Raman studies of oxide minerals: a retrospective on cristobalite phases

Raman studies of oxide minerals: a retrospective on cristobalite phases

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Abstract
A brief review of early Raman studies of oxide minerals is given, emphasizing aspects yet to receive modelling. To these are added extensive unpublished infrared data on α- and β-cristobalite SiO_2 and $AlPO_4$, following a soft mode and its damping from 132 cm^{-1} at 20 K to about 80 cm^{-1} just below the $AlPO_4$ α–β transition temperature and from 155 to 125 cm^{-1} in SiO_2 (the transitions are of first order). Rather good data exist on the α- and β-cristobalite phases of $AlPO_4$ and BPO_4 single crystals (not powders) which are discussed in terms of the more recent controversy regarding β-cristobalite SiO_2. The α–β cristobalite phase transition in $AlPO_4$ doubles the primitive cell size on cooling, with a probable D_{2d} to D_2 point group symmetry reduction: β-$AlPO_4$ is likely to be $I\bar{4}2d$ (D_{2d}^{12}) with $Z = 1$ formula group, and α-$AlPO_4$ to be $C222_1$ (D_2^5). For $AlPO_4$ our results favour the model of Liu *et al* (1993 *Phys. Rev. Lett.* **70** 2750) over that of Swainson and Dove (1993 *Phys. Rev. Lett.* **71** 3610). The point group symmetries appear to be the same in cristobalite SiO_2, so that the previously proposed tetragonal space group symmetry D_4^4 ($P4_12_12$) for α-SiO_2 and the O_h^7 ($Fd3m$) phase for β-SiO_2 are only slow time averages that do not control selection rules or electronic band structures.

1. Introduction

Shortly after argon-ion lasers were invented at Bell Laboratories in the early 1960s they were used for Raman spectroscopy on a variety of crystals. Oxides were favoured, because of their availability in large size and high transparency. These served as paradigms for early phonon studies and, in some cases, of structural phase transitions. Subsequently the different families emphasized in the early work have become important for different groups of scientists: the silica structures have remained of importance to mineralogists and hence are particularly appropriate for this special issue honouring Professor Salje. Of these, cristobalite phases have had perhaps the greatest attention because of controversy regarding their β-phase structure. The scheelites have been of interest because of the early use of tungstate and molybdate scheelites as laser host lattices, and subsequently, because of phase transitions in related vanadates. The

wurtzite ZnO has had a renaissance lately in terms of blue light-emitting diodes, and the use of ultraviolet lasers for Raman spectroscopy, which was first used on ZnO. Quartz studies have benefited from the recent availability of a large family of phosphates and arsenates isomorphic with α-quartz, and from the incommensurate phase now known to lie at temperatures 3 K wide between the α- and β-phases.

2. Specific families

2.1. Wurtzites, scheelites, and quartz

The initial Raman work emphasized simple crystals with diatomic unit cells and a single optical phonon branch, such as wurtzites [1, 2]. One of the main interests was in understanding modes in which Coulombic splittings between transverse (TO) and longitudinal (LO) branches was large compared with anisotropy (due to crystal fields) between modes with polarization along the optic axis (extraordinary A_1 modes) and those with polarization perpendicular to the optic axis (ordinary E modes). CdS and ZnO were popular choices, with a resurgence of interest caused by the availability of resonant Raman scattering (laser wavelength matching semiconductor bandgap, using not only Ar-ion lasers but He–Cd at wavelengths of 441.6 and 325.0 nm) [3–5], which was ideal for ZnS and ZnO. The first extension of this work to crystals with many optical phonon branches was on quartz [6, 7]. A detail of interest in that regard was the discussion of why non-cubic crystals should often preferably be cut with faces at 45° to the principal crystallographic axes; this permits the propagation of phonons in the scattering experiment to be precisely along the crystallographic axes and hence of pure (e.g., E (LO) or A_1 (TO)) symmetry. Other geometries, in which the phonons propagate at 45° to the principal axes generally result in mixed symmetry, such as quasi-longitudinal (polarization a few degrees away from propagation direction) or quasi-A_1 symmetry (polarization a few degrees away from the n-fold principal axis). The quasi-longitudinal modes are not forbidden in infrared absorption or reflection and are often called Berreman modes.

2.2. Scheelites

Also featured in the 1960s were the scheelites [8, 9]. $CaWO_4$, $CaMoO_4$ and isomorphs such as $SrWO_4$ and $BaWO_4$ were grown at Bell Laboratories as host lattices for rare earth ions for laser oscillators. Of particular spectroscopic interest were the Davidov splittings of phonon branches due to the presence of two formula groups per unit cell, and lattice modes that were in phase or out of phase in the two neighbouring tungstate ions [10]. This family has retained significant academic interest [11], including as a laser host material, and also for its high-pressure phases.

2.3. Quartz structures

Both alpha- and beta-quartz were studied extensively [12, 13] before the incommensurate phase was discovered between them. The alpha–beta phase transition in isomorphic aluminium phosphate (berlinite) received a comparable amount of attention [14], due in part to the Fano-like interference processes observed for the soft optic mode in this material [15, 16], as in quartz [17, 18] or the KDP (potassium dihydrogen phosphate) isomorphs [19, 20]. Of special interest in the early lattice dynamical work on berlinite were the effective charges of Al-, P-, and O-ions, which were [14] about $+2.3$, $+2.5$, and -1.2, respectively, rather than the nominal valence values of $+3$, $+5$, and -2. The strong differences between nominal valence charges and effective charges has remained of paramount interest in lattice dynamics, sometimes implying an unexpected degree of covalency [21].

Table 1. Corresponding Raman-only optical phonon frequencies (experimental values) in α- and β-cristobalite isomorphs (cm^{-1}).

α-SiO$_2$	β-SiO$_2$	α-BPO$_4$	α-AlPO$_4$	β-AlPO$_4$
121		79 (theory[b])	99	143
233	292	230	188	270
380	402 (B$_2$?[a])	450	388	402
426		475	—	
1076	1077 (A$_1$?[a])	1114	996	995

[a] Assumes symmetries given by Leadbetter *et al* [31] and Ng and Calvo [99].
[b] There is absolutely no Raman mode seen in this frequency range; theoretical estimate is from [100].

Rather less cited are the vibrational spectra of other quartz isomorphs, such as AlAsO$_4$, GeO$_2$, GaPO$_4$, and GaAsO$_4$ [22, 23], but these continue to be studied in detail [24a, 24b, 24c, 24d, 24e]. Relatively new materials such as FePO$_4$ have also been reported [24c]. Surprisingly little lattice dynamics has been published on these quartz isomorphs. Some, especially GaPO$_4$, have commercial interest as piezoelectric transducers [24b] and other devices, including light-emitting diodes [24d]. It is especially interesting in the context of the present review, emphasizing cristobalite, that a direct phase transition in GaPO$_4$ from the α-quartz phase to the β-cristobalite phase has been reported [24e]. A primary concern in the past few years has been neutron scattering studies of high-pressure phase transitions in FePO$_4$, GaPO$_4$, and AlPO$_4$ [24f, 24g, 24h, 24i, 24j, 24k, 24l, 24m].

2.4. Other silica structures: reexamination of cristobalite phases

A significant effort was made to characterize other silica structures, such as the α- and β-cristobalite phases [25] of SiO$_2$, BPO$_4$ and AlPO$_4$, as well as the rutile family of oxides: cassiterite SnO$_2$ [26, 27], GeO$_2$ [28], stishovite [29], and others (tridymite, coesite, etc). Of special interest was the soft-mode phonon broadening in cristobalite [30], whose phase transition character—displacive or order–disorder—was controversial. SiO$_2$, AlPO$_4$, BPO$_4$, and GaPO$_4$, among others, all exist in cristobalite phases. The α–β cristobalite phase transition in AlPO$_4$ doubles the unit cell upon cooling, and this also occurs in cristobalite SiO$_2$. Therefore, both cristobalite SiO$_2$ and AlPO$_4$ have a soft mode (their α–β transitions are largely displacive), and this is an underdamped soft mode which would be viewed as at the Brillouin zone boundary in the body-centred tetragonal (bct) β-phase (and hence Raman inactive). As shown in figure 1, the soft mode in α-AlPO$_4$ has an infrared frequency 132 cm^{-1} at 20 K, 120 cm^{-1} at room temperature, and softens to less than 110 cm^{-1} at 170 °C. The soft mode in α-AlPO$_4$ shows slightly more softening than for the transition in α-cristobalite SiO$_2$, where the lowest-frequency infrared mode is at 155 cm^{-1} at 20 K (figure 2) and softens to only 125 cm^{-1} at the transition temperature, as shown in figure 3 (this mode is not seen in α-cristobalite BPO$_4$; only the next higher A$_1$ mode at 230 cm^{-1} appears). The halfwidth of this mode broadens from about 20 cm^{-1} at ambient to >60 cm^{-1} as the transition temperature T_0 is approached from low temperature. Thus it would appear that cristobalite AlPO$_4$ is not more displacive than other members of the family, but that it is slightly less first-order than in cristobalite SiO$_2$. The comparison with SiO$_2$ is not surprising because there is no significant ionic mass change (Al + P)/2 = Si. A comparison of A$_1$ symmetry mode frequencies is given in table 1, and for E, B$_1$/B$_2$ and A$_2$ symmetry modes in tables 2 and 3, respectively. α-cristobalite SiO$_2$ has often been considered to have space group symmetry $P4_12_12$ (D$_4^4$) with $Z = 4$ formula groups per primitive cell. Swainson and Dove emphasize that this a time-averaged structure, as discussed below. However, they do not conclude, as we do here, that this is not the 'true'
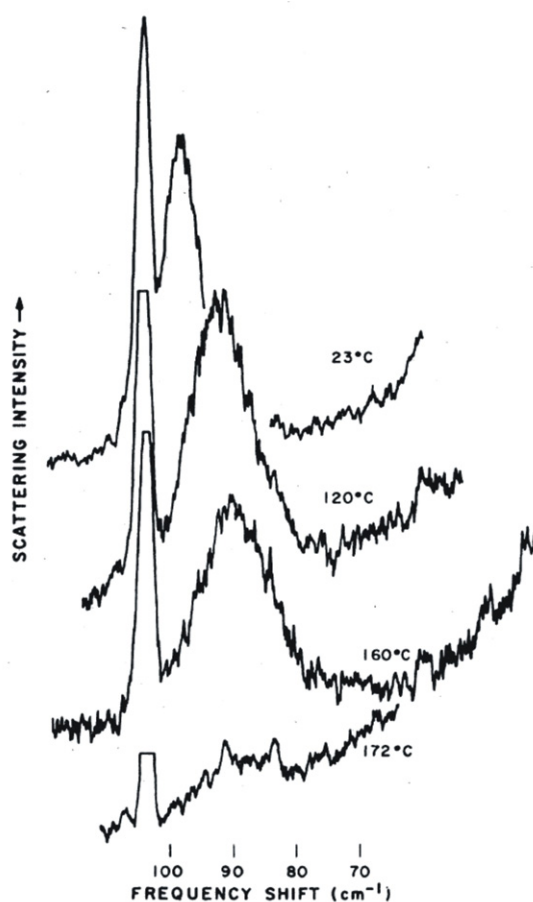
Figure 1. Raman spectra of the soft mode in the α-cristobalite phase of AlPO$_4$ [25].

structure in the sense that it will not characterize Raman or infrared selection rules; these occur on a ps timescale, whereas nuclear magnetic resonance (NMR) occurs on a μs scale and x-ray diffraction (XRD) on a scale of seconds. Based upon the x-ray powder diffraction work of Leadbetter and Wright [31], α-AlPO$_4$ is thought to be $C222_1$ (D_2^5) with $Z = 2$ formula groups per primitive cell, and β-AlPO$_4$ to be $I\bar{4}2d$ with $Z = 1$ formula group per primitive cell. Note that both D$_{2d}$ and D$_4$ point groups are tetragonal, so they are not trivial to distinguish. However, the D$_4^4$ space group suggested for the α-phase assumes an O$_h$ point group for the β-phase. Our Raman and infrared data, discussed below, favour a D$_{2d}$ β-phase. Since the phase transition is nearly second order (with a soft mode), it follows that the α–β phases must satisfy a subgroup– group relationship; but D$_4$ is not a subgroup of D$_{2d}$. Therefore if the β-phase is indeed D$_{2d}$, the α-phase is probably D$_2$ in both SiO$_2$ and AlPO$_4$. This line of argument is very important, because it might permit the resolution of the unambiguous structure of the β-phase merely from data on the α-phase: if it can be definitively established that α-SiO$_2$ or α-AlPO$_4$ is D$_4^4$, then the β-phases must be O$_h$ and not D$_{2d}$. These experiments on the α-phases might be much easier, but must be on a fast timescale.

It is not trivial, however, to distinguish the α-cristobalite structure even from that of α-quartz by Raman spectroscopy alone, because in each case there are four strong
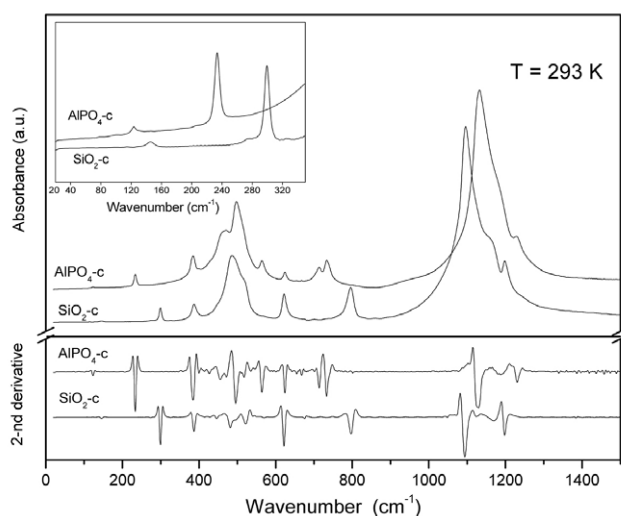
Figure 2. Infrared spectra of α-cristobalite SiO_2 and $AlPO_4$.

lines of totally symmetric symmetry; and differentiating D_4 from D_2 would be much more difficult (the eight E-symmetry modes of D_4 each split into $B_2 + B_3$, but the latter representations are both infrared and Raman active, so each E mode would become a quartet of $B_2(TO) + B_2(LO) + B_3(TO) + B_3(LO)$ and unlikely to be resolvable). In table 1 only A-symmetry modes in BPO_4 or $AlPO_4$ which would be A_1 in a D_4-phase for α-SiO_2 are listed, not those which would be B_2. Note in particular that cristobalite $AlPO_4$ has a rather conventional displacive, cell-doubling transition.

There has been considerable discussion in the literature about the structure of β-cristobalite SiO_2 above $T_0 = 267\,^\circ C$. Wyckoff gives [31] two different structures, both cubic. Weak x-ray diffraction lines have been indexed as T^4 ($P2_13$) by Simon and McMahon [32]. Bates inferred a cubic O_h^7 ($Fd\overline{3}m$) space group symmetry, based upon his observation of only three Raman lines from powder in the β-phase, two of which he inferred are due to disorder-allowed odd-parity lines [33]. This structure would have only a single Raman-active mode, which he assigns as being at 777 cm^{-1}. Later, Etchepare *et al* [34] considered both the D_4 and O_h point group symmetries. Our results are compatible with it being an ordered D_{2d}^{12} space group ($I\overline{4}2d$) with $Z = 2$ formula groups per primitive cell. That means that it has the same number of atoms per primitive cell as does β-cristobalite $AlPO_4$. The new spectral observations in our present work are first that sharp Raman lines of quite narrow linewidths persist into the β-phases of both SiO_2 and $AlPO_4$, showing that these phases cannot be highly disordered, and second, that the number of Raman lines and the absence of any large linewidth broadening implies a displacive phase transition in each case which doubles the primitive cell, and that the associated soft mode is underdamped right up to the transition temperature in each case (the transitions are of first order). This rules out any interpretation as an order–disorder transition. Our results support the statement of Bates [33] that 'Raman spectra of cristobalite showed that the structure of this material should not be employed as a lattice model for noncrystalline SiO_2'.

The observation of the lowest totally symmetric soft mode near 100 cm^{-1} in α-cristobalite $AlPO_4$, originally by Nicola *et al* [25, 30], was rarely cited in the cristobalite work that followed; this work is useful primarily because its underdamped soft mode established unambiguously that the α–β phase transition is displacive, not order–disorder, and doubles
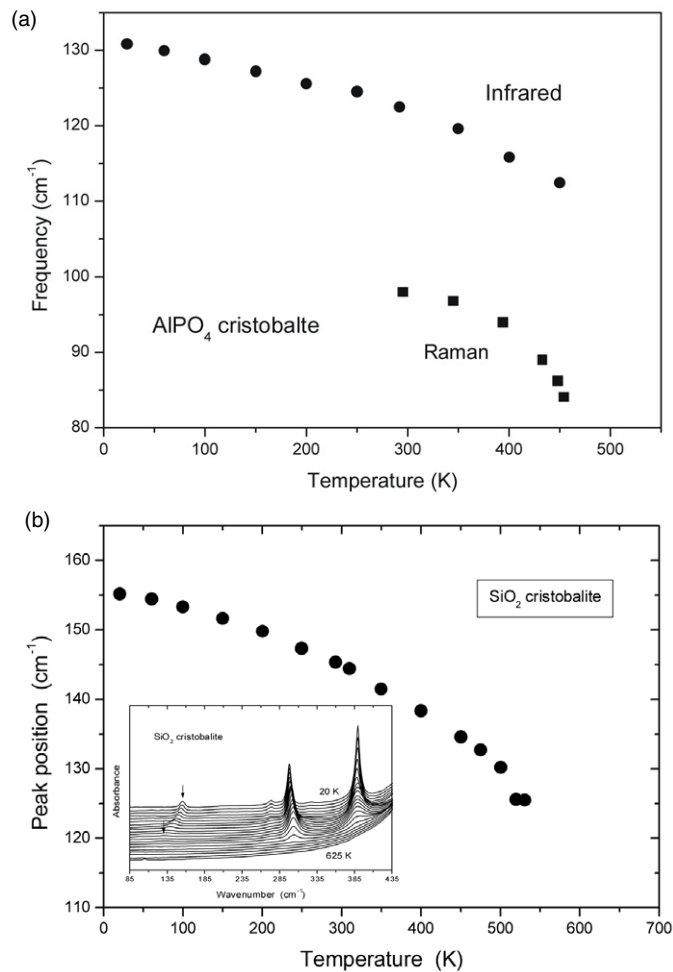
Figure 3. Raman and infrared frequencies of the lowest-energy phonon branch in the α-cristobalite phase of (a) AlPO$_4$ and (b) SiO$_2$ ([25] and present work). Not shown in (b) is the Raman mode, which lies at 121 cm^{-1} at 81 K, 110 cm^{-1} at 298 K and 95 cm^{-1} at 541 K (T_0—2 K) [33]. This mode would be described as a zone-boundary acoustic branch in the β-phase, which has a smaller primitive crystallographic cell.

the primitive unit cell (i.e., is antiferrodistortive). It is of special interest because the lowest-frequency (neutron) mode in β-cristobalite SiO$_2$ is near 40 cm^{-1} and has been discussed in terms of the similar broad peak in amorphous silica. Although this has been described as a rigid-unit mode (RUM) in which the oxide tetrahedral groups remain rigid in a dynamic O$_h$ cubic structure [35–41], it can probably be described equally well as arising from a transverse acoustic mode at the Brillouin zone boundary in a simplified unit cell picture with a D$_{2d}$ β-phase [42–44]. Note that it is not very broad in the α-phase. A great deal of work has been carried out in this department over the past decade on the α–β cristobalite transition in silica [35–41], but equally data with equally good signal to noise and resolution on cristobalite AlPO$_4$ have been cited rarely.

Because Al- and P-ions are not equivalent, the symmetry labelling in the silica cristobalite and aluminium phosphate cristobalite can be different. Correlation tables are given in [25].

Table 2. Corresponding infrared- and Raman-active optical phonon frequencies (experimental values) in α-cristobalite isomorphs (cm^{-1}).

E symmetry[a]				
α-SiO$_2$	β-SiO$_2$	α-BPO$_4$	α-AlPO$_4$	β-AlPO$_4$
		121	145	
275	292	286	279	270
380(TO)		380	482	450
401(LO)				
485		534	533	
		612		
785(TO)	777	832	713	
796(LO)				
1086(TO)		1048	1013	1017
1188(LO)				
1195(TO)			1124	1125
1204(LO)		1262		

B$_1$/B$_2$ symmetry[b]			
α-SiO$_2$	α-BPO$_4$	α-AlPO$_4$	β-AlPO$_4$
B$_1$—(79[b])	—	—	—
B$_1$—(94[b])	—	—	—
B$_2$ 275	—	—	—
B$_1$ 368	—	—	—
B$_2$ 416 (416[b])	—	—	—
B$_2$—(759[b])	920	—	—
B$_1$—(762[b])	970	924	920
B$_1$—(1092[b])			
B$_2$ 1193	—	1124	1125

[a] Eight pairs of transverse TO and longitudinal LO modes expected in α-phase; assignments are only probable.
[b] Theoretical values: Etchepare *et al* [34].

Table 3. Corresponding infrared-only optical phonon frequencies from infrared studies in α-cristobalite isomorphs (cm^{-1}).

α-SiO$_2$	α-AlPO$_4$
145	123
495	426
620	623
1162	1230

In the α-phases, there are eight totally symmetric modes of A symmetry in D$_2$ point group AlPO$_4$ which are infrared and Raman active; these become four A$_1$ Raman-active modes in SiO$_2$ and four B$_2$ infrared-active modes if the structure of the latter is D$_4$. However, even in the AlPO$_4$ D$_2$ point group structure four of them are weak in the infrared and four are weak in the Raman effect, since these intensities depend upon the difference in mass and charge of Al- and P-ions, which is actually rather small, as shown by Scott [14]. Therefore as expected, only four strong A-symmetry Raman lines are found in α-AlPO$_4$. The symmetry of the Raman-active mode near 110 cm^{-1} in SiO$_2$ and 99 cm^{-1} in AlPO$_4$ has been under some dispute, but it is clearly the soft mode in this system, and soft modes (at least one component, if degenerate)

must be totally symmetric and Raman active in the low-temperature phase of any material with a displacive phase transition ('Worlock's Lemma'); therefore this mode is unlikely to be of E symmetry, as proposed by Bates or by Etchepare *et al*. Bates assigned this mode as an unresolved doublet E(TO + LO) purely on the basis that such a mode exists at almost the same frequency (128 cm^{-1}) in α-quartz [6, 12], but this comparison with quartz is not a rigorous argument. If it were indeed an E-symmetry mode, it would be unrelated to the α–β phase transition and expected to occur in BPO$_4$, where it is absent. Because it is instead the soft mode triggering the α–β phase transition, it is not observed in BPO$_4$, because only the α-phase of cristobalite BPO$_4$ has been observed, the transition presumably occurring at very high temperatures (and hence the soft mode renormalized to rather high frequencies and not readily identifiable). All of the early work by Bates and Etchepare *et al* was carried out on powders from which polarization information could not be obtained. The work by Scott's group [21, 25] was on single crystals, which yielded some polarization and mode symmetry information. However, sample size (about 0.1 mm diameter) did not permit cutting and orienting sample faces so as to make symmetries unambiguous. These specimens were grown from a flux of V$_2$O$_3$. Most of the product were berlinite crystals, and the cristobalite AlPO$_4$ specimens were picked out by hand.

Some thermal hysteresis is known for β-cristobalite phases. Thus, it is possible that the 'extra' Raman or infrared lines persisting above 500 K might be due to a coexistence of α- and β-phases. However, the sharpness of the underdamped soft mode makes it unlikely that a well-defined α-phase persists above T_0. Bates found that no α-phase Raman lines persisted more than 10 °C above the transition at 267 °C. The presence of strong infrared lines at 270, 380, 470, 733, and 1100 cm^{-1} in β-AlPO$_4$ up to $T = 600$ K (327 °C) in our work makes it very unlikely that the material can be cubic O$_h$ point group, since the measured transition temperature in our specimens was at 473 ± 3 K; however, the infrared data for cristobalite silica are much less clear on this point, because the absorptions are weaker.

Extensive NMR data exist on β-cristobalite SiO$_2$, mostly from Kirkpatrick's group in Illinois [45]. Although these have generally been interpreted in terms of a disordered cubic structure, it is important to remind ourselves of the differences between Raman and NMR data: Raman data measure on an optical timescale of about 10^{-14} s and on an optical wavelength length scale of 100 nm; NMR measures on a MHz timescale (μs) and is purely local (nearest neighbours). In several other phase transition systems NMR data were used to conclude erroneously that the transition was order–disorder, whereas Raman and infrared spectroscopy showed unambiguously that it was displacive. Tris-sarcosine calcium chloride (TSCC) is the most notorious example [46, 47]. We note that in the low-temperature phase of both cristobalite and TSCC the NMR data imply a continuous change in lattice parameters as the transition temperature is approached from below; this is not the signal expected for an order–disorder transition.

Etchepare *et al* consider O$_h$ and D$_4$ point groups for β-cristobalite SiO$_2$ (not D$_{2d}$). The D$_4$ point group structure of β-cristobalite would have three modes (A$_1$ + 2B$_1$) found only in the Raman effect; two modes (2A$_2$) found only in the infrared; and four modes (4E) found in both. By comparison, the proposed O$_h$ structure would have only one Raman line of F$_{2g}$ symmetry and two infrared lines of F$_{1u}$ symmetry. Etchepare *et al* assign the F$_{2g}$ mode at 777 cm^{-1} and the F$_{1u}$ modes at 1077 and 450 cm^{-1}. They assign the strong A$_1$ mode at 230 cm^{-1} in the α phase as the soft mode responsible for the α–β phase transition, which is clearly incorrect. It is not clear that the D$_{2d}$ structures proposed for β-cristobalite are exactly the same in SiO$_2$ and AlPO$_4$ (since Al- and P-ions are distinguishable). Leadbetter and Wright suggest D$_{2d}^9$ space group for AlPO$_4$ but D$_{2d}^{12}$ for SiO$_2$. In the D$_{2d}$ point group symmetry ($Z = 2$) assumed for β-cristobalite AlPO$_4$ there are 2A$_1$ + A$_2$ + B$_1$ + 3B$_2$ + 4E modes of long wavelength ($q = 0$),
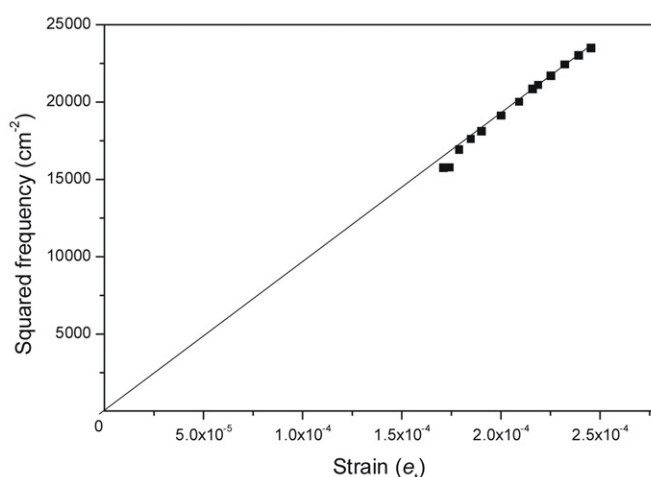
Figure 4. The squared band frequency for the 145 cm^{-1} band versus the strain. The linear fit passing through the origin indicates that the 145 cm^{-1} is a soft mode proportional to the order parameter and approaching zero at the transition.

seven modes of which are both Raman and infrared active: $3B_2 + 4E$. In addition, there are three Raman-only modes: $2A_1 + B_1$. The one A_2 mode is silent. But for SiO_2 we calculate $A_1 + 2A_2 + 2B_1 + 2B_2 + 4E$, which still gives only three Raman-only modes ($A_1 + 2B_1$), but six infrared and Raman modes instead of seven. We do not see all these predicted modes: we measure in β-SiO_2 five out of the predicted nine lines—one Raman-only at 402; plus four infrared lines at 292, 777, 1077, and 1160 (all ± 5 cm^{-1}). In β-$AlPO_4$ we measure a total of six lines of the predicted ten. Thus, these lines are more numerous than predicted for an O_h phase, but not as many as predicted for D_{2d}. They are compatible with the D_{2d} point groups but do not unambiguously prove them; they would be equally compatible with D_4.

It is perhaps more revealing to concentrate on small splittings of groups of infrared or Raman lines. It the archetype cubic O_h phase hypothesized for β-cristobalite, there will be only one F_{2g} Raman line (near 777 cm^{-1}) and two F_{1u} infrared lines (near 450 and 1077 cm^{-1}); there are two F_{2u} modes that are both infrared and Raman forbidden. If the symmetry is reduced from O_h to D_{2d}, these will each split: F_{2g} into $A_1 + E$ and F_{1u} into $A_2 + E$, of which the A_2 and E modes will be further split into TO + LO components. If we examine the cristobalite SiO_2 infrared absorption data in figure 4, we see that the doublet near 1100 cm^{-1} is still resolved at 650 K, and those in $AlPO_4$ at both about 450 and 1150 cm^{-1} resolved at 600 K, well into the β-phases (figure 5). In addition, the line near 750 cm^{-1} (790 cm^{-1} in SiO_2) is still moderately strong in infrared absorption (figure 6), forbidden for F_{2g}. This makes a cubic symmetry unlikely. Intensities for other modes near the α–β transition temperature are shown in figure 7.

High-pressure studies of the cristobalite phase transition have been useful also, including the study of cristobalite $GaPO_4$ [48].

2.5. Rutile family

Some early effort was made on Raman spectroscopy of rutile structures, including TiO_2 (rutile) [49], GeO_2 [50], SnO_2 (cassiterite) [51, 52], and SiO_2 (stishovite) [53]. The latter is of considerable interest to geologists and mineralogists [54].
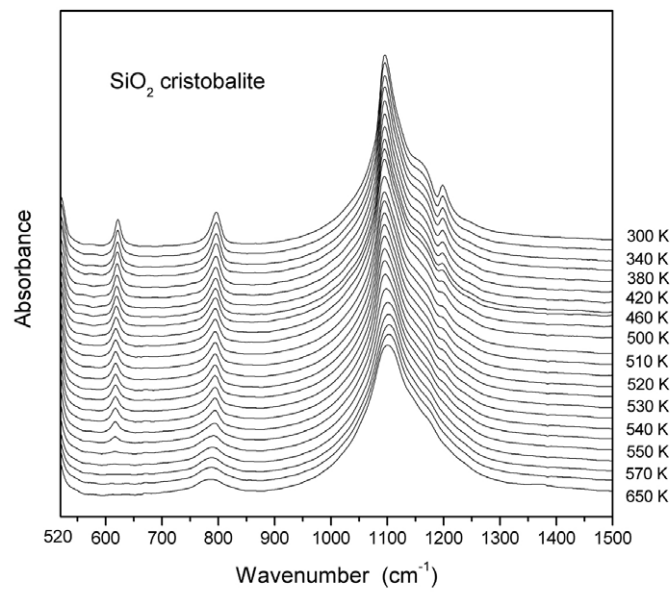
Figure 5. Infrared absorption in cristobalite SiO_2 from 500 to 1500 cm^{-1}, showing persistence of doublet structure near 1100 cm^{-1} up to 650 K. Note that there are too many lines for the O_h space group of references [40, 41].
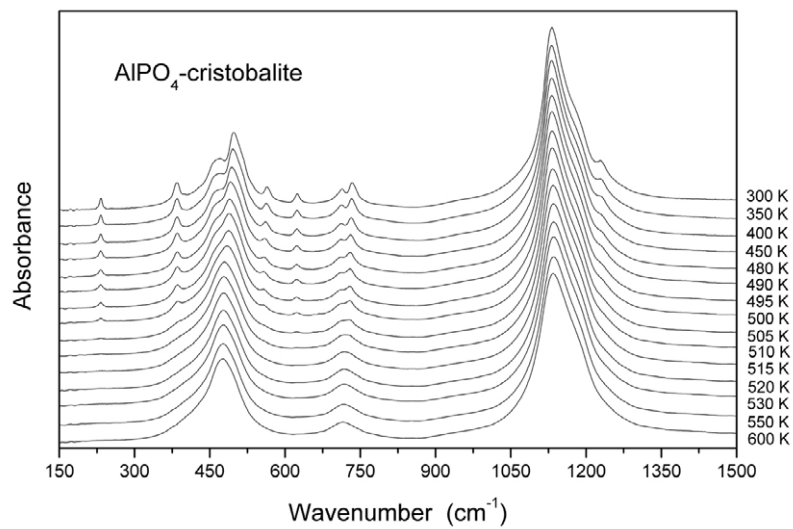

Figure 6. Infrared absorption in cristobalite $AlPO_4$ from 150 to 1500 cm^{-1}, showing persistence of doublet structure near 450 and 1100 cm^{-1} up to 600 K.

2.6. Calcite family

Both calcite and dolomite received early emphasis [55], with more recent studies applying the spectroscopy to mineralogical aspects [56–59]. Subsequently the three phases of potassium nitrate (including a reentrant ferroelectric phase) accessible at atmospheric pressure were
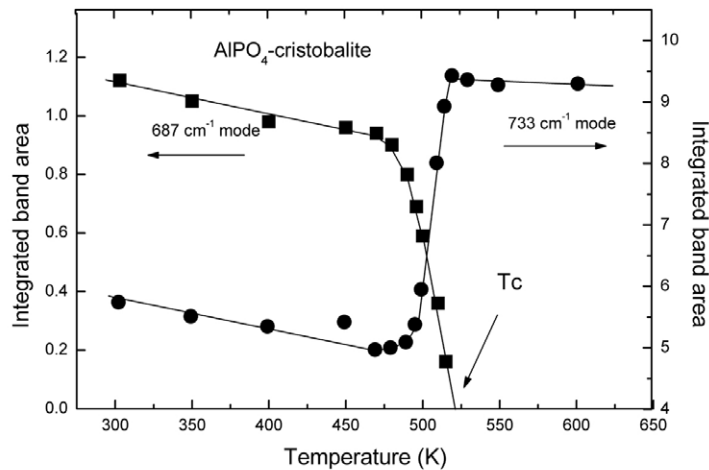
Figure 7. Graph of the intensities versus temperature for some phonon modes near 687 and 733 cm^{-1} in cristobalite AlPO$_4$.

studied in detail [60]. Particularly interesting was the great increase in the temperature range over which the ferroelectric phase is stable in thin-film form [61–63]. This stability appears to be due to stress, and a very similar effect is present with hydrostatic pressure. These effects have not yet been modelled with 'Pertsev diagrams' [64], although *ab initio* calculations have been initiated [65]. An early Raman study of KNO$_3$ in Paris was incorrectly modelled [66], assuming a wrong primitive unit cell (twice the real size), which had been controversial and incorrect [67, 68] until 1973 [69].

3. Systems with no Raman effect

3.1. Perovskites

In their ideal cubic structure, ABO$_3$ perovskites have no first-order Raman effect; all ions sit at centres of inversion, so that all long-wavelength ($q = 0$) phonon branches are of odd parity (F$_{1u}$ or F$_{2u}$). Most of these are infrared active but some are 'silent' (forbidden in both infrared or Raman spectra). All of these modes are Raman allowed in the present of a dc electric field, however, and this has permitted their extensive study [70–72], with SrTiO$_3$ the most studied [73]. More recently the multiferroic perovskite BiFeO$_3$ has been of great interest [74]. Cubic phase perovskite materials have no first-order Raman effect, as discussed above. We note that bismuth ferrite is a simple cubic perovskite only at very high temperatures, as shown in the Raman study of Haumont *et al* [74]. However, work near the bismuth ferrite melting temperature by Okuyama claimed six or eight first-order Raman lines [74]; these in reality are non-lasing emission lines from their Ar-ion laser (e.g. the 521 nm Ar$^+$ line occurs near 100 cm^{-1} shift from the 488 nm lasing transition).

3.2. Relaxors

Relaxors are materials which have some short-range ordering in nanoclusters and thereby exhibit dielectric peaks resembling those in ferroelectrics; however, the temperature at which

11

the dielectric susceptibility peaks is strongly frequency dependent, and often there are few other indications of a symmetry-breaking phase transition. The relaxor (nano-ordered) ferroelectrics such as PMN (lead magnesium niobate, $PbMg_{1/3}Nb_{2/3}O_3$) [75, 76], PST (lead scandium tantalate) [77, 78] or SBN (strontium barium niobate) [79–81] have been of great device interest because they permit strains of about 2%, about an order of magnitude greater than those in conventional ferroelectric oxides. PST is interesting because its non-cubic phase symmetry has remained controversial (even more so than β-cristobalite SiO_2), and its transition temperature and degree of ordering depends strongly upon thermal processing. SBN is interesting because unlike most perovskite oxide relaxors it is strongly uniaxial and not pseudo-cubic.

4. Theoretical approaches

4.1. Ab initio

Recently, *ab initio* modelling has favoured such systems because they typically have small unit cells, high symmetry, and hence rather a small number of optical phonon branches. Effort has been on understanding the covalent Ti–O bonding [82], the sequences of phase transitions [83], and the temperature–stress diagrams [64].

4.2. Critical exponents

Very near transition temperatures for continuous (second-order) phase transitions, it is expected that fluctuations in the order parameter ϕ dominate dynamics. This requires that $\langle \phi^2 \rangle \gg \langle \phi \rangle^2$. Unfortunately that is probably true only within a few mK of ferroelectric or ferroelastic phase transitions, because both Coulombic forces and strain, respectively, are unscreened and very long range. Therefore, unlike magnets, these structural phase transitions are expected to exhibit mean-field data at all feasible measuring temperatures near the transition. It is useful to point out, however, that Raman data give very accurate values of the critical exponent γ' which is the exponent describing the divergence of dielectric constant with temperature in a ferroelectric or the stress–strain compliance in a ferroelastic (the soft mode frequency $\omega(T)$ is proportional not to $(T_c - T)^\beta$, as is sometimes erroneously assumed (true only in mean field), but to $(T_c - T)^{\gamma'/2}$, from the Lyddane–Sachs–Teller relationship), from both soft-mode frequencies and Raman intensities also; the intensities are proportional to combinations of β and γ' [84–86]. Here β is the exponent that describes the temperature dependence of the order parameter (spontaneous polarization in a ferroelectric).

Many recent attempts to evaluate true critical exponents in such materials seem to ignore these issues.

5. Applications

In thin-film form these materials are of considerable interest as ferroelectric random access memories (FRAMs) [87–89]. Those which are simultaneously magnetically and ferroelectrically ordered have been very trendy as potential RAMs which can be magnetically read but electrically erased and rewritten.

6. Summary

We have tried to provide a short review that details the early Raman studies of minerals. Oddly enough, these were not done in a mineral physics laboratory, but at Bell Laboratories, where

interest was in the laser Raman technique *per se* and in certain synthetic minerals as host lattices for rare earth laser ions. Some of the early x-ray crystallography was wrong due to the inability to localize light ions such as oxygen with precision: this often arose because the published x-ray crystallographic data on, for example, KNO_3, $SrTiO_3$, and $LaAlO_3$, all had the size of the primitive unit cell wrong and hence the wrong space group symmetry (although the correct point group). In the past three years a number of materials isomorphic with quartz or cristobalite have been studied (e.g., $FePO_4$), and it seems timely to do renewed lattice dynamical studies of these, now that a large set is available. It might be possible to 'data-mine' some of the early work reviewed here, particularly regarding the α–β transitions in cristobalite $AlPO_4$, which to our knowledge have not been modelled. Clearly the dispute between Liu *et al* and Swainson and Dove regarding the structure of β-cristobalite has not been resolved, and the extensive data on cristobalite $AlPO_4$ given in the present manuscript may be helpful in that regard. Our results support the $I\bar{4}2d$ structure originally inferred by O'Keefe and [90], for which the model calculations of Liu *et al* [42–44], and more recently Ramos *et al* [91], Yang *et al* [92] and Bourova *et al* [93] or Iarlori *et al* [94] add credibility. We think that our Raman studies are probably more reliable than most reported earlier because some were obtained from single crystals and not powders or pressed pellets. Although there are many very recent models of β-cristobalite [95], most seem to be based on powder spectra [96]. Because of the large strain associated with surfaces and interfaces in powders, such spectra can in principle appear more disordered than those from single crystals and therefore imply a disordered structure that is not intrinsic nor characteristic of bulk single crystals. However, in such cases the neutron diffraction lines would be broadened, and this was not the case [97]. However we can reconcile the 'extra' Raman lines in the β-cristobalite phases of SiO_2 or $AlPO_4$ with the neutron crystallography of SiO_2 and its implied O_h cubic phase not in terms of strain but in terms of different timescales. Our conclusion is that cristobalite $AlPO_4$ is definitely D_{2d} in its β-phase and D_2 in its α-phase and fits the theory of Liu *et al*; the structures of cristobalite SiO_2 are probably the same as those of $AlPO_4$. We emphasize that these are the structures measured on a ps optical timescale. We think that this is the important timescale because it determines electronic band structures and optical selection rules [98]. However, on slower timescales the dynamical hopping from site to site will produce an averaged D_4 symmetry for α-SiO_2 and O_h for β-SiO_2 [35–41].

Acknowledgments

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