Single-crystal Vibrational Spectrum of Topaz and some Comments on Spodumene

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Nearly all of the 93 optically active modes of topaz have been observed and assigned to symmetry species using the techniques of single-crystal spectroscopy. Preliminary data are given for spodumene.

ALTHOUGH much is known about the i.r. spectra of silicate minerals and, to a lesser extent, their Raman spectra [1-3] very little work has been done using orientated single crystals in polarised light. Such studies are an essential prerequisite to full understanding of what are often very complex spectra since silicate minerals commonly have large unit cells of low symmetry. We have recently deduced assignments for beryl [4] and benitoite,[5] systems in which the structures and selection rules are particularly helpful in leading to an understanding of the manner of construction of the spectra. We now report single-crystal i.r. and Raman data for topaz, and some fragmentary data for spodumene. The low symmetry of spodumene means that we can only produce a list of numbers classified by symmetry label. Topaz has much higher symmetry [6] and, although the constituent atoms of the large unit cell are on low-symmetry sites and contribute to all-symmetry species, yields spectra capable of further interpretation. Our results provide a firm data base for theoretical studies of topaz.

EXPERIMENTAL

A piece of topaz of side *ca.* 1 × 1 × 1 cm^3 was cut from a large colourless block of excellent optical quality. Topaz commonly shows cleavage parallel to (001) faces [7] and this appeared to be the case with our specimen. Examination under the polarising microscope revealed two orthogonal extinction directions in the cleavage plane of the original block: our experimental sample was cut off parallel to one of these directions and a further face was cut at right angles, parallel to the second extinction. Both cut faces were polished, first with boron carbide grit 1 000 and then with alumina.

Preliminary study of the single-crystal Raman spectra revealed significant departures from the theoretical predictions, indicating an incorrect choice of axes. Weissenberg photographs of a small chip clearly showed that, in terms of the axis set given by Wyckoff,[6] the cleavage plane was (010). In our discussion we use the axes $x = a_0$ (4.649 9), $y = b_0$ (8.796 8), and $z = c_0$ (8.390 9) where the cell parameters are in parentheses. The same specimen of topaz was used for i.r.-reflectance and Raman studies. Since completion of our work Kovaleva [8] has published a factor-group analysis (f.g.a.) of topaz and shown i.r.-reflectance spectra for the 400—1 200 cm^{-1} region. In comparing her f.g.a. with ours, B_{1g} and B_{2g} and B_{1u} and B_{2u} species must be interchanged. Comparison of our three i.r. spectra with Kovaleva's shows very good agreement, apart from some minor details which may well be due to differing amounts of OH as opposed to F in our respective crystals; *but* this agreement requires the assumption that she has mislabelled her crystal axes in a system that is inconsistent with the axis set chosen for f.g.a. The equivalence between our two sets of spectra is B_{3u} $(E \parallel a) \equiv B_{1u}$ $(E \parallel c)$, B_{2u} $(E \parallel b) \equiv B_{3u}$ $(E \parallel a)$, and B_{1u} $(E \parallel c) \equiv B_{2u}$ $(E \parallel b)$ where Kovaleva's notation is the first half and ours the second half of each pair.

A small natural face parallel to the *c* axis of a specimen of spodumene was enlarged slightly by polishing. The orientation of this crystal was determined by reference to known forms of this mineral, and by measurement of interfacial angles: it was confirmed by observation of extinction directions.

Raman spectra were obtained using a Coderg T800 instrument and 514.5- or 488.0-nm excitation. Infrared spectra were recorded by the reflectance technique due to the impossibility of cutting slices sufficiently thin for transmission work. Extinctions between the three spectra were good. Spectra in the 200—1 500 cm^{-1} region were recorded using a Perkin-Elmer 225 machine in conjunction with the reflectance unit described previously.[9] The 40—500 cm^{-1} region was covered using a Beckman-RIIC FS-720 Fourier spectrometer with an RS7F reflectance module. These reflectance data were not analysed directly, but the frequencies quoted were read from the records, taking the positions at which the reflectivity begins to increase sharply reading from low to high frequency.

TABLE 1

I.r. wavenumbers (cm^{-1}) for single-crystal topaz

$B_{1u}(z)$	$B_{2u}(y)$	$B_{3u}(x)$		
175w	178w			
		208w		
292w	291vs	268vs		
310w		309vs		
336w	335vs			
375ms	364m	389vs		
420w		419ms		
444vs	450ms	463ms		
489vs	473w	489vs		
513vs	520ms			
	545s	544wm		
		572w		
609vs	611vs	610vs		
ca. 760vw				
875w		857s	ν_1	ν(Si–O)
895vs	870ms	936vs	ν_3	
995vs	995vw [a]	*ca.* 985(sh)	[b]	

[a] Not a fundamental. [b] This region is complicated and appears to contain a further oscillator.

RESULTS AND DISCUSSION

Topaz.—The data shown in Tables 1 and 2 and in Figures 1 and 2 were all collected at ambient temperature after trial runs had confirmed earlier experience that

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[1] 'The Infrared Spectra of Minerals,' ed. V. C. Farmer, The Mineralogical Society, London, 1974.

[2] A. N. Lazarev, 'Vibrational Spectra of Mineral Silicates,' Consultants' Bureau, New York, 1962.

[3] 'Infrared and Raman Spectroscopy of Lunar and Terrestrial Minerals,' ed. C. Karr, Academic Press, New York, 1975.

[4] D. M. Adams and I. R. Gardner, *J.C.S. Dalton*, 1975, 1502.

[5] D. M. Adams and I. R. Gardner, *J.C.S. Dalton*, 1976, 315.

[6] R. W. G. Wyckoff, 'Crystal Structures,' 2nd edn., Interscience, New York, 1968, vol. 4.

[7] I. Kostov, 'Mineralogy,' Oliver and Boyd, Edinburgh, 1968.

[8] L. T. Kovaleva, *Zhur. priklad. Spektroskopii*, 1975, **22**, 311.

[9] D. M. Adams and M. M. Hargreave, *J.C.S. Dalton*, 1973, 1426.

the spectra of silicate minerals at low temperature differ insignificantly from those obtained at room temperature.

Theory. Topaz, $Al_2(OH,F)_2SiO_4$, is an orthosilicate containing discrete $[SiO_4]^{4-}$ anions. Each aluminium atom is octahedrally co-ordinated to four oxygens from silicate groups, the remaining two positions being filled by OH or F. The lattice is of symmetry [6] *Pnma* (D_{2h}^{16}), $Z = 4$. The silicon and half the oxygen atoms are on C_s sites with all the other atoms on general sites: the f.g.a. is shown in Table 3. Since the Si–O–Al bonding has considerable directionality [10] the decomposition of N_T into contributions from internal and external modes is little more than an aid to discussion and should not be taken to indicate anything about the bonding. In α-Al_2O_3, in which the metal is in distorted octahedral co-ordination, optically active transverse optic (TO) phonons [11] are found as high as 751 cm^{-1}, which may be taken to imply that bands at similar frequencies should be expected in topaz due to Al–O bonds. In interpreting the spectra the only reliable guide is the vector of optically allowed modes: $N_{\text{opt.}} = 15A_g + 12B_{1g} + 15B_{2g} + 12B_{3g} + 14B_{1u} + 11B_{2u} + 14B_{3u}$.

TABLE 2

Raman wavenumbers (cm^{-1}) and intensities (arbitrary units) * for topaz

	Band	Symmetry species	$z(xx)y$	$z(yy)x$	$y(zz)x$	$z(yx)y$	$z(xz)x$	$z(yz)y$
	155	A_g	6	25	24			
	165	B_{1g}				68		
	171	B_{3g}						6
	191	B_{3g}						8
	237	B_{2g}					100	
	242	A_g	49	100	100	16		15
	266	B_{2g}					37	
	270	A_g	100	100	100	22		20
	273	B_{2g}					40	
	288	A_g/B_{1g}	100	100	90	53	14	
	292	B_{3g}						20
	315	B_{1g}				68		10
	334	A_g	81	8	38	15	4	
	351	B_{3g}						6
	360	B_{2g}					48	
	369	B_{1g}				20		
	373	B_{3g}						33
	380	B_{2g}					15	
	402	B_{1g}				8		
	405	A_g	39	14	16			
	424	B_{1g}				18		
	441	B_{3g}						10
	460	A_g	62	6		8	6	
	474	B_{3g}						10
	482	B_{3g}						27
	491	A_g		6	8			
	495	B_{2g}					17	
	499	B_{1g}				8		
	509	B_{1g}				22		
	521	A_g		2	66			
	549	B_{2g}					35	
	561	A_g	1	19	19			
	599	B_{1g}				10		
	641	B_{3g}						10
	646	A_g	2	3				
	682	B_{3g}						6
	706	B_{1g}				16		
	843	B_{2g}					4	
ν_1	854	A_g	40	1	4	10	6	
	908	B_{2g}					32	
ν_3	926	A_g/B_{2g}	50		88	12	36	
	938	A_g		64				
	984	B_{3g}						100
	1 006	B_{1g}				42		
	1 008	B_{2g}					35	
δ(OH)	1 166	$A_g/B_{1g}/B_{3g}$	14			20		10
ν(OH)	3 655	A_g		10				

* (*xx*), (*yy*), and (*zz*) spectra were recorded at 0.5 cm^{-1} spectral slit width, (*xy*), (*yz*), and (*zx*) spectra at 3.25 cm^{-1}. The intensities in the two sets cannot be compared directly.

Excellent single-crystal i.r.-reflectance and Raman spectra have been reported for another orthosilicate, forsterite (Mg_2SiO_4).[12,13] A normal-co-ordinate analysis (n.c.a.) [14] has been made on the basis of these data. Bonding between Mg^{2+} and $[SiO_4]^{4-}$ is weaker than between Al^{3+} and $[SiO_4]^{4-}$ and results in a clear gap of *ca.* 200 cm^{-1} in the 600—800 cm^{-1} region for forsterite. This allows the ν(Si–O) region to be treated separately

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[10] D. M. Adams, 'Inorganic Solids,' Wiley, Chichester, 1974.

[11] S. P. S. Porto and R. S. Krishnan, *J. Chem. Phys.*, 1967, **47**, 1009.

[12] J. L. Serroin and B. Piriou, *Phys. Status Solidi*, 1973, **55**, 677.

[13] V. Hohler and E. Fünck, *Z. Naturforsch.*, 1973, **B28**, 125.

[14] V. Devarajan and E. Fünck, *J. Chem. Phys.*, 1975, **62**, 3406.

TABLE 3

Factor-group analysis and correlation scheme for topaz

(*a*) Factor-group analysis

D_{2h}	N_T *	T_A	T	R	$N_{vib.}$	ν(Si–O)	Activities
A_g	15		8	1	6	3	x^2, y^2, z^2
B_{1g}	12		7	2	3	1	xy
B_{2g}	15		8	1	6	3	xz
B_{3g}	12		7	2	3	1	yz
A_u	12		7	2	3	1	
B_{1u}	15	1	7	1	6	3	z
B_{2u}	12	1	6	2	3	1	y
B_{3u}	15	1	7	1	6	3	x

(*b*) Correlation scheme

Ion, T_d	Site, C_s (xz)	Crystal, D_{2h}
$\nu_1\ a_1$	A'	$6A' \xrightarrow{\times 4} 6(A_g + B_{2g} + B_{1u} + B_{3u})$
$\nu_2\ e$	$A' + A''$	
ν_3, ν_4, t_2	$2A' + A''$	$3A'' \longrightarrow 3(B_{1g} + B_{3g} + A_u + B_{2u})$

* N_T = Total number of unit-cell modes: T_A = acoustic, T = optic branch modes; R = rotatory modes of $[SiO_4]^{4-}$; $N_{vib.}$ = internal modes of $[SiO_4]^{4-}$ of which ν(Si–O) forms a part.

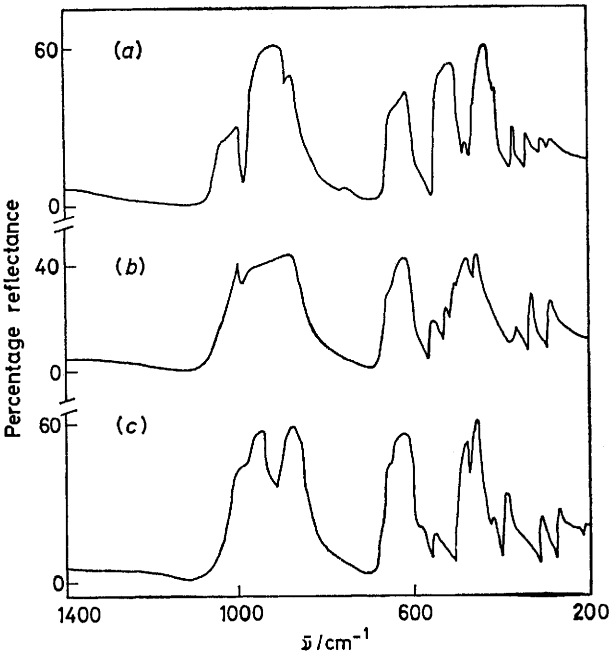

FIGURE 1 Infrared-reflectance spectra of single-crystal topaz: (*a*) B_{1u} (*z*), (*b*) B_{2u} (*y*), and (*C*) B_{3u} (*x*)

although, in fact, neither set of workers was able to find a fully consistent interpretation of the data.[12-14] At 600 cm^{-1} the ν_4 and ν_2 anion modes tail off into an extensive series of lattice modes with which they become significantly mixed. Our Raman data for topaz (Table 2) show a much smaller gap in the region below ν(Si–O), although the i.r. data show only one (very weak) feature in this intermediate region: bands in the 600—800 cm^{-1} region must be considered good candidates for ν(Al–O), where the oxygen is from $[SiO_4]^{4-}$.

A further complication arises from the effect of OH or F being distributed on one set of (general) Wyckoff sites. {The presence of hydroxyl is clearly demonstrated by the Raman bands at 1 166 cm^{-1} [δ(OH)] and 3 655 cm^{-1} [ν(OH) non-hydrogen-bonded].} Not only will this allow appearance of ν(Al–F) modes, it may also affect the other modes by virtue of the disordering it introduces.

The ν(Si–O) *assignment.* The Raman data in the 850—1 050 cm^{-1} region are in perfect agreement with predictions for ν(Si–O). One A_g and one B_{2g} band is present at significantly lower energy than the other two in these species, implying that $\nu_1 < \nu_3$. The same

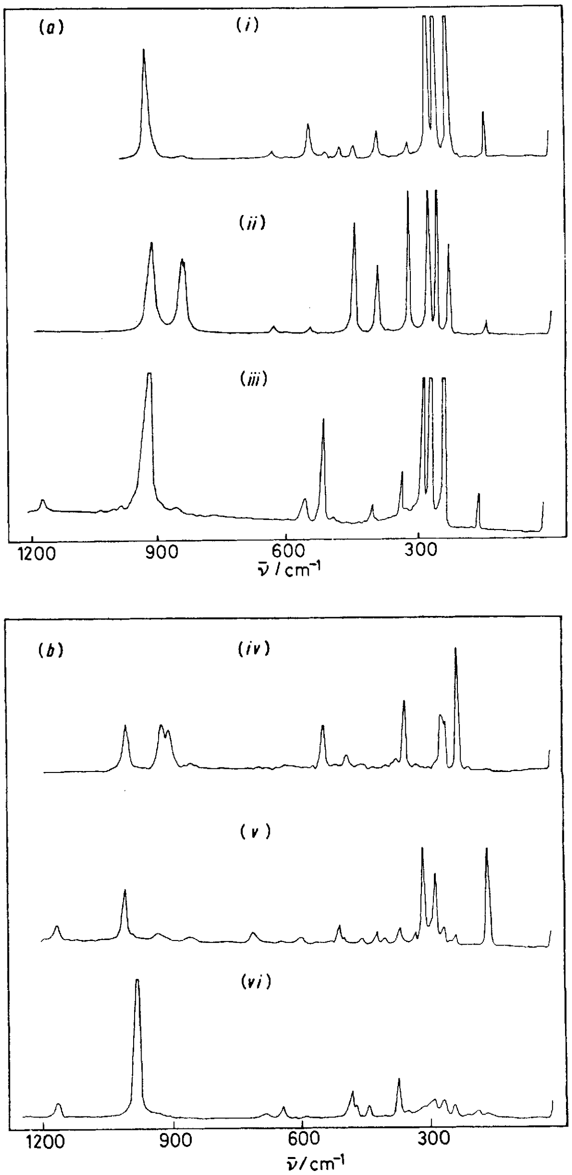

FIGURE 2 Raman spectra of single-crystal topaz; (*a*) diagonal tensor components (*i*) $z(yy)x$, (*ii*) $z(xx)y$, (*iii*) $y(zz)x$; (*b*) off-diagonal terms (*iv*) $z(xz)x$, (*v*) $z(yx)y$, (*vi*) $z(yz)y$

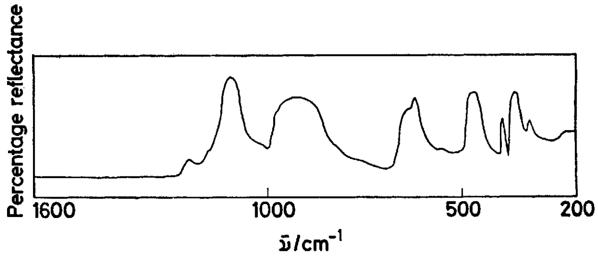

FIGURE 3 The B_u reflectance spectrum of spodumene

conclusion follows from the B_{1g} and B_{3g} bands at 1 006 and 984 cm^{-1} respectively, which can only originate in ν_3 of $[SiO_4]^{4-}$ since these are significantly higher than the bands attributed to ν_1.

As is common in i.r.-reflectance spectra (not only of minerals), there are some second-order features which must be distinguished from regions of reflectance due to fundamentals before assignment can be attempted. On the present evidence we have no *a priori* means of making such a distinction, although one could be made in principle experimentally by studying the thermal dependence of the spectra to very high temperature and extracting the contributions of the cubic and quartic anharmonicities for the various oscillators. Our chief guide for the present is internal consistency (including Raman data), backed up by experience of i.r.-reflectance spectroscopy.

A single ν(Si–O) mode is expected in the B_{2u} spectrum: we find one very broad region of reflectance, corresponding to a very intense absorption, with a TO frequency at 870 cm^{-1}. Since this is the dominant feature we regard it as due to the fundamental and attribute the weak feature at *ca.* 1 000 cm^{-1} to second-order processes. In the B_{1u} spectrum three bands are expected: we find three and regard these as the fundamentals sought. Kovaleva observed a secondary feature on the highest of these bands: we do not regard it as a fundamental although the possibility cannot yet be excluded. There is a similar ambiguity in our B_{3u} spectrum in which we find an oscillator at *ca.* 990 cm^{-1} not reported by Kovaleva. (It should be noted that Kovaleva reports reflectance *maxima*, not TO oscillator frequencies.)

Subject to these reservations, we deduce the following assignment for the ν(Si–O) region: the wavenumbers (cm^{-1}) attributed to the site-field modes are arithmetic averages of the observed site plus correlation-field splittings.

Ion, T^d	Site, C_s	$\xrightarrow{\times 4}$ Crystal, D_{2h}				
	$2A'$	$2A_g$	$+ 2B_g$	$+ 2B_{1u}$	$+ 2B_{3u}$	Range
ν_3, T_2	(981, 921)	926	926	895	936	41
		938	1 008	995	985	70
	A''	B_{1g}	$+ B_{3g}$	$+ B_{2u}$	$+ A_u$	
	(953)	1 006	984	870		136
ν_1, A_1	A'	A_g	$+ B_{2g}$	$+ B_{1u}$	$+ B_{3u}$	
	(874)	854	908	875	857	54

The assignments for A' site modes show high internal consistency and reasonable site-plus-correlation-field splittings of up to 70 cm^{-1}. The A'' assignment seems less satisfactory at first sight as the B_{2u} component is rather far removed from the others: had we chosen the weaker feature at *ca.* 1 000 cm^{-1} from this region of the reflectance spectrum the splitting would have been very small indeed, perhaps too small. The B_{1g}, B_{3g}, and B_{2u} ν(Si–O) assignments seem to us the least ambiguous of all in this work, and we prefer to accept them at face value. We note, however, that a similar difficulty arose in assigning one of the ν_3 i.r. components in forsterite:[14] the final assignment gave ν_3 a range of *ca.* 130 cm^{-1} and ν_1 a range of 16 cm^{-1}.

The region below ν(Si–O). The numbers of modes found, compared with those predicted, are:

	A_g	B_{1g}	B_{2g}	B_{3g}	B_{1u}	B_{2u}	B_{3u}
f.g.a.	12	11	12	11	11	10	11
Observed	11	10	7	10	11	9	10

It is clear that the spectrum of topaz has been almost completely established. The absence of i.r. bands below 175 cm^{-1} and Raman bands below 155 cm^{-1} is consistent with a lattice structure in which only light atoms are involved. Comparison with other orthosilicates suggests that none of the bending modes of $[SiO_4]^{4-}$ is above 650 cm^{-1}. Accordingly, we regard the weak Raman bands at 682, 706, and 843 cm^{-1}, and the very weak i.r. features at *ca.* 760 cm^{-1}, as due to either Al–O(Si) bond stretching or to second-order processes. ν(Al–OH) and ν(Al–F) are most probably in the region below 650 cm^{-1} for which no assignment is meaningful in the absence of a full n.c.a., although the 400—650 cm^{-1} region must be primarily due to the components of ν_2 and ν_4 of the anion, and the bands below 400 cm^{-1} to lattice modes.

Spodumene.—This material is a pyroxene, $LiAlSi_2O_6$, with symmetry[6] $C2/c$ (C_{2h}^6) and a bimolecular primitive cell. Chains with an (Si_2O_6) repeat are parallel to the c axis. Unfortunately, our specimen exhibited broad and intense fluorescence, precluding Raman study by single-crystal methods. With 488-nm excitation of the crystal in arbitrary orientation the following bands could be detected above noise level: 134, 190, 254, 300, 360m, 397, 446, 523, 590, 712vs, and 1 076 cm^{-1} (all weak unless otherwise indicated).

The unfavourable face development of our sample, upon which it was possible to grind only a small face parallel to the c axis, also made i.r. reflectance of marginal applicability. The following bands (cm^{-1}) were located in the 200—1 600 cm^{-1} region.

$A_u(E \parallel c)$	229, 270, 444, *ca.* 500, 1 008, *ca.* 1 050
$B_u(E \perp c)$	325, 358, 392, 463, 619, *ca.* 650, 890, 1 085, 1 205

F.g.a. predicts, for the optic branch, $14A_g + 16B_g + 13A_u + 14B_u$, where all g modes are Raman active and all u modes are i.r. active. Of these, ν(Si–O) accounts for $3(A_g + B_g + A_u + B_u)$.

The Raman spectrum is unusual in showing only one (very weak) band in the ν(Si–O) region at 1 076 cm^{-1}. However, the i.r. spectra show exactly the required number. In contrast with topaz (which contains discrete $[SiO_4]^{4-}$ groups), but like beryl[4] and benitoite[5] (which have linked SiO_4 tetrahedra), the i.r. spectra of spodumene show bands at $>1\,100$ cm^{-1} which are correlated with the Si–O–Si bridges. The bands at 890 and 1 008 cm^{-1} are therefore attributed to ν(Si–O) of non-bridged bonds. The region of the i.r. spectra below ν(Si–O) shows $\frac{3}{11}A_u$ and $\frac{6}{11}B_u$ modes. Further discussion is of little value in the absence of data from a better specimen.

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