

The structure of particles and the structure of crystals: information from vibrational spectroscopy

William B. White*

Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA

Vibrational spectra, particularly Raman spectra provide useful information on the internal structure, bonding, and state-of-order of materials ranging from bulk crystals to nanoscale particulates. Spectra of bulk crystals contain first order phonons excited at the center of the Brillouin zone. Disorder produces a broadening of Raman lines due to breakdown of strict translational symmetry. Structural disorder can be distinguished from dipolar disorder in strongly polar materials by the temperature dependence of the line shapes. At particle sizes in the nanoscale range, new phenomena appear due the effects of phonon confinement. These include mode wavenumber shifts and line broadening, the appearance of zone boundary phonons, the appearance of surface phonons, and the appearance of extremely low wavenumber bands due excitation of bulk resonances of the particle. One must distinguish between purely nanocrystal effects due to phonon confinement and the increased structural disorder that often accompanies extreme reduction in particle size. The present paper reviews these concepts and the underlying theory with the aim of making Raman spectroscopy a useful characterization tool for particulate ceramic materials.

Key words: Raman Spectra, Particulates, Order/Disorder.

Introduction

The structure of crystalline solids is reflected in their vibrational spectra. Bond lengths, bond strengths, atomic masses, and the arrangement of atoms within the unit cell are the primary factors controlling frequency and intensity of infrared absorption and Raman scattering bands. The theoretical foundation for the vibrations of macroscopic single crystals is well established [1]. When the objects of interest are ceramic particles on either a micro or nano size scale, other factors must be considered. Deviations from ideal structural order on the atomic scale are a consideration on any size scale from bulk crystals to nanoparticles. In addition, however, the particle size itself becomes a parameter at a certain size scale below which the vibrations of crystal particles deviate from the behavior of bulk crystals.

The objective of the present paper is to summarize and review the phenomena that appear in the vibrational spectra of crystals and crystalline particles of ceramic interest and to indicate ways in which vibrational spectroscopy can be used as a characterization tool. Examples are drawn mainly from earlier work by the author and his research group.

Reference Points: Free Molecules and Bulk Crystals

To provide a reference for what follows, there follows an extremely brief review of the vibrational characteristics of molecules and crystals. The vibrational physics of defect-free, well-ordered bulk crystals (admittedly an idealized concept) define one end of a continuum of spectral responses. We can consider the modifications of idealized behavior as the crystal becomes smaller and as it becomes more disordered. With respect to both particle size and disorder, however, the isolated molecule marks the opposite end of the continuum. An isolated molecule is the smallest possible particle but it is also a highly ordered particle.

Molecular Vibrations

– Localized Molecular Resonances

A molecule can be considered as a purely mechanical system with atoms represented by balls with certain masses and the bonds represented by springs with certain Hooke's law constants. The molecule will vibrate with resonance frequencies determined by the masses and the spring constants. The free molecule has $3n$ degrees of freedom where n is the number of atoms in the molecule. Three of these are translations of the molecule along the x , y , and z coordinate directions and another three are rotations of the molecule around the coordinate axes. The $3n-6$ internal degrees of freedom are vibrations with mechanical frequencies that fall into the infrared range of the electromagnetic spectrum.

*Corresponding author:
Tel : +1-814-865-1152
Fax: +1-814-865-2326
E-mail: wbw2@psu.edu

Relating vibrational frequencies to atomic masses and bond force constants requires solving the n -body equations of motion, done with great elegance long ago [2]. Except for the introduction of a zero-point energy, quantum mechanics gives the same results as classical mechanics.

– Mode Classification and Selection Rules

The vibrational frequencies and the energies associated with them are real physical properties of the vibrating molecule and as such must be invariant under all symmetry operations of the molecular point group. Consideration of the transformations of the atomic displacements during vibration under the various symmetry operations allows the vibrational modes to be classified according to the irreducible representations of the molecular point group [3]. In order for the molecular vibrations to be observed, the mechanical resonances must either couple directly with the electromagnetic field to produce an infrared absorption spectrum or they must interact through the molecular polarizability to produce Raman scattering. Only those modes that have the same symmetry as some component of the time derivative of the molecular dipole moment will appear in the infrared spectrum and only those modes that have the same symmetry as some component of the polarizability tensor will appear in the Raman spectrum.

– Lineshapes of Molecular Spectra

Ideal Raman bands are Lorentzian. They can be most easily described in terms of peak wavenumber, peak intensity and the full width at half maximum. Band widths for isolated molecules are in the range of a few wavenumbers. The width varies depending on molecular geometry and on the symmetry of the vibration. Symmetrical modes tend to be more narrow than antisymmetrical ones.

Crystal Vibrations

– Phonons and Phonon Band Structure

Unlike molecular vibrations, excitations of the fundamental vibrational modes of crystals can migrate through the crystal giving these packets of excitation some of the characteristics of particles and the name *phonons*. Crystal vibrations have characteristic frequencies (usually expressed in wavenumbers, cm^{-1} , rather than frequency) and also characteristic momenta expressed by the wavevector, $\mathbf{k}$. Unfortunately wavevector also has units of inverse length and is also expressed in units of cm^{-1} although these are not wavenumbers. The overall vibrational structure of a crystal can be displayed as a band diagram (Fig. 1), not intrinsically different from the band diagrams used to describe the behavior of electrons in crystals. Here, however, the band diagram refers to phonons, not electrons.

Because crystal vibrations are mechanical resonances migrating through the crystal, they have a shear wave component, called the transverse mode and a pressure

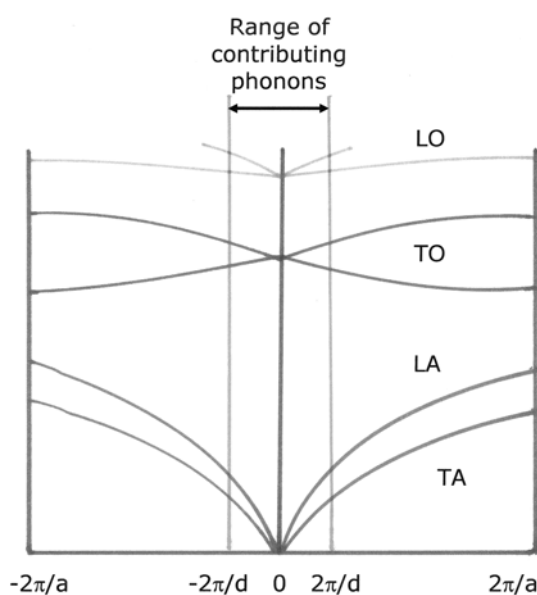


Fig. 1. Schematic phonon band structure diagram showing optic and acoustic branches. Definition of symbols: LO = longitudinal optic mode; TO = transverse optic mode; LA = longitudinal acoustic mode; TA = transverse acoustic mode.

wave component called the longitudinal mode. In contrast to molecular spectra, each vibrational mode appears on the phonon band diagram with a separate transverse and longitudinal component. In addition, there is a set of motions that correspond to in-phase motion of all atoms in the crystal. These are the acoustic modes which also have transverse and longitudinal components.

A correct representation of the phonon band structure would be a four-dimensional figure with three spatial coordinates to describe the components of the wavevector plus an energy coordinate. In order to show at least part of the band structure on a flat sheet of paper, the custom has been to plot energy as a function of wavevector along selected crystallographic directions. The $\mathbf{k}=0$ point is the center of the Brillouin zone, and the various vibrational branches are drawn along the specified directions to the boundary of the zone.

– Counting Modes

In the limit of small displacements, each atom in a crystal has three degrees of freedom with possible displacements along the x -, y -, and z -axes. Thus an entire crystal would have $3nN$ vibrational degrees of freedom, where n is the number of atoms in the unit cell and N is the number of unit cells that make up the crystal. However, translational symmetry requires that all unit cells vibrate alike, reducing the number of degrees of freedom at the zone center to $3n$ where it must be kept in mind that n refers to the primitive unit cell, not necessarily the crystallographic cell. Three of these, corresponding to all atoms moving in the same direction, are the acoustic modes. The remaining $3n-3$ degrees of freedom may or may not appear in the spectra as distinct Raman or infrared bands. In high

symmetry crystals some of the modes will be degenerate, that is two or three modes are required by symmetry to have exactly the same energy and thus appear in the spectra as a single band. Some will be forbidden by symmetry to couple with either the electric field for infrared absorption or the polarization fluctuation for Raman scattering. Calculations based on the factor group of the crystal will classify the modes according to their symmetry transformation properties and thus identify the degeneracies. These calculations also determine the selection rules.

The spectra of crystals with relatively small unit cells and a limited number of atoms usually display all of the modes expected from symmetry arguments. As the number of atoms in the unit cell increases, experimental results account for fewer and fewer of the calculated number of modes. There are a number of reasons: accidental degeneracy – two or more modes with close to the same wavenumber – weak bands lost in the measurement noise, and more low wavenumber bands because of the complex torsional motions possible in large unit cells. Overall, it means that simple mode counting is not a very definitive way of confirming structure from spectra for large and complex unit cells.

– Selection Rules

Transitions between the vibrational ground state and the vibrational excited states are controlled by the symmetry properties of the operator that couples the transition as well as by the symmetry of the crystal. Three selection rules are of relevance here.

The $\mathbf{k} = 0$ (momentum conservation) selection rule.

The wavevector, $\mathbf{k}$, varies from 0 to $2\pi/a$ or 0 to about 10^8 cm^{-1} . Infrared photons at 10^2 to 10^3 cm^{-1} or laser excitation for Raman scattering at about 10^4 cm^{-1} have only a tiny fraction of the momentum of the crystal phonon dispersion curves. Thus first order infrared absorption and Raman scattering is limited to the center of the Brillouin zone, $\mathbf{k} = 0$. This selection rule will be weakened for disordered crystals or for small particles.

Infrared radiation is coupled to vibrational transitions by changes in the dipole moment during the execution of the vibration. This coupling requires that the crystal vibration have the same symmetry as some component of the dipole moment. In non-cubic crystals, the infrared spectra will be polarized.

Raman scattering is coupled to vibrational transitions by changes in the polarizability during the execution of the vibration. The polarizability is a second rank symmetric tensor. By proper orientation of the crystal, the incident laser beam, and the scattered beam, spectra coupled by independent components of the tensor can be measured. In general, the polarization is lost for polycrystalline or particulate materials.

– Temperature Dependence

The intensities of Raman bands have both a frequency dependence and a weak temperature dependence often normalized to a reduced intensity by

$$I_R = \frac{I(\omega)}{\omega[n(\omega) + 1]} \quad (1)$$

In the above equation, the temperature dependence of the Raman intensity is given by the Bose temperature

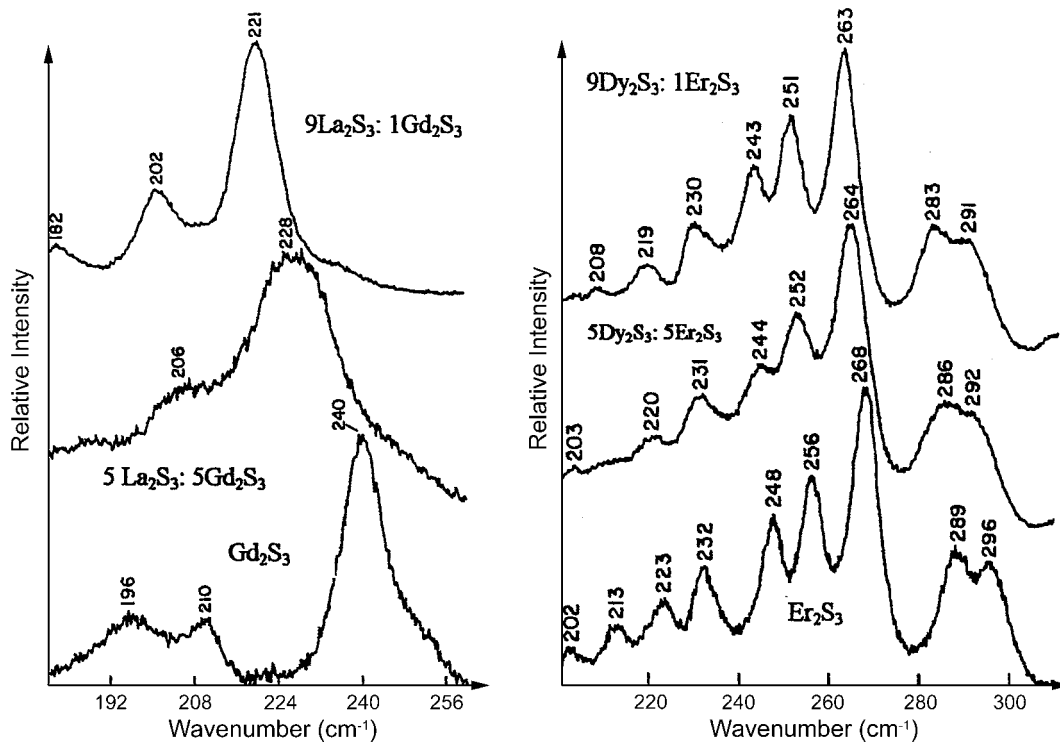


Fig. 2. Raman spectra for two series of rare earth sulfide solid solutions. Spectra from Knight and White [4].

factor, n .

$$n(\omega) = \left[\exp\left(\frac{h\omega}{2\pi k_B T}\right) - 1 \right]^{-1} \quad (2)$$

The anomalous change in band width with temperature that is observed in what below is called dynamic disorder is to be compared with the intrinsic temperature dependence.

Disorder in Bulk Crystals

Structural Disorder

– Substitutional Solid Solutions

In a pure, defect-free, stoichiometric crystal, every ion is on a specified lattice site and every unit cell is strictly identical to every other unit cell. Substitution of a similar but not identical ion introduces disorder into the system. Although the unit cell changes size in a uniform fashion and there is no clustering or phase separation of the substituted ion, the translational symmetry is to some degree broken. In terms of the physics, the local electric fields and local polarizability no longer replicate exactly from cell to cell depending on the mismatch in size (or charge) of the ion being substituted.

The effect of creating a small variation in the local field through substitution of ions of the same charge but different ionic radius is illustrated with the case of solid solutions between rare earth sesquisulfides [4]. La_2S_3 - Gd_2S_3 solid solutions have the orthorhombic α -

type structure. The Raman spectra consist of a few broad bands (Fig. 2). Dy_2S_3 - Er_2S_3 solid solutions have the monoclinic δ -type structure with more complex Raman spectra. For both solid solutions there is a pronounced increase in Raman band width along the solid solution series. The ionic radius of La^{3+} is 130 pm [5] compared to 119 pm for Gd^{3+} (for 8-fold coordination). In contrast, the ionic radius of Dy^{3+} is 105 pm compared with 103 pm for Er^{3+} (for 6-fold coordination), a much smaller mismatch. The mismatch is clearly reflected in the Raman band widths (Fig. 3). For both solid solution series, the line width increases with substitution, reaches a maximum near the middle of the series, and then decreases toward the opposite end member. However, there is a much greater increase in Raman band width at intermediate compositions for the La-Gd system compared with the Dy-Er system.

– Defect Solid Solutions

The system CaO - ZrO_2 is a classic example of a solid solution series dominated by defects. For pure ZrO_2 , the cubic fluorite structure is unstable at ambient temperature and reverts to the monoclinic baddeleyite structure. Introduction of CaO stabilizes the cubic structure. Ca^{2+} substitutes for Zr^{4+} so there is both a

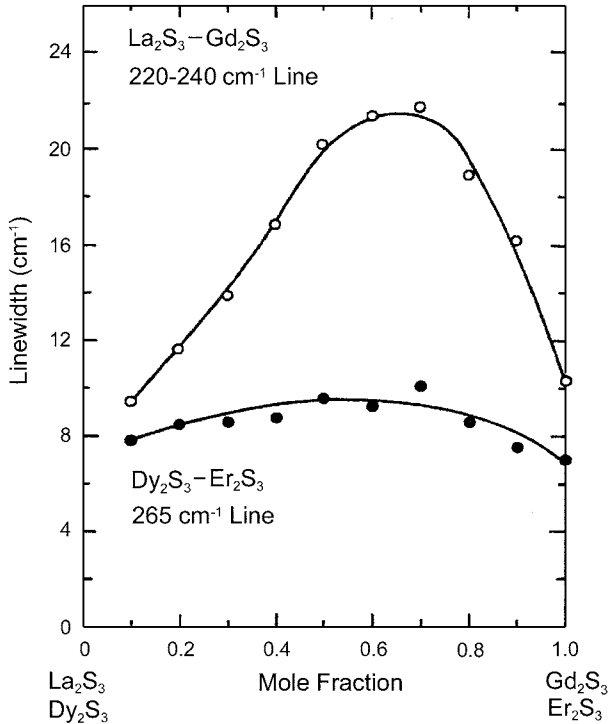


Fig. 3. Variation in Raman band width for two rare earth sulfide solid solutions showing effect of ionic size mismatch. Data from Knight and White [4].

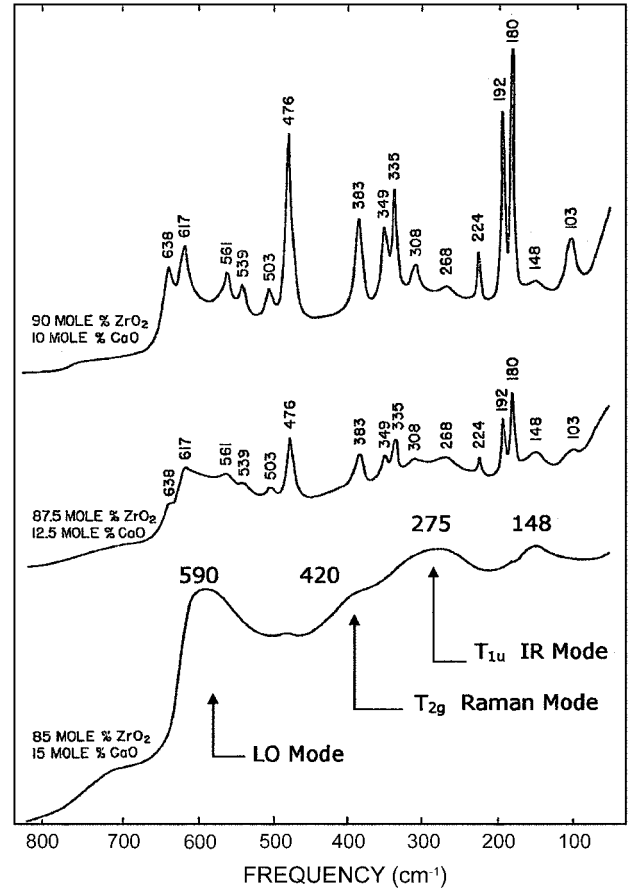


Fig. 4. Raman spectra for a sequence of ZrO_2 - CaO solid solutions. Upper two spectra are from two-phase region. Bottom spectrum is of single-phase lime-zirconia solid solution with fluorite structure. Data from Keramidas and White [6].

size and charge imbalance. To compensate for the charge mismatch, every Ca^{2+} is compensated by omitting an oxygen ion from the anion sublattice. The cubic solid solution should be written $\text{Zr}_{1-x}\text{Ca}_x\text{O}_{2-x}$ so in these solid solutions, there are strongly altered local fields on both cation and anion sublattices.

The effect of this type of structural disorder on the Raman spectrum is dramatic. Figure 4, from the rather old work of Keramidas and White [6], shows Raman spectra for three compositions in the CaO-ZrO_2 system. The 10% lime composition is in the two-phase region dominated by the highly ordered baddeleyite structure with sharp Raman bands. There are a large number of bands because of the low symmetry structure. The 15% lime composition is cubic zirconia. The X-ray diffraction patterns are sharp and indicative of a well-ordered fluorite structure on the X-ray scale. The Raman spectrum is a continuum with a few broad humps.

The interpretation is that this highly defective structure has forced a complete breakdown of all selection rules. The broad band at 590 cm^{-1} corresponds to the longitudinal component of the T_{1u} mode. The fluorite structure has a single T_{2g} Raman mode which would be expected around 465 cm^{-1} . The weak shoulder near 420 cm^{-1} may be this mode. The feature at 275 cm^{-1} corresponds closely to the normally infrared-active T_{1u} mode. None of the specific features are very strong and all are superimposed on a broad scattering continuum. The breakdown of the $k=0$ selection rule allows contributions from phonons throughout the Brillouin zone, producing the observed continuum. At the concentration of defects in lime-stabilized zirconia, the Raman scattering maps the density of states in the phonon band structure rather than specific modes at the zone center.

Dynamic Disorder

Disorder can be introduced into crystal structures without vacancies and without deviation from ideal composition. Molecular units within crystals may be locked into a single orientation or there may be multiple possible orientations. If the barrier to reorientation is small, some molecular units may take one orientation and some another thus introducing disorder within the structure. The NH_4^+ ion is the best studied example. The ammonium halides exhibit a series of polymorphs corresponding to a locked-in orientation, multiple orientations, and, at higher temperatures, free rotation of the NH_4^+ ion. Structures with orientable dipoles can also exhibit dynamic disorder. This can arise from structures containing ions with lone-pair electrons such as Pb^{2+} and Bi^{3+} and it can arise in structures in which off-center cations produce strong local dipoles. The perovskite structure ferroelectrics are examples. The characteristic feature of dynamic disorder in the Raman spectra is a strong temperature dependence of Raman band widths.

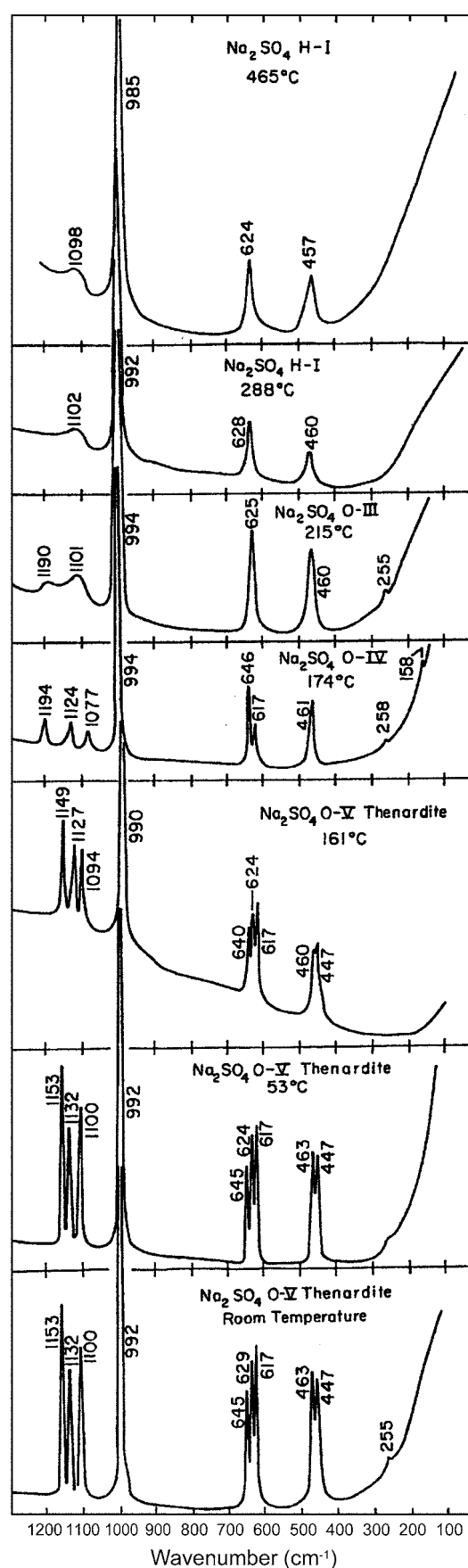


Fig. 5. Raman spectra for the Na_2SO_4 polymorphs as a function of temperature.

– Orientational Disorder

The NH_4^+ ion exhibits orientational disorder at low temperature because the molecule is so compact that it is nearly spherical. However, similar effects are seen with other tetrahedral molecules although usually at somewhat higher temperatures. The sulfate ion is a case in point. Figure 5 shows a sequence of Raman spectra of Na_2SO_4 taken at successively higher temperatures. At low temperatures, the compound takes the orthorhombic thenardite structure ($\text{Na}_2\text{SO}_4\text{-V}$). At higher temperature there is a sequence of phase transitions [7]. Both $\text{Na}_2\text{SO}_4\text{-III}$ and $\text{Na}_2\text{SO}_4\text{-I}$ have structures in which the SO_4^{2-} ion is disordered between alternate orientations within the structure.

The bands seen in the Raman spectra of Figure 5 are the internal modes of the SO_4^{2-} ion. The group of three bands near 1100 cm^{-1} are the triply degenerate antisymmetric stretch with the degeneracy removed by the low symmetry of the host structure. In the low temperature polymorphs, these bands are sharp and well-defined. In the high temperature polymorphs the bands are broadened and smeared together because of the orientation disorder of the sulfate ion.

– Dipole Disorder

As an example of dipole disorder, Figure 6 presents the Raman spectra of $\alpha\text{-Bi}_2\text{O}_3$ taken from the work of Betsch and White [8]. The structure itself is well-ordered. The disorder arises from the Bi^{3+} ion which has an outer shell containing lone-pair $6s^2$ electrons. As a result, the Bi^{3+} ion is non-spherical. The lobe of charge can take multiple orientations within the structure. Because the outer electron shell is highly polarizable, bismuth oxide has a very intense Raman spectrum but at room temperature, the band widths are very broad. As the temperature is lowered, the bands sharpen considerably. This is because the Bi^{3+} ion is gradually frozen into the lowest minimum in the multiple well

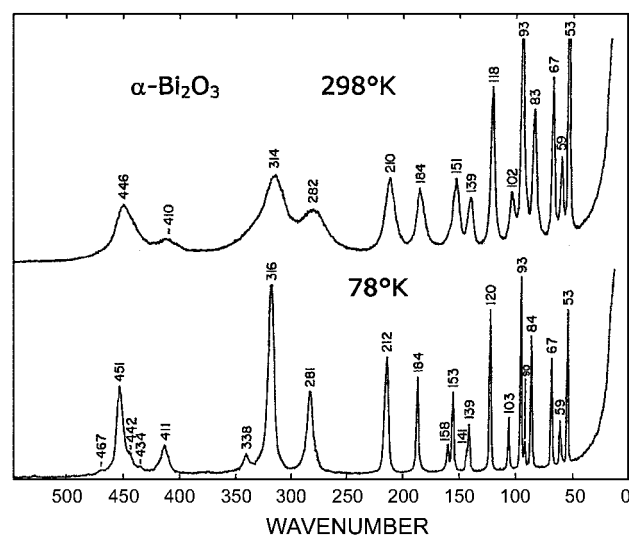


Fig. 6. Raman spectra of $\alpha\text{-Bi}_2\text{O}_3$ at room temperature and at liquid nitrogen temperature. Data from Betsch and White [8].

potential. There is no phase transition in this case. The ordering proceeds gradually with decreasing temperature. This behavior is typical, not only for lone pair ions, but for many ferroic compounds with orientable dipoles.

Disorder and Size Effects in Particulates

Loose Particles, Aggregates, and Dense Ceramics

– For Reference: Disorder at Larger Size Scales

The behavior of the Raman spectra of disordered materials, illustrated by the examples above, is summarized in the sketch in Figure 7. Substitutional disorder can be distinguished from orientational disorder by the temperature dependence of the line width. Orientational disorder, which does not require any atomic movement, tends to produce band widths that decrease rapidly with decreasing temperature as the molecule or dipole tends to freeze into its lowest energy configuration. First order, zone-center Raman lines have only a small intrinsic temperature dependence as given by equations (1) and (2) so that the broadening induced by structural disorder is largely independent of temperature.

The Raman spectrum of a crystal with a small number of defects is essentially that of the well-ordered crystal with the same number of bands obeying the same selection rules. Increasing the concentration of defects increases the band width. In general, the magnitude of broadening at any given defect concentration is related to the polarization of the material. Materials with high intrinsic polarization show greater broadening compared with materials with a smaller polarization. At some defect concentration, which depends on the structures and on the ions, there will be a breakdown of selection rules. Bands appear which are forbidden as first order Raman scattering at the center of the Brillouin zone. With a further increase in the concentration of defects, the effective translational symmetry will be lost, the $\mathbf{k} = 0$ selection rule will be completely broken, and all phonons will contribute to the Raman scattering. The resultant spectrum will be

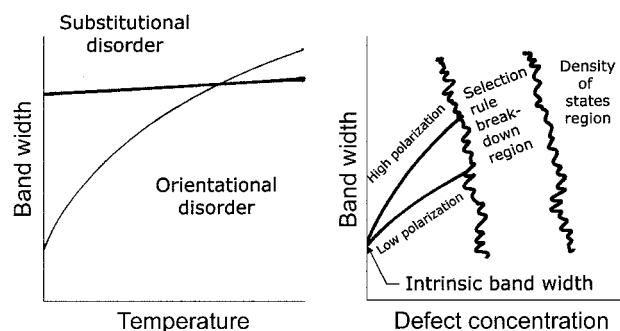


Fig. 7. Sketch showing relation of Raman band widths to temperature for types of disorder and the relation of Raman band width to concentration of defects.

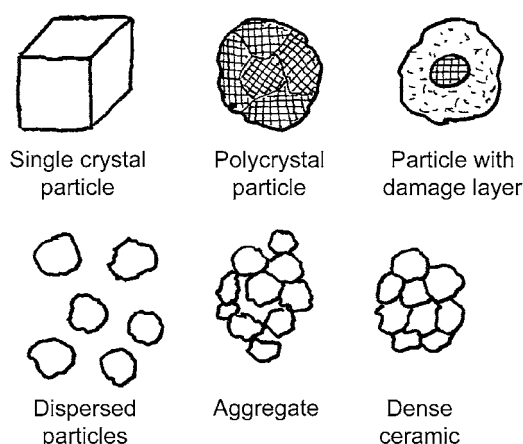


Fig. 8. Cartoon showing structural arrangements of particulate materials.

closely related to the density of states of the material.

It is to be emphasized that the phenomena described above are observed in crystals which give sharp, well-ordered X-ray diffraction patterns. There need be no breakdown in crystallinity as such. Measurements, such as X-ray diffraction, that are sensitive only to an average unit cell will assess the material as crystalline.

– Morphological/Structural Considerations

Application of Raman spectroscopy to particulate matter introduces some further complications. Figure 8 sketches some of the possibilities for particulate materials. The individual particles might take the form of very small single crystals. Particles might be polycrystalline. They might have a core of crystalline material surrounded by a damage layer which might or might not be at least partially crystalline. The particles might be dispersed so that there is no effective contact between them. They might form a loose aggregate. They might be compacted and sintered to various degrees with the ultimate limit of a dense ceramic where grain boundaries are of atomic thicknesses.

In addition to whatever disorder exists at the atomic scale, particle size becomes an additional parameter. Furthermore, the state of aggregation is also a parameter which at the present time has not been very thoroughly investigated. Down to a certain limit, a well ordered particle gives the same spectral response as the bulk material. Below that limit, effects of quantum confinement begin to appear. Some of the phenomena that have been identified are listed below.

- Small downshifts in TO mode wavenumbers.
- Broadening of first order phonon modes.
- Decrease in the separation of longitudinal and transverse modes (LO-TO).
- Changes in relative band intensities, especially multiphonon modes.
- Appearance of zone boundary phonons in the Raman spectra.
- Appearance of surface phonons between TO and LO.

- Appearance of a low wavenumber “particle band” due to bulk resonances of the particle.

A selection of these phenomena will be illustrated below.

Coherence Length and Phonon Confinement

– Implications of Small Size Scales

It has long been known that infrared spectra of polar particulates are highly distorted from the correctly measured spectra of bulk materials. The effect of long range polarization is related to the separation of transverse and longitudinal modes. For strongly covalent materials transverse and longitudinal modes nearly overlap so that infrared spectra measured on powders embedded in a dielectric medium such as KBr are quite accurate. Compounds with an intermediate degree of polar character such as carbonates, sulfates, and silicates produce usable spectra but with significant band distortion. The powder infrared spectra of strongly ionic compounds such as most oxides are so highly distorted as to be useless.

Raman spectroscopy is a valuable characterization tool for particulate materials because the Raman band shapes remain accurate at least down to the micrometer size scales typical of ceramic materials. At smaller size scales new effects begin to appear. Several phenomena come into play. As sketched in Figure 1, at small particle sizes the reciprocal of the particle diameter becomes a significant fraction of the Brillouin zone, relaxing selection rules. The particle size becomes comparable to the phonon mean free path. Extracting numerical values for the threshold size for phonon confinement is difficult and substantially model dependent. Many researchers have used some modification of the expression for Raman line shape published by Campbell and Fauchet [9].

$$I(\omega) = \int \frac{|C(0, q)|^2}{(\omega - \omega(q))^2 + \left(\frac{\Gamma_0}{2}\right)^2} d^3 q \quad (3)$$

Various forms have been used for the confinement function $C(0, q)$. One of these is the Gaussian form

$$|C(0, q)|^2 = \exp\left(-\frac{q^2 L^2}{4}\right) \quad (4)$$

L in this equation is the correlation length. Some results obtained by various authors are summarized in Table 1 [10-13]. Phonon confinement effects will not be an important consideration in the Raman spectra of microcrystalline materials but became very important at the nano-scale.

– Band Widths and Particle Size

The broadening of Raman lines due to particle size is illustrated in Figure 9 for some representative compounds. The line widths measured for CeO_2 and Ge increased only slightly with decreasing particle size.

Table 1. Threshold for Onset of Phonon Confinement Effects

Material	Particle Size (nm)	Source
Ge in SiO ₂	20	Fujii et al. [10]
ZnTe	40	Hayashi et al. [11]
SiC	40	Sasaki et al. [12]
CeO ₂	10	Kosacki et al. [13]
ZrO ₂ :0.16Y	0.4	Kosacki et al. [13]

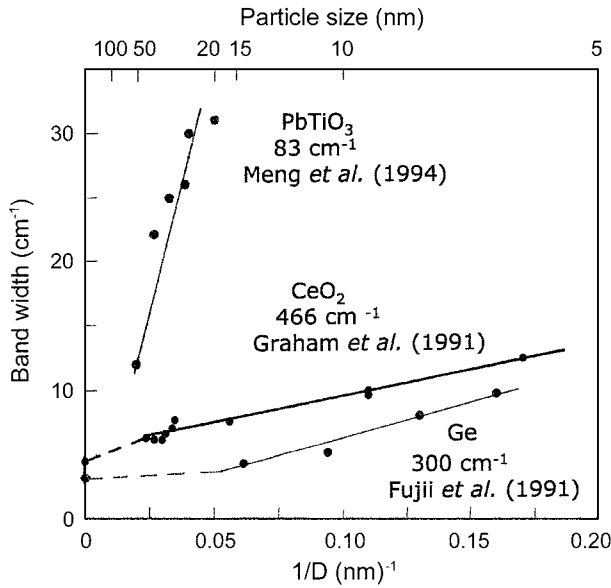


Fig. 9. Relation of Raman band width to particle size for three compounds. Approximate band wavenumber for each compound is given. Numerical data for PbTiO₃ from Meng et al. [14], for CeO₂ from Graham et al. [15], and for germanium from Fujii et al. [10].

The measurement for PbTiO₃ was on a soft mode which proves to be much more sensitive to phonon confinement.

– Zone Boundary Phonons

Possibly the best example of new Raman bands arising in samples of small particle size is graphite. The main vibrational mode of single crystal graphite occurs at 1580 cm⁻¹ (Fig. 10). It is often referred to in the literature as the “G-band”. In small particle graphite, a second band, called the “D-band” appears at 1357 cm⁻¹. This band has been assigned to a first order zone-boundary phonon at the [0001] M point in the Brillouin zone. It was recognized quite early by Tuinstra and Koenig [16] that the ratio of D-band to G-band intensities scales with particle size. Figure 10 shows a more recent evaluation of available data [17]. The dispersion curve for graphite is flat near the [0001] zone boundary with a correspondingly high density of states. As a result, for the smallest particle sizes, the zone-boundary phonon is more intense than the zone-center phonon. In general, the zone-boundary phonons appears in the same region of the spectrum as the zone-center phonons with similar line shapes and similar intensity.

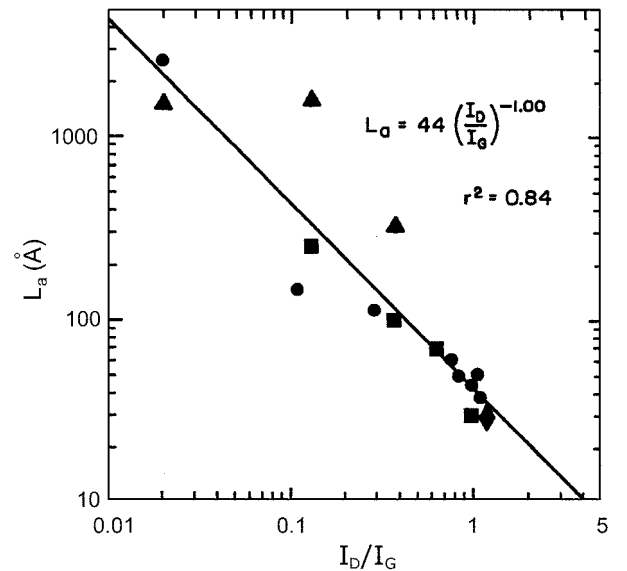
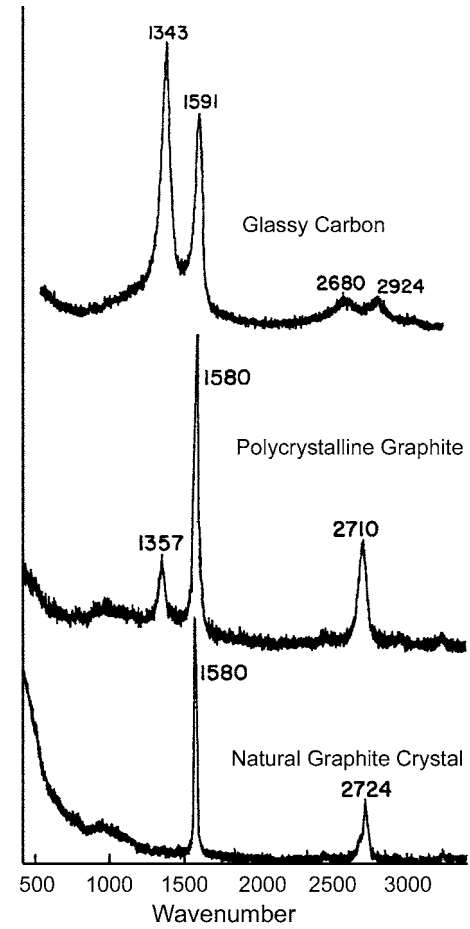


Fig. 10. Raman spectra of three graphitic carbons and the relation of the ratio of the 1350 cm⁻¹ D-band intensity to the 1580 cm⁻¹ G-band intensity to particle size. Data from Knight and White [17].

Bulk States and Surface States

A unique feature of small particle spectra is the appearance of a new band at very low wavenumbers. This “particle peak” is the result of vibration of the entire particle, in effect an acoustic mode. Although it

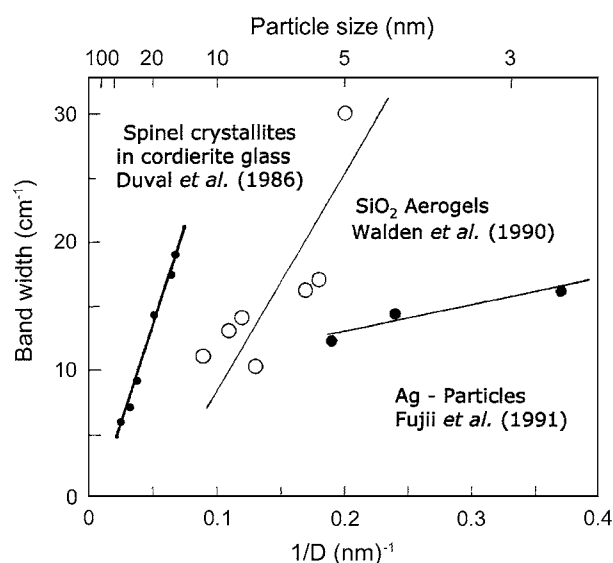


Fig. 11. Relation of the band wavenumber for the low wavenumber “particle peak” to particle size for three compounds. Numerical data for spinel particles from Duval et al. [18], for silica aerogels from Walden et al [19], and for silver particles embedded in silica from Fujii et al. [20].

is necessary to use special spectrometers that can make measurements close to the exciting line, particle peaks have been observed in a variety of materials. Figure 11 shows several examples. Because these are spherical resonances of the entire particle, the wavenumber of the particle peak scales inversely with the particle size. The relationship has been described

$$\omega = \frac{Cv_l}{2ac} \quad (5)$$

The proportionality constant, C , describes the order of the spherical vibration. It has numerical values ranging from 0.7 to 0.85 depending on which modes are deemed to be dominant. $2a$ is the particle diameter, v is the sound velocity in the particle, and c is the velocity of light.

Figure 11 illustrates well the diversity of particles that produce a particle peak in their Raman spectra. The spinel crystallites are ionic oxide nuclei formed by heat-treating glass of cordierite composition. Silica aerogels were shown by transmission electron microscopy to have a particulate structure with “particles” in the 5-10 nm size range. As a result, the particle peak is rather broad and the peak wavenumber not so well defined as the other materials. Surprisingly, small particles of metallic silver, dispersed in a silica film, give a well-defined particle peak. Because silver has only one atom in the primitive unit cell, it has no zone-center vibrational spectrum. This is good evidence that the particle peak is indeed an acoustic resonance of the entire particle.

Conclusions

This paper is intended to show the range of order/disorder and particle size phenomena that can appear in the Raman spectra. The small particle measurements that appear in the literature have been made on well-defined and well-dispersed particles. Further investigations into the effects of aggregation would be instructive. It would be particularly interesting to know the packing density required to convert the spectra of individual particles into the spectra of a bulk material. Application of Raman spectroscopy as a characterization tool requires careful distinction between modifications of Raman line shape due to disorder in the bulk crystal from modifications due to particle size.

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