with two exceptions: (1) For those phases containing oxygen ions not coordinated to silicon, vibrations occurring at $\nu > 1,080\text{ cm}^{-1}$ that are attributable to Be–O(H) stretching must be treated separately in the model in order to calculate C_V accurately. (2) Minerals consisting entirely of interlocking Si and Be tetrahedra (i.e., phases without Al or OH) can be modeled by one optic continuum representing all optical modes. These results, along with the occurrence of very low energy lattice vibrations for Be-silicates within Al, suggests that although Be–O bonds are generally weaker than neighboring Si–O bonds, Be mimics the network-forming characteristic of Si to a limited extent.

SiO_2 polymorphs (except for stishovite), and Al_2SiO_5 polymorphs can be predicted accurately from their vibrational spectra.

Previous studies on vibrational properties of beryllium minerals are incomplete, except for single-crystal Raman and *infrared* (IR) studies of bromellite (Loh 1968; Arguello et al. 1969) and beryl (Adams and Gardner 1974). Mid-IR powder data exist for all six phases (e.g., Plyusnina 1963; Moenke 1974), but far-IR spectra have been reported only for beryl (Adams and Gardner 1974). Far-IR modes are not expected for bromellite. Polarized reflectance mid-IR spectra has also been measured on phenakite at elevated temperatures by Gervais et al. (1973). Powder Raman data have been measured for phenakite (Narayanan, 1950) and at frequencies above 300 cm^{-1} for euclase (Griffith 1969).

In this report, IR and Raman powder spectral data covering the range of the anticipated fundamental vibrational modes of six beryllium minerals (Table 1) are presented and compared with previous work. Single-crystal absorption spectra of beryl are presented and compared to powder and reflectance spectra. Several alternative band assignments differentiating Be–O from Si–O stretching vibrations are constructed by applying factor group analysis (e.g., Fately et al. 1971) to the above data and by comparison with their structural analogues. Heat capacities predicted using Kieffer's (1979a, b, c, 1980) method for the alternative band assignments are shown to generally correspond with calorimetric measurements, such that band assignments that are most strongly constrained by symmetry and the experimental data give C_V closest to experiment. We suggest that the discrepancy between experimental and calculated heat capacity can aid in making band assignments. Our calculations of the heat capacity for the beryllium aluminosilicates utilizing these detailed band assignments provide a strong and positive test of the general validity of Kieffer's (1979c) model.

Introduction

Vibrational spectra of six phases in the system $\text{BeO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ have been measured, and then used to calculate heat capacities through the method of Kieffer (1979 a, b, c, 1980). This system was chosen because beryllium aluminosilicates are stoichiometric, fully ordered, relatively pure, and form a wide variety of structures from a relatively small number of distinct cation polyhedra. Data are not presented for the subsystem $\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ because essentially complete spectroscopic data exist in the literature, and because Kieffer (1980) and Salje and Werneke (1982) have shown that heat capacity of corundum,

Experimental

Mid-infrared absorption spectra were obtained from KBr pellets at 4 cm^{-1} resolution with a Nicolet 7199 Fourier transform IR spectrometer. For far-IR spectra ($550-50\text{ cm}^{-1}$), finely ground powders were dispersed in petroleum jelly on sheets of polyethylene and true spectral features were revealed by monitoring peak intensity as a function of sample thickness. Single crystal spectra were acquired using a Barnes/Spectra-Tech FTIR microscope

from a cleavage flake of beryl that was first ground and polished to about 20 μm thickness and then sputter-etched until a hole was formed in the center of the crystal. Ion-thinning (Tighe 1976) is necessary in order to achieve appropriate thicknesses for transmission of mid-IR wavelengths. Mid-IR spectra were obtained at 2 cm^{-1} resolution with an HgCdTe detector (detection range 5,000–400 cm^{-1}) from a 60 μm by 70 μm area of the beryl crystal that had an average thickness of 2 μm . Far-IR spectra were obtained with a liquid-helium-cooled bolometer (detection range 370–70 cm^{-1}) from a 300 μm by 500 μm area having an average thickness of 15 μm .

Raman spectra were measured at 1 cm^{-1} resolution by using a computer controlled spectrometer (Jobin Yvon "Ramanor HG-2S,") and the 488.0 nm excitation line from a Spectra-Physics Ar⁺ ion laser. Phenakite and euclase spectra were collected from powders in a capillary tube. Chrysoberyl and bertrandite spectra were taken on unoriented single crystals because intensities from powders were weak.

The phases studied in this work are described in Table 1. The low amounts of impurities present are unlikely to affect the vibrational spectra. Hemingway et al. (1986) determined heat capacities for the phenakite, bertrandite, beryl and euclase samples from 5 to 800 K, and C_p for chrysoberyl from 300 to 800 K.

Description of Spectra and Band Assignments

IR and Raman spectral data presented here generally agree with previously determined band positions and relative intensities (Plyusnina 1963; Griffith 1969; Gervais et al. 1972, 1973; Moenke 1974; Adams and Gardner 1974). Beryllium aluminosilicate bands are sharp, in accordance with their stoichiometry and complete degree of positional ordering (Figs. 1 and 2). Except for bromellite, many bands are present owing to the large number of elements and the low symmetry (Table 1).

Despite the plethora of data and the general agreement, assigning bands for the phases containing both Be and Si is controversial. The difficulty occurs because the extent to which the high energy region is occupied only by Si–O stretches or by a mixture of Be–O and Si–O stretches cannot be determined *a priori*. Several intense bands exist in the high frequency region (900–1,300 cm^{-1}) even for silicon-free phases (Fig. 1, top). In view of band assignments for silicate minerals, the high frequency bands of bromellite and chrysoberyl must be Be–O stretching vibrations. Hence, some proportion of the high frequency bands in both regions of Be-silicates are probably Be–O stretching modes, as suggested by Plyusnina (1963) and Moenke (1974). Information on the proportion of Be–O and Si–O stretching bands in the high energy regions is crucial to heat capacity calculations because Kieffer's (1979b) method relies on proper enumeration of modes in the Si–O stretching region. Incorrect enumeration of the internal modes leads to an improper density of states over all energy, and thus to a generally incorrect heat capacity. Correct enumeration can be approached by comparing the number of observed bands to the number predicted for the two limiting origins for the high energy bands: for case # 1, Si–O bonds are assumed have stronger force constants than Be–O bonds, so that SiO_4 tetrahedra vibrate as separate groups, and at higher energies. In case # 2, Be–O and Si–O bonds

Table 1. Description of minerals

Mineral	Formula	Z ^a	Symmetry ^b	Structure ^b	Origin	Chemistry ^c	Source	Sample number
Bromellite	BeO	2	C _{6v}	Wurtzite: "framework" of BeO ₄ tetrahedra	Synthetic	No impurities	John White (NMNH)	NMNH # 115234
Chrysoberyl	Al ₂ BeO ₄	4	D _{2h} ¹²	Olivine: isolated BeO ₄ tetrahedron, Al octahedra link tetrahedra	Colatine, Espirito Santo, Brazil	3.1 wt% Fe ₂ O ₃ (= 2.5 mole% BeFe ₂ O ₄)	John White (NMNH)	NMNH # R15231
Phenakite	Be ₂ SiO ₄	6	C _{3i}	"Framework" of SiO ₄ and BeO ₄ tetrahedra	San Miguel di Pracacaba, Brazil	No impurities	John White (NMNH)	NMNH # B21152
Bertrandite	Be ₄ Si ₂ O ₇ (OH) ₂	2	C _{2v} ¹²	Incomplete "Framework": each Be links OH that is not bonded to a Si ₂ O ₇ group	Albany, Maine	No impurities	R. Gaines (Maine) M. Barton (UCLA)	Field Msm. Nat. Hist. # 6969
Beryl	Be ₃ Al ₂ Si ₆ O ₁₈	2	P _{6h} ²	Layers of Si ₆ O ₁₈ rings linked laterally and vertically by BeO ₄ tetrahedra and AlO ₆ octahedra	Synthetic	0.37 wt% Cr ₂ O ₃ (replacing Al ₂ O ₃)	Richard M. Mandel (Vacuum ventures)	
Euclase	BeAlSiO ₄ (OH)	4	C _{2h} ⁵	"Chains" of alternating SiO ₄ and BeO ₃ OH tetrahedra. AlO ₆ octahedra link chains	Minas Gerais, Brazil	No impurities	John White (NMNH)	NMNH # 121350

^a Number of formula units per Bravais (primitive) cell

^b Wyckoff (1969) pp. 91, 159, 199–200, 230–231, 278–279, 283–284, 528

^c Detailed chemical analyses of these samples are given in Barton (1986) and Hemingway et al. (1986). All samples appear to be stoichiometric

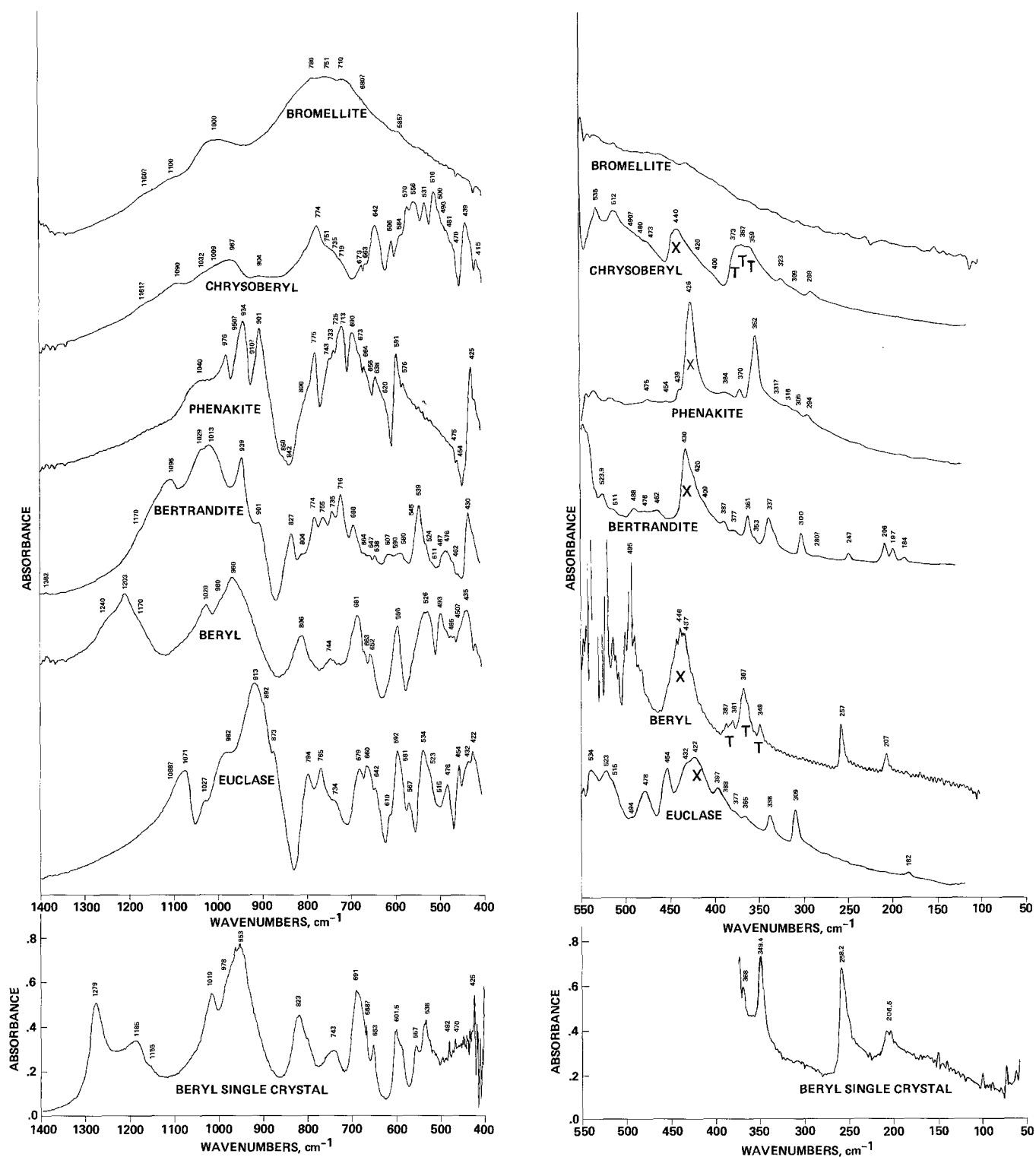


Fig. 1. IR powder spectra of six minerals in the $\text{BeO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system. Top, powder spectra. Resolution is 4 cm^{-1} . Spectra are offset for clarity, and are labeled by mineral name. Intensities are arbitrarily scaled. Right, mid-IR region. Weak bands near $1,170\text{ cm}^{-1}$ may be artifacts. Bottom, single crystal absorption spectra of beryl. Peaks in the E_u polarization are much more intense than those in A_{2u} . Resolution of 2 cm^{-1} . Sample area was $60\text{ }\mu\text{m}$ by $70\text{ }\mu\text{m}$. Thickness is about $2\text{ }\mu\text{m}$. Left, far-IR region. Weak water vapor peaks were not subtracted from the bromellite spectrum. For beryl, interference fringes are apparent. Bottom, far-IR absorption spectra of a single-crystal of beryl from $380-80\text{ cm}^{-1}$. Peaks in the E_u polarization are much more intense than those in A_{2u} . Sample area was $300\text{ }\mu\text{m}$ by $500\text{ }\mu\text{m}$; thickness about $15\text{ }\mu\text{m}$.

RAMAN

INTENSITY

CHYRSOBERYL

PHENACITE

BERTRANDITE

EUCLASE

WAVENUMBER, cm^{-1}

1400

1200

1000

800

600

400

200

0

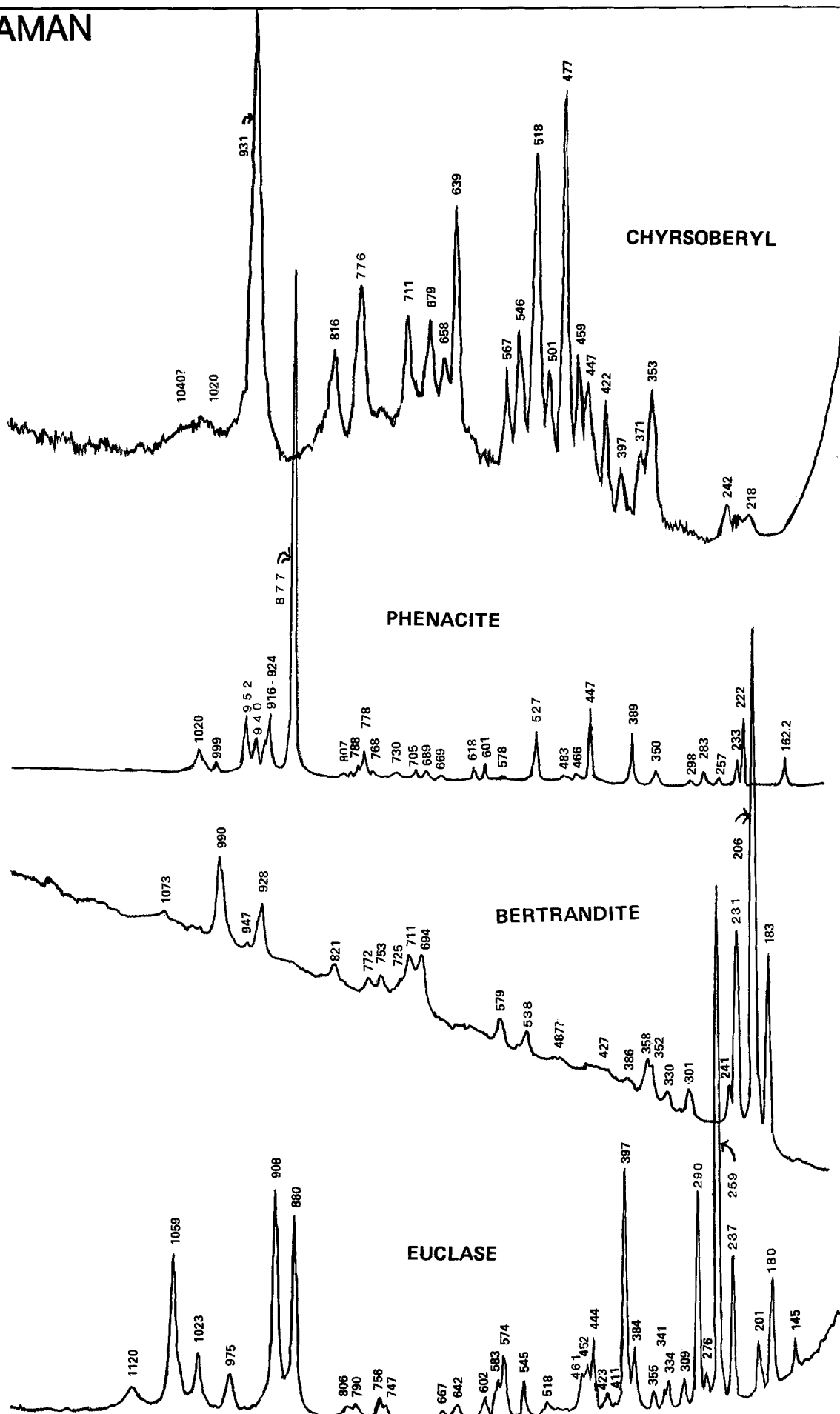


Table 2. Factor group analysis of Raman and IR modes

Mineral	Modes ^a												
Bromellite ^b	type	A_1			B_2		E_1		E_2				
	Nopt	1			2		1		2				
	$\nu(\text{BeO})$	1			1		1		1				
	$\nu(\text{BeO}_4)$	ν_1			ν_3, ν_4		$2\nu_3$		$2\nu_2, 2\nu_4$				
	Activity	I, R			—		I, R		R				
Chrysoberyl ^c	type	A_g		B_{1g}	B_{2g}	B_{3g}	A_u		B_{1u}	B_{2u}		B_{3u}	
	Nopt	11		11	7	7	10		9	13		13	
	$\nu(\text{BeO})$	2		2	1	1	1		1	2		2	
	$\nu(\text{BeO}_4)$	$\nu_1, \nu_2, 2\nu_3, 2\nu_4$		as A_g	ν_2, ν_3, ν_4	as B_{2g}	as B_{2g}		as B_{2g}	as A_g		as A_g	
	Activity	R		R	R	R	—		I	I		I	
Phenakite ^d	type	A_g			E_g		A_u			E_u			
	Nopt	21			21		20			20			
	$\nu(\text{Si—O})$	3			3		3			3			
	$\nu(\text{SiO}_4)$	$\nu_1, 2\nu_2, 3\nu_3, 3\nu_4$			as A_g		as A_g			as A_g			
	Activity	R			R		I			I			
Bertrandite	type	A_1			A_2				B_1	B_2			
	Nopt	23			21				20	23			
	$\nu(\text{Si—O})$	3			3				3	3			
	$\nu(\text{SiO}_4)$	$\nu_s(\text{Si—O—Si}), \nu_s(\text{SiO}_3), 2\nu_{as}(\text{SiO}_3)$			$\nu_{as}(\text{Si—O—Si}), \nu_s(\text{SiO}_3), 2\nu_{as}(\text{SiO}_3)$				as A_2	as A_1			
	Activity	I, R			R				I, R	I, R			
Beryl ^e	type	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_{1g}	E_{2g}	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_{1u}	E_{2u}
	Nopt	7	9	7	6	13	16	5	6	9	8	16	12
	$\nu(\text{Si—O})$	2	2	1	1	2	4	1	1	2	2	4	2
	$\nu(\text{Be—O})$	0	1	1	1	2	1	0	1	1	1	2	1
	$\nu(\text{Ring})$	7	7	5	5	10	14	5	5	7	7	14	10
Euclase	Activity	R	—	—	—	R	R	—	I	—	—	I	—
	type	A_g			B_g			A_u			B_u		
	Nopt	24			24			23			22		
	$\nu(\text{Si—O})$	3			3			3			3		
	$\nu(\text{SiO}_4)$	$\nu_1, 2\nu_2, 3\nu_3, 3\nu_4$			as A_g			as A_g			as A_g		
	Activity	R			R			I			I		

^a Acoustic modes are not included here. A and B modes are not degenerate, E modes are doubly degenerate, F modes are triply degenerate

^b c.f. Loh 1968

^c c.f. Iishi 1978

^d c.f. Gervais et al. 1973

^e c.f. Adams and Gardner 1974

are treated equivalently, leading to complete intermixing of Si—O and Be—O bands at high energy. Methods for enumerating the modes are as follows.

For both cases, *factor group analysis* (FGA) predicts the number and symmetry (i.e., polarization) of the vibrational modes present in each mineral. This method (discussed in detail by Fately et al. 1971 and by Farmer and Lazarev 1975) requires knowledge of only the mineral structure and the number and placement (site symmetry) of the constituent atoms. In addition to the total number of optical vibrations (N_{opt} in Table 2), FGA gives the approximate number of vibrations involving the stretching bands $\nu(\text{Si—O})$ or $\nu(\text{Be—O})$ by summing the number of vibrations involving Si or Be.

For case #1, in which Si—O bonds dominate, the number of asymmetric (ν_3) and symmetric (ν_1) stretching vibrations can be exactly determined by considering how the degeneracies of the vibrations of an isolated SiO_4 (BeO_4

for bromellite and chrysoberyl) tetrahedron of T_d symmetry are lifted when the tetrahedron is located in a lower symmetry site (the correlation method: Fately et al. 1971; Farmer and Lazarev 1975). This method implicitly assumes that the Si—O bond is stronger than the Be—O bond whereas application of FGA requires no assumption about bond strengths. For bromellite, the total number of ν_3 and ν_1 stretching vibrations agrees with the total number of $\nu(\text{Be—O})$. For bertrandite, the correlation method was applied to the vibrations of an isolated Si_2O_7 group as determined by Farmer and Lazarev (1975) and Lazarev (1975). The number of stretching vibrations (Table 2) agree for both approaches. However, for chrysoberyl, phenakite, and euclase, the number of asymmetric (ν_3) stretching vibrations equals those for $\nu(\text{Si—O})$ or $\nu(\text{Be—O})$ as determined by FGA (Table 2), suggesting that FGA alone may underestimate the number of stretches.

In case #1, the number of Si—O stretching modes can

Fig. 2. Raman spectra of beryllium aluminosilicates. Resolution is 1 cm^{-1} . Bertrandite and chrysoberyl spectra were obtained from unoriented single crystals. Phenakite and euclase spectra were obtained from powders

Table 3. Enumeration of vibrational modes and bands

Mineral	No. of IR bands ^a		No. of raman bands ^a		Total modes ^b	Inactive	Case 1: Si—O stretches ^c		Case 2-KS ^d		
	expected	observed	expected	observed			CM ^e	KS ^d	# Si—O	# Be—O	# Be—OH
Bromellite	1–2 ^e	4 see text	2–4	6 see text	12	2	4 ^f	4 ^f		4	
Chrysoberyl	13–35	33	11–36	22	84	10	16 ^f	16 ^f		16	
Phenakite	20–40	33	21–42	30	126	0	24	24	12	24	
Bertrandite	25–71	44	23–87	23	94	0	16	14	8	12	4
Beryl	14–20	23 see text	16–36	33	174	36	36	36	30	12	
Euclase	23–45	35	24–48	34	100	0	16	16	10	6	4

^a The number of bands is less than or equal to the number of modes because of degeneracy

^b Includes optical, acoustic, and OH bands

^c Enumerated by the correlation method

^d Enumerated by Keffer's (1976) polymerization scheme

^e For powder spectra accidental degeneracy of bands in the different polarizations can give a spectrum with less bands than the sum of the number of bands expected for each polarization

^f Be—O stretching modes were enumerated because those phases do not contain Si

also be determined from Kieffer's (1979b) polymerization scheme by assuming that only Si participates in the network formation. Except for bertrandite, the number of Si—O stretching bands determined by the correlation method agrees with the number of Si—O stretching modes determined from Kieffer's (1979b) polymerization scheme (Table 3). Thus, Kieffer's polymerization scheme is generally correct and can be substituted for the more accurate and more involved correlation method.

All of the above counting schemes are self consistent in that if Si—O bonding is much stronger than Be—O bonding then the Si—O stretching frequencies should occur at higher frequencies. For case # 1, the number of Be—O stretches can also be determined by FGA. These bands should occur at lower frequency.

For case # 2 in which Be—O and Si—O bonds are approximately equal strength, the correlation method cannot be readily used to determine the number of stretching bands because Si and Be are often on sites with different symmetries. Instead, Kieffer's (1979b) polymerization scheme was used to calculate the number of Be—O and Si—O stretching vibrations (indicated in Table 3). Except for euclase, the number of Be—O and Si—O stretches are always greater than the number of Si—O stretches determined for case # 1.

In the following sub-sections the number of bands observed will be compared to those predicted for the two cases in order to evaluate the proportion of Be—O and Si—O stretches in the high energy region.

OH Bands

Bertrandite and euclase structurally incorporate stoichiometric hydrogen. In accord with the number of OH[−] in their Bravais cells (Table 1) both minerals should have four bands in the fundamental absorption region of "water" near 3,600 cm^{−1}. Euclase possesses a doublet in the IR and two distinct unequal peaks in the Raman, whereas bertrandite has two strong-to-moderate bands in both spectra (Fig. 3). Additional weak bands in the OH region probably arise from impurities such as clay or other alteration

(Moenke 1974). Possibly, the weaker, lower energy bands of bertrandite are due to Van der Waals bonding of hydrogen to nearby oxygens.

Bromellite

All vibrational modes of bromellite are related to the bending and stretching of the BeO₄ tetrahedra according to the correlation method (Table 2). The number of bands expected for the IR and Raman active symmetries were observed by Loh (1968). Higher resolution spectroscopy (Arguello et al. 1969) and pressure studies (Kourouklis et al. 1985) have confirmed Loh's deduction that the *A*₁ and *E*₂ bands overlap.

The IR modes are split into longitudinal and transverse optic components (Table 4a), resulting from vibration of the atoms either parallel (LO) or perpendicular (TO) to the direction of propagation. A large difference in LO and TO frequencies is expected for the highly directional BeO bond (Adams and Gardner 1974). Peaks in the powder spectra (Fig. 1) do not correspond well with the bands in the single crystal reflection spectra (Table 4a) because the powder spectra contain varying combinations of TO and LO components depending on the distribution of particle size and orientation (e.g., Farmer 1974).

Each band can be unambiguously assigned if *v*₄ is greater than *v*₂ as generally occurs. From the IR and Raman band assignments (Table 4a), the inactive frequencies in *B*₂ are predicted as 911 cm^{−1} (the average of the *v*₃ LO and TO frequencies) and as 684 cm^{−1} for *v*₄.

Inelastic neutron scattering experiments (INS) by Brugger et al. (1967) and Ostheller et al. (1968) show that two of the acoustic branches depend nearly sinusoidally on wave vector *K* as Kieffer (1979c) assumed in her model; however, one of the acoustic branches is independent of *K* at high *K*, which may cause the errors in calculating the low temperature heat capacity. Few of the optical bands were observed by Ostheller et al. (1968): one at 333 cm^{−1} in the center of the Brillouin zone is dispersed to 250 cm^{−1} along [0001] and to 650 cm^{−1} along [0110], in fair agreement with lattice dynamic calculations of Ramani et al. (1976).

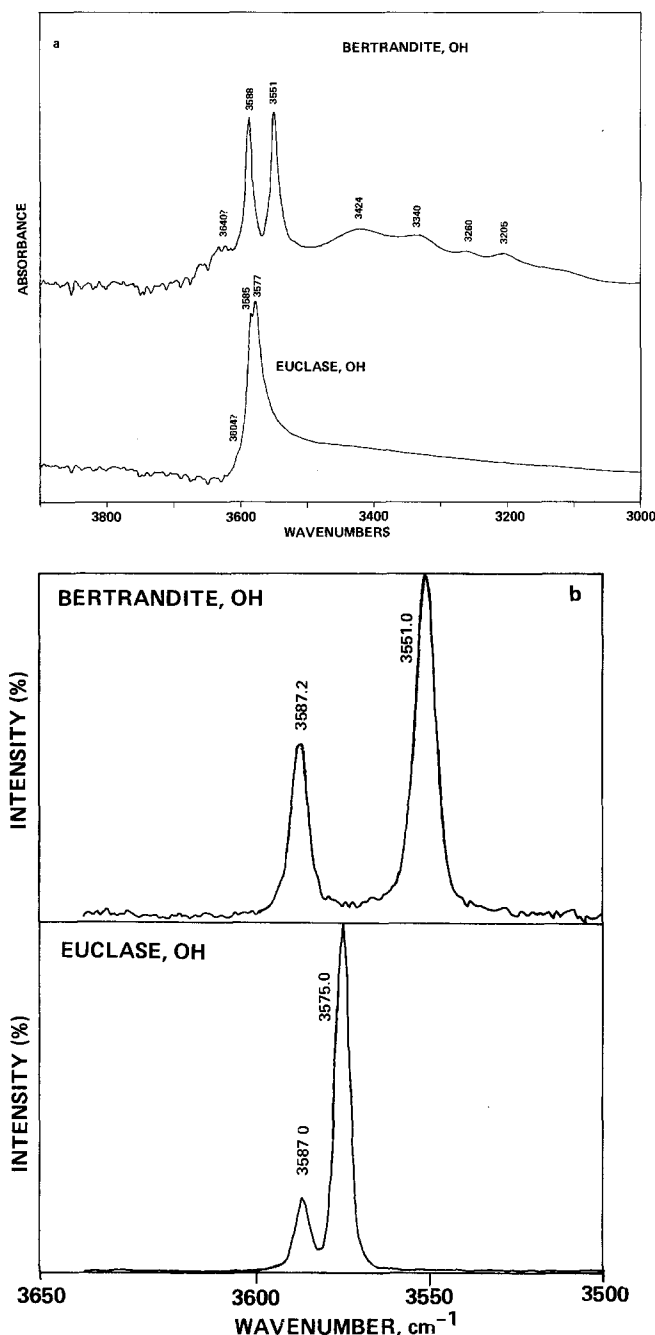


Fig. 3a, b. OH⁻ bands in bertrandite and euclase. Intensities are arbitrarily scaled. (a) Infrared spectra. (b) Raman spectra

One dispersionless band was observed with a frequency of 667 cm^{-1} that resembles two of the optical bands. Precise identification is not possible based on this incomplete data set.

Chrysoberyl

The number and symmetry of vibrational modes in chrysoberyl must be identical to that of isostructural olivine. Differences in atomic mass, ionicity, and bond strength will create different vibrational energies for the same atomic motion. Hofmeister (in prep.) has made a detailed assignment of forsterite's vibrational bands on the basis of single-crystal absorption and reflection data, FGA, and chemical and isotopic substitution experiments of Paques-Ledent and Tarte (1973) and Kovach et al. (1975). Construction of a band assignment by analogy was feasible because nearly all IR bands predicted by FGA (Table 3) were observed in chrysoberyl (Table 4b). IR spectra of the two minerals appear similar above $\sim 700\text{ cm}^{-1}$ and below $\sim 440\text{ cm}^{-1}$ because (1) high energy vibrations of tetrahedra that are not linked to other tetrahedra in the olivine structure should not significantly differ from the vibrations of an isolated tetrahedron; and (2) low energy vibrations should vary only with mass and force constant if these vibrations involve simple translations of the M-site atom as assigned. Obvious correspondence is not expected for the intermediate energy vibrations, because these probably involve combinations of lattice motions. Assigning the IR band at 535 cm^{-1} as a rotation instead of an Al—O modes as Plyusina (1963) suggested is preferred because bertrandite (which lacks aluminum) has a similar band at 542 cm^{-1} . IR peaks at 751 and 735 cm^{-1} were assigned as ν_1 stretching motions of the BeO_4 tetrahedra in accord with the low ν_1 frequency in bromellite (678 cm^{-1}).

The absence of a significant portion of the Raman bands (Table 3, 4b) makes assignment by analogy difficult. As an additional constraint, any Raman band having the same energy as an IR band was given the identical assignment. Despite this requirement, assignment of the lowest energy stretching vibrations of Be—O in chrysoberyl remains ambiguous (Table 4b).

Both the bromellite and chrysoberyl assignments contain Be—O stretching frequencies of 690 to $1,100\text{ cm}^{-1}$. Similar values are expected for other Be-minerals because all possess nearly the same average Be—O distance of $1.64 \pm 0.02\text{ \AA}$ (Hazen and Au 1986; Hazen et al. 1986).

Table 4a. Bromellite: vibrational frequencies and assignments

Powder IR this work	Reflectance IR Loh 1968	Raman crystal Arguello et al. 1969	Symmetry	Assignment
1,100	1,098	1,097	E_1 (LO)	ν_3
1,000	1,083	1,081	A_1 (LO)	ν_1
781—710	724	722	E_1 (TO)	ν_3
680, 585?	680	678	A_1 (TO)	ν_1
		684	E_2	ν_4
		338	E_2	ν_2

Table 4b. Chrysoberyl: vibrational frequencies and comparison with forsterite

Chrysoberyl			Forsterite			Forsterite			Chrysoberyl	
Powder IR		Assign- ment	Powder IR Akaogi et al. 1984 ^a	Reflectance IR Hofmeister in prep. ^d		Raman Xtal Iishi 1978 ^d	Powder Griffith 1969		Powder Raman this work	
This work	Plyusnina 1963									
1,161?	1,161	overtone								
1,090	1,103	ν_3	990	988–991	$B_{3u} \nu_3$	976 $B_{1g} \nu_3$			1,040?	ν_3
1,032	1,052	ν_3		984–996	$B_{2u} \nu_3$	966 $A_g \nu_3$	950		1,020	ν_3
1,009	1,008	overtone				922 $B_{3g} \nu_3$			931	ν_3
967	963	ν_3	960	950–961	$B_{3u} \nu_3$	884 $B_{2g} \nu_3$			816	ν_3
904		ν_3	890	865–957	$B_{1u} \nu_3$	866 $B_{1g} \nu_3$				
774	774	ν_3	870	865–961	$B_{2u} \nu_3$	856 $A_g \nu_3$	860		776	ν_3
751	754	ν_1	840	841–842	$B_{3u} \nu_1$	839 $B_{1g} \nu_1$			747	$\nu_1(\nu_3?)$
735		ν_1		828–844	$B_{2u} \nu_1$	826 $A_g \nu_1$	823		711	$\nu_1(\nu_4?)$
719?		overtone								
673		ν_4								
663		ν_4				632 $B_{1g} \nu_4$			679	ν_4
642	641	ν_4	615	601–644	$B_{3u} \nu_4$	609 $A_g \nu_4$	606		658	ν_4
606	600	ν_4	570	543–573	$B_{1u} \nu_4$	595 $B_{3g} \nu_4$			639	ν_4
584	581	ν_4	540	520–572	$B_{2u} \nu_4$	588 $B_{2g} \nu_4$				
570	571	ν_2		502–583	$B_{1u} \nu_2$	583 $B_{1g} \nu_4$			567	ν_4
556	541	$\nu_2?$	510	504–511	$B_{2u} \nu_4$	546 $A_g \nu_4$	546		546	ν_4
~531	535	R	480	505–511	$B_{3u} \nu_4$					
				463–482	$B_{1u} R$					
			470	452–488	$B_{2u} \nu_2$	441 $B_{2g} \nu_2$				
511	515	ν_2	436 ^a	434–463	$B_{3u} \nu_2$	434 $B_{1g} \nu_2$				
500?		?	425 ^a	412–450	$B_{1u} R?$	424 $A_g \nu_2$			518	ν_2
490?		?	415 ^a	418–438	$B_{2u} R?$	418 $B_{1g} R$				
481		?	403 ^b	405–430	$B_{3u} T(M_I)?$	412 $B_{3g} \nu_2$			501	ν_2 or R
473		?	384 ^a	398–408	$B_{2u} T(M_I)?$					
440		?	364 ^a	377–388	$B_{3u} R?$	376 $B_{3g} R$	380		477	R
				365–371	$B_{1u} T(M_I)?$	368 $B_{2g} R$				
420–415		?		345–375	$B_{2u} T(\text{mixed})?$					
						340 $A_g R$			459	R
400.5		$T?$	321 ^a	319–321	$B_{3u} T(\text{mixed})?$	329 $A_g T$	327		447	T
373.4		T	300 ^a	309–313	$B_{1u} T(M_I)$	324 $B_{2g} R$				
				300–308	$B_{2u} T(M_I)$	318 $B_{3g} R$				
				309–313	$B_{3u} T(M_I)$	318 $B_{1g} T$				
366.7		T	295 ^a	293–299	$B_{1u} T(M_I)$	305 $A_g T$			422	T
359.2		T		290–298	$B_{2u} T(M_I)$					
				294–297	$B_{3u} T(M_I)$					
322.6		T	278 ^a	276	$B_{1u} T(M_{II})$	272 $B_{3g} T$			397	T
				268–276	$B_{2u} T(M_{II})$	260 $B_{1g} T$			371	T
				275–276	$B_{3u} T(M_{II})$					
						244 $B_{2g} T$				
						227 $A_g T$				
						226 $B_{3g} T$				
						224 $B_{1g} T$				
309.8		T	199 ^b	200–201	$B_{3u} T(\text{SiO}_4)$	192 $B_{1g} T$			242	T
289.1		T	142 ^b	142–144	$B_{2u} T(M_{II})$	183 $A_g T$			218	T
					+ ? $T(\text{SiO}_4)$	142 $B_{2g} T$				

^a Paques-Ledent and Tarte, 1973^b Kovach et al. 1975^c R indicates an SiO_4 rotation, T a translation^d Polarizations are for the Pbnm orientation. B_{1u} , Ellz. B_{2u} , Elly. B_{3u} , Ellx.

Phenakite

For phenakite, which has a network of BeO_4 and SiO_4 tetrahedra, we first consider case # 1 (Si–O bonds dominate). The low site symmetry removes all degeneracies of the “isolated” Si–O_4 tetrahedra so that six asymmetric ν_3 and 2 symmetric ν_1 stretching vibrations are expected. Gervais et al. (1973) assigned modes observed from reflec-

tance spectra as internal to SiO_4 (ν_1 , ν_2 , ν_3 or ν_4) or external based on the frequency of the band and the temperature dependence of its width. Part of this assignment is thought to be incorrect for the following reasons: The A_u frequency at 964 cm^{-1} is not readily detectable in the reflection spectra of Gervais et al. (1973) and may be an artifact of the computer generated fit. Assignment of the $1,019 \text{ cm}^{-1}$ E_u band as an overtone (Table 4c) may not be correct because

Table 4c. Phenakite: vibrational frequencies and assignments

Powder IR this work		Reflectance IR Gervais et al. 1973 ^a			Raman powder			
					This work		Griffith 1969	Narayanan 1950
1,040	ν_3 (SiO)	1,022	A_u	ν_3 (SiO)				
	ν_3 (SiO)	1,019	E_u	overtone	1,020	ν_3 (SiO)		1,022
976	ν_3 (SiO)	997	A_u	ν_3 (SiO)	999	ν_3 (SiO)	980	1,010
950?	ν_3 (SiO)	970	E_u	ν_3 (SiO)	952	ν_3 (SiO)	950	949
		964?	A_u					
934	ν_3 (SiO)	931	E_u	ν_3 (SiO)	940	ν_3 (SiO)		937
910	ν_3 (BeO)	922	A_u	e	924	ν_3 (SiO)		
					916	ν_3 (SiO)	916	918
901	ν_3 (SiO)	898	A_u	ν (SiO)				
	ν_3 (BeO) or ν_1 (SiO)	893	E_u	ν_3 (SiO)				
					877	ν_3 (SiO)	877	879
850	ν_3 (BeO) or ν_1 (SiO)							
842	ν_1 (SiO)?							
800	ν_1 (SiO)	792	A_u	ν_1 (SiO)	807	ν_1 (SiO)		805
					788	ν_1 (SiO)		
775	ν_1 (BeO)	778	E_u	e	778	ν_1 (BeO)	776	
					768	ν_1 (BeO)		
743		741	A_u	e				
733		734	E_u	e	730			726
725		719	A_u	e				
713		711	A_u	$e?$	705			705
		710	E_u	e				
690, 673		683	E_u		689		686	
664, 656					669		668	
638, 620		636	A_u	$e?$	618			
					601	ν_4 (SiO)		
591	R (SiO)	590	E_u	ν_4 (SiO)				
576	ν_4 (SiO)	577	A_u	ν_4 (SiO)	578	ν_4 (SiO)		580
	ν_4 (SiO)	544	A_u	ν_4 (SiO)				
					527	ν_4 (SiO)		526
475	ν_4 (SiO)				483	ν_4 (SiO)	486	485
454	ν_4 (SiO)				466	ν_4 (SiO)		
439.4	ν_2 (SiO)	429	A_u	ν_2 (SiO)	447	ν_4 (SiO)	444	446
425	R (SiO)	420	E_u	ν_2 (SiO)				
384.5	ν_2 (SiO)				389	ν_2 (SiO)		383
370.0	ν_2 (SiO)	357	E_u	ν_2 (SiO)				
352.4	ν_2 (SiO)	348	A_u	ν_2 (SiO)	350	ν_2 (SiO)		348
330.9?							322	
316.5								
304.7								
294.1					298			
					283			279
					257			255
					233			230
					222			223
								184
					162.2			161

^a e indicates an external or lattice vibration

the 1,019 cm^{-1} band (Gervais et al. 1973) is as intense as the Si—O (ν_3) stretching bands, whereas an overtone should be discernably weaker. If the 1,019 cm^{-1} band is one of the ν_3 vibrations of Si, then the 893 cm^{-1} band observed in the E_u polarization by Gervais et al. (1973) must either be ν_1 , according to symmetry (Table 2), or possibly a Be—O stretch. Alternatively, the 1,019 cm^{-1} band could be a Be—O stretch, but it is more likely that the 893 cm^{-1} band seen only in reflectance measurements is a Be—O stretch because its energy matches ν_3 (Be—O) in chrysoberyl, but is significantly higher than that of most ν_1 vibra-

tions of SiO_4 tetrahedra. In this case, the 850 cm^{-1} band observed only in the powder could be the ν_1 (Si—O) mode in E_u predicted by the correlation method (Table 4c). One moderately high energy band at 775 cm^{-1} is assigned as an asymmetric Be—O stretch by analogy to chrysoberyl.

All six bands observed in the Raman spectra of phenakite above 919 cm^{-1} were assigned to ν_3 . The ν_1 , ν_2 , and ν_4 frequencies were estimated (Table 4c) by analogy to the IR band assignment. Bands near 770 cm^{-1} are tentatively assigned as Be—O symmetric stretching.

The number of bands observed is only consistent with

that predicted by symmetry analysis if the two "extra" bands observed in the IR are Be—O stretches. Some Be—O stretches could also be present at high energy in the Raman because 25 percent of the Raman bands were not observed. The spectral data thus indicates that to some extent the Be—O bond competes with the Si—O bond in phenakite.

If phenakite vibrates according to case 2, then two Si—O and four Be—O stretches are expected for each symmetry (Table 3; note that E modes are degenerate). This number is in agreement with the observations in that 12 bands occur in the IR and 11 bands occur in the Raman above 750 cm^{-1} (Table 4c). Thus complete intermixing of Be—O and Si—O stretching for phenakite is also consistent with the data. Differentiating between the two cases requires single-crystal absorption and Raman data.

Bertrandite

Application of the correlation method (case # 1) to bertrandite structure implies that 16 Si—O stretching bands will be present (Table 2). Six bands were observed at high frequencies ($900\text{--}1,134\text{ cm}^{-1}$) in the IR spectra. However, in Lazarev's (1975) analysis of thortveitite ($\text{Sc}_2\text{Si}_2\text{O}_7$), only seven of the nine vibrations of the Si_2O_7 group allowed by symmetry appear in the spectra at high frequency: two occur near 650 cm^{-1} . In thortveitite, intense bands are produced at $1,160\text{ cm}^{-1}$ by the asymmetric stretching of the bridging oxygen, at 900 cm^{-1} by the asymmetric stretching of the SiO_3 groups, and at 850 cm^{-1} by the symmetric stretching of the SiO_3 groups. By analogy, the strong bands in bertrandite at $1,096$, $1,013$, and 939 cm^{-1} are assigned to $\nu_{\text{as}}(\text{Si—O—Si})$, $\nu_{\text{as}}(\text{SiO}_3)$ and $\nu_s(\text{SiO}_3)$, respectively (Table 4d). Very high frequency weak shoulders observed at $1,170$ and $1,382\text{ cm}^{-1}$ may be artifacts, but Plyusnina (1963) reported peaks at the same positions. We associate the weak peaks with Be—O stretching vibrations as Plyusnina (1963) proposed. The bertrandite structure has two different OH ions connecting the two Be atoms (Hazen and Au 1986), which would produce at least two Be—OH stretching modes as assigned (Table 4d).

Raman bands were assigned by analogy. Although only half of the Raman bands predicted were observed (Table 3), the duplication of three out of four of the Raman bands by the IR (Table 2) results in this assignment being less tentative than it might at first appear.

For case # 2, the high energy region of both the IR and Raman should have two Be—OH, four Si—O, and six Be—O stretching bands (Table 3). Powder IR data would suggest that two Be—OH bands occur at $1,170$ and $1,391\text{ cm}^{-1}$, four Si—O bands between $1,000$ and $1,134\text{ cm}^{-1}$, and at least five Be—O bands between 760 and $1,000\text{ cm}^{-1}$. Some of the bands could be LO and TO components, but given that only 60 percent of the expected bands were observed (Table 3), we conclude that the high energy region of bertrandite could contain a mixture of Si and Be stretching bands.

Beryl

In contrast to bromellite, the powder spectrum of beryl closely resembles its single-crystal absorption (Fig. 1) and reflection data with one exception (discussed below). The excellent match can be attributed to the presence of a large number of modes with generally small LO—TO splittings

in beryl as opposed to bromellite's few modes that have large LO—TO splittings, in that mixing of the two components in a powder has little effect when the splittings are small. A large number of modes also tends to obscure the differences. We suggest that most silicates and Be-minerals will behave as beryl, whereas most oxides will behave as bromellite.

Gervais et al. (1972) used the temperature dependence of the calculated half-widths of the reflection spectra to differentiate internal vibrations of the Si_6O_{18} rings from external vibrations or lattice modes (case # 1). One problem with their analysis is that in order to fit the spectra with the Kramers-Kronig relations, bands were postulated at 979 cm^{-1} in E_{1u} and at 975 cm^{-1} in A_{2u} (Table 4e), which were not observed in the reflectance spectra. In general, Kramers-Kronig analysis does not acceptably duplicate spectral data for crystals with large unit cells (E. Salje, pers. comm. 1985), mostly due to of the large number of vibrational modes. As discussed by Adams and Gardner (1974), the postulated 975 cm^{-1} A_{2u} band is an artifact because without it, the total number of bands observed in A_{2u} exactly matches the six bands predicted. Four Si—O stretching modes are predicted in E_{1u} by application of FGA. The three intense modes above 900 cm^{-1} in the reflectance spectra (Table 4d) are certainly three of the four predicted Si—O stretching bands of beryl (Adams and Gardner 1974). The fourth band in E_{1u} is assigned to the sharp band at $1,279\text{ cm}^{-1}$ in the single-crystal spectra. Adams and Gardner (1974) considered this band to be a LO with the TO component occurring at $1,200\text{ cm}^{-1}$. The $1,279$ and $1,185\text{ cm}^{-1}$ bands ($1,290$ and $1,200\text{ cm}^{-1}$ in reflectance data), however, must be two distinct modes, because these two bands are clearly separated in the single-crystal absorption spectrum of mostly TO component (Fig. 1), such that the higher energy band ($1,279\text{ cm}^{-1}$) is more intense than the lower energy peak at $1,185\text{ cm}^{-1}$, which is not consistent with LO—TO splitting of one mode. For this assignment (Table 4e), the LO—TO splitting is large only for the highest energy mode in the A_{2u} polarization, which involves an Si—O—Be stretching motion in accord with the symmetry of the mineral (Adams and Gardner 1974).

Raman spectra of Adams and Gardner (1974) possess the same number of modes at frequencies above 900 cm^{-1} as the number of stretching modes predicted from FGA (Table 4e). In accord with the symmetry of beryl, all A_{1g} modes are ring motions (Adams and Gardner 1974).

For case # 1, FGA predicts two Be—O stretching bands in each of E_{1u} and E_{1g} , and one in each of A_{2u} and in E_{2g} (Table 2). Four bands between 730 and 823 cm^{-1} are assigned to these motions (Table 4e). Possibly, the E_{1u} band at 700 cm^{-1} could also be a Be—O stretch, although this energy seems too low. It is possible that two remaining weak Be—O stretches could be among the missing modes ($1E_{1u}$, $2E_{1g}$, and $1E_{2g}$; Tables 2, 3 and 4d).

Case # 2 can be ruled out for beryl because the FGA analysis for case # 1 gives a smaller total number of Be and Si modes (Table 2) than Kieffer's method (Table 3), and the number of observed bands is slightly less than the number predicted from FGA for case # 1.

Euclase

For case # 1, six asymmetric Si—O stretching bands are expected above about 900 cm^{-1} in both Raman and IR

Table 4d. Bertrandite vibrational frequencies

Powder IR			Raman	
This work	Plyusnina 1963	Assignment	This work	Assignment
3,588	3,584	$\nu(\text{OH})$	3,587.2	$\nu(\text{OH})$
3,551	3,546	$\nu(\text{OH})$	3,551.0	$\nu(\text{OH})$
1,382?	1,391	$\nu_s(\text{BeOH})$		
1,170?	1,170	$\nu_s(\text{BeOH})$		
1,134	1,133	$\nu_{as}(\text{SiO}_3)?$		
	1,122			
1,096		$\nu_{as}(\text{Si}-\text{O}-\text{Si})$	1,073?	$2\nu_{as}(\text{Si}-\text{O}-\text{Si})$
1,029	1,030	$\nu_{as}(\text{SiO}_3)$		
1,013		$\nu_{as}(\text{SiO}_3)$		
	987	$\nu_s(\text{SiO}_3)?$	990	$8\nu_{as}(\text{SiO}_3)$
	956		947	$4\nu_s(\text{SiO}_3)$
939	935	$\nu_s(\text{SiO}_3)$	928	
901	898	$\nu_s(\text{SiO}_3)$		
827	829		821	
804	783			
774	777		772	
755			753	
735	733		725?	
716	719		711	
	691			
688	675	$\nu_s(\text{Si}-\text{O}-\text{Si})?$	694	$2\nu_s(\text{Si}-\text{O}-\text{Si})?$
664?				
647				
638	637	$\nu_s(\text{Si}-\text{O}-\text{Si})?$		
607	610			
590?				
580			579	
545.4	546		538	
539	541			
523.9	524			
511				
487	485		487?	
476				
462				
430			427	
420				
409				
387			386	
377				
361			358	
353			352	
340				
336			330	
330				
300			301	
280?				
247			241	
			231	
206			206	
197				
184			183	

spectra (Table 2). The six strong bands in the IR above 873 cm^{-1} are thus assigned as ν_3 (Table 4f). The strong IR bands near 800 cm^{-1} are most likely ν_1 symmetric stretching vibrations (Table 4f) as postulated for phenakite. The weak IR band at $1,088\text{ cm}^{-1}$ may be an artifact, but is more likely associated with Be—OH; as in bertrandite, euclase has OH anions that are not bonded to Si (Hazen and Au 1986). Four nearly identical Be—OH bonds exist in the Bravais cell (Table 1), so that one (or two close)

stretching frequency is expected in each of the Raman and IR spectra. The three Be—O stretches expected for each symmetry according to FGA (Table 2) are associated with bands near 730 to 770 cm^{-1} .

The Raman spectrum of euclase resembles the IR, and is assigned analogously (Table 4f). About one quarter of the predicted modes were not observed, making these assignments in Table 4f tentative.

For case # 2, the number of Be—O and Si—O stretches

Table 4e. Beryl: vibrational frequencies, polarizations, and assignments

IR						Raman	
Single Xtal this work	Powder this work	Assign-ment	Reflectance (Lo-To)			Powder Griffith, 1968	Single crystal Adams and Gardner 1974
			Adams and Gardner 1974		Gervais et al. 1972		
					Sym-metry		
1,279	1,240 sh	$\nu(\text{SiO})$			E_{1u}		
1,185	1,203	$\nu(\text{SiO})$	1,290–1,200	$\nu(\text{SiO})$	1,283–1,196 $\nu(\text{Si-O})$	1,175 ν_s	1,243 E_{2g} $\nu(\text{Si-O})$
1,155 sh	1,170 sh	LO of A_{2u}			–1,054 A_{2u}		1,225 E_{2g} $\nu(\text{Si-O})$
1,019	1,020	$\nu(\text{SiO})$	1,032–1,014	$\nu(\text{Si-O})$	–1,016 $\nu(\text{Si-O})$		1,125 A_{1g} $\nu(\text{Si-O})$, in ring
					–979 ^a $\nu(\text{Si-O})$		1,068 A_{1g} $\nu(\text{Si-O})$, in ring
					–975 ^a $\nu(\text{Si-O})$		1,012 E_{1g} $\nu(\text{Si-O})$
978?	980	$\nu(\text{SiO})$	1,100–924	$\nu(\text{Si-O-Be})$	1,100–916 $\nu(\text{Si-O})$		1,005 E_{2g} $\nu(\text{Si-O})$
					–975 ^a $\nu(\text{Si-O})$		918 E_{1g} $\nu(\text{Si-O})$
953	960	$\nu(\text{SiO})$	1,002–958	$\nu(\text{Si-O})$	995–955 $\nu(\text{Si-O})$	860 ring stretch	914 E_{2g} $\nu(\text{Si-O})$
823	806	$\nu(\text{BeO})$	828–796	$\nu(\text{Si-O})?$	825–803 e		772 E_{2g} $\nu(\text{BeO})$
743	~744	$\nu(\text{BeO})$	772–734		771–733 e		770 E_{1g} $\nu(\text{BeO})$
691	681	$\nu(\text{BeO})$	706–682		703–674 e		686 A_{1g} ring
668? ^c	663 ^c				$E_{1u}??^c$	684 ring stretch	685 E_{2g}
653	652		660–656		–652 E_{1u}		583 E_{1g}
602,590 sh	590		615–596		608–588 E_{1u}	645	626 A_{1g} ring
557	526		564–528		560–515 e		583 E_{2g}
					–519? E_{1u}		565 E_{2g}
538?	517		554–532		–537 A_{2u}		529 E_{1g}
482	495		510–492		502–488 e	470	450 E_{1g}
470,425	~450,435	$R(\text{SiO}_4)$	484–419		473–423 A_{2u}		444 E_{2g}
>373 ^b	387,381	$T(\text{SiO}_4)$	387–376		–382 E_{1u}		424 E_{2g}
368.4	367	$T(\text{SiO}_4)$	376–361		375–362 e		397 E_{2g}
349.4	349	$T(\text{SiO}_4)$	350–342		–350 e	400	396 A_{1g} ring
258.2	257		262–252		E_{1u}	343 ring	383 E_{1g}
206.5	207		210–201		A_{2u}	323 de-form	324 A_{1g} ring
							318 E_{2g}
							297 E_{1g}
							291 E_{2g}
							254 E_{1g}
							214 A_{1g} rotation of ring
							188 E_{1g}
							187 E_{2g}
							146 E_{2g}
							145 E_{1g}

^a These peaks were not observed but were added in order to fit the reflection data

^b Data are not available between 420 and 370 cm^{-1} for the single crystal

^c This could be one of the missing bands or an LO component of the 652 cm^{-1} band

is 16 (Table 3). This is equal to the total number of bands observed above 750 cm^{-1} , suggesting that this is a valid approximation to euclase spectra. However, the fact that roughly one third of the bands have not been observed shows that case #1 which indicates a larger number of stretches is the better approximation.

Detection and Assignment of Low Energy Vibrations

One problem in vibrational spectroscopy is to decide whether or not all bands have been observed. This difficulty is exacerbated for weak, low frequency bands. Moreover, the position of the lowest energy band affects strongly the low temperature heat capacity calculated from vibrational spectra. Enumeration of the bands serves as a check; however, the number observed is often less than that expected (Table 3), frequently due to accidental degeneracy. Lower energy IR or Raman bands probably do not exist; but the inactive symmetries can contain the lowest frequency, which

may cause problems in calculating beryl and chrysoberyl heat capacities.

Assignments for the various common features are now considered. For all phases except bromellite, an asymmetric band is prominent at 425–440 cm^{-1} (marked by “ $\times$ ” in Fig. 1, left), and was assigned as a rotation of the BeO_4 tetrahedra in chrysoberyl. This assignment is supported by the fact that an easily distinguishable band is likely to have a similar cause for all five minerals and that a rotation would be common to all five phases.

Modes below 350 cm^{-1} in silicates are generally considered to be translations. Aluminum translations in chrysoberyl found at about 350 cm^{-1} are marked by “T” in Figure 1. Beryl contains a similar pattern; however, euclase, which also has Al, lacks this pattern. Instead, the far-IR spectra of euclase most closely resembles that of bertrandite, which has no heavy cation (Fig. 1). This similarity suggests that the lowest energy modes in euclase are lattice deformations. For beryl, two intense bands that are found

Table 4f. Euclase: vibrational frequencies

Powder IR			Raman		
This work	Moenke 1974	Assignment	This work	Griffith 1969	Assignment
3,604?					
3,585		$\nu(\text{OH})$	3,587		$\nu(\text{OH})$
3,577	3,580	$\nu(\text{OH})$	3,575		$\nu(\text{OH})$
1,088?		$\nu_s(\text{Be}-\text{OH})$	1,120		$\nu_s(\text{Be}-\text{OH})$
1,071	1,072	$\nu_3(\text{SiO})$	1,059		$\nu_3(\text{SiO})$
1,027		$\nu_3(\text{SiO})$	1,023		$\nu_3(\text{SiO})$
982	980	$\nu_3(\text{SiO})$	975	945	$\nu_3(\text{SiO})$
913	915	$\nu_3(\text{SiO})$			$\nu_3(\text{SiO})$
982		$\nu_3(\text{SiO})$	908	912	$\nu_3(\text{SiO})$
873		$\nu_3(\text{SiO})$	880	882	$\nu_3(\text{SiO})$
			806		$\nu_1(\text{SiO})$
794	776	$\nu_1(\text{SiO})?$	790		$\nu_1(\text{SiO})$
765		$\nu_s(\text{BeO})?$	756		
734	726		747		
679					
660	665		667	665	
642			642		
610			602		
592	595				
581			583		
567			574	560	
534	540	$R(\text{SiO}_4)$	545	540	
523					
515			518	515	
494					
478	480				
			461	464	
454	455		452		
432		$R(\text{SiO}_4)$	444		
422	427	$R(\text{SiO}_4)$	423		
			411		
397			397		
388			384		
377					
365					
			355		
			341		
338			334		
309			309		
			290		
			276		
			259		
			237		
			201		
182			180		
			145		

below the inferred pattern of Al translational motions must also be deformations. We suggest that translations may be distinguished from deformations in the far-IR because the former are discernably weaker.

All of the beryllium silicates have low energy modes ($145\text{--}180\text{ cm}^{-1}$). If Moenke's (1974) interpretation that Be and Si vibrations are coupled is correct, then low frequency bands are expected because the position of the lowest energy band in silicates generally decreases as polymerization increases (Kieffer 1985). The lower charge on Be lends to a directionality of the Be—O bond as compared to the three-dimensional character of the Si—O bond. The di-

Table 5. Options used to model C_V for Be-Al-Silicates

Case	Option	Mineral	Description
1 ^a	2	Phases with Si	The Einstein oscillators are assumed to all be Si—O stretching modes and to all occur in the high energy region. The correlation method was used to enumerate bands.
	2a	Phases with Si	$\nu_3 > 800\text{ cm}^{-1}$ and $\nu_1 \leq 800\text{ cm}^{-1}$
	2b	Phases with Si	ν_3 and $\nu_1 > 800\text{ cm}^{-1}$
	2c	Bertrandite	Kieffer's polymerization scheme was used to enumerate the Si—O stretching bands
	2d	Phenakite, beryl	Gervais et al's (1972, 1973) assignments for IR bands and Adams and Gardner's (1974) assignments for the Raman bands were used.
	2e	Phenakite, beryl	Modifications of Gervais et al's (1972, 1973) assignments were used.
	2a + Be	Bertrandite, euclase	As 2a with the addition of Be—OH oscillators at very high frequencies.
	2b + Be	Bertrandite, euclase	As 2b with the addition of Be—OH oscillators.
	3	Phases without Si	The Einstein oscillators were assumed to all be Be—O stretching bands and were enumerated according to the correlation method.
	3a	Chrysoberyl	$\nu_3(\text{BeO}_4) > 774\text{ cm}^{-1}$ and $\nu_1(\text{BeO}_4) \sim 750\text{ cm}^{-1}$
	3b	Chrysoberyl	$\nu_3 > 800\text{ cm}^{-1}$ and $\nu_1 \sim 775\text{ cm}^{-1}$
	3c	Chrysoberyl	$\nu_3 > 774\text{ cm}^{-1}$ and $\nu_1 \sim 725\text{ cm}^{-1}$
	3d	Bromellite	Loh's (1968) assignment and an estimate for the inactive frequencies were used.
2 ^b	1	All	All optic frequencies are included in the continuum.
	4	Bertrandite, Phenakite	Be—O and Si—O modes intermixed in the high energy region. Be—OH oscillators are separated.

^a Si—O stretches assumed to account for all bands in the high energy region

^b Si—O and Be—O stretching bands intermixed in the high energy region

rectionality is manifest in the low energy of the lattice modes in euclase, suggesting that Be and Si are equally effective in bonding along the chains, as opposed to the higher energy of the lattice bands in phenakite and bertrandite, suggesting that Be does not bond as strongly as Si in a framework. The existence of very low energy modes in structures classified as nesosilicates suggests that applying FGA to isolated SiO_4 groups in minerals that have a light cation which could compete with bonding of oxygen to silicon is not entirely justified.

Table 6. Parameters used in all options for calculating C_V

Mineral	V cm ³ /mole	α μK ⁻¹	B_T Mbar	$U_3 = V_{VRH, p}$ km/s	$V_{VRH, s}$ km/s	U_2 km/s	U_1 km/s	$\nu_i(\text{IR})$ cm ⁻¹	$\nu_i(\text{Raman})$ cm ⁻¹
Bromellite ref.	8.315	13.8 + 0.011 T Skinner 1966	2.24 Cline et al. 1967	12.16	7.410	7.503	7.265	680 Loh 1968	338 Arguello et al. 1969
Chrysoberyl	29.18	13.8 + 0.011 T See text	2.40 Wang et al. 1975	11.0	6.56	6.75	6.39	289 this work	218 this work
Phenakite	37.19	14 + 0.00865 T See text	2.0854 Yeganeh-Haerj and Weidner 1985	10.748	5.812	5.780	5.730	294 this work	162 Narayanan 1950
Bertrandite	91.28	32 + 0.00865 T See text	0.72 Hazen and Au 1986	Assumed equal to phenacite's (see text)				184 this work	183.3 this work
Beryl	200.56	-0.5 + 0.00865 T Schlenker	1.918 Yoon and Newnham 1973	8.46	5.61	5.65	5.57	207 Adams and Gardner 1974	145
Euclase	46.57	14 + 0.00865 T See text	1.60 Hazen et al. 1986	Assumed equal to phenacite's (see text)				182 this work	145 this work

Calculation of Heat Capacity

Summary of Kieffer's (1979) Model

Heat capacity, $C_V(T)$ was calculated from the lattice dynamics model of Kieffer (1979a, b, c, 1980). Her method approximates the total vibrational spectrum from IR and Raman frequencies and the three acoustic velocities. Heat capacity is relatively insensitive to the details of the spectrum, except at temperatures below 50 K, because the thermodynamic functions are averages over the vibrational density of states. For this reason, Kieffer's model (1979a, b, c, 1980) yields accurate estimates of $C_V(T)$ and entropy $S(T)$ for many classes of minerals (typical differences between calculated and experimental values are ± 30 –50 percent at 50 K, ± 5 percent at 298 K, and ± 1 percent at 700 K). Minerals tested so far include Mg_2SiO_4 polymorphs (Akaogi et al. 1984), aluminosilicates, pyroxenes, feldspars, garnets, calcite, and some oxides and salts (Kieffer 1980).

Kieffer's (1979c) method can be summarized as follows. The primitive cell has $3s$ total degrees of freedom (where s is the number of atoms in a primitive cell). Three of the $3s$ vibrational modes are acoustic: these are determined from the acoustic velocities of the one longitudinal and the two shear waves by assuming that frequency varies sinusoidally with wave vector K (dispersion). The remaining $3s - 3$ modes are optical. Isolated high-energy modes (such as O–H or Si–O stretching) are enumerated in accordance with structural linkage and represented as separate Einstein oscillators of frequency ν_{Ei} . The optic continuum that contains the remaining optical modes is estimated from far-IR, mid-IR, and Raman spectra. The scant INS data available for minerals suggests that only the dispersion of the lowest energy mode will affect calculation of the thermodynamic functions. Kieffer (1979c) assumed that at the Brillouin zone edge the lowest frequency ν_i is reduced to

$$\nu_i(K) = \nu_i(0)(1 + M_2/M_1)^{-1/2}, \quad (1)$$

where M_1 and M_2 are masses of the atoms involved such that $M_1 > M_2$.

The assumed vibrational spectrum is thus a combination of three acoustic branches, an optic continuum, and Einstein oscillators. Data required for the model are acoustic velocities, unit cell characteristics, and IR and Raman frequencies. To compare C_V to the experimentally derived C_P , in-

formation on the bulk modulus (B_T), volume (V), and the thermal expansivity (α) are needed, because

$$C_P = C_V + TV\alpha^2 B_T. \quad (2)$$

Details of the Frequency Distribution of the Vibrational Bands

We have shown that (1) bromellite and chrysoberyl spectra can be approximated as consisting of internal BeO_4 vibrations and external lattice vibrations; (2) beryl and euclase spectra can be treated as the sum of internal SiO_4 vibrations, secondary lower energy Be–O stretching modes, and lattice vibrations, and that (3) phenakite and bertrandite may be either behave as in (2) above or as if the internal vibrations of SiO_4 and BeO_4 are mixed in the high energy region. In addition, bertrandite and euclase contain distinguishable Be–OH stretching bands. Nevertheless, several options (Table 5) are reasonable for the spectroscopic modelling of C_V for each of the minerals because the assignments for the individual Si–O and/or Be–O stretching modes are not unique. The differences in density of states $g(\nu)$ are generally small as indicated in Figure 4. The different effect on C_V for each of the options will be discussed in detail in the following section.

Dispersion was included as a variable to allow for the possibility of lower energy modes. INS data shows that bromellite's lowest energy mode at 338 cm^{-1} was dispersed to 245 cm^{-1} along $[0001]$ and to 636 cm^{-1} along $[0110]$ (Ostheller et al. 1968). For Option 3, which separates the modes, an average frequency (i.e., no dispersion), may be the best approximation, but for the optic continuum, 245 cm^{-1} should be used as the lower cutoff. This amount of dispersion is similar to using the mass of the oxygen atom for M_1 and M_2 in Equation (1), which is the approximation Kieffer (1980) used for minerals lacking a heavy cation. For the Be-silicates, dispersion could either be ignored or be modelled as O *vs.* O. For the Al and Si bearing phases, the lowest mode is most likely to involve Al *vs.* O. For chrysoberyl, in analogy to forsterite, the lowest energy mode could also be Al *vs.* BeO_4 .

Parameters common to all options for modelling C_V are listed in Table 6, along with thermodynamic quantities needed to relate C_V to C_P . Thermal expansivity (α) of chrysoberyl has been measured only near room temperature

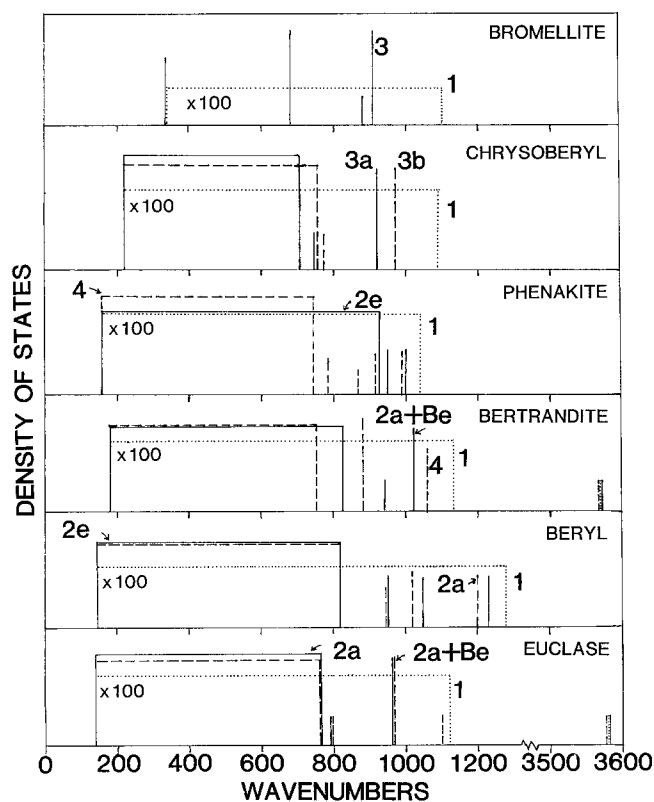


Fig. 4. Density of states vs. frequency for selected models, as described in Tables 5, 6 and 7. Optic continua (boxes) are drawn at $\times 100$ actual height to facilitate comparison to Einstein oscillators

(α is $15.3 \times 10^{-6}/\text{K}$ at 273 K: Fizeau 1888), so that its temperature dependence was approximated by $d\alpha/dT$ of bromellite, which is the only other Si-free phase. This approximation is reasonable because chrysoberyl's assumed slope is similar to that of the structural analog forsterite ($0.018 \times 10^{-6}/\text{K}^2$: Suzuki et al. 1979). For phenakite, bertrandite, and euclase, the temperature dependence of α was approximated from $d\alpha/dT$ measured for bromellite, rather than $d\alpha/dT$ of beryl because its behavior is anomalous for a silicate. The intercepts of phenakite, bertrandite, and euclase were determined from the approximately inverse relationship of bulk modulus with thermal expansivity at room temperature (Sumino and Andersen 1984, Fig. 4). The approximation described above will have little effect, because the correction from experimentally determined C_P to C_V (Eq. 4) is small (on the order of 1 to 2%) over 0 to 800 K. Assuming a maximum error in estimating α of 50 percent, then the resulting error induced in calculating C_V from C_P is less than 2 percent.

Because acoustic velocities have not been measured for bertrandite and euclase, the values were approximated from those of phenakite. Phenakite was selected because its structure is the most similar. This approximation will contribute at most an error of 0.5 percent in $C_V(T)$ for bertrandite and euclase, owing to their large number of optic modes.

Results from Modeling C_V

The heat capacities calculated from Kieffer's (1979c) approach and the parameters varied for each of the options

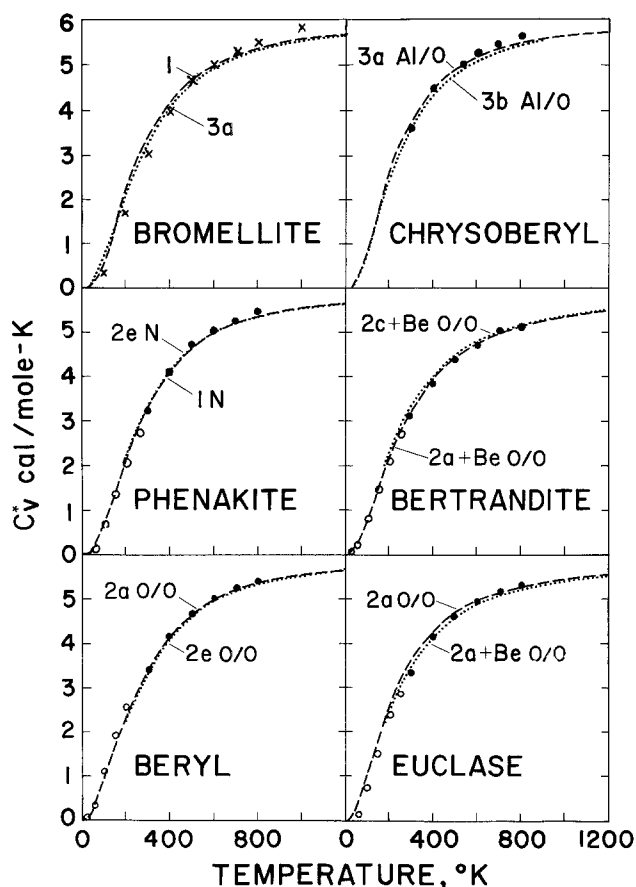


Fig. 5. Heat capacity at constant volume vs. temperature. The two models (described in Tables 5, 6, and 7) which gave C_V closest to the experimental values are depicted here. Circles are experimental data of Hemingway et al. (1986); open circles indicate low temperature data. Crosses, experimental values of Chase et al. (1974)

are listed in Table 7, along with C_V derived from Hemingway et al.'s (1986) results. Models for which the difference between experimental and calculated C_V are less than 5 percent at 298 K and 3% at temperatures greater than 500 K are acceptable. Three temperatures were sufficient in constraining the curve. We chose 700 K because it is low enough that anharmonic effects and the C_P to C_V correction will not interfere, 500 K as a middle point, and 298 K because this is sufficiently high that the acoustic modes will not significantly affect C_V here. Figure 5 compares C_V calculated for two of the possible options with experimental values of Hemingway et al. (1986) for each of the six minerals. At 100 K and below differences are ± 20 percent, which is generally closer than previous results at low temperature. The worse fit above 600 K can be attributed to errors in estimating α for the C_P to C_V correction. First, each mineral is discussed individually, and then the results are generalized under "conclusions".

Acceptable C_V 's were predicted for bromellite by omitting dispersion for both the optic continuum model (1), for and the model consisting entirely of Einstein oscillators (option 3e). The match ($< 2\%$ from 200–700 K) is closer than that usually achieved. The same options (3e and 1) that included dispersion overestimate C_V at $T < 298$ K. This overestimation of C_V at temperatures below 298 K likely arises from the contribution of the acoustic branches (one of which is nearly constant instead of sinusoidally depend-

Table 7. Parameters and results for spectroscopic models of C_V

Mineral	Model #	Dispersion	ν_u	ν_{E1}	q_{E1}	ν_{E2}	q_{E2}	ν_{E3}	q_3	ν_4	q_4	Heat capacity				Max. error %			
												at 50K	at 100K	at 298K	at 500K		at 700K		
Bromellite	Expt. data ^c																		
	1	None	1,100										0.016	0.32	3.036	4.607	5.263	—	
	1	See text	1,100										0.042	0.446	3.078	4.506	5.124	2.6	
	3e	None		338	0.167	684	0.250	882	0.083	911	0.250		0.051	0.569	3.283	4.534	5.145	8.1	
	3e	See text		245	0.167	684	0.250	882		911	0.250		0.046	0.527	3.113	4.569	5.164	2.5	
Chrysoberyl													0.084	0.329	3.199	4.569	5.164	5.3	
	Expt. data ^b												nd	nd	3.574	4.931	5.471	—	
	1	O/O	1,090										0.137	0.707	3.139	4.550	5.148	12.2	
	1	None	1,090										0.079	0.509	3.011	4.458	5.094	15.7	
	3a	O/O		750	0.048	920	0.142						0.160	0.904	3.722	4.904	5.368	4.4	
	3a	Al/O	711	750	0.048	920	0.142						0.131	0.828	3.682	4.886	5.359	3.2	
	3a	Al/BeO ₄	711	750	0.048	920	0.142						0.114	0.776	3.652	4.872	5.351	2.2	
	3a	None	711	750	0.048	920	0.142						0.085	0.663	3.580	4.840	5.333	2.5	
	3b	O/O	754	775	0.048	970	0.142						0.153	0.850	3.587	4.815	5.313	2.9	
	3b	Al/O	754	775	0.048	970	0.142						0.126	0.778	3.546	4.797	5.303	3.1	
	3b	Al/BeO ₄	754	775	0.048	970	0.142						0.110	0.728	3.516	4.783	5.295	3.2	
	3b	None	754	775	0.048	970	0.142						0.086	0.622	3.444	4.750	5.277	3.7	
	3c	O/O	673	725	0.048	920	0.142						0.168	0.959	3.821	4.957	5.399	6.9	
	3c	Al/BeO ₄	673	725	0.048	920	0.142						0.120	0.823	3.751	4.927	5.383	5.0	
	3c	None	673	725	0.048	920	0.142						0.091	0.706	3.679	4.895	5.365	1.9	
	Phenakite	Expt. data ^b												0.086	0.632	3.237	4.674	5.327	
1		None	1,040										0.134	0.689	3.257	4.615	5.192	2.5	
1		O/O	1,040										0.224	0.876	3.384	4.680	5.229	4.5	
2a		None		862	0.047	955	0.143						0.141	0.739	3.401	4.710	5.251	5.0	
2a		O/O	813	862	0.047	955	0.143						0.234	0.927	3.504	4.757	5.278	8.2	
2b		None	850	920	0.095	1,000	0.095						0.136	0.705	3.296	4.638	5.206	2.2	
2b		O/O	850	920	0.095	1,000	0.095						0.226	0.886	3.399	4.686	5.233	5.0	
2d		None	922	950	0.050	1,000	0.050						0.137	0.711	3.331	4.667	5.226	2.9	
2d		O/O	922	950	0.050	1,000	0.050						0.228	0.898	3.446	4.723	5.257	6.5	
2e		None	922	950	0.060	1,000	0.060						0.135	0.697	3.285	4.636	5.206	2.3	
2e		O/O	922	950	0.060	1,000	0.060						0.225	0.880	3.397	4.690	5.236	4.9	
4		None	743	786	0.048	867	0.032	917	0.055				0.150	0.814	3.597	4.831	5.325	11.1	
4		O/O	743	786	0.048	867	0.032	917	0.055				0.254	1.018	3.698	4.877	5.350	14.0	
Bertrandite		Expt. data ^b												0.211	0.808	3.122	4.394	5.009	
		1	None	1,134										0.112	0.565	2.873	4.240	4.864	7.9
		1	O/O	1,134							3,570	0.042		0.179	0.738	3.010	4.313	4.907	3.6
	2a	None		940	0.042	1,000	0.085	1,100	0.021	3,570	0.042		0.122	0.670	3.244	4.498	5.028	3.6	
	2a	O/O	825	940	0.042	1,000	0.085	1,100	0.021	3,570	0.042		0.203	0.868	3.362	4.553	5.058	3.9	
	2a + Be	None	825	940	0.042	1,020	0.106	1,280	0.042	3,570	0.042		0.160	0.828	3.219	4.432	4.975	7.9	
	2a + Be	O/O	825	940	0.042	1,020	0.106	1,280	0.042	3,570	0.042		0.196	0.828	3.219	4.432	4.975	3.1	
	2c	None	825	940	0.042	1,000	0.064	1,100	0.021	3,570	0.042		0.124	0.685	3.298	4.537	5.052	5.6	
	2c	O/O	825	940	0.042	1,000	0.064	1,100	0.021	3,570	0.042		0.200	0.888	3.420	4.593	5.084	9.5	
	2c + Be	None	825	940	0.042	1,025	0.085	1,280	0.042	3,570	0.042		0.121	0.656	3.161	4.418	4.970	1.2	
	2c + Be	O/O	825	940	0.042	1,025	0.085	1,280	0.042	3,570	0.042		0.199	0.848	3.276	4.472	5.000	4.9	
	4	None	755	880	0.128	1,060	0.085	1,280	0.042	3,570	0.042		0.121	0.653	3.120	4.383	4.946	1.3	
	4	O/O	755	880	0.128	1,060	0.085	1,280	0.042	3,570	0.042		0.197	0.838	3.222	4.428	4.971	3.2	
	Beryl	Expt. data ^b												0.278	0.170	3.439	4.673	5.246	
		1	Al/O	1,280										0.191	0.701	2.839	4.244	4.936	17
		1	O/O	1,280										0.218	0.745	2.870	4.261	4.947	16
2a		O/O	820	946	0.055	1,020	0.076	1,200	0.076				0.264	0.938	3.373	4.622	5.200	1.9	
2a		Al/O	820	946	0.055	1,020	0.076	1,200	0.076				0.230	0.887	3.348	4.601	5.173	2.6	
2a		None	820	946	0.055	1,020	0.076	1,200	0.076				0.165	0.767	3.284	4.581	5.157	5.5	
2b	O/O	820	960	0.069	1,020	0.069	1,200	0.069				0.264	0.938	3.376	4.627	5.184	1.8		

Euclase		820	960	0.069	1,020	0.069	1,200	0.069	0.230	0.887	3.351	4.615	5.177	2.6
2b	Al/O	820	960	0.069	1,020	0.069	1,200	0.069	0.165	0.767	3.287	4.586	5.161	4.4
2b	None	820	960	0.069	1,020	0.069	1,200	0.069	0.264	0.938	3.388	4.640	5.193	1.5
2d	O/O	820	930	0.069	1,000	0.069	1,200	0.069	0.230	0.887	3.363	4.629	5.187	2.2
2d	Al/O	820	930	0.069	1,000	0.069	1,200	0.069	0.165	0.767	3.300	4.600	5.171	4.0
2d	None	820	930	0.069	1,000	0.069	1,200	0.069	0.264	0.938	3.370	4.616	5.175	2.0
2e	O/O	820	945	0.069	1,050	0.069	1,230	0.069	0.230	0.887	3.345	4.605	5.169	2.7
2e	Al/O	820	945	0.069	1,050	0.069	1,230	0.069	0.165	0.767	3.281	4.575	5.153	4.6
2e	None	820	945	0.069	1,050	0.069	1,230	0.069	0.120	0.719	3.357	4.628	5.190	
Expt. data ^b									0.239	0.848	3.123	4.389	4.958	7.0
1 + Be	O/O	1,070					1,100	0.040	0.209	0.801	3.093	4.374	4.950	7.9
1 + Be	Al/O	1,070					1,100	0.040	0.081	0.693	3.020	4.336	4.928	10.0
1 + B	None	1,070					1,100	0.040	0.285	1.039	3.575	4.692	5.149	6.4
2a	O/O	765	792	0.04	962	0.12			0.248	0.985	3.550	4.680	5.142	5.7
2a	Al/O	765	792	0.04	962	0.12			0.178	0.858	3.487	4.652	5.129	3.8
2a	None	765	792	0.04	962	0.12	1,100	0.040	0.273	0.992	3.443	4.595	5.086	2.6
2a + Be	O/O	765	792	0.04	962	0.12	1,100	0.040	0.238	0.940	3.420	4.585	5.080	2.1
2a + Be	Al/O	765	792	0.04	962	0.12	1,100	0.040	0.173	0.820	3.360	4.558	5.066	2.4
2a + Be	None	765	792	0.04	962	0.12	1,100	0.040	0.272	0.986	3.457	4.616	5.102	3.0
2b	O/O	806	878	0.04	980	0.12			0.237	0.934	3.432	4.604	5.095	2.2
2b	Al/O	806	878	0.04	980	0.12			0.171	0.813	3.368	4.575	5.080	3.2
2b	None	806	878	0.04	980	0.12	1,100	0.040	0.261	0.941	3.330	4.522	5.041	2.8
2b + Be	O/O	806	878	0.04	980	0.12	1,100	0.040	0.228	0.892	3.306	4.511	5.035	3.0
2b + Be	Al/O	806	878	0.04	980	0.12	1,100	0.040	0.166	0.777	3.246	4.484	5.020	3.3
2b + Be	None	806	878	0.04	980	0.12	1,100	0.040						

^a Maximum error incurred between 200 and 700 K. ^b Experimental heat capacities from Hemingway et al. (1986). ^c Experimental C_V for bromellite from Chase et al. (1974).

ing on K) because the acoustic branches constitute a large fraction (1/4) of the modes, and because at lower temperatures, the lowest energy modes become increasingly important. Apparently, larger v_l compensates for the excess contribution of the acoustic branches. The close approximation of option 3e to C_V at high temperature lends credence to estimation of the B_2 frequencies as 684 and 911 cm^{-1} (v_4 and v_3). Option 1 probably gives good results because its density of states is a spreading out of the delta functions used for model 3 (Fig. 4).

Option 3a for chrysoberyl predicts $C_V(T)$ well, implying that the assignment for Al_2BeO_4 (Table 4b) based on Hofmeister's (in prep.) assignment for Mg_2SiO_4 is valid, at least for the high energy modes. Slight variations of the assignment (option 3b and 3c) are less successful in deriving C_V (> 5% difference over 298–700 K: Table 7). Model 3 partitions more modes to lower energy (Fig. 4), thus leading to a higher C_V at low temperature for model 3. Other variations of model spectra were even less satisfactory.

For phenakite, option 2 and the sole optic continuum give reasonable values for C_V . These approximations for the total spectrum accurately reproduce the experimental heat capacity from Kieffer's (1979c) method because in phenakite there is no large gap in frequency between the high energy bands and the continuum, so that separating a few bands as Einstein oscillators does not alter the density of states. However, option 4 overestimates C_V by 10 percent over 150 to 800 K, suggesting that treating Be–O and Si–O bonds as equivalent overestimated the oscillators between 200 and 800 cm^{-1} (Fig. 4). For this reason, we suggest that the Si–O stretching bands account for the modes above 900 cm^{-1} as assumed in option 2, and that the optic continuum (option 1) gave satisfactory results simply because phenakite has nearly a constant density of states. A few Be–O stretches are present in the high energy region (i.e., the mode at 922 cm^{-1}) but complete intermixing of Be and Si stretching modes can be ruled out by the failure of model 4 to reproduce C_V . Our modification of Gervais et al. (1973) band assignment gives slightly better results, but the difference is too small to favor one assignment over the other.

For bertrandite, agreement is surprisingly good (difference ~4%) for all options enumerating stretching bands, even though only about half of the expected bands were observed. The calculation of C_V may be affected by inclusion of these missing bands in the model, depending on their distribution in frequency, so that the conclusions here are tentative. The high energy region cannot consist entirely of Si–O stretching vibrations, because models 4 and 2c with the largest number of Si–O stretching bands (Table 5) most closely approach C_V (Table 7). A heat capacity (reduced by roughly 10% at lower temperatures) that is close to the measured value results if additional Einstein oscillators are included for Be–O(H) stretching in the high energy region (options 4 and 2a + Be), thus corroborating the assignment of IR bands at 1382 and 1,170 cm^{-1} as Be–O(H) stretching modes. These vibrations were excluded from the continuum model (option 1) presented here because the value predicted for C_V was about 20 percent lower than the experimental value. Even if an artificially low high-energy cutoff (v_u) is used as listed in Table 7, the heat capacity is still lower than that measured. The continuum option apparently distributes too many vibrations in the high energy region (Fig. 4). We cannot be certain that total mode mixing occurs in bertrandite because $g(v)$ for model's 2a +

Be and 4 are similar (Fig. 4) despite the contrasting assumptions.

All models of the density of states in beryl except the continuum approximate C_V well (1–4 percent difference). All options enumerating $\nu(\text{Si}-\text{O})$ give similar values for C_V because the density of states (Fig. 4) is strongly constrained by the data. The large number of inactive modes must have a similar distribution in frequency: otherwise a difference in $g(\nu)$'s would lead to erroneous values for C_V . The strong departure of C_V calculated from experiment for the continuum model corroborates the spectral evidence that stronger bonding occurs within the Si_6O_{18} rings than across the $\text{Si}-\text{O}-\text{Be}$ linkages joining the rings. If $\text{Si}-\text{O}-\text{Be}$ linkages were as strong as $\text{Si}-\text{O}-\text{Si}$ linkages, then the resulting framework should produce vibrations that could be modelled as a continuum as it was for phenakite and bromellite.

For euclase, the optic continuum gave a poor match of C_V with experimental results (>10% difference), as expected for an aluminum-bearing phase without continuously linked tetrahedra. Models with a larger portion of modes at high energy (2a+Be, 2b; see Fig. 4) resulted in the closest match for C_V . Some of the high energy modes are associated with Be, because including just the Si modes does not result in a large enough density of modes at high frequency. If the uppermost bands are treated as Be–O(H) stretching bands (option 2a+Be) then a much closer approximation to the calorimetric C_V results (Table 7). The improvement in calculated C_V produced by the addition of very high energy oscillators implies that assignment of Be–O(H) stretching to very high energy modes is correct, and confirms Plyusnina's (1963) deduction.

Discussion and Conclusions

Kieffer (1980) has shown that her model, which requires enumeration only of isolated $\text{Si}-\text{O}$ and OH stretching modes, can be used to successfully predict the heat capacity of most minerals. For the six beryllium aluminosilicates examined here, however, band partial assignments for $\text{Si}-\text{O}$ and $\text{Be}-\text{O}$ stretching modes in the high energy region are needed to accurately calculate C_V . In fact, it is highly likely that better agreement between model and experimental values for C_V may be obtained for *all* minerals by utilizing band assignments to construct $g(\nu)$.

The varying degree of correspondence between calculated C_V and C_V derived from calorimetric C_P for the different options suggest that some of the band assignments are better representations of the vibrational character of these minerals than others. The best agreement between calculated and experimental C_V was found for the minerals having band assignments that were most strongly constrained by the spectral data and by symmetry. The band assignment of bromellite is completely constrained by the spectral data and by symmetry and leads to a model that closely reproduces (1–4 percent difference) the calorimetry. For phenakite and beryl, which have reasonably well constrained band assignments, almost all models give C_V close to experiment. The band assignments of chrysoberyl, bertrandite, and euclase are not well constrained and do not produce models that accurately reproduce experimentally derived C_V unless specific assumptions are made. If it is assumed that the model will give a value of C_V closest to experiment for the most accurate band assignment, then the departure of

the model from experiment can be used to support the best band assignment consistent with spectroscopy. The assignment for chrysoberyl given in Table 4b is likely valid, because it is the only band assignment that gives acceptable heat capacity (<5% difference at $T < 500\text{K}$). For bertrandite and euclase, the only models that give reasonable values for C_V are those that enumerate separately the very high frequency bands which are attributed to Be–OH stretching, which implies that this assignment made on the basis of structural considerations is correct.

The varying degrees of correspondence of the alternative band assignments used in modeling can be used to ascertain the minimum amount of mixing of Be–O stretching vibrations with $\text{Si}-\text{O}$ stretching in the high energy region. The general correspondence of C_V for options that enumerate $\text{Si}-\text{O}$ stretching bands suggests that Be–O stretching accounts for a minor part of the high frequency region, with the possible exceptions of phenakite and bertrandite. For minerals containing Be and not Si, Be–O stretching bands clearly replace $\text{Si}-\text{O}$ stretching bands in the high frequency region and act in the same manner. If both tetrahedrally coordinated Be and Si are present in a mineral then the proportion of $\text{Si}-\text{O}$ vs Be–O stretching bands in the $800\text{--}1,300\text{ cm}^{-1}$ region depends on the structure of the mineral. The high energy region of beryl consists entirely of $\text{Si}-\text{O}$ stretching vibrations, as the strong bonding within the six-member rings would imply. Phenakite definitely has a small number of Be–O oscillators mixed in with the $\text{Si}-\text{O}$ modes, but the Be–O modes clearly cannot dominate as indicated by the failure of model 4. Bertrandite and euclase, which have oxygen ions coordinated only to Be and not to Si possess Be–O(H) stretching bands at very high frequency ($>1,100\text{ cm}^{-1}$) that must be included as Einstein oscillators for Kieffer's (1979c) method to closely approximate the experimental heat capacity. Otherwise, the high frequency region of euclase consists entirely of $\text{Si}-\text{O}$ stretching bands, implying that Be–O bonding is secondary to $\text{Si}-\text{O}$ bonding. The information on bertrandite is insufficient to make this distinction.

In apparent contradiction to the above results, examination of the relative energy of the lowest energy band in the six phases implies that Be contributes along with Si to the lattice modes in all Be-silicates. This contradiction can be ascribed to the fact that the high energy stretching vibrations involve only nearest neighbors, whereas the low energy modes inherently involve forces between distant atoms.

In the calculations presented here, dispersion was treated as a variable. The omission of dispersion gave acceptable values for the heat capacity for all phases. For bromellite, bertrandite, and phenakite the omission of dispersion is only slightly better than modelling dispersion as Al or O vibrating against oxygen. For chrysoberyl, the only phase with isolated BeO_4 tetrahedra, the possible dispersion factors gave slightly better results than not using dispersion. For beryl or euclase, either Al/O or O/O dispersion gave better results than omitting dispersion. The above agrees with results of Akaogi et al. (1984) who found that in modelling Mg_2SiO_4 polymorphs that dispersion has a minor effect on entropies and C_V . We agree with Ross et al. (1986) that it is best to omit dispersion when no constraining experimental data (such as low temperature C_P or INS data on structural analogues) are available.

In conclusion, Kieffer's model can successfully model

C_V for beryllium aluminosilicates provided that complete and accurate vibrational spectra are available and that approximately correct assignments of the high energy bands have been made. Similar problems in calculating C_V are likely to be encountered with silicates containing boron, vanadium or phosphate groups that vibrate at similar energies. Our results give confidence that spectroscopy will continue to be useful in determining C_V , S , and free energies of minerals. Even more importantly, this method has unique potential in determining thermodynamic properties of rare or metastable phases and of minerals under the extreme physical conditions of the earth's interior.

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