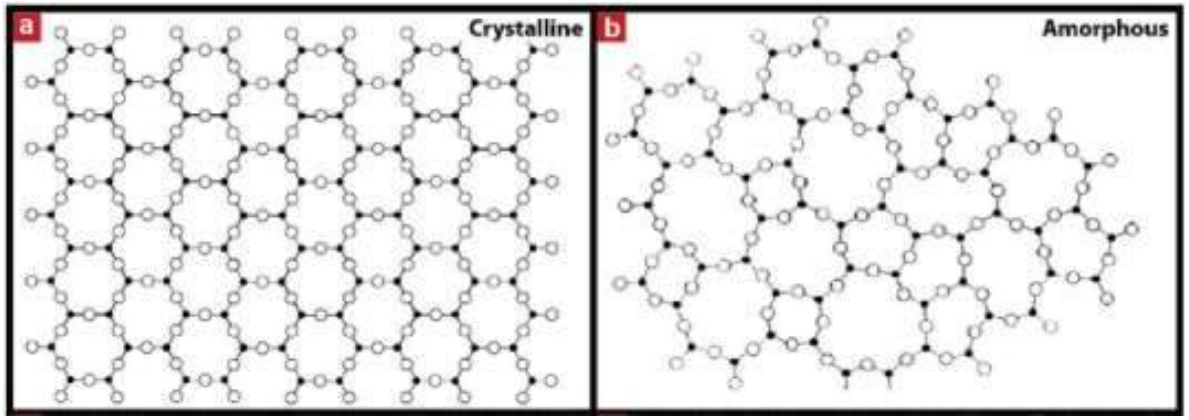
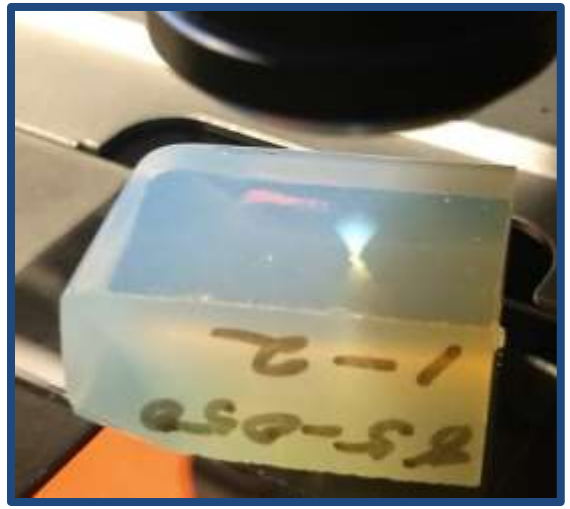
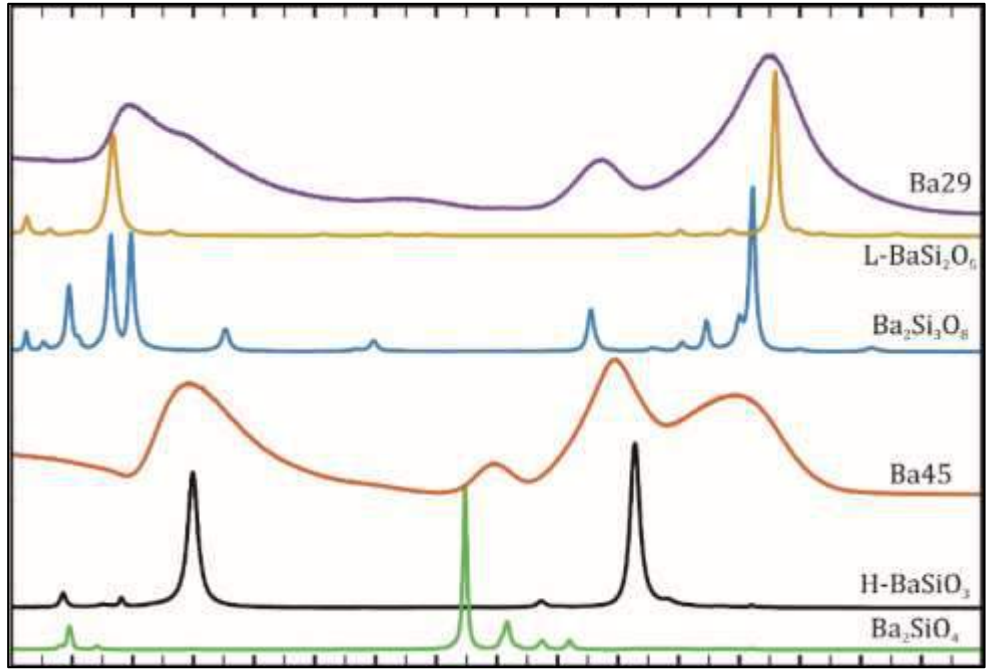
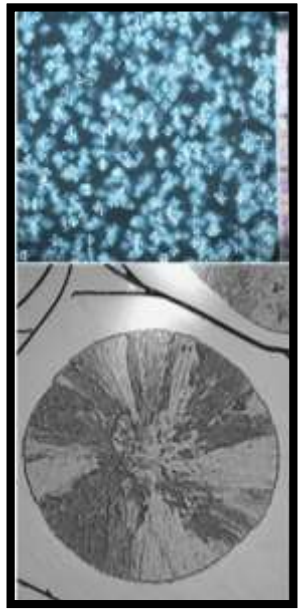
SILICATE GLASSES & GLASS-CERAMICS INVESTIGATIONS BY RAMAN SPECTROSCOPY

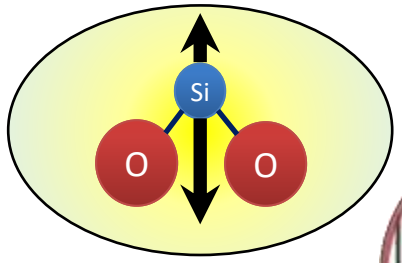


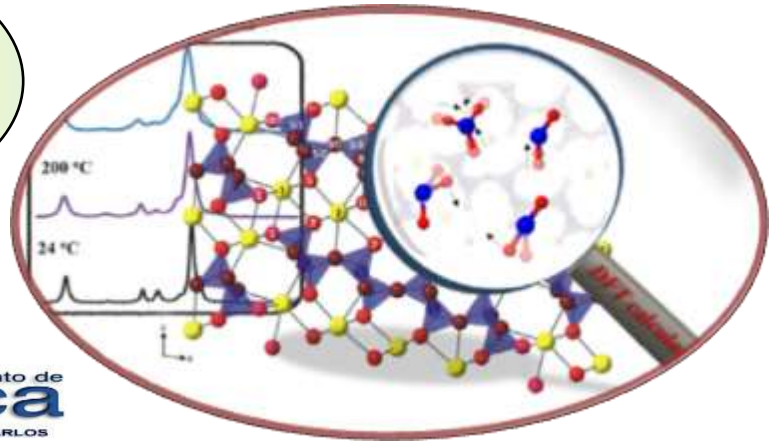


Sir C.V. Raman & K.S. Krishnan discovered the Raman effect in 1928







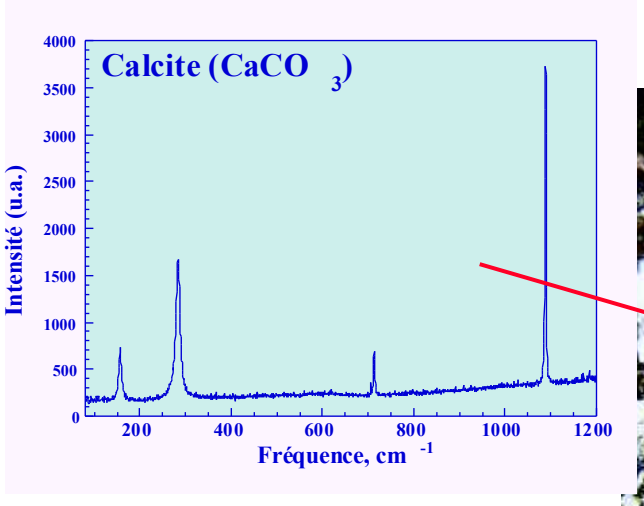


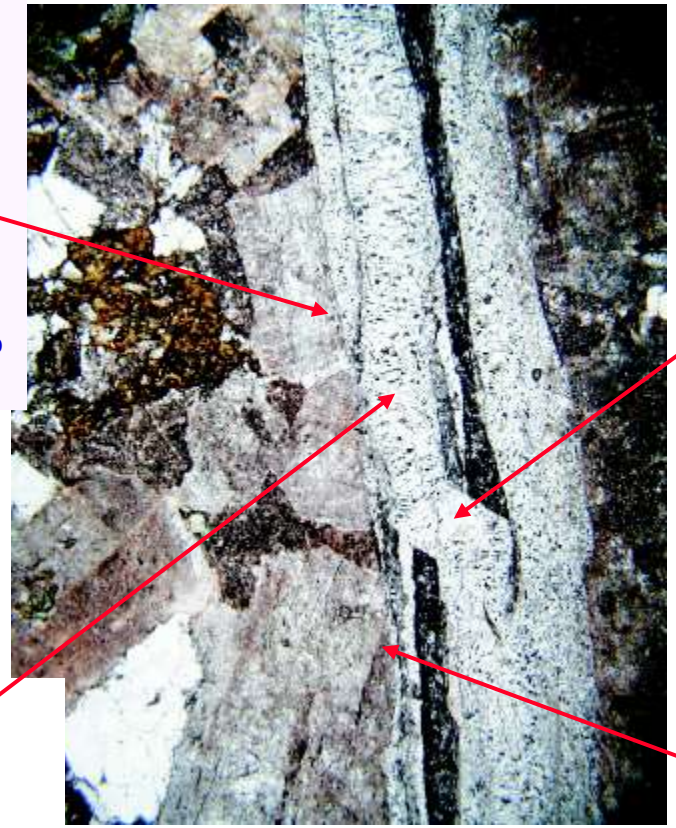
Departamento de Física
UNIVERSIDADE FEDERAL DE SÃO CARLOS

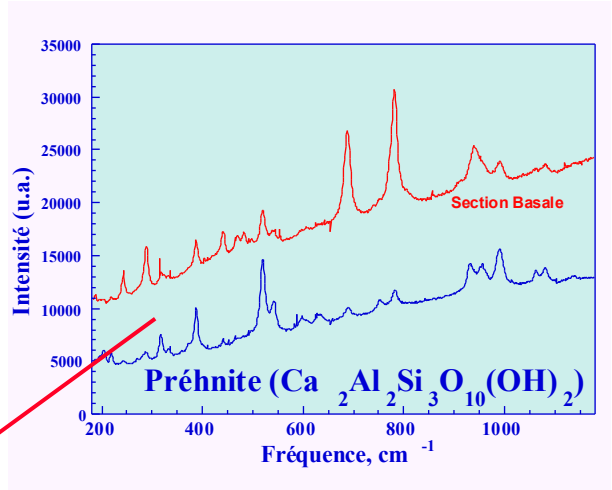
Benjamin J A Moulton, Raman Spectroscopy Webinar Dec. 22nd, 2020 from UFSCar, São Carlos, Brazil

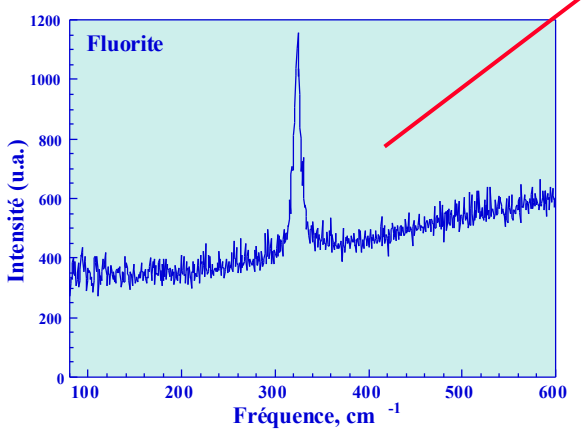
Polymineralic Ceramic or Granite

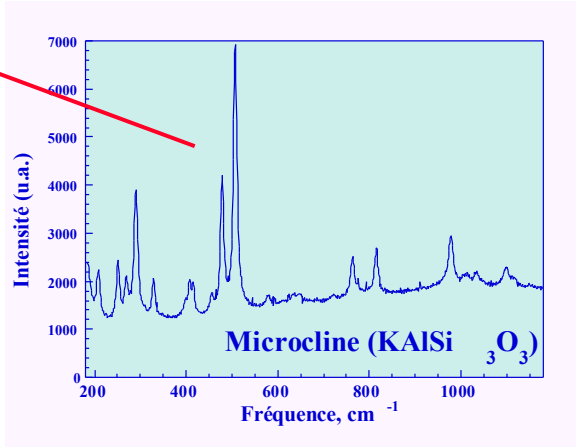
"Fingerprinting"



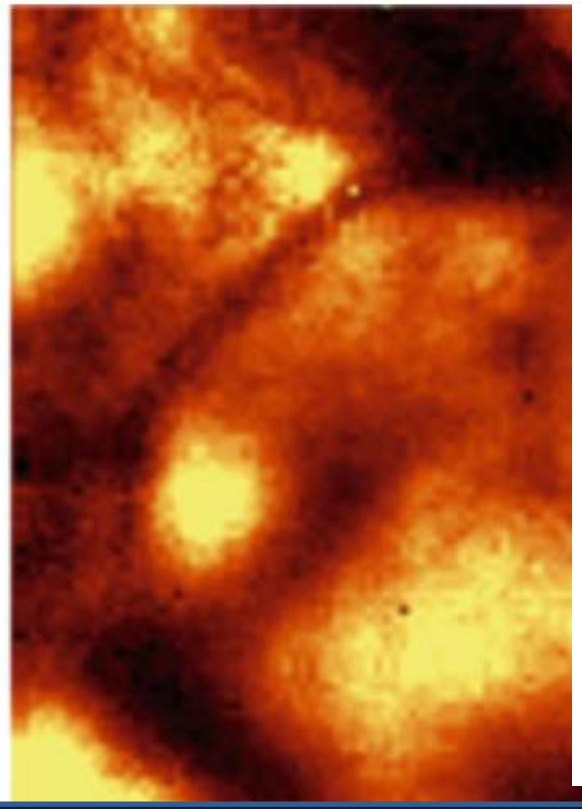


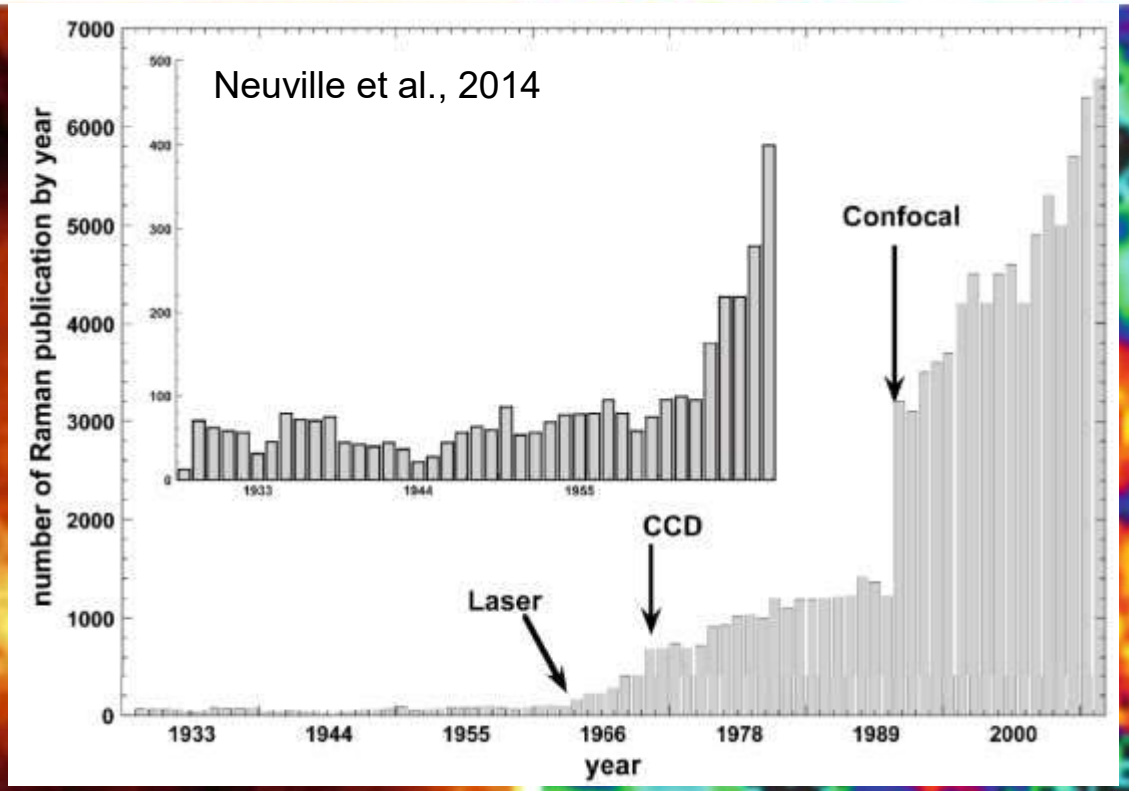


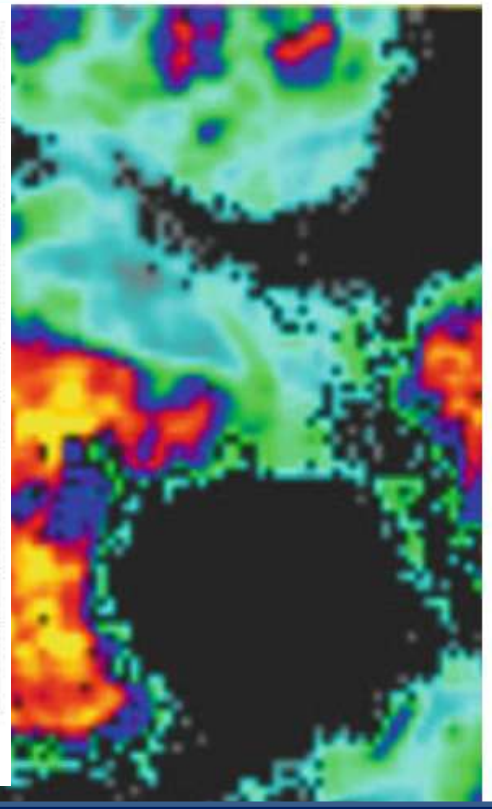




Phase identification in ceramics







No other technique can give you as much information as quickly & easily!
Use of Raman in research in every industry is increasing exponentially!
But what is it & how is it used for glass/ceramic science?

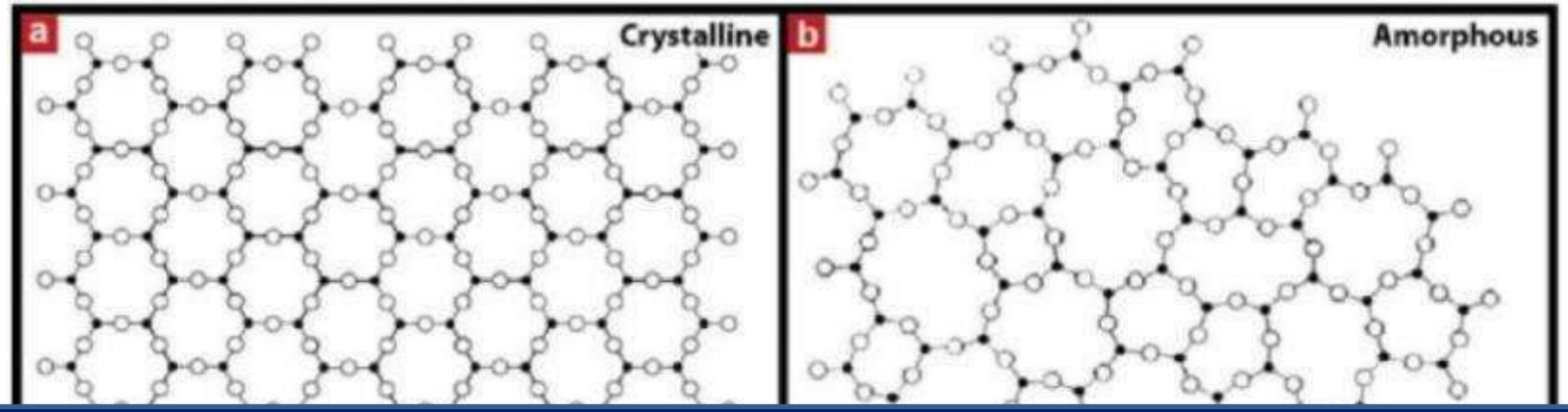
Fries & Steele, 2010 Chapter 6: Raman spectroscopy and confocal Raman imaging in mineralogy & petrography.

Overview for today:

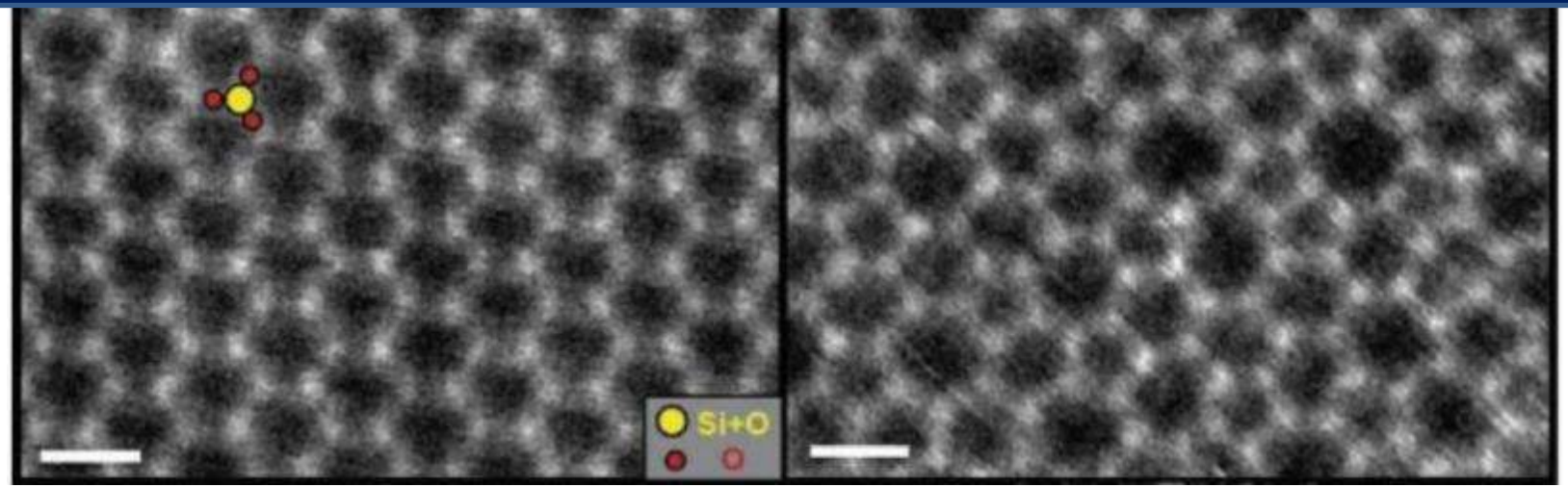
1. Glass versus Crystal structure
2. What is Raman scattering?
3. Glass spectra and how we quantify them?
4. Exemplar studies

Structure: Crystal vs. Glass

6-membered ring structures **Amorphous SiO_2 network**



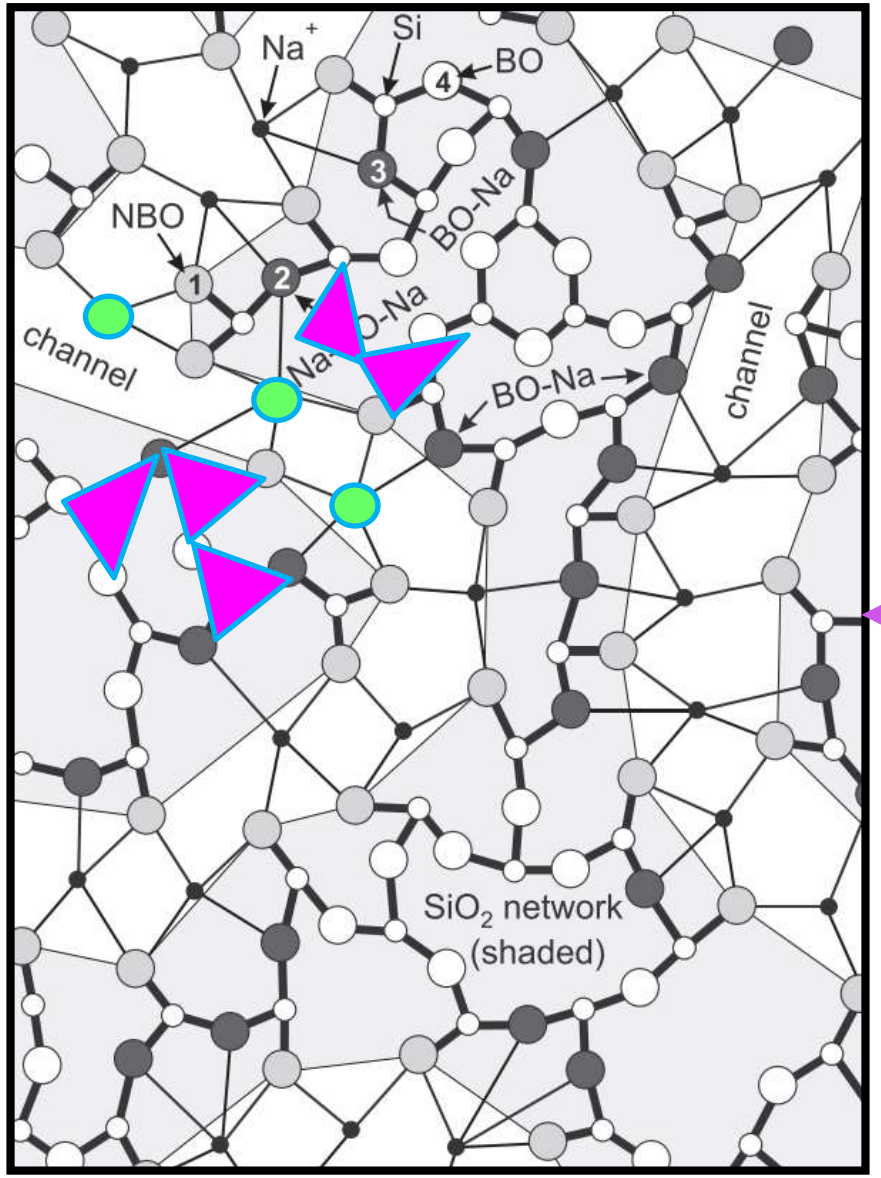
The structural difference between crystal and glass (liquid) is in the long range order; translational symmetry is broken.



Huang et al., 2012 Nanoletters 12:1081-1086

TEM Images of SiO_2 film

Modified Random Network Model (Greaves, 1985)

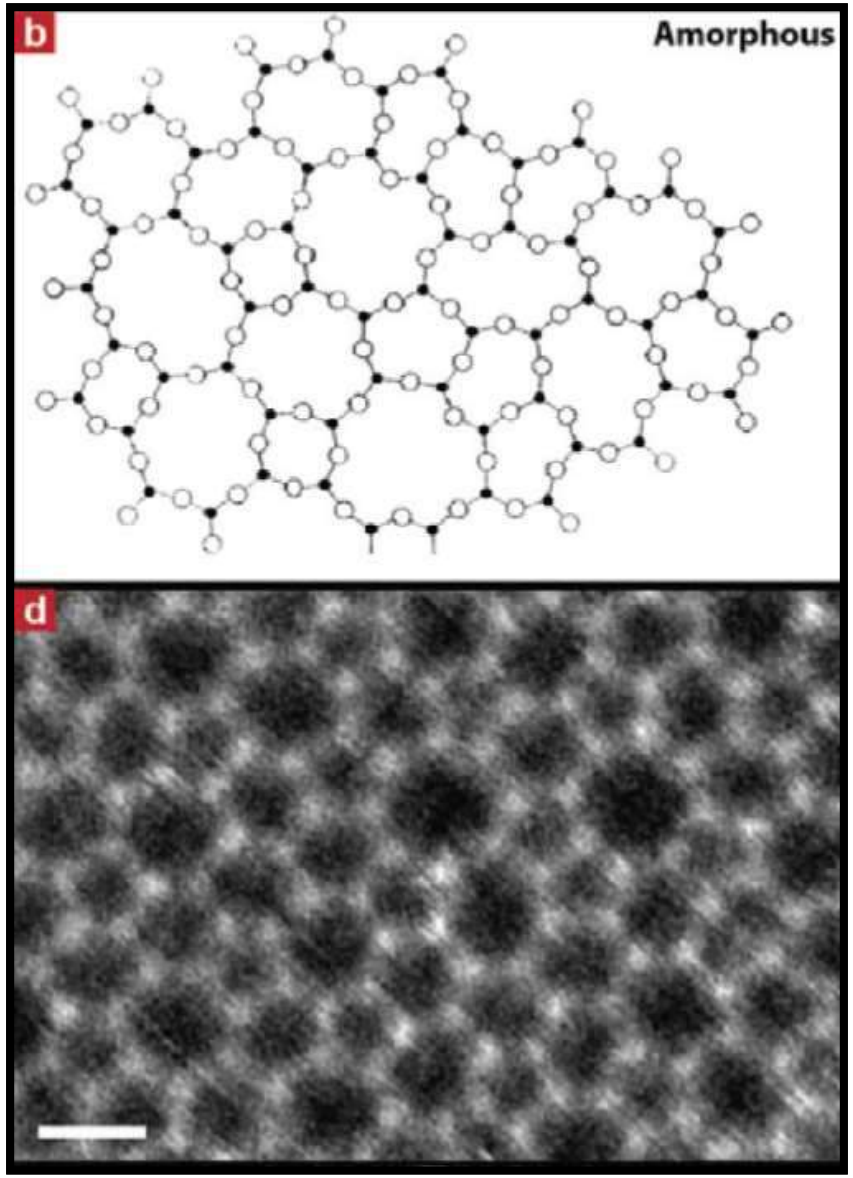


Nesbitt et al., 2015, JNCS, 409:139

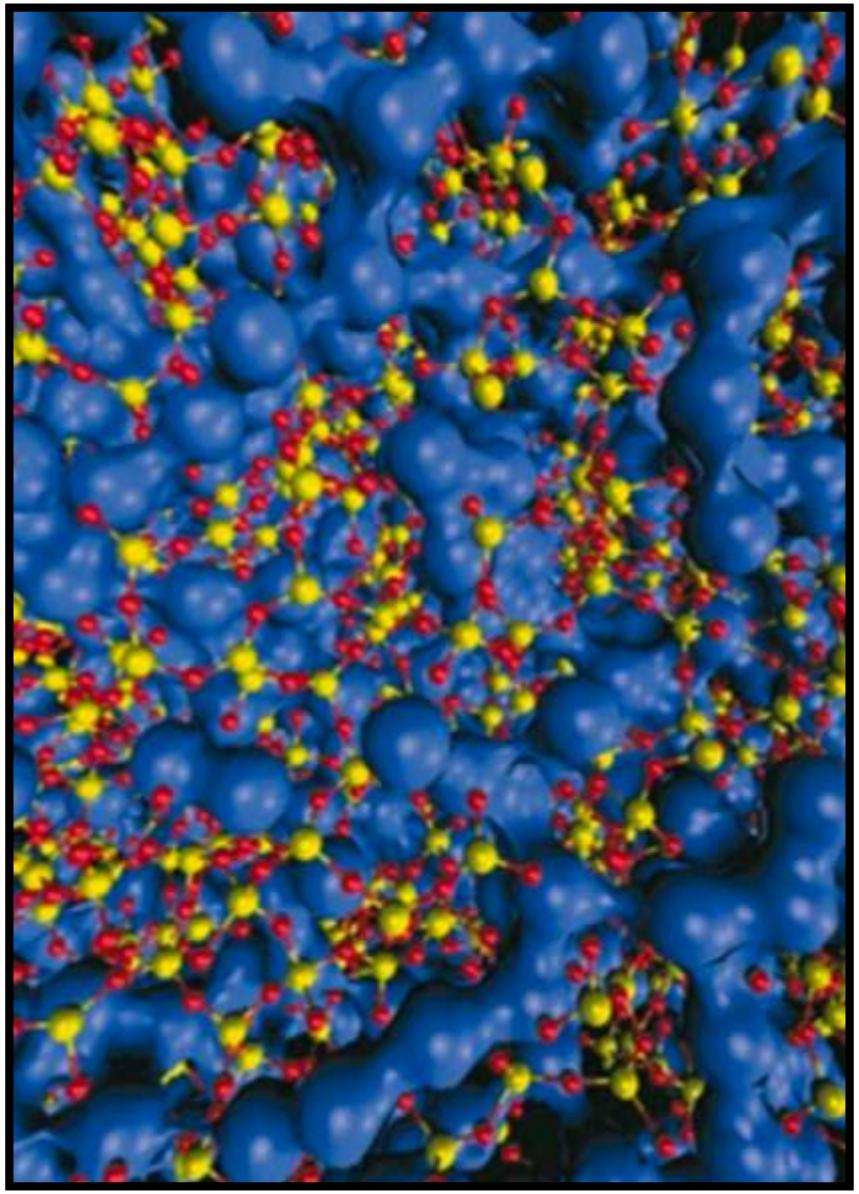
$xSiO_2 + (1-x)MO$

$M = Na_2, Li_2, Ca, K_2, Ba$, etc..

Continuous Random Network (Zachariasen, 1932)



Modified Random Network Model



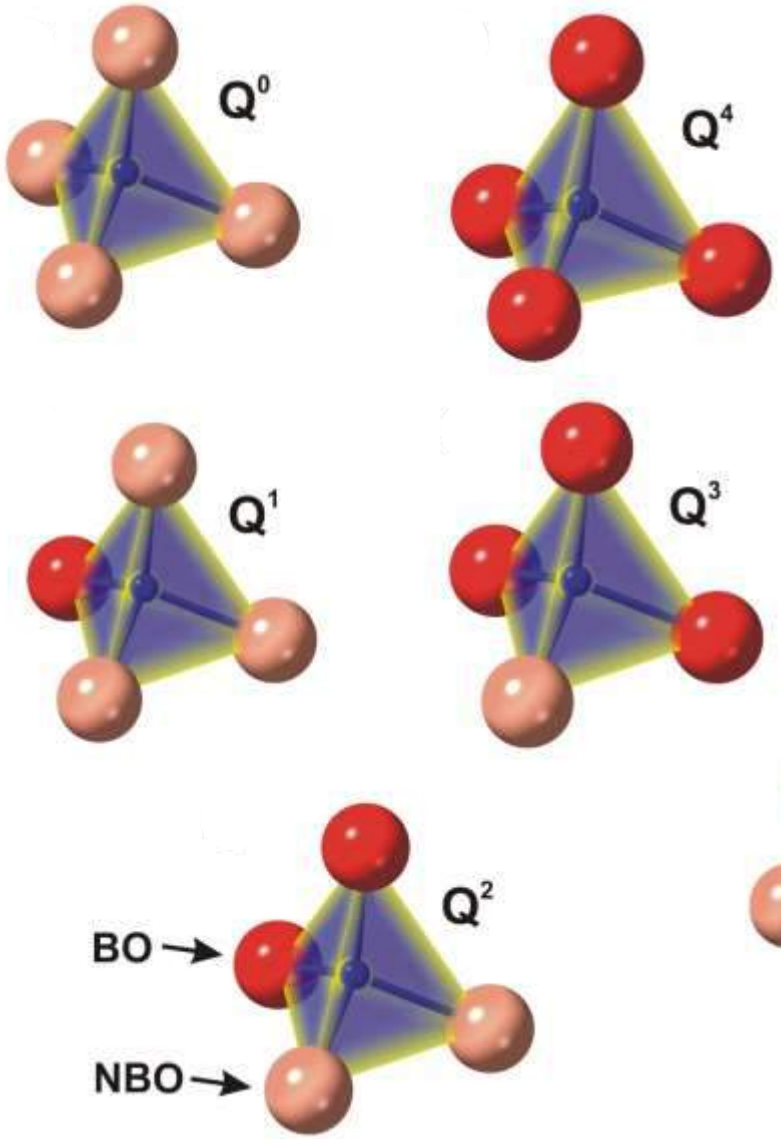
Meyer et al., 2004 Phys Rev B 93, 027801

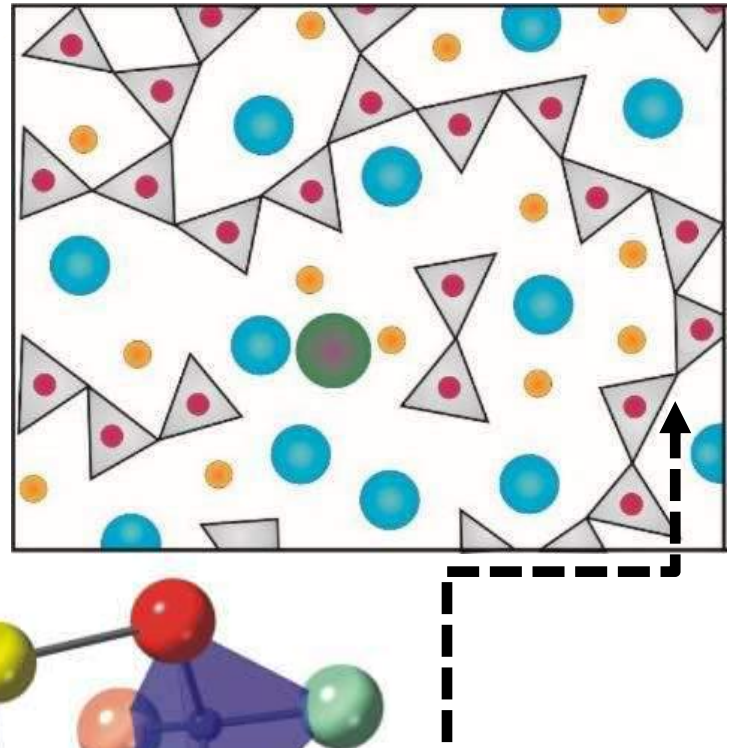
Network Formers – cations (CN=4) which have strong (covalent) bonds with oxygen (e.g. Si, B, P, Ge, Al, Ti) → high field strength

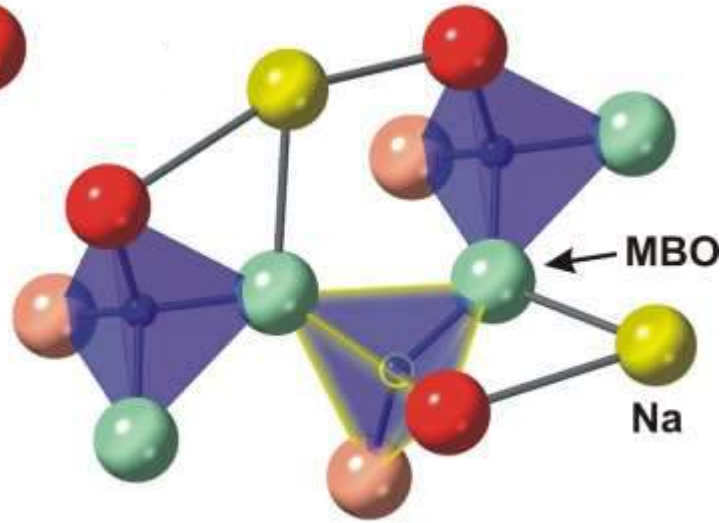
Network Modifiers – cations (CN=5-8+) which have weak (ionic) bonds with the oxygen (e.g. Na, K, Ca, Ba, Sr, Rb, etc.)

Oxygen "glues" the tetrahedral (formers) and modifier networks together.

Tetrahedron Connectivity: Q^n species (n = # of BO)





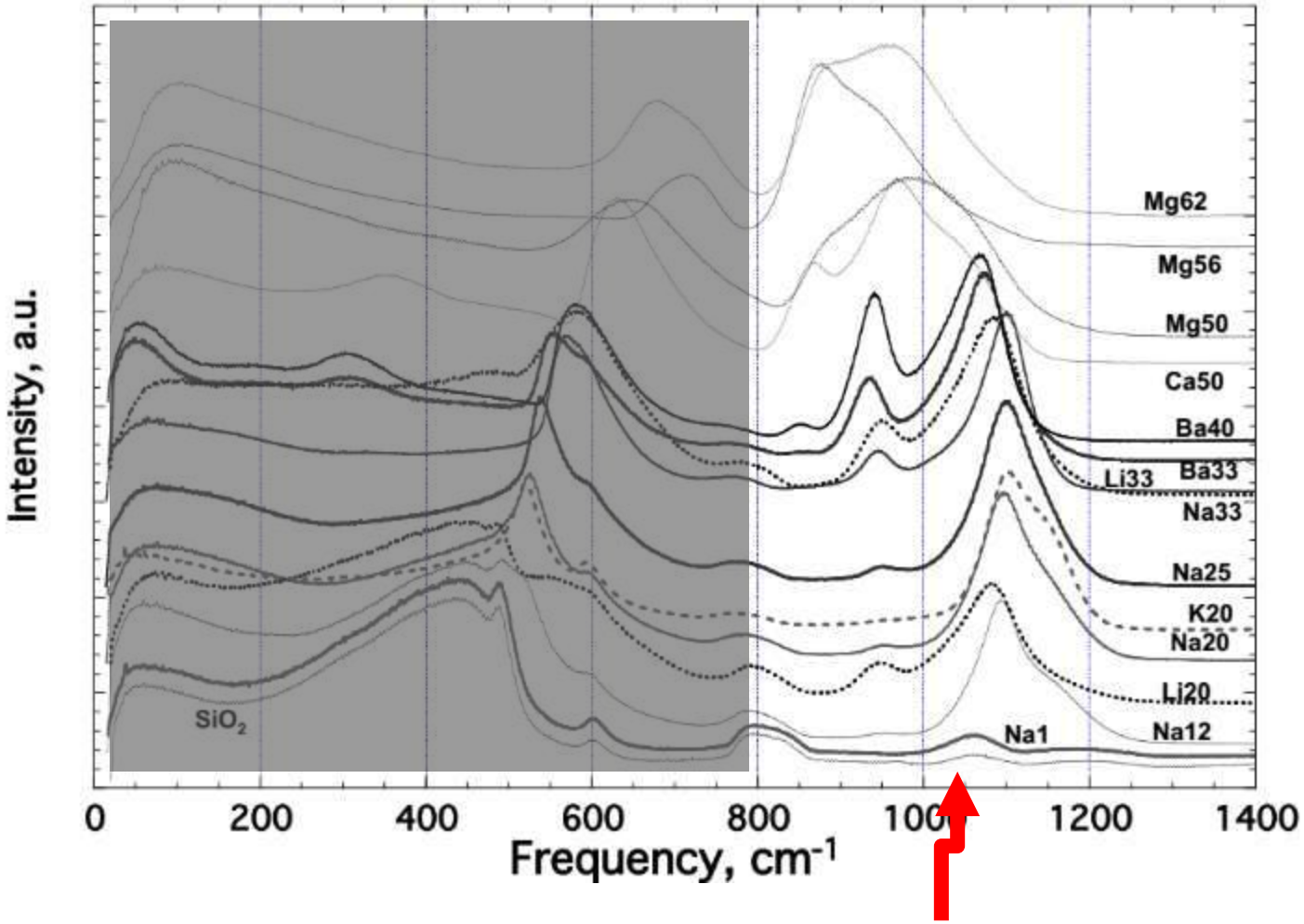


Q^n species:
n = # of bridge oxygen (BO) per tetrahedron (Q)

Moulton & Henderson, 2021

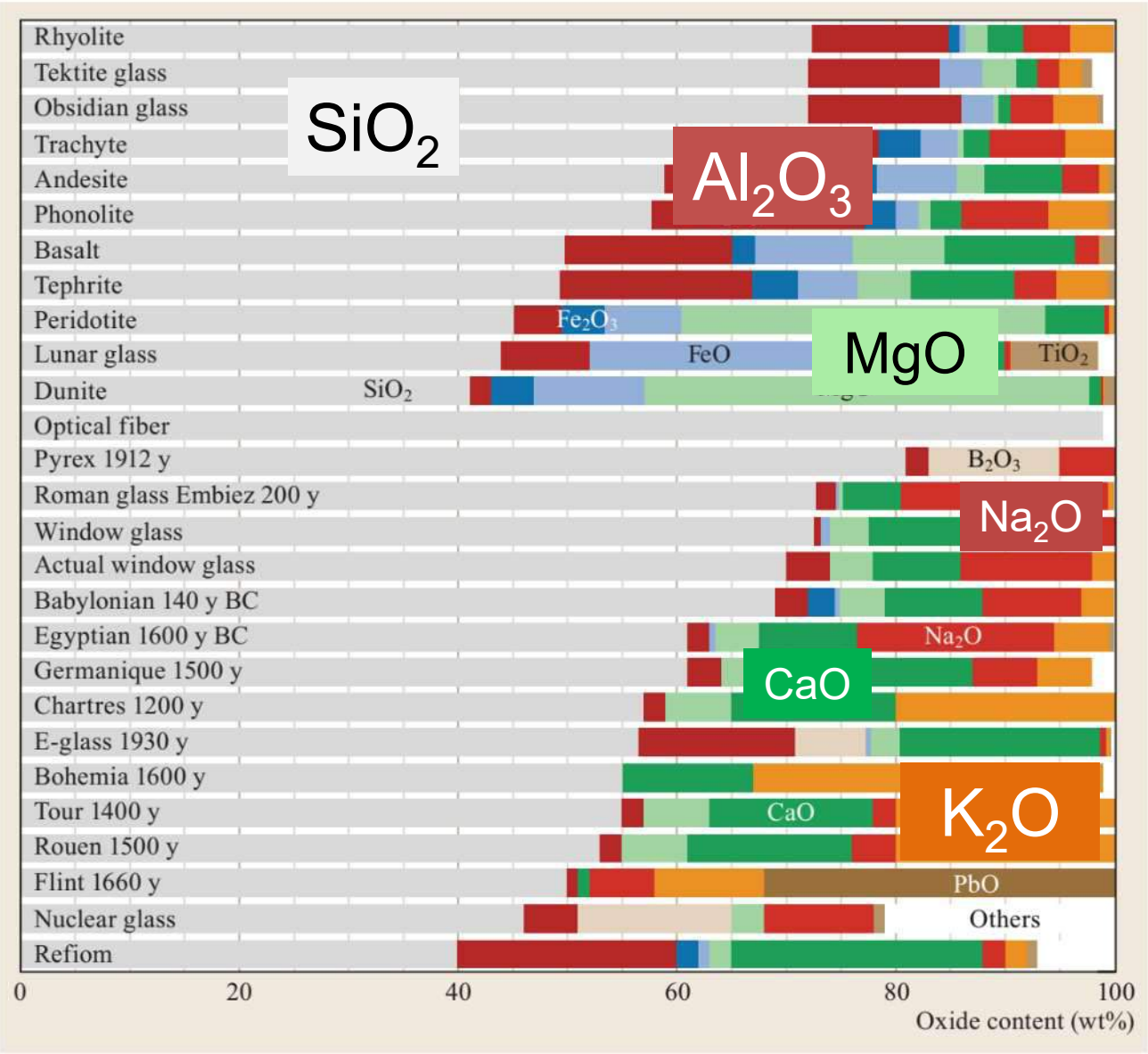
Alkali- & Alkaline earth-silicate glasses

Neuville et al., 2014: RiMG Vol. 78:509-541



Raman peaks originate from the Q^n species.

Glass compositions: Why are binaries important?



← Natural & synthetic glasses

Glasses are frozen liquids which have solid-like properties.

Why binary SiO_2-MO (or M_2O) systems? (M = Na, Ca, Fe, etc.)

- Most glasses contain 3-4 components which constitute the bulk chemistry
- **SiO_2 ± Al_2O_3 ± CaO ± MgO ± K_2O ± Na_2O ± FeO** are major elements in most silicate glasses.

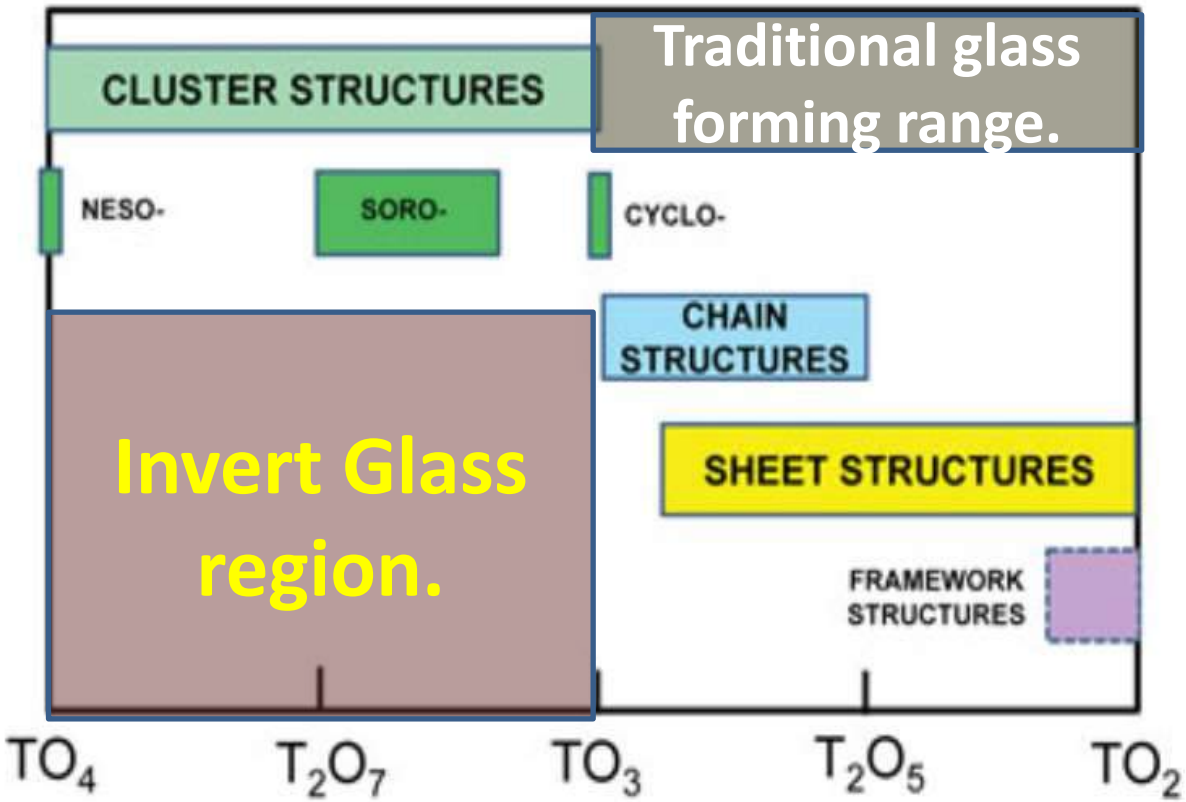
LeLosq, Cicconi, Greaves, Neuville (2019) Ch 13: Silicate glasses. Springer Handbook of Glass. https://doi.org/10.1007/978-3-319-93728-1_13

Terminology: Equivalent terms

Hawthorne, Uvarova, Sokolova (2019)
Min Mag. 83:3-55. doi:10.1180/mgm.2018.152

Mineralogy -	Generic -	Composition -	Q^n
Nesosilicate	= Orthosilicate	= SiO_4	= Q^0
Sorosilicate	= Pyrosilicate	= Si_2O_7	= Q^1
Cyclosilicates	= Ring silicates	= SiO_3	= Q^2
Inosilicates	= Metasilicate	= SiO_3	= Q^2
Phyllosilicates	= Disilicate	= Si_2O_5	= Q^3
Tectosilicates	= Framework	= SiO_2	= Q^4

A structural hierarchy for silicate minerals.



Q^n :	Q^0	Q^1	Q^2	Q^3	Q^4
%SiO_2:	33	~40	50-60	55-100	>80

The fundamental difference #2 between crystals and liquid/glass structure is that silicate liquids always contain a distribution of 2-4 Q^n units whereas most crystals contain only 1 type of Q^n.

Break #1: Any questions about glass structure?

Before we turn to Raman spectroscopy…

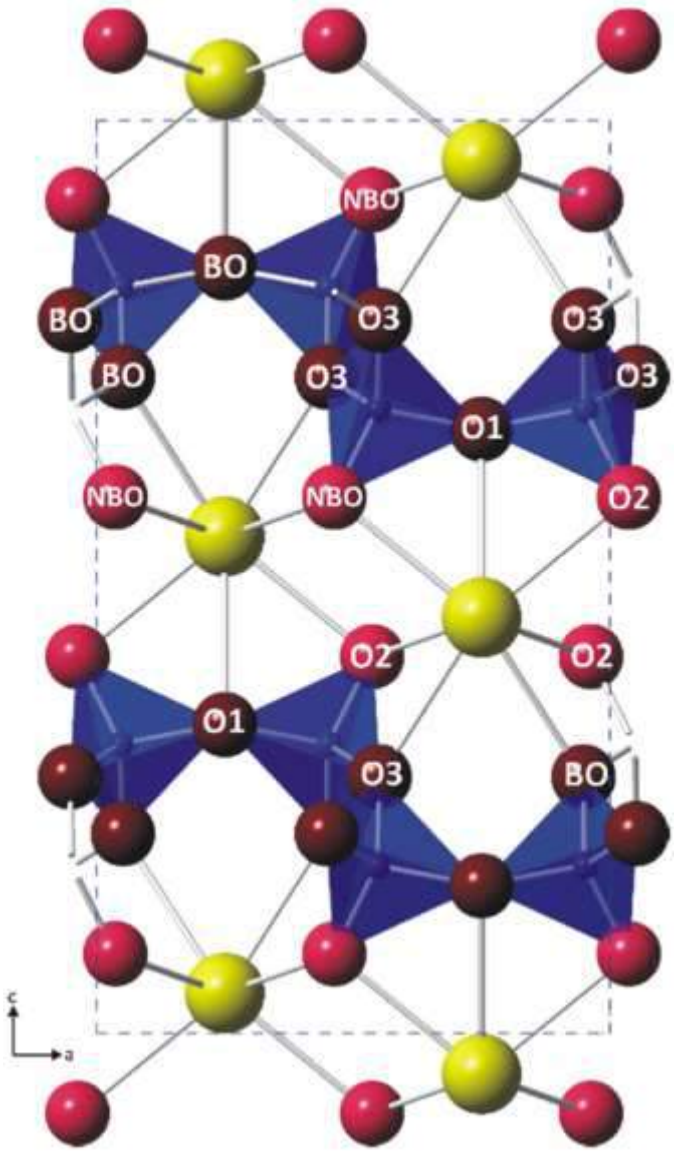
Recommended article:

GS Henderson. **2005**. Canadian Mineralogist, Vol. 43, pg. 1921-1958

The Structure of Silicate Melts: A Glass Perspective.

Vibrational normal modes in crystalline materials

Sanbornite, low-$BaSi_2O_5$



See Diem 2015 Modern Vibrational Spectroscopy for more details.

$$\Gamma_{\text{vib}} = \Gamma_{3n} - \Gamma_{\text{trans}} - \Gamma_{\text{rot}}$$

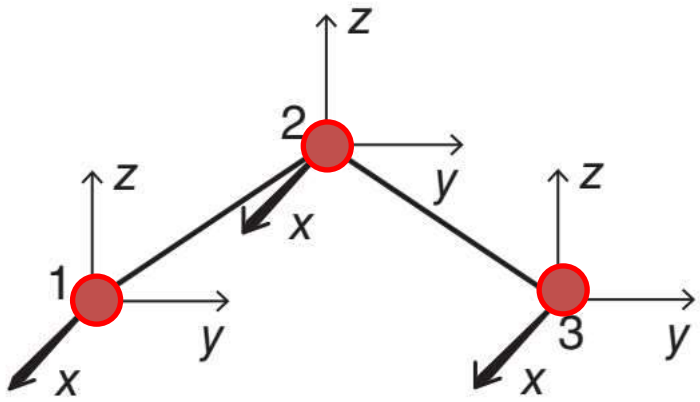
3n-6 *vibrational degrees of freedom* (Γ_{vib}), ***n*** *is the # of atoms / unit cell*

→ vibrational density of states.

Normal to axis, 'Q' = X, Y, or Z.

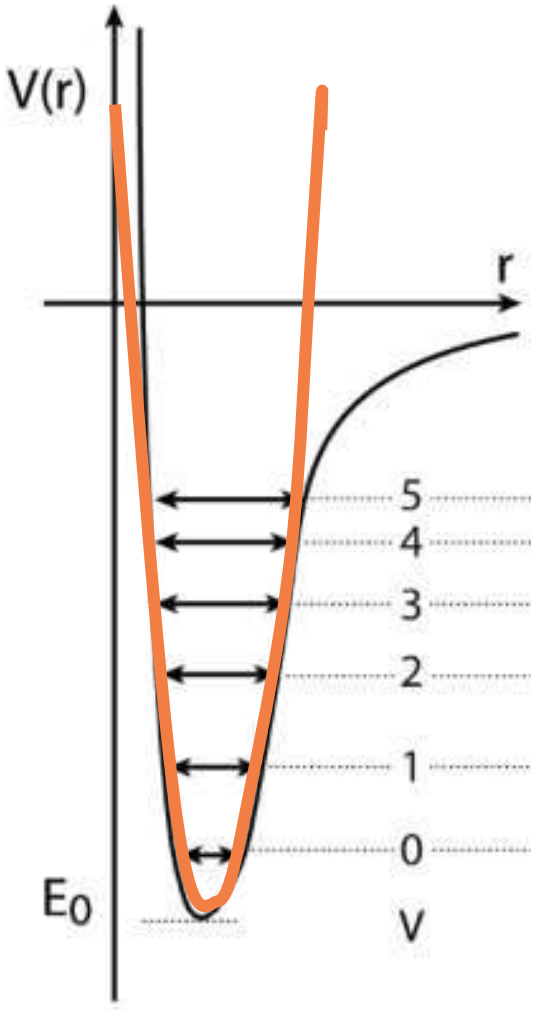
e.g. $BaSi_2O_5$ (sanbornite, Z=4),
32 atoms / unit cell.

3*32-6 = **90 normal modes**



Gomes, **Moulton**, et al. (2021) Spectrochim Acta Part A. 248:119130. https://doi.org/10.1016/j.saa.2020.119130

Vibrational frequency, ν



The **harmonic approximation** treats the Morse curve as a simple parabola which represents a A-X molecule connected by a spring (*bond*).

Hooke's Law

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

K – is the force constant

μ – is the reduced mass

$$\mu = \frac{M_A M_B}{M_A + M_B}$$

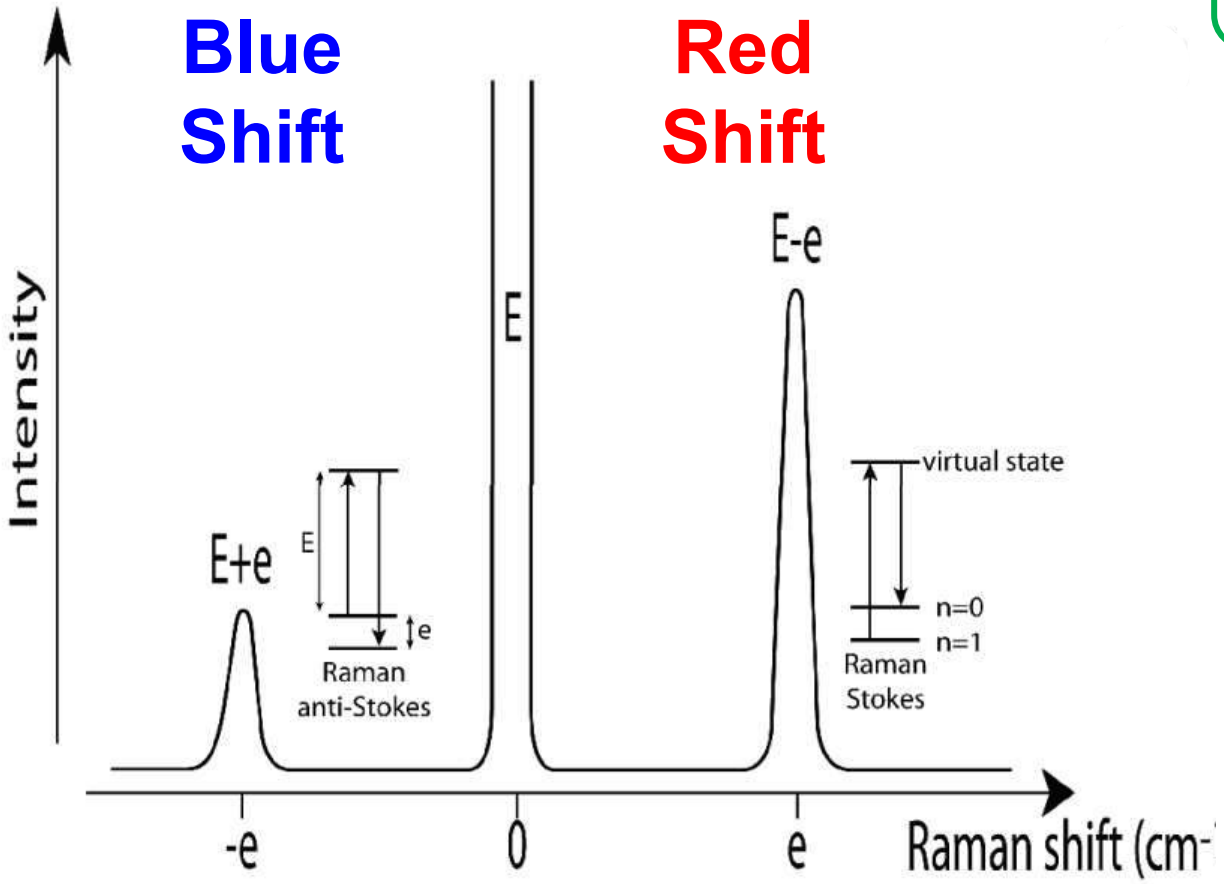
Vibrational modes are described as phonons.

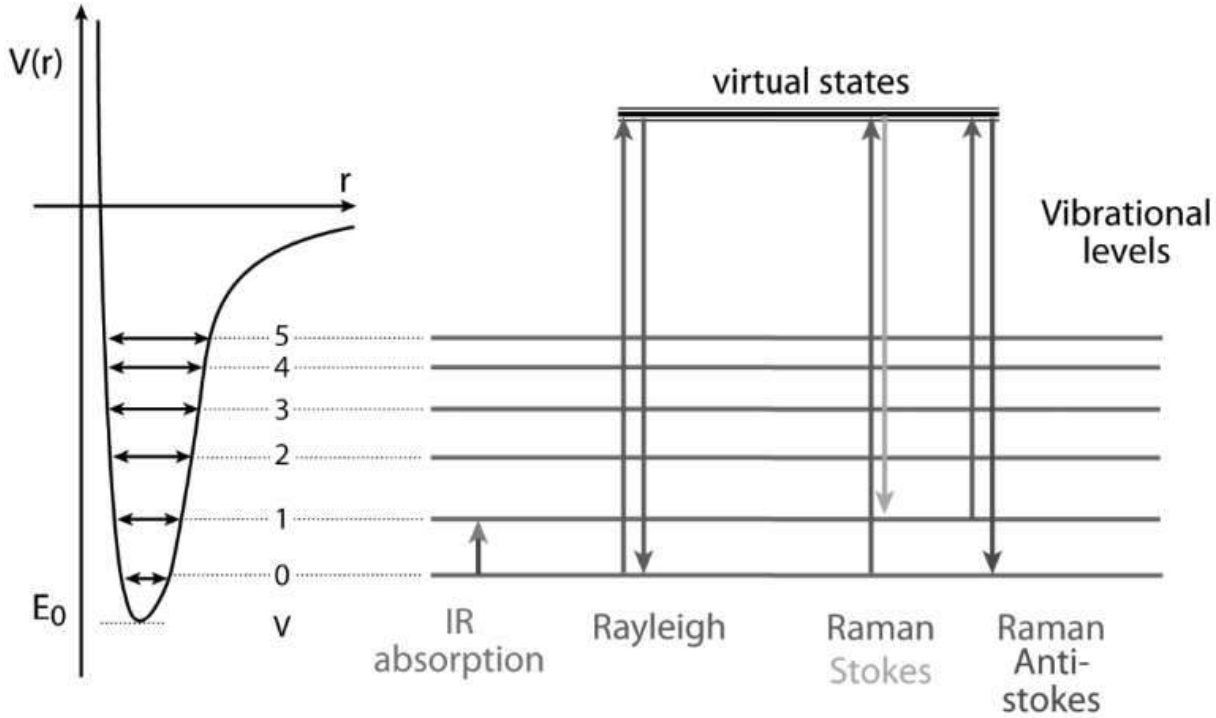
Rayleigh versus Raman scattering (Stokes + Anti-Stokes)

$$\mu_{induced} = \underbrace{\alpha_0 E_0 \cos \omega t}_{\text{Rayleigh}} + \frac{1}{2}\frac{\partial \alpha}{\partial Q} Q_0 E_0 [\underbrace{\cos(\omega - \omega_0)t}_{\text{Stokes}} + \underbrace{cos(\omega + \omega_0)t}_{\text{Anti-Stokes}}]$$

$$\boxed{\frac{\partial \alpha}{\partial Q} \neq 0}$$

Raman scattering



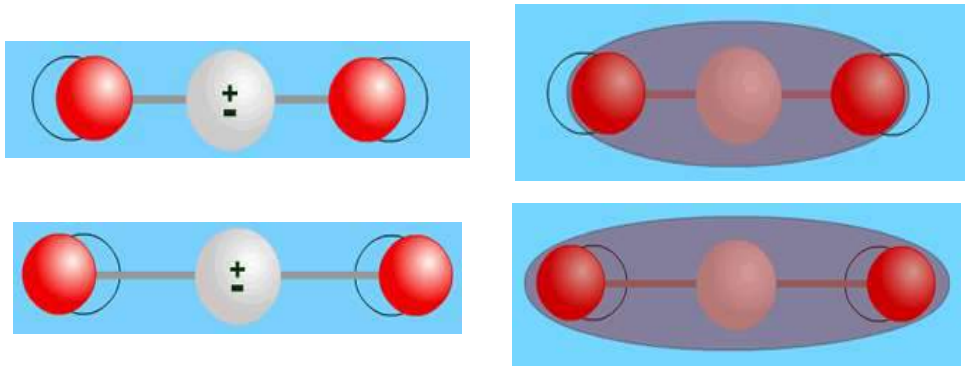


Neuville et al., 2014: RiMG Vol. 78:509-541

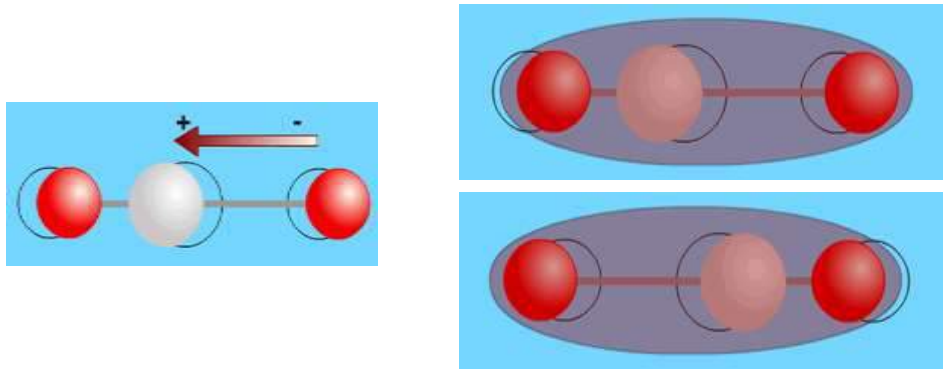
Raman selection rule: e.g. 2 modes of CO_2

www.chemgapedia.de/vsengine/vlu/vsc/de/ch/3/anc/ir_spek/methoden.vlu.html

$\nu_1 = 1354\ cm^{-1}$



$\nu_3 = 2396\ cm^{-1}$



$$\frac{\partial \alpha}{\partial Q} \neq 0$$

+ and - center of charge remain the same despite stretching

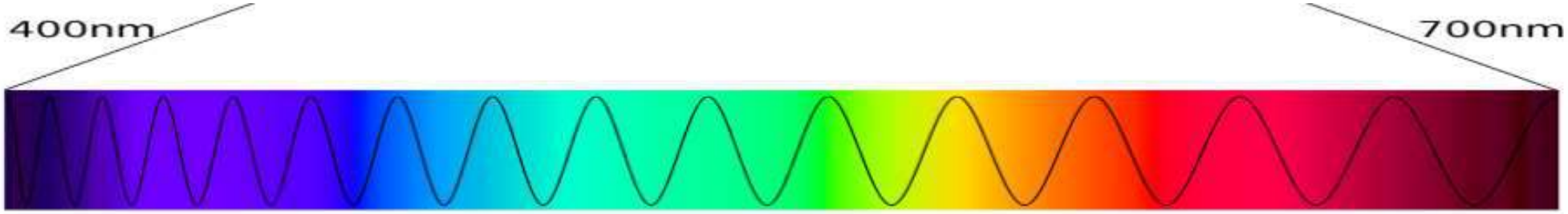
symmetric stretching
constant dipole

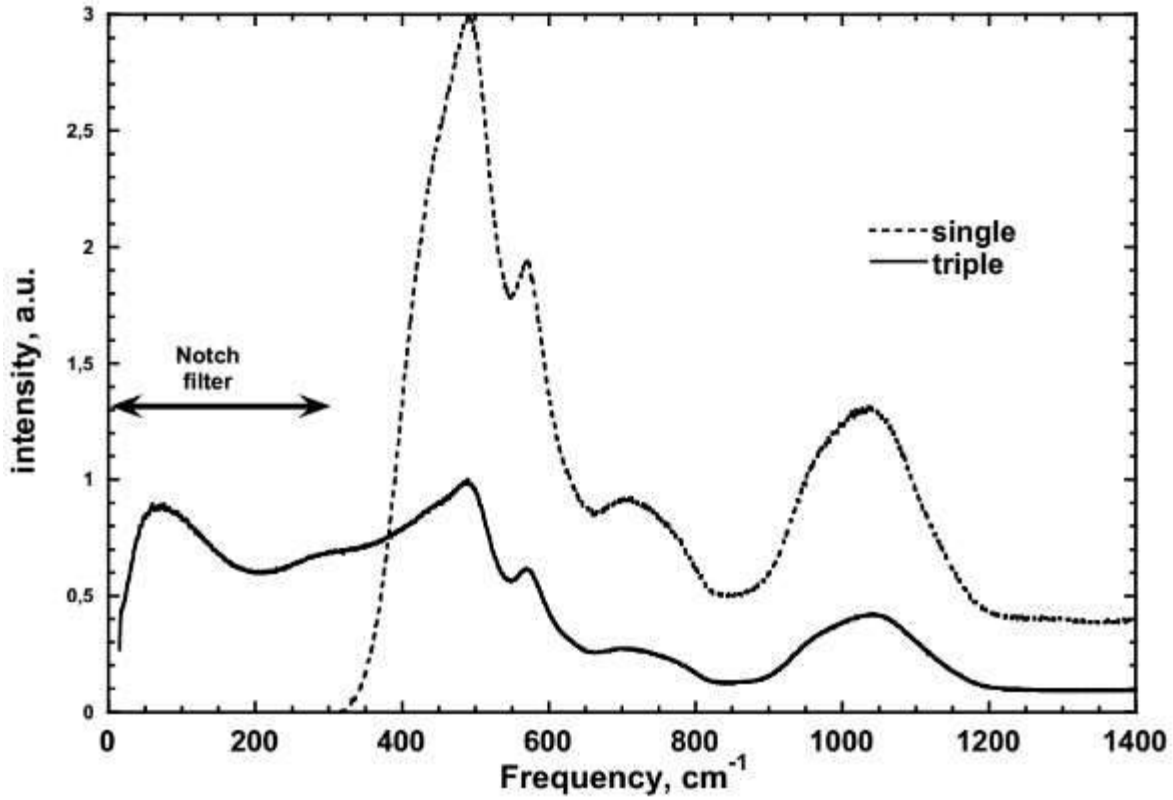
Raman active
IR inactive

- and + center of charge change within vibration

asymmetric stretching
change of dipole

Raman inactive
IR active





For a 532 nm laser

$$\Delta\nu = (1/\lambda_0 - 1/\lambda_{vibration})$$

$$\Delta\nu = 1000\ cm^{-1}$$

wavelength: **532 nm – 562 nm**

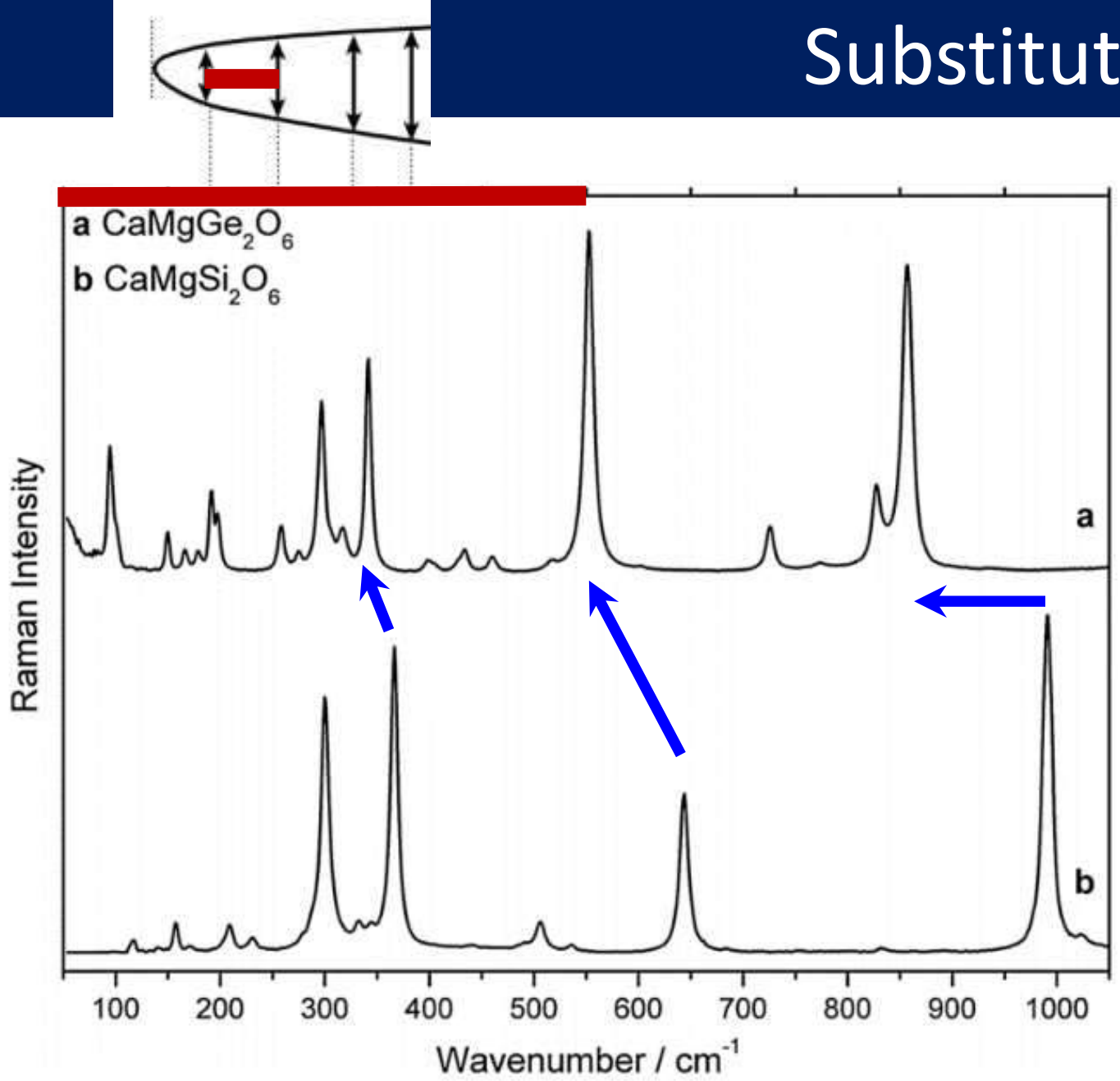
Frequency = Wavenumbers = Raman shift

Absolute **Relative**

532 nm = 18797 cm^{-1} = 0 cm^{-1} Raman shift

Neuville et al., 2014: RiMG Vol. 78:509-541

Substitution of Ge for Si in diopside



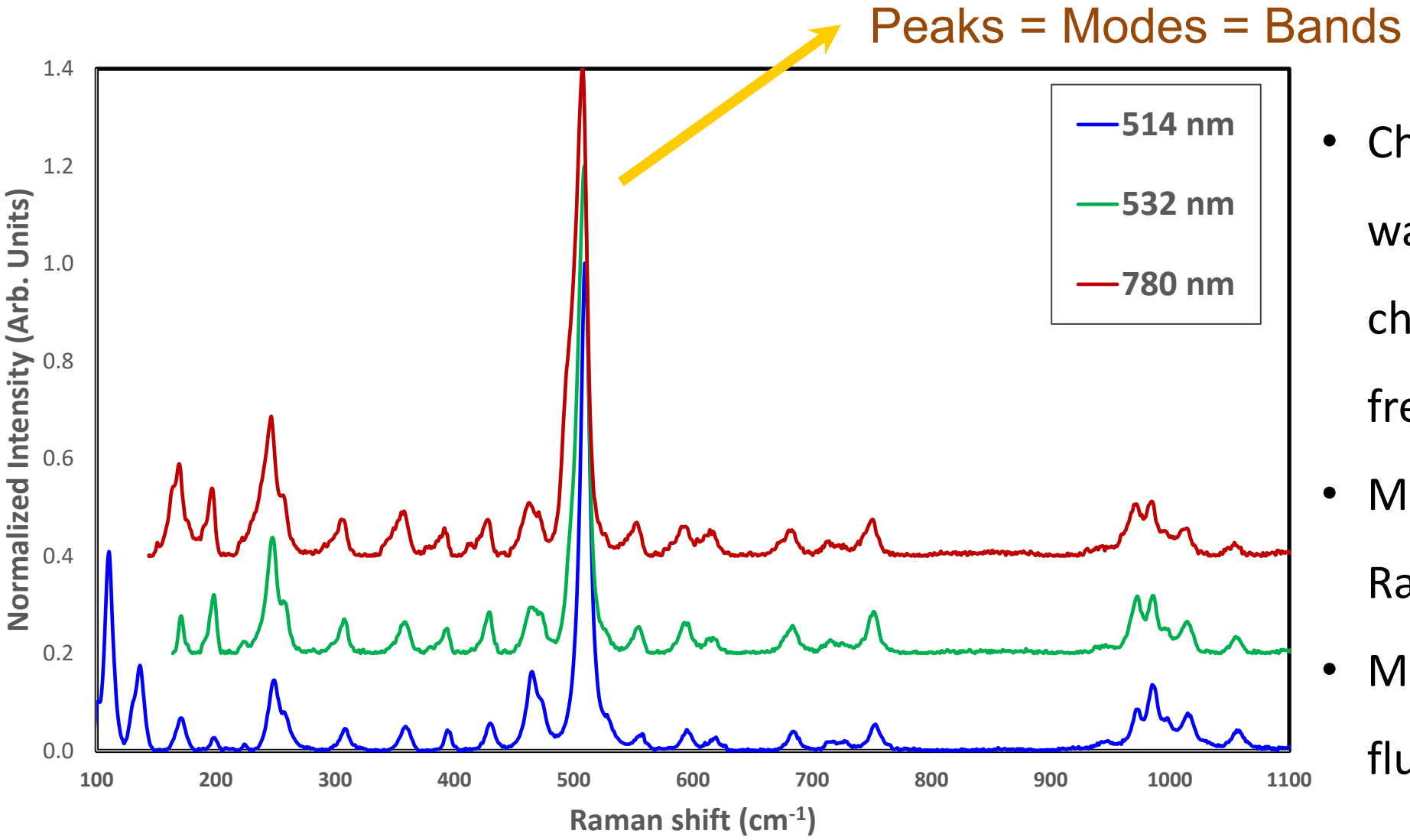
Peaks involving Si or Ge shift dramatically while those related to Ca or Mg don't shift much!

This means that analogies between **isostructural phases** can provide insightful interpretations, even when one may not know absolute vibrational identities.

To determine which vibrations are Raman active requires knowledge of the crystal / molecular symmetry & Group Theory.

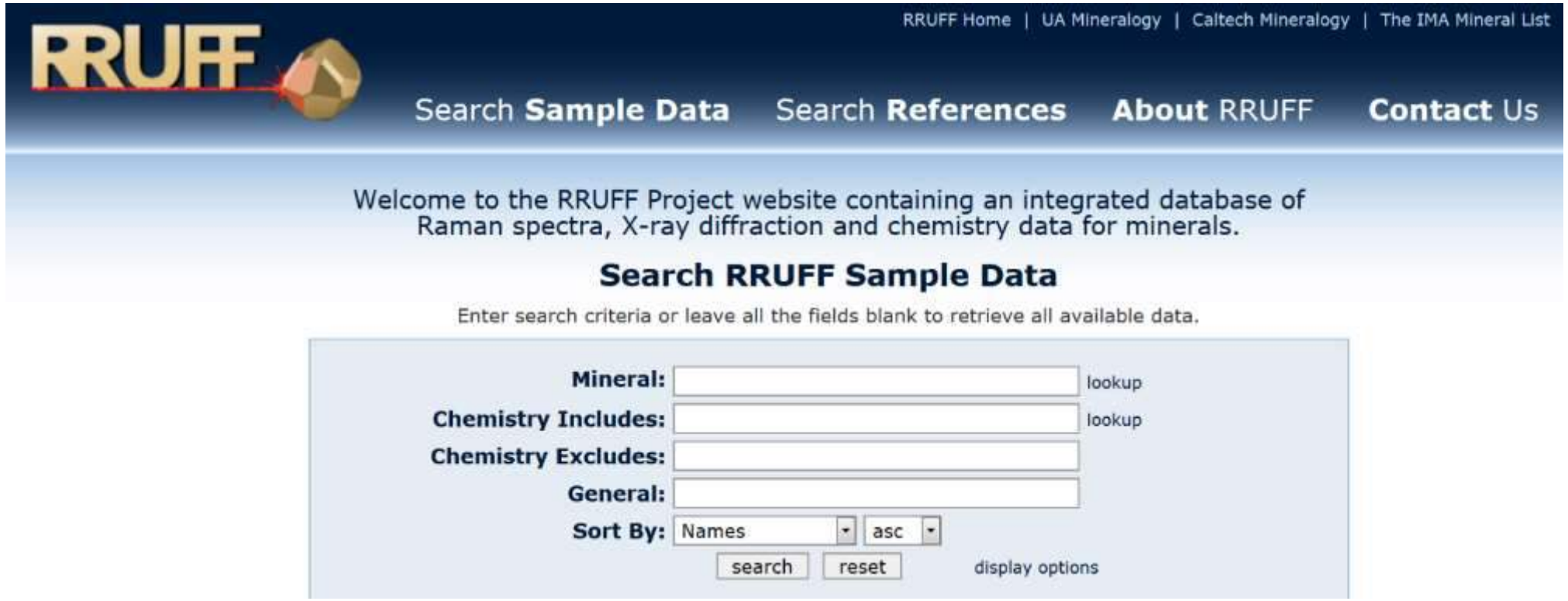
Lambruschi et al., 2015 J. Raman Spec. 46:586-590

Example of Celsian, $BaAl_2Si_2O_8$



- Changing the laser wavelength should not change the mode frequency.
- Modes that shift are not Raman modes!
- May be due to fluorescence, etc…

RRUFF™ Raman Database - rruff.info



Contains: >14 000 high resolution Raman spectra, X-ray Diffraction Spectra, Chemical Analysis for minerals. But no glass spectra…

Barbara Lafuente, R. T. Downs, H. Yang, and N. Stone

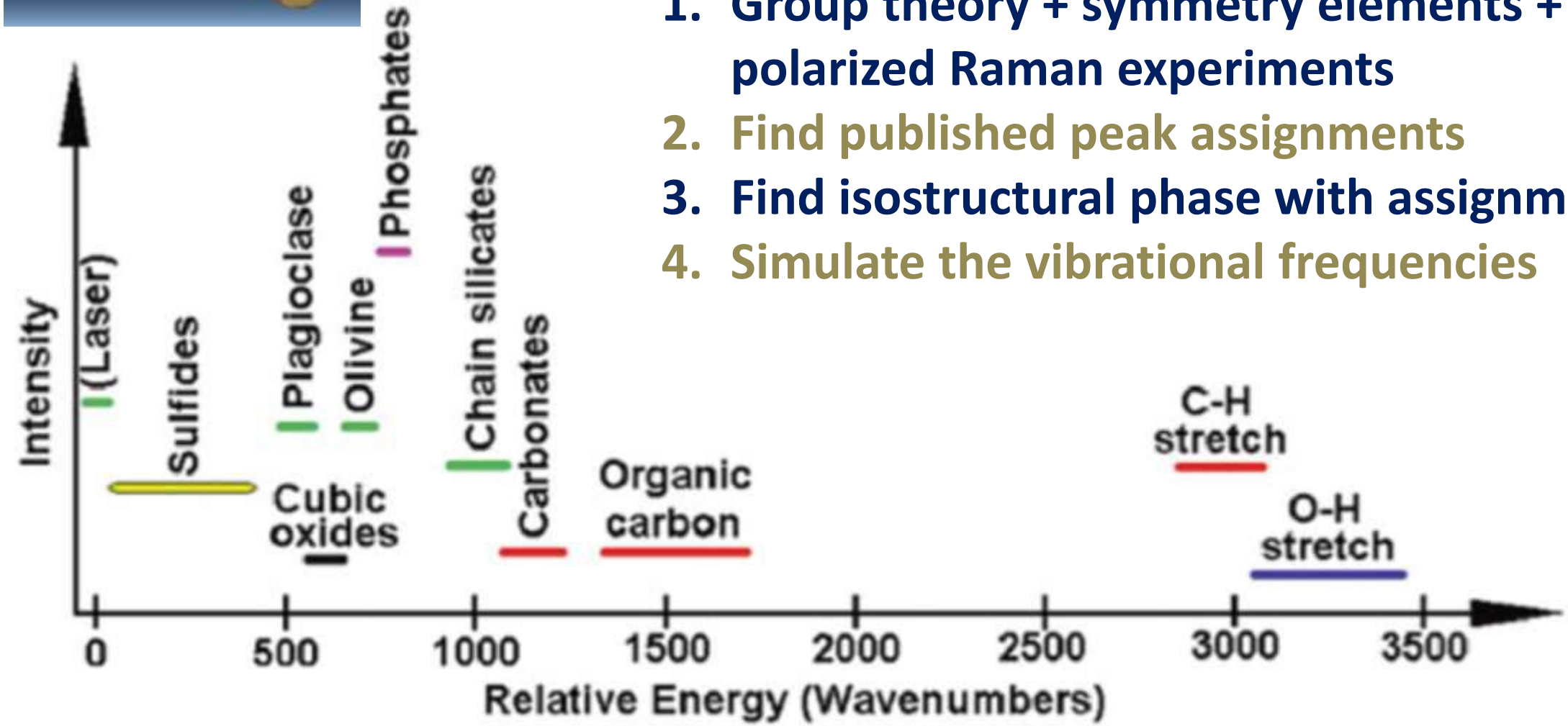
1 The power of databases: The RRUFF project

Thomas Armbruster, Rosa Micaela Danisi (Eds.) 2015
HIGHLIGHTS IN MINERALOGICAL CRYSTALLOGRAPHY by De Gruyter

How do I know the vibrations origin?

For crystals:

1. **Group theory + symmetry elements + polarized Raman experiments**
2. **Find published peak assignments**
3. **Find isostructural phase with assignments**
4. **Simulate the vibrational frequencies**



Fries & Steele, 2010

Raman Open Database

SOLSA

ROD Home

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Accessing ROD Data

Search

Add Your Data

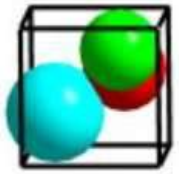
Deposit your data
Manage depositions

Raman Open Database

Open-access collection of Raman spectra used for the SOLSA H2020 project.

All data on this site have been placed in the public domain by the contributors.

Currently there are **1133** entries in the ROD.
Latest deposited structure: 1000679 on **2019-**



ICG

International Commission on Glass

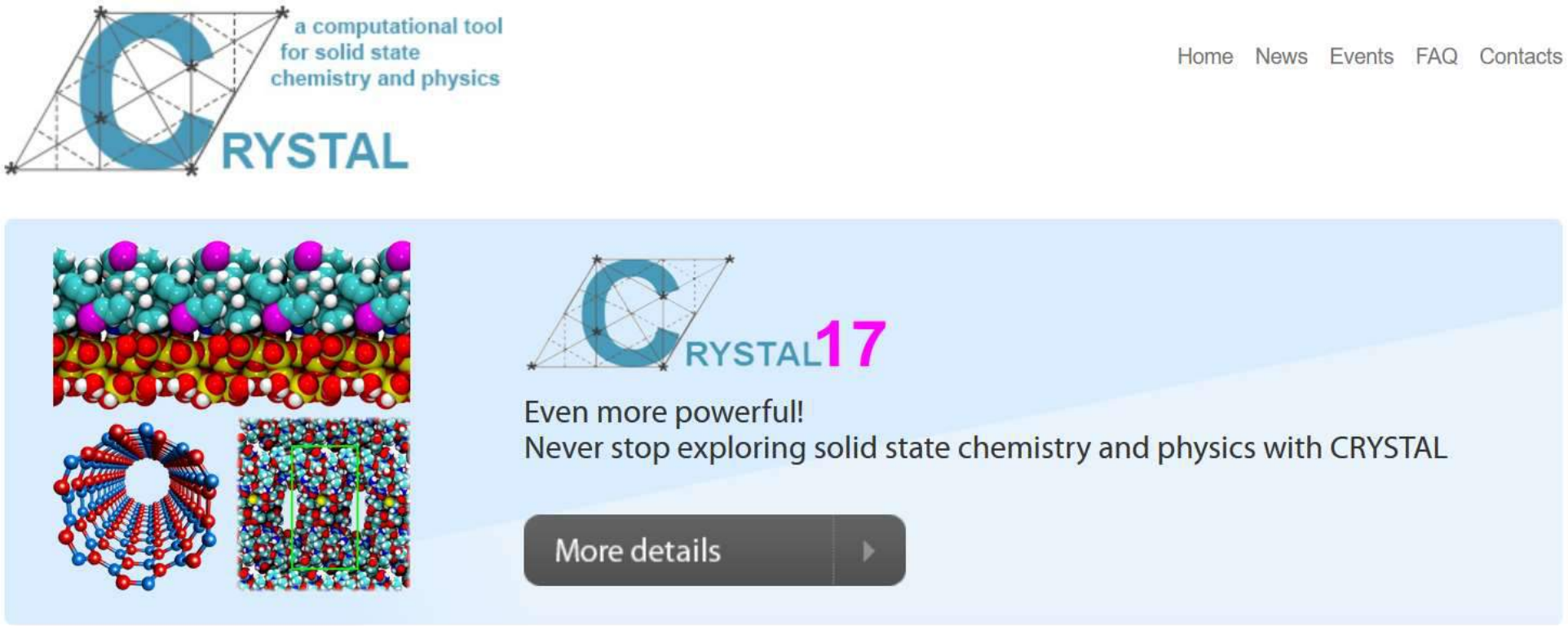
Home About Committees People

TC26: Structure & Vibrations

Currently under development by the Technical Committee 26 of the International Commission on Glass.

https://solsa.crystallography.net/rod/

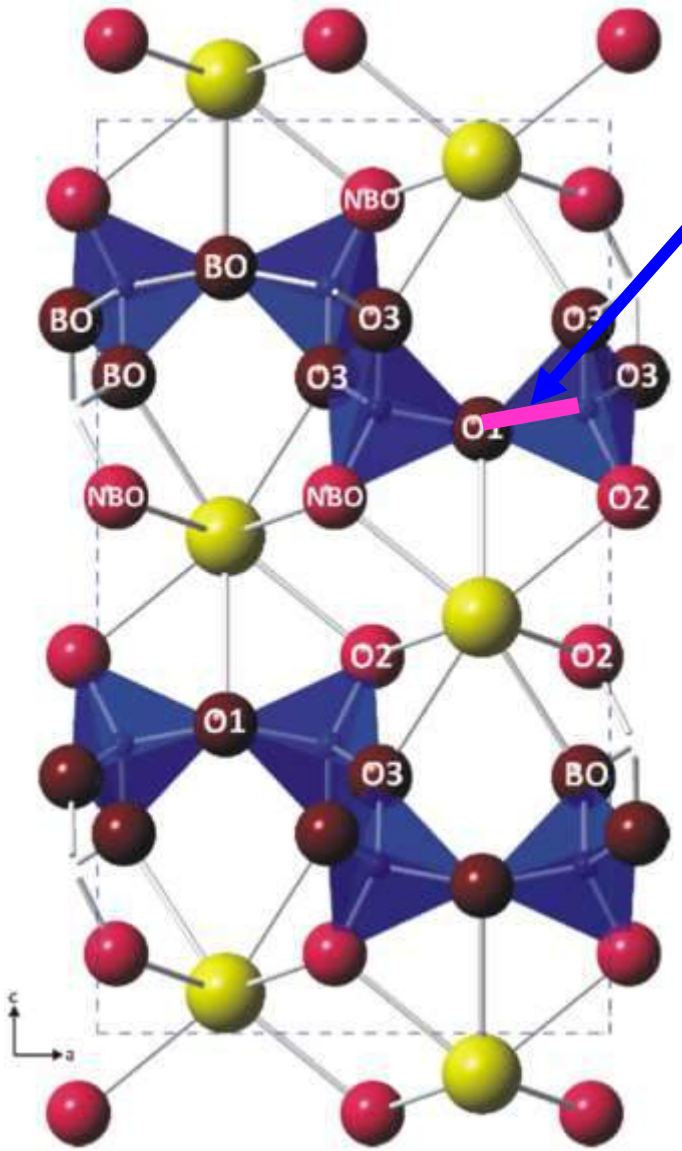
DFT simulations of vibrational modes



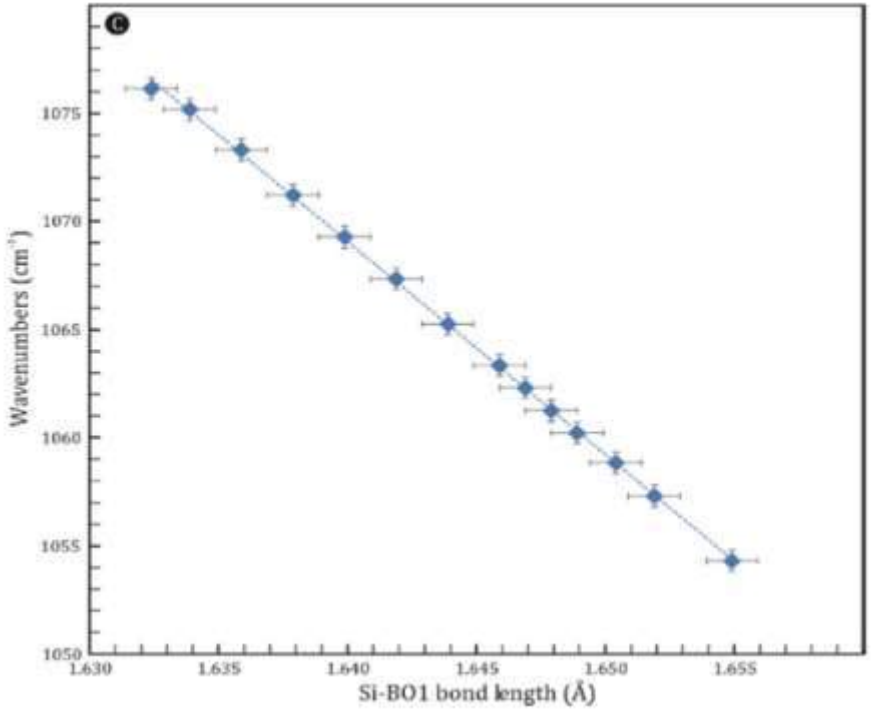
Ab initio determination of the normal modes may be done using CRYSTAL, Vienna Ab initio Simulation Package (VASP), Quantum Espresso, TRAVIS, among others…

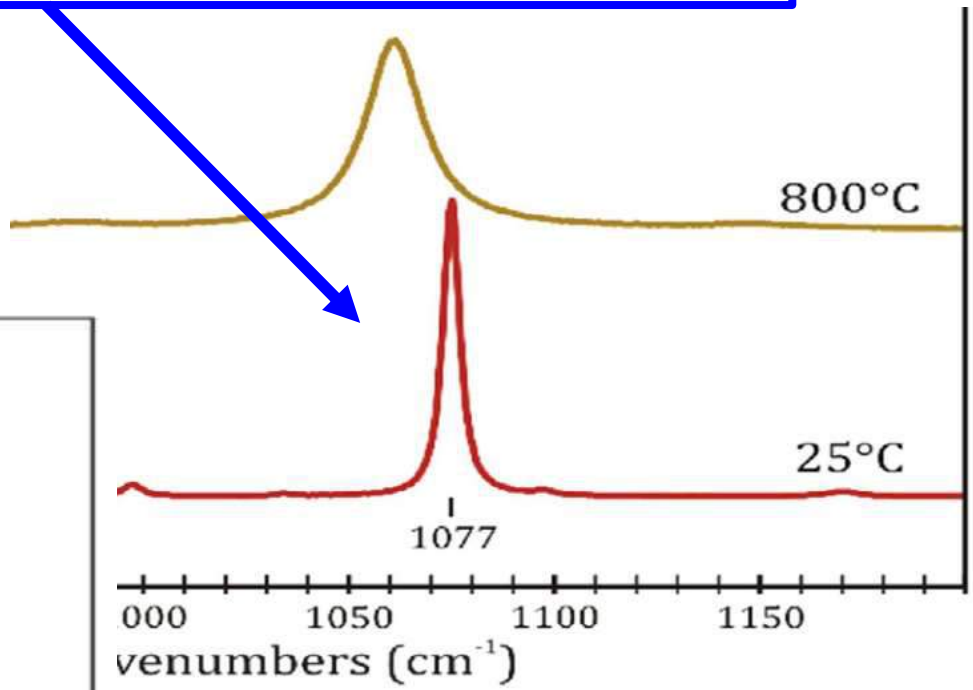
DFT simulations of vibrational modes

Sanbornite, low-$BaSi_2O_5$



1077 cm^{-1} mode originates from the Si-O1 stretch.



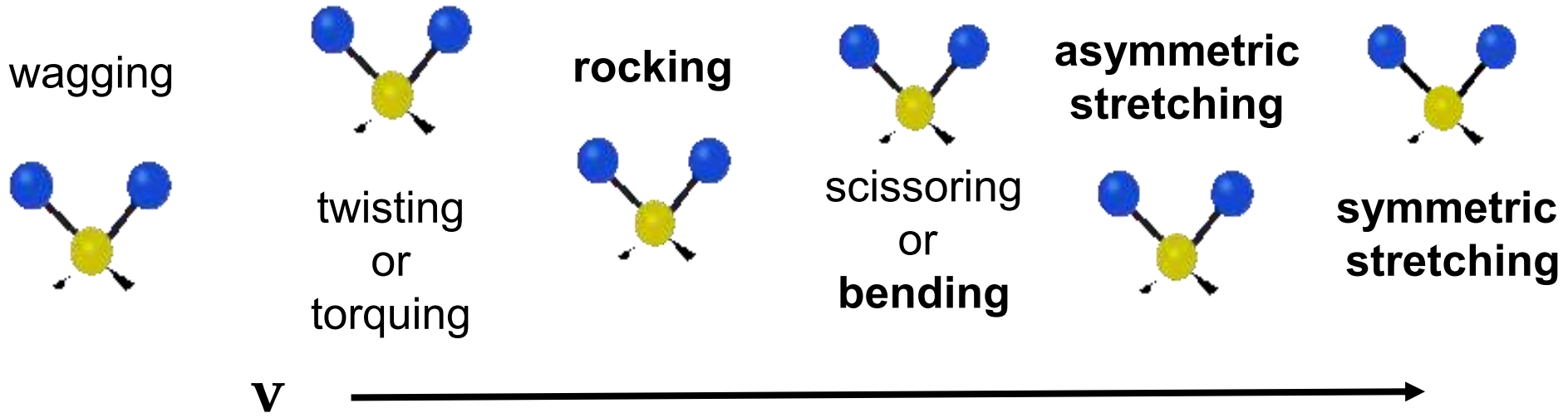


Gomes, **Moulton**, et al. (2021) Spectrochimica Acta Part A. 248:119130. https://doi.org/10.1016/j.saa.2020.119130

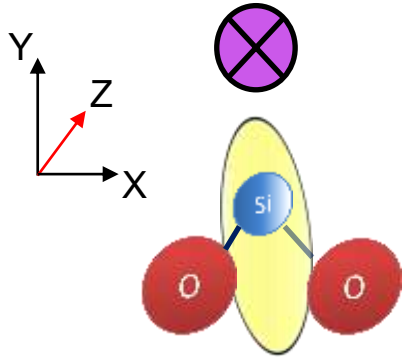
Vibrational Motions: Deformation + Bending + Stretching modes

Stretching, bending, deformation aka 'lattice' (= rocking, twisting, wagging) modes

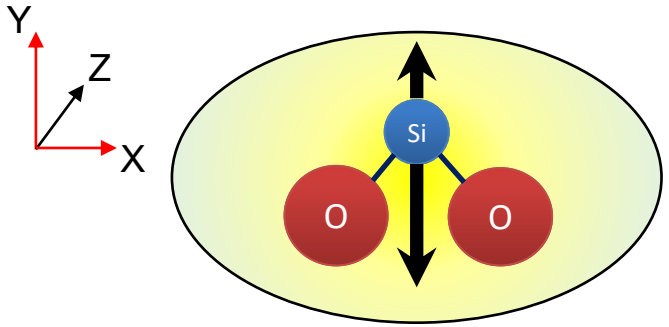
In solids:



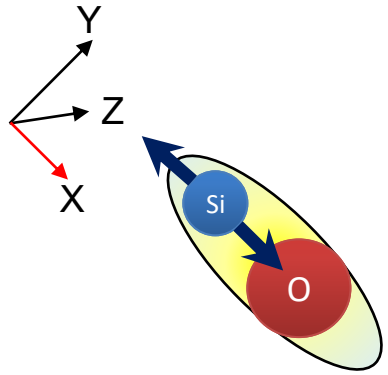
In amorphous solids:



Rocking: Out-of-plane (±Z)

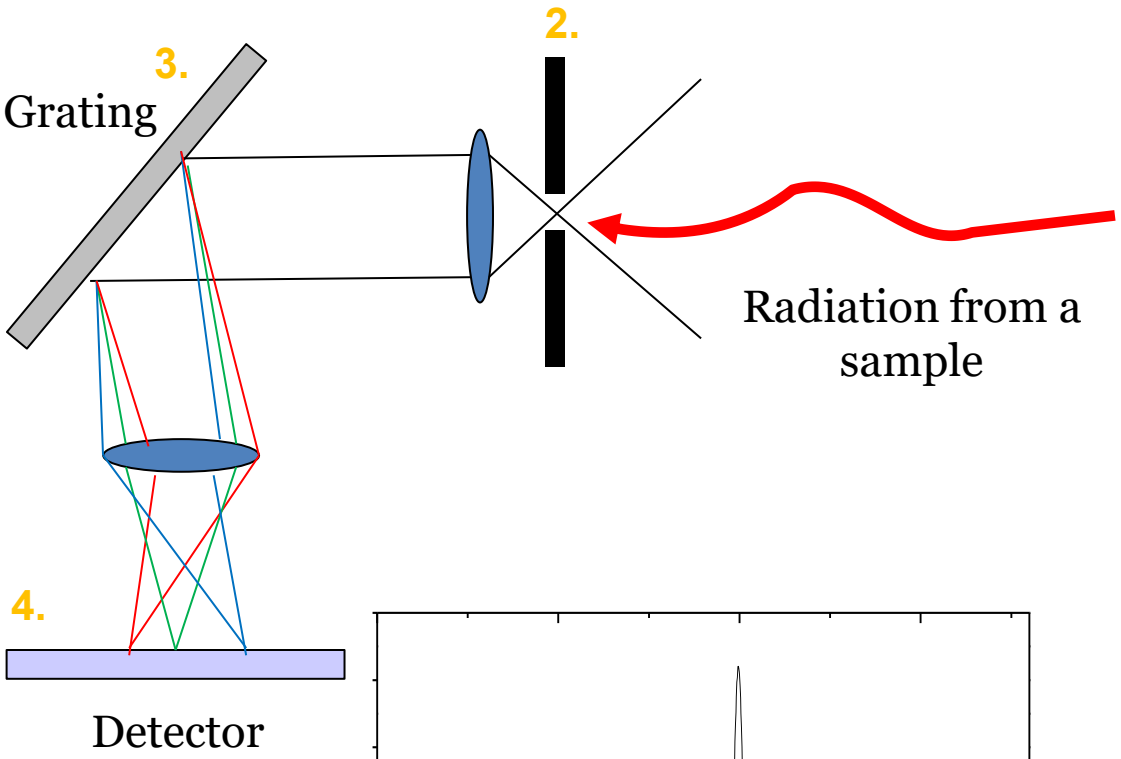


Bending: Within X-Y plane



Stretching: Along the bond(s)

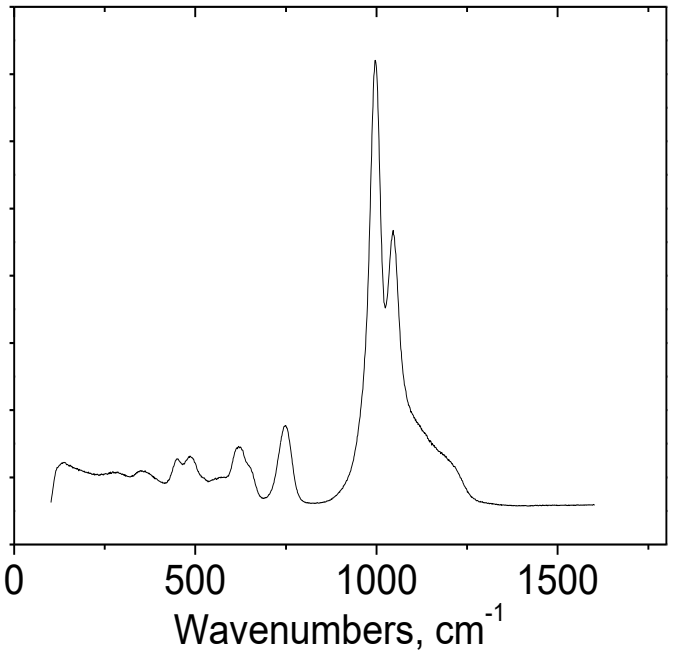
Classical Raman scattering



System basics:

1. laser
2. Rayleigh rejection filter
3. grating (resolution)
4. CCD detector

- Liquids
- Solids
- Powders
- Gases



Parameter	Value (Type)
Excitation Wavelength	514.5; 488 nm 532 nm 633 nm 785 nm 1064 nm
Power	0 – 500 mW
Geometry	Backscattering, 90

Laser Wavelengths & their use

- ✓ Blue/green lasers are good for inorganic materials, resonance Raman experiments and surface enhanced Raman scattering (SERS).

- ✓ Red/near infra-red are good for fluorescence suppression.

- ✓ Red/near-IR low energy, high power good for long measurements (imaging / mapping)

- ✓ Ultra-violet lasers are good for resonance Raman on bio-molecules (such as proteins, DNA, and RNA), & fluorescence suppression.

Raman Scattering: Intensity

$$I \sim \nu^4 I_0 N \left(\frac{\partial \alpha}{\partial Q}\right)^2$$

ν – excitation frequency of the laser

(MOST IMPORTANT ν^4)

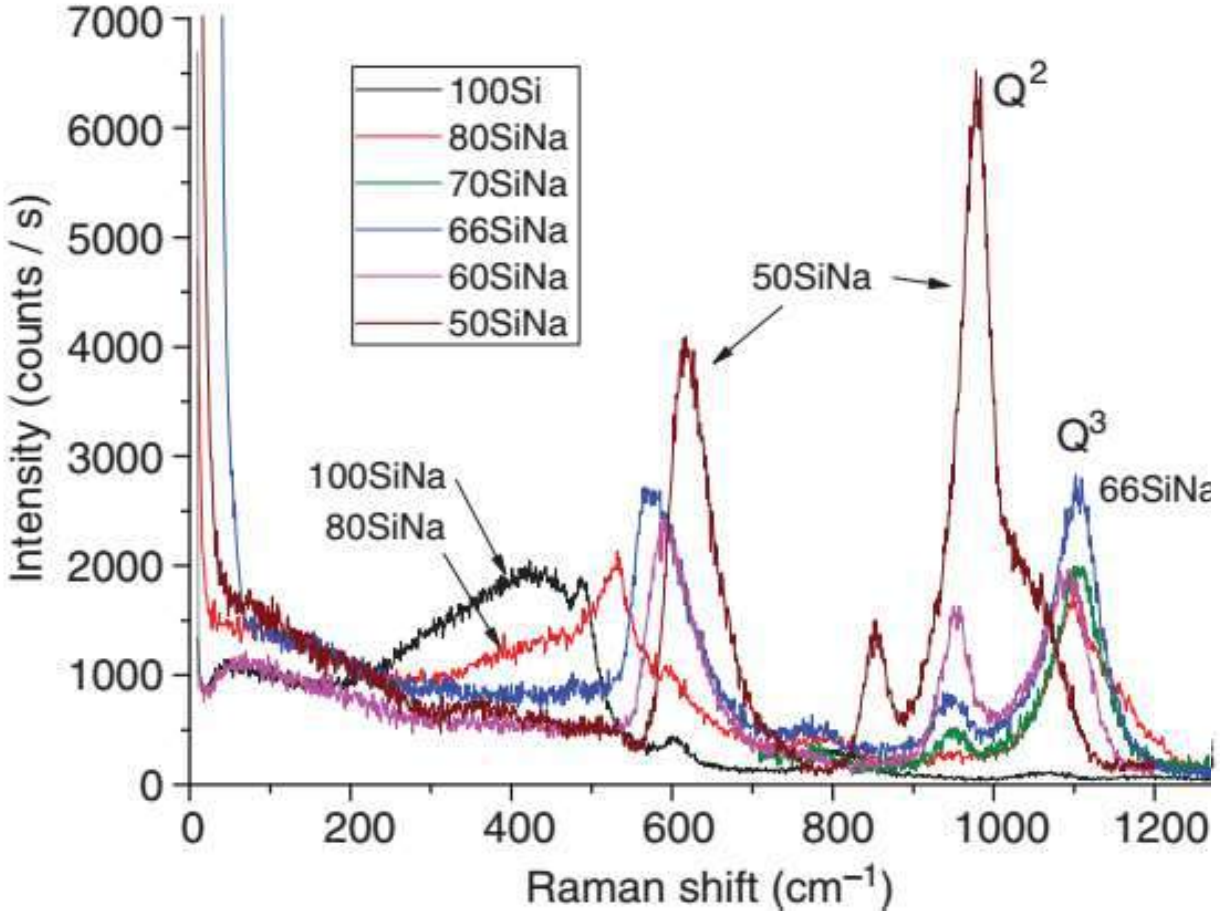
I_0 - intensity of the excitation laser

N – number of scattering molecules

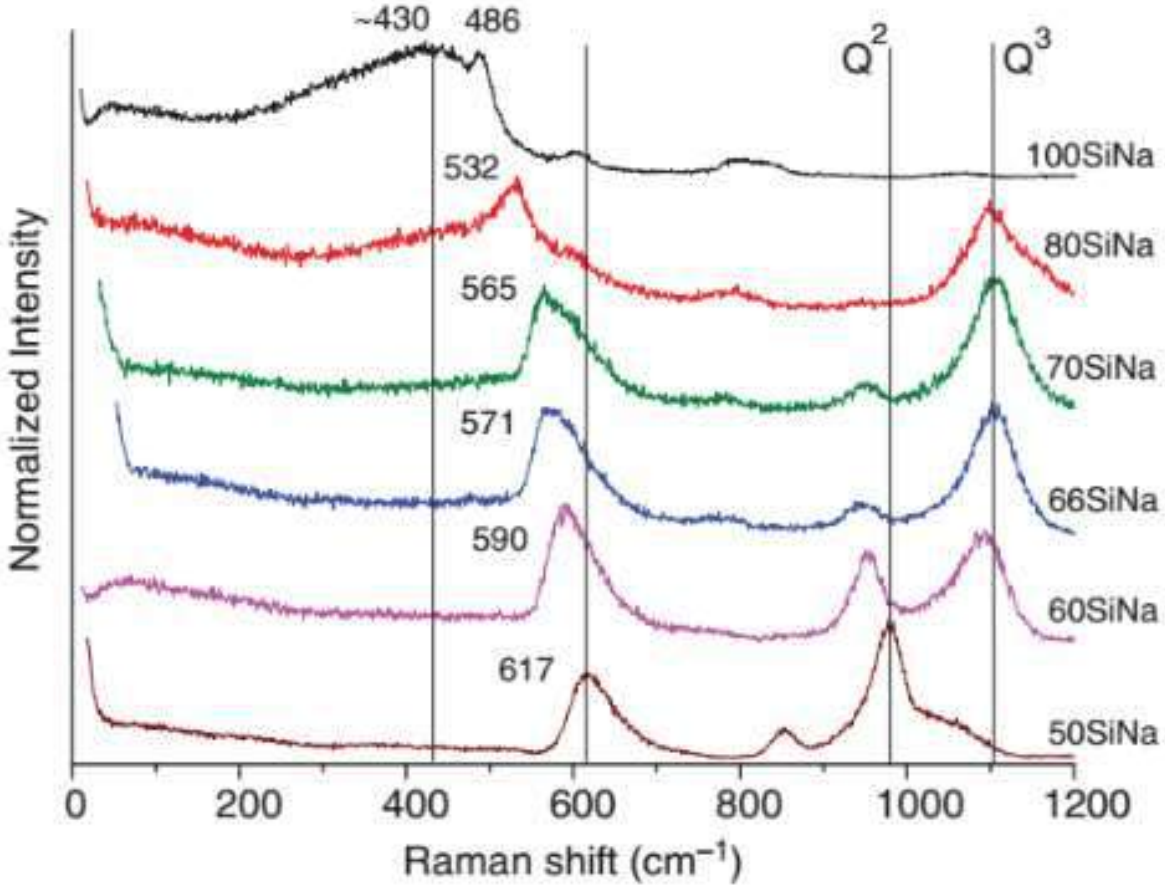
$\frac{\partial \alpha}{\partial Q}$ - polarizability

Raman Scattering: Normalized Intensity

Raw spectra



Intensity Normalized Spectra



Intensity or Area normalize

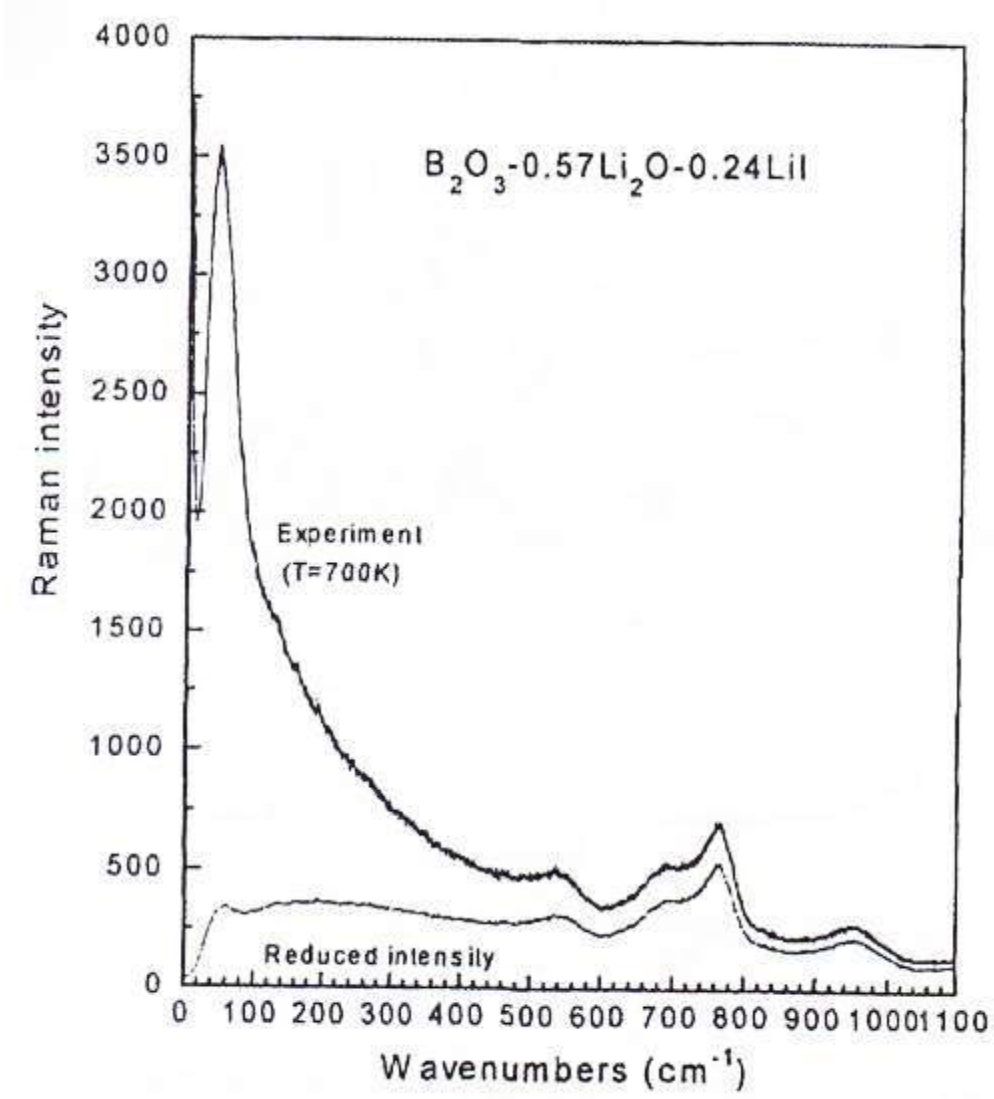
It is the relative intensities that are important, not the absolute!

Almieda & Santos, 2015 – Modern Glass Characterization

Intensity Corrections

$$I_{reduced} = \frac{I_{observed}}{\exp(-\frac{\hbar\omega}{k_B T})+1}$$

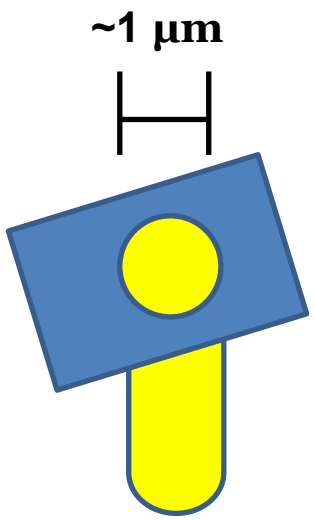
- In glasses, the Raman signal at low frequencies (<~400 cm^{-1}) is typically enhanced
- The low frequency region has a strong temperature dependence → thermal vibrational modes
- <100 cm^{-1} lies the **Boson peak**
- The boson peak origin is debated…



http://fy.chalmers.se/OLDUSERS/brodin/

Estimated Sampling Volume: 14 µm^3

Lateral resolution → $$d_{lat} = \frac{0.61\lambda}{NA}$$



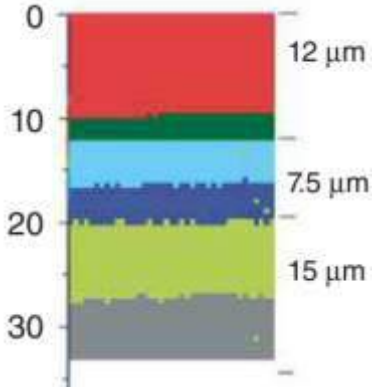
λ= 532 nm, N_a= 0. 35 (50x) d_{lat}=0.92 µm

Axial (depth) resolution → $$d_{ax} = \frac{2n\lambda}{(NA)^2}$$

λ=532 nm, n = 1.6, N_a= 0. 35 (50x) d_{ax} =14 µm

Caution: The true sampling volume is much larger depending on pinhole, refractive index, crystallization, heterogeneities, surface, etc...

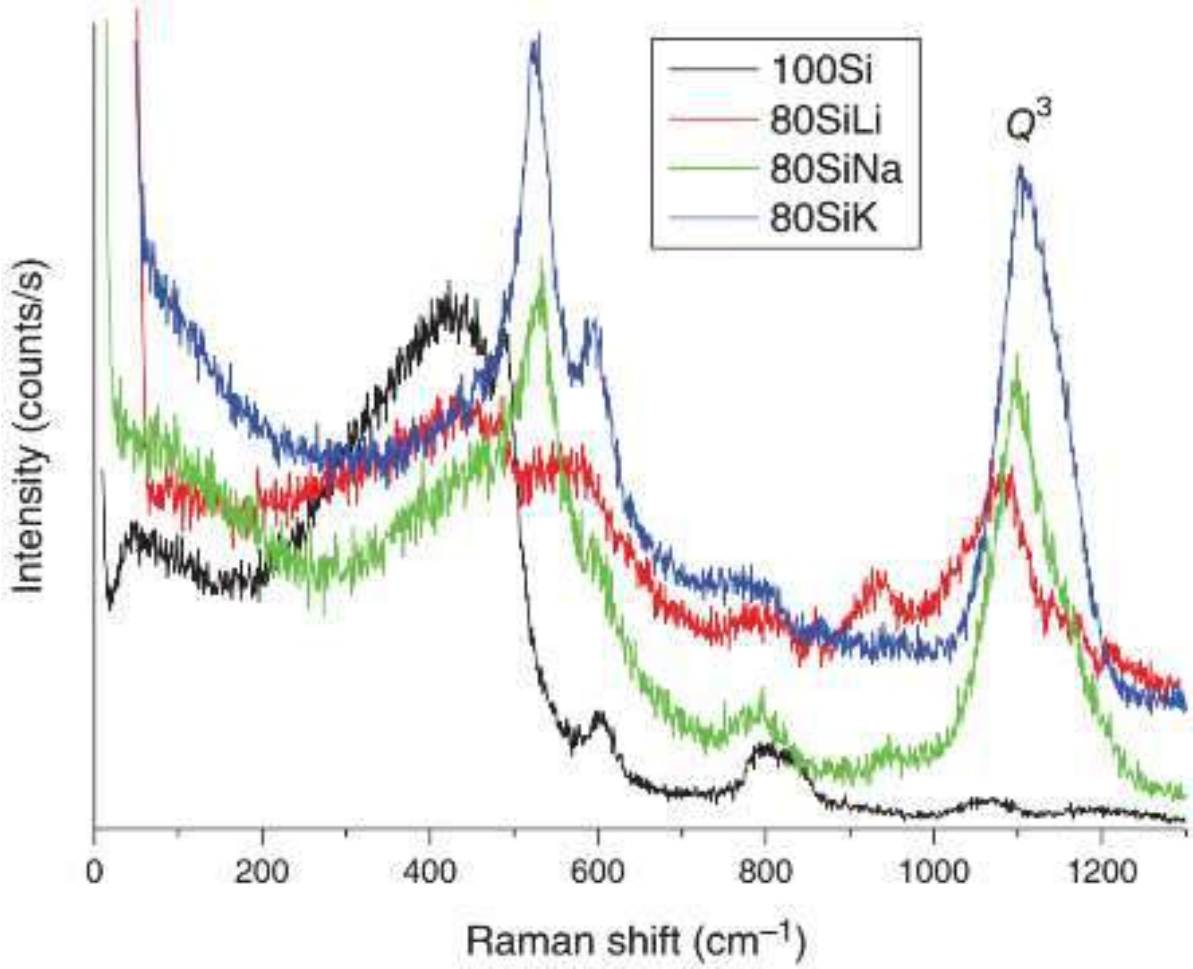
Better to test your equipment with a layered material such as laminated film →



For more info see: Diem, 2015. Modern Vibrational Spectroscopy and Micro-Spectroscopy. Wiley.

Spectral Quality depends on…

- Experimental parameters (quality of lens, grating, detector, stage setup, etc…)
- The size of the confocal hole
- Microscope objective (NA)
- Excitation wavelength (λ_0)
- Surface of the sample
- Sample colour
- Sample homogeneity
- Refractive index



Almieda & Santos, 2015 – Modern Glass Characterization

Advantages & Disadvantages

Pros	Cons
Any material can be investigated!	Difficult to quantify!
Excellent spatial / depth resolution	Not good for strongly fluorescent samples
Non-destructive (mostly)	Complimentary techniques (NMR, XPS, IR)
No required sample preparation	Inconsistent data treatment…
Minutes (or seconds) for quality spectra	Questionable interpretations persist…
In situ high Temperature / Pressure	
Much more sensitive than XRD	

Stay focused on your goal!

Keep experimenting to gain experience!

Break #2: Any questions about Raman basics?

Before we turn to dealing with glass spectra?

Recommended introduction to spectroscopy:
M Diem. **2015**. **Modern Vibrational Spectroscopy and Micro-Spectroscopy.** John Wiley & Sons Ltd. 411 pg book.

Overview for today:

1. Glass versus Crystal structure
2. What is Raman scattering?
3. Glass spectra and how we determine glass structure?
4. Exemplar studies

Is there a theory of Raman for glasses?

"In conclusion, there is no single theory for accurately predicting the first order
vibrational spectra of glassy materials, […]"

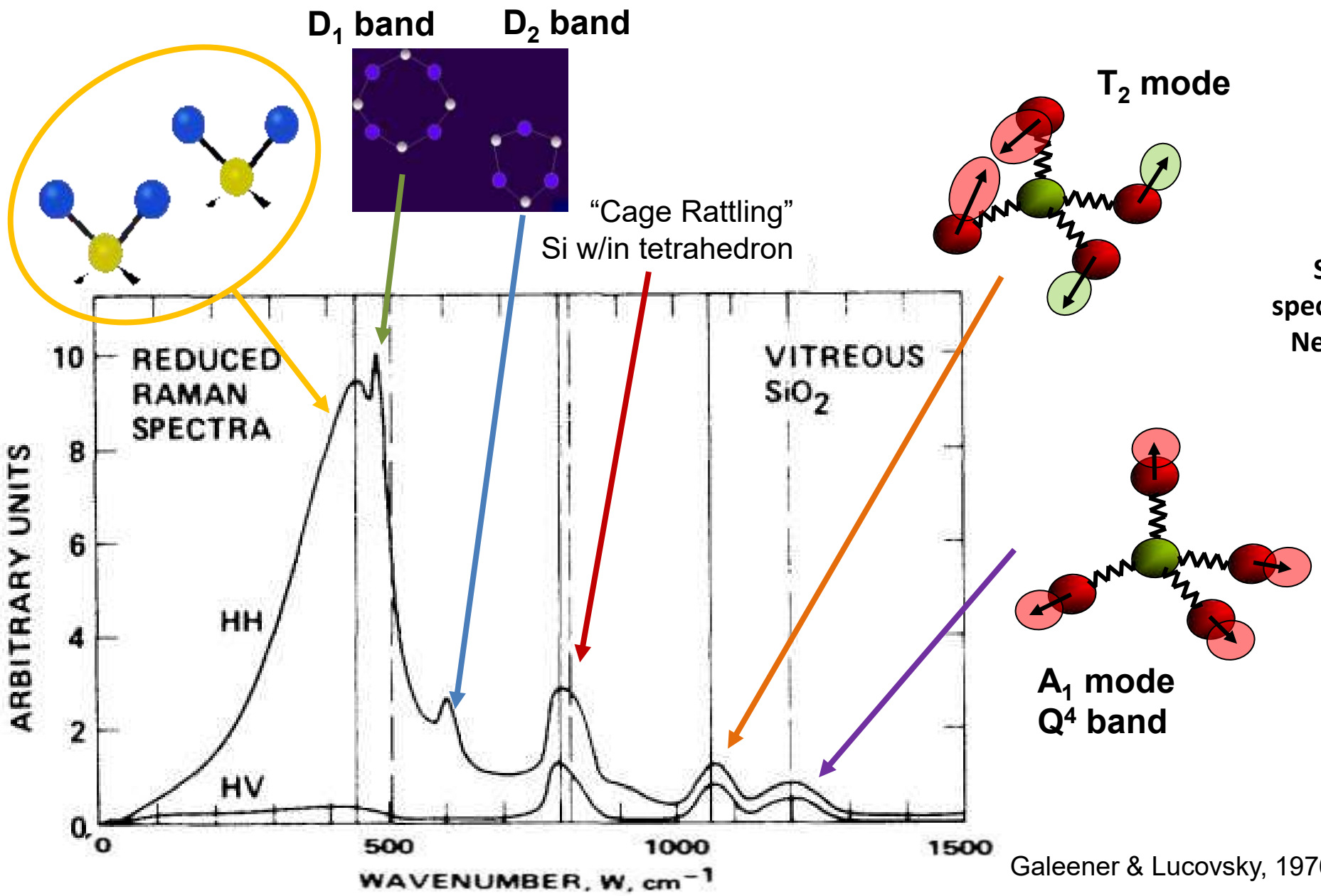
"Compositional variations, whenever possible, are also very helpful in assigning the Raman spectra of glasses."

Prof. R. M. Almeida & Prof. L. F. Santos

Raman spectroscopy of glasses

In Modern Glass Characterization (2015)

The Raman Spectrum of SiO_2



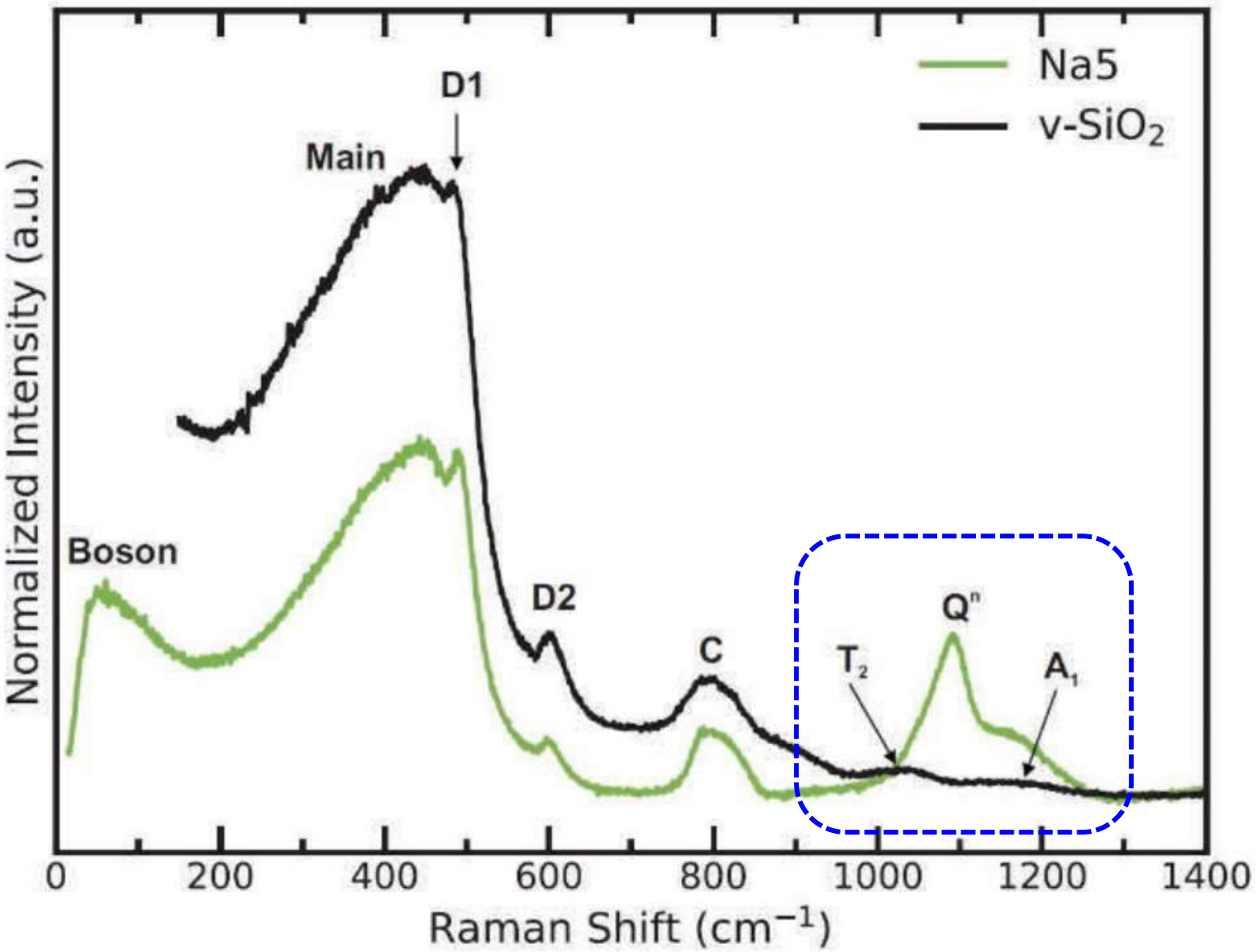
SiO_2 polymorphs spectra can be found in Neuville et al., 2014, RiMG

Galeener & Lucovsky, 1976; Sarnthien et al., 1997

What happens when Na_2O is added to SiO_2?

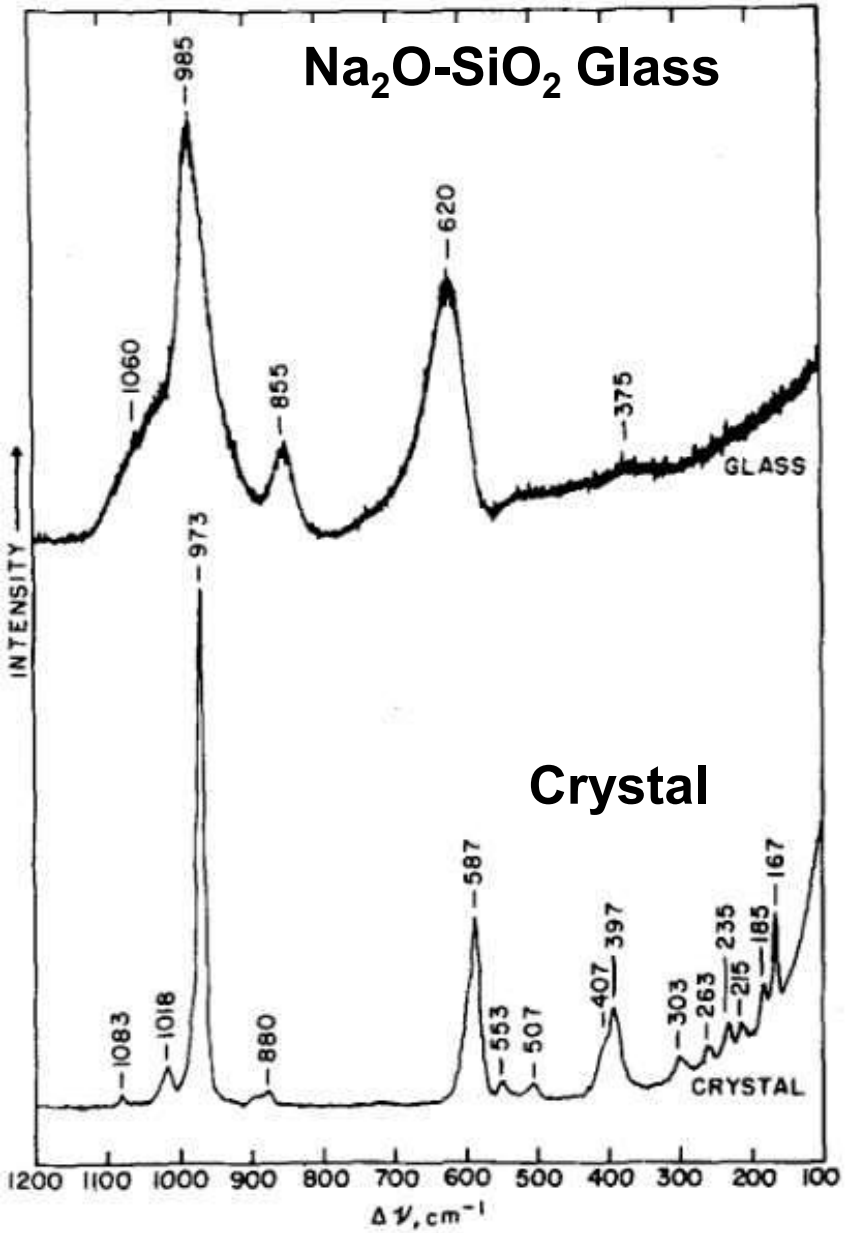
Q^n modes are strongly polarizable compared to SiO_2 modes.

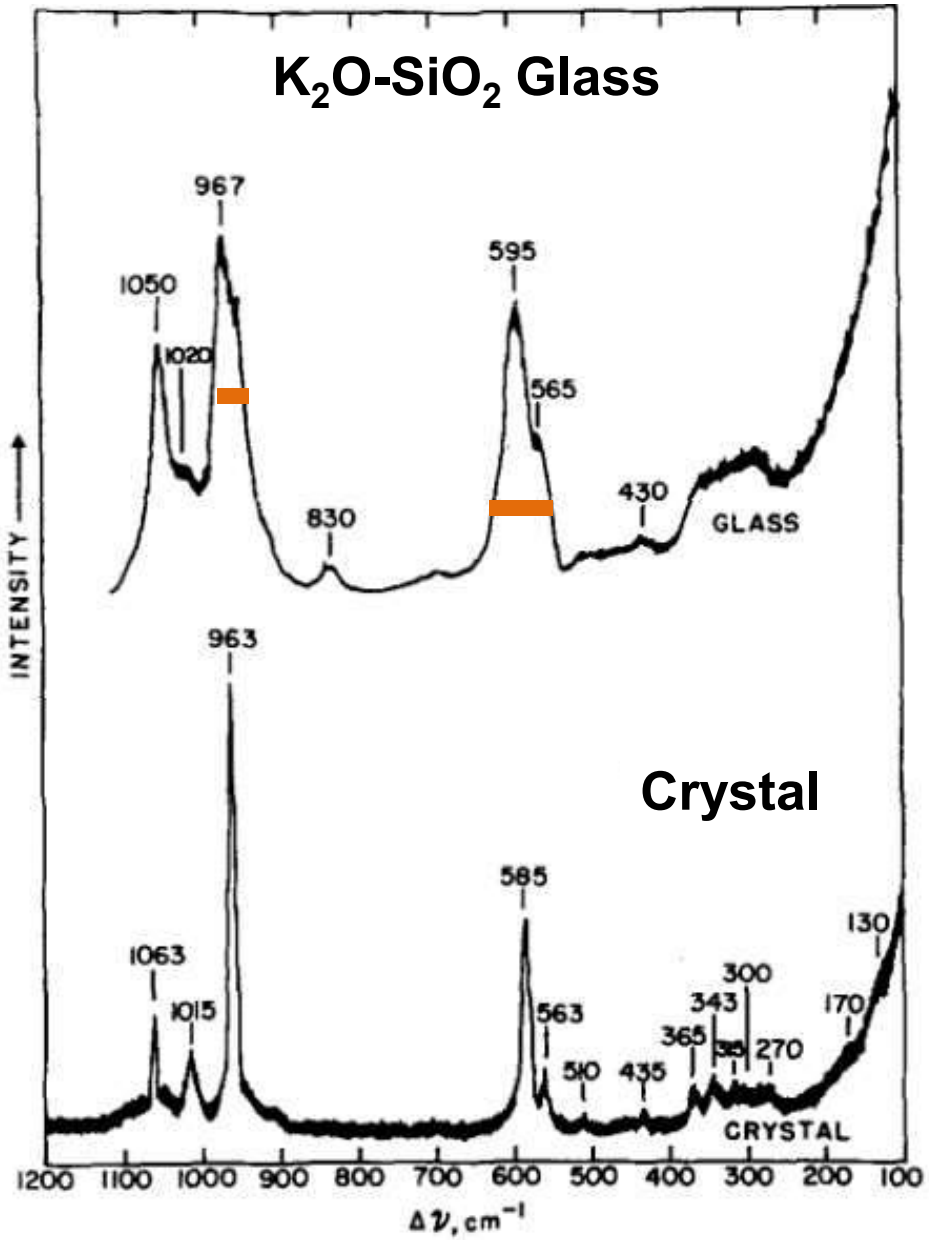
Is polarizability change for Q^n affecting SiO_2 bands as well?



Henderson & Stebbins, 2021. Reviews in Mineralogy & Geochemistry.

Seminal work: Brawer & White ('75) Metasilicates



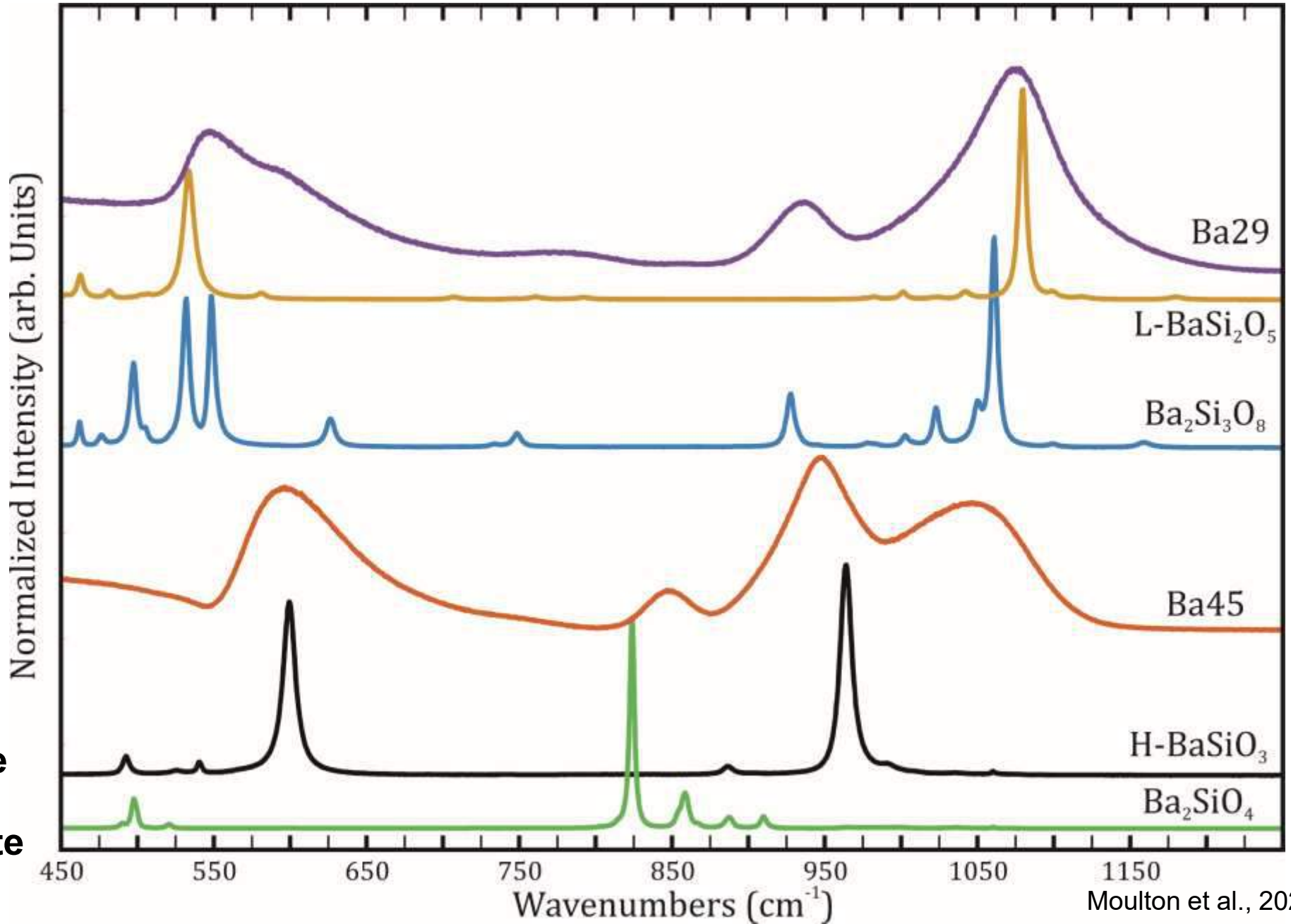


Modes in the crystalline solid & in the glass are found at very similar frequencies.

More (& broader) modes are observed in the glass.

Brawer & White, 1975. J Chem. Phys. 63(6)2421-2432.

Crystal vs. Glass spectra of the $BaO\text{-}SiO_2$ system



SiO_2 (mol. %)

71

66.6

60

55

50

33.3

Q^3 - Disilicate

Q^2 - Metasilicate

Q^0 - Orthosilicate

Moulton et al., 2021, under review

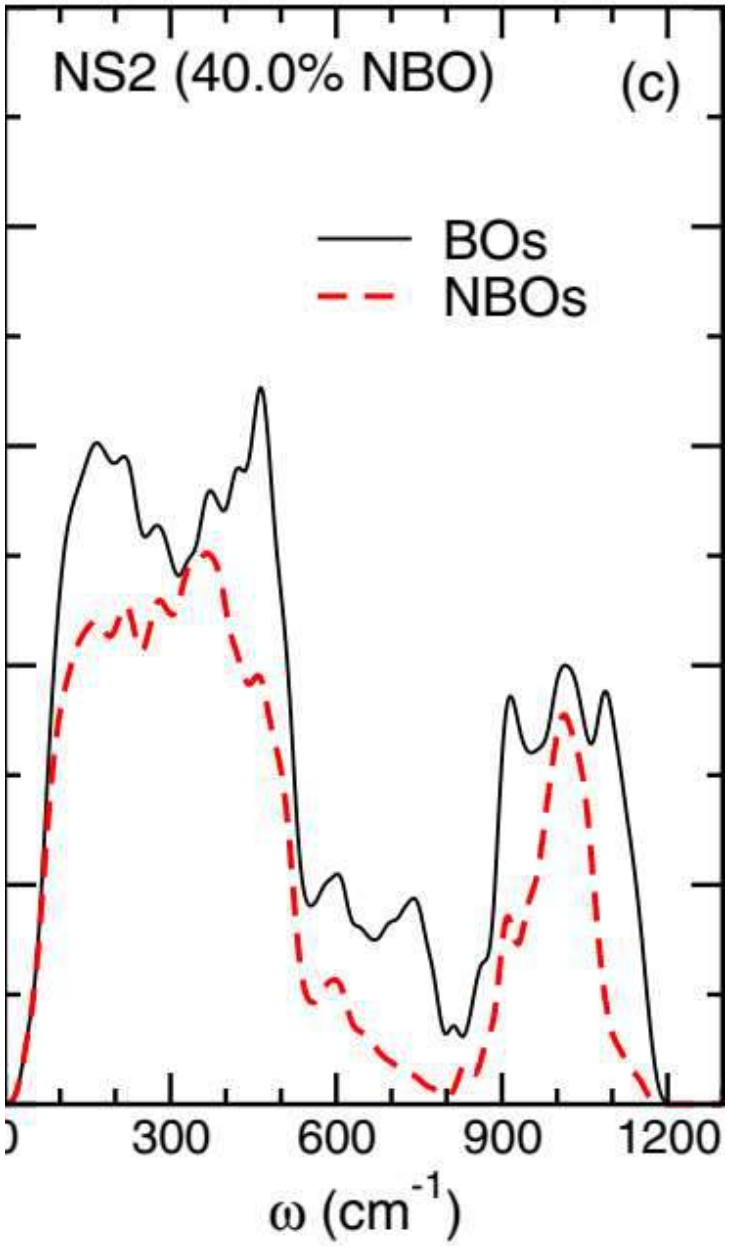
Vibrational modes in Na_2O-$2SiO_2$ glass

In many glass studies:

low frequency (<700 cm^{-1}) ~ **Si-O-Si**

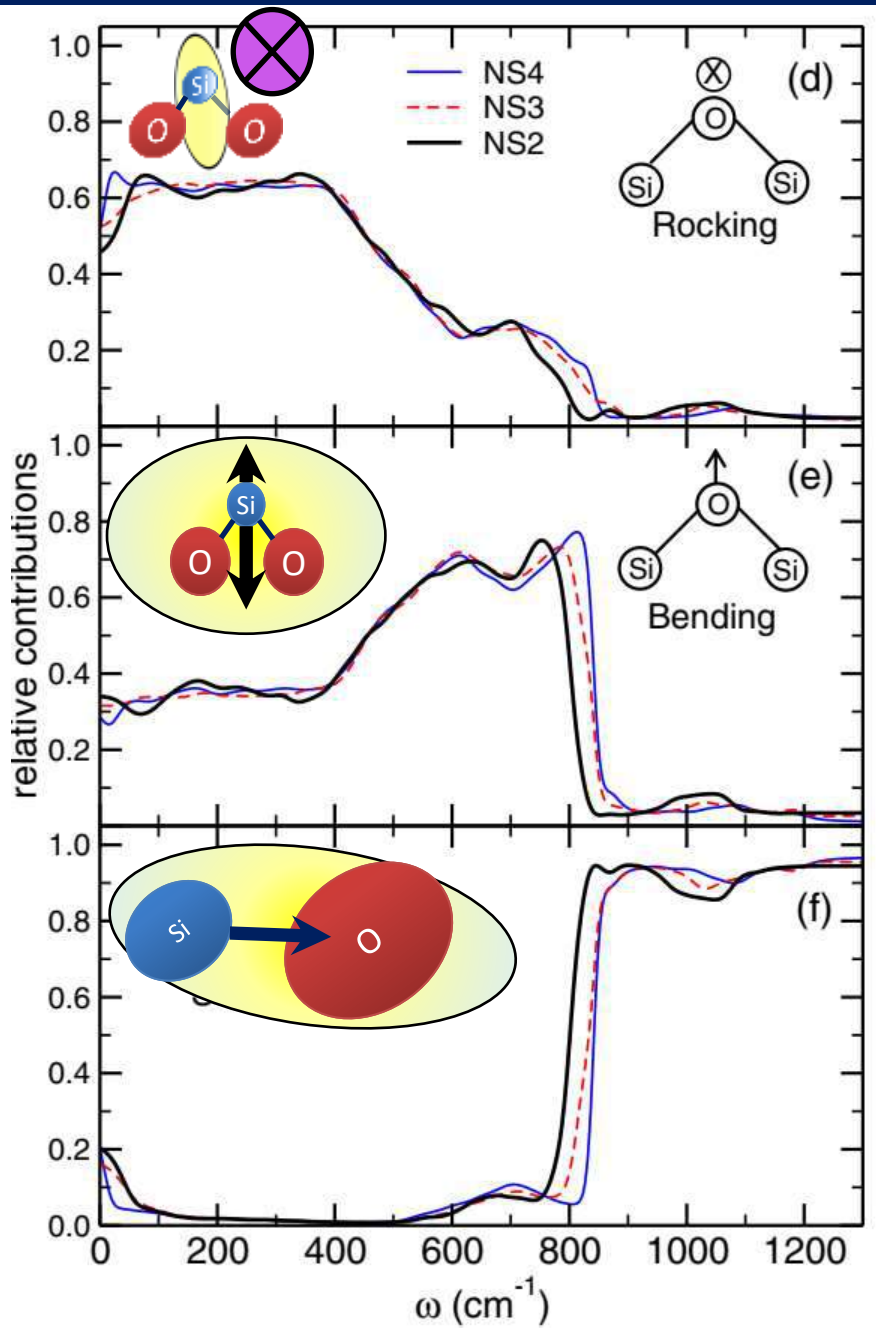
high frequency (>800 cm^{-1}) ~ **Si-NBO**

BO and NBO contribute ≈ equally at all frequencies.



Kilymis, Ispas, Hehlen, Peuget, Delaye (2019) Phys Rev B 99: 054209

Deformation + Bending + Stretching modes in Na_2O-$2SiO_2$ glass



← **When the vDOS is divided by motions:**

Rocking: <400 cm^{-1}

Bending: 400-800 cm^{-1}

Note: **Bend+Rock overlap entirely.**

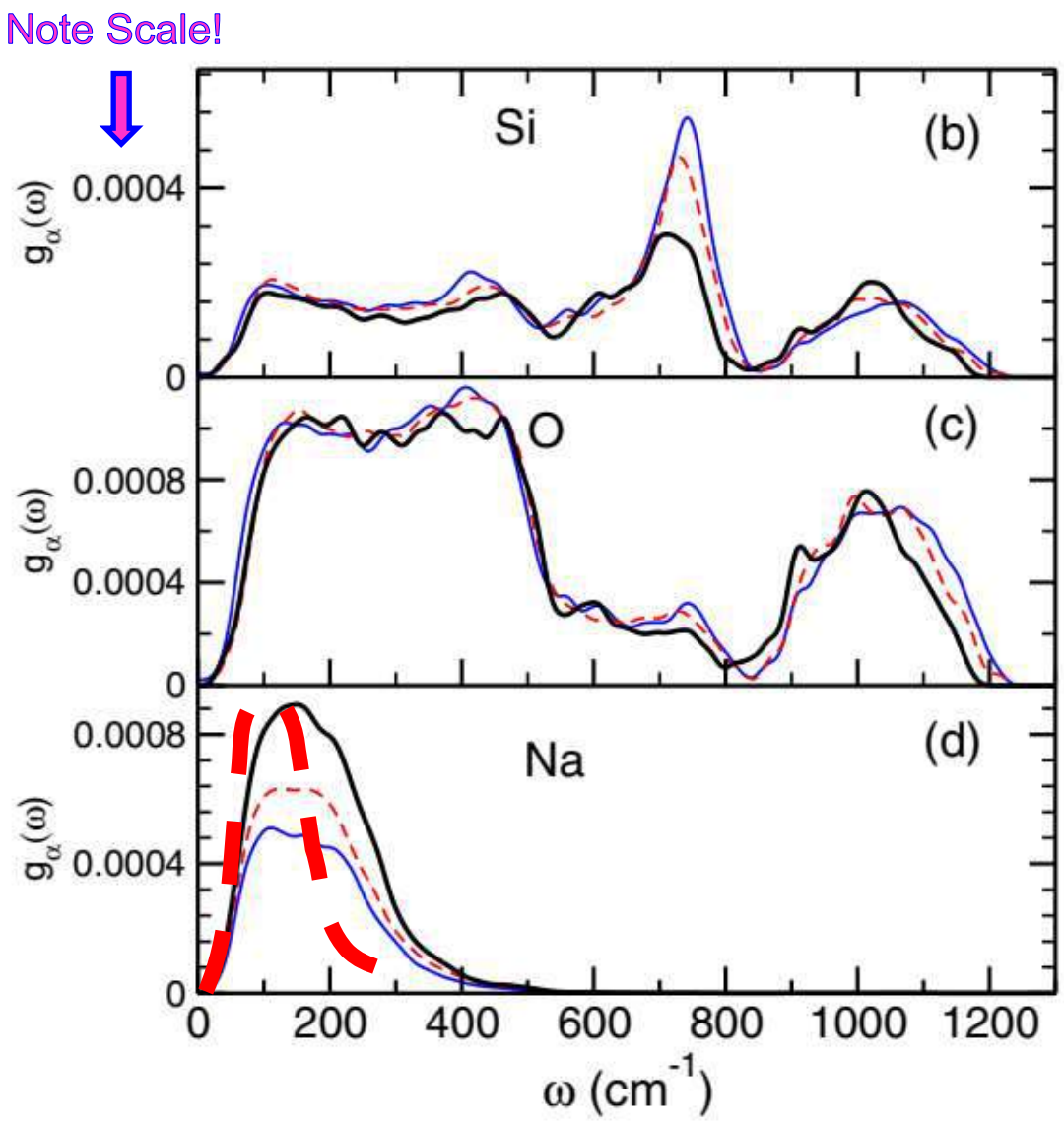
Pure bending or rocking motions are almost non-existent in glasses.

Stretching: >800 cm^{-1}

Although these ranges are sensitive to composition these trends are essentially true for all silicates (crystal or glass).

Kilymis, Ispas, Hehlen, Peuget, Delaye (2019) Phys Rev B 99: 054209

Vibrational modes in Na_2O-$2SiO_2$ glass



← When the vDOS is divided by element:

(b) Si contributes broadly but weakly.

(c) Signal comes from O

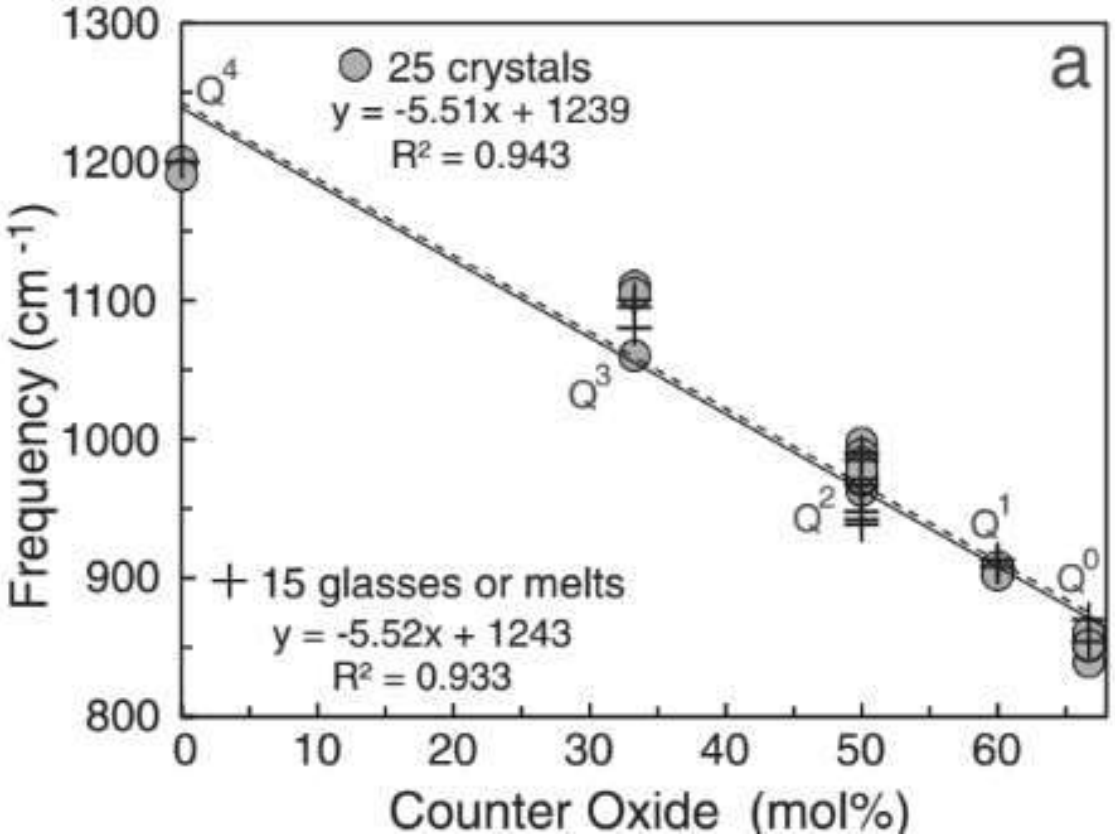
(d) Na contributes <500 cm^{-1}

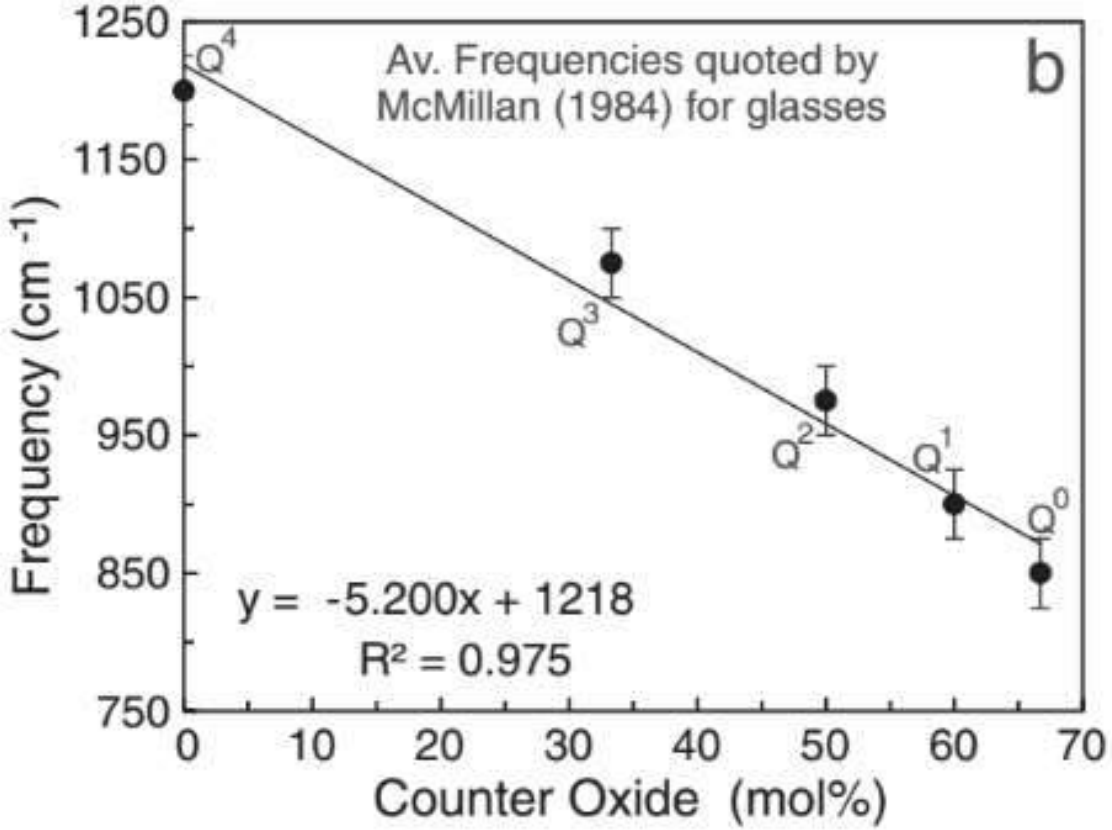
If Na was switched for Ba (- - -), the distribution would shift to lower frequencies.

Oxygen dominates the signal (except perhaps near the boson peak)

Kilymis, Ispas, Hehlen, Peuget, Delaye (2019) Phys Rev B 99: 054209

Q^n modes in Crystals vs Glasses

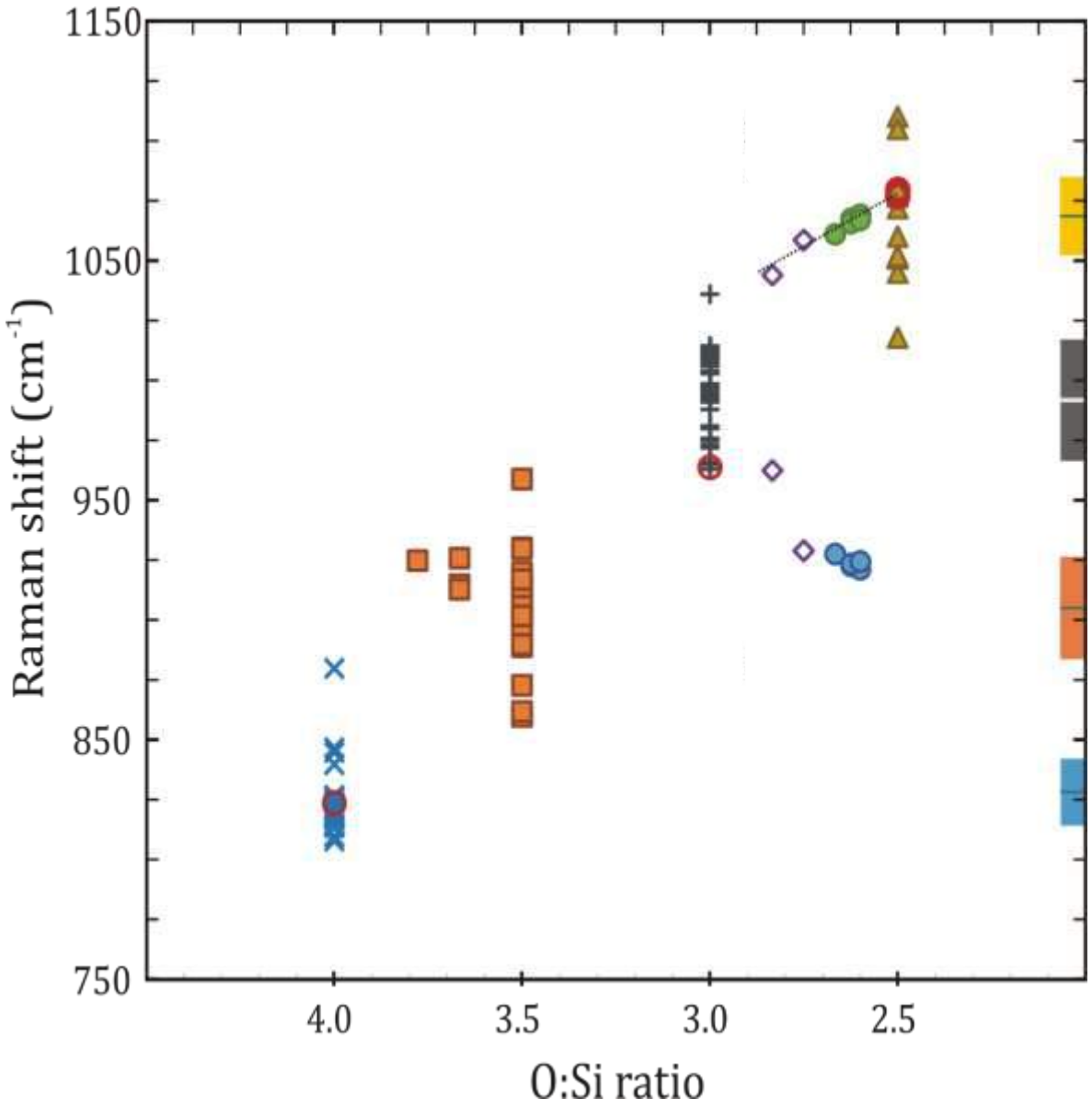




- **Q^n species in crystals are also found in the glasses.**
- **Glass are made of networks with multiple Q^n species.**

McMillan, 1984; Nesbitt et al., 2017 Chem. Geol. 461:13-22

Q^n response in Crystals Raman



- **~160 crystals**
- **Variety of symmetries**
- **Variety of composition**

Q^n bands have specific frequency ranges – with slight overlap.

Moulton et al., 2021, under review

Raman spectra of glass vs. crystal:

In crystals:

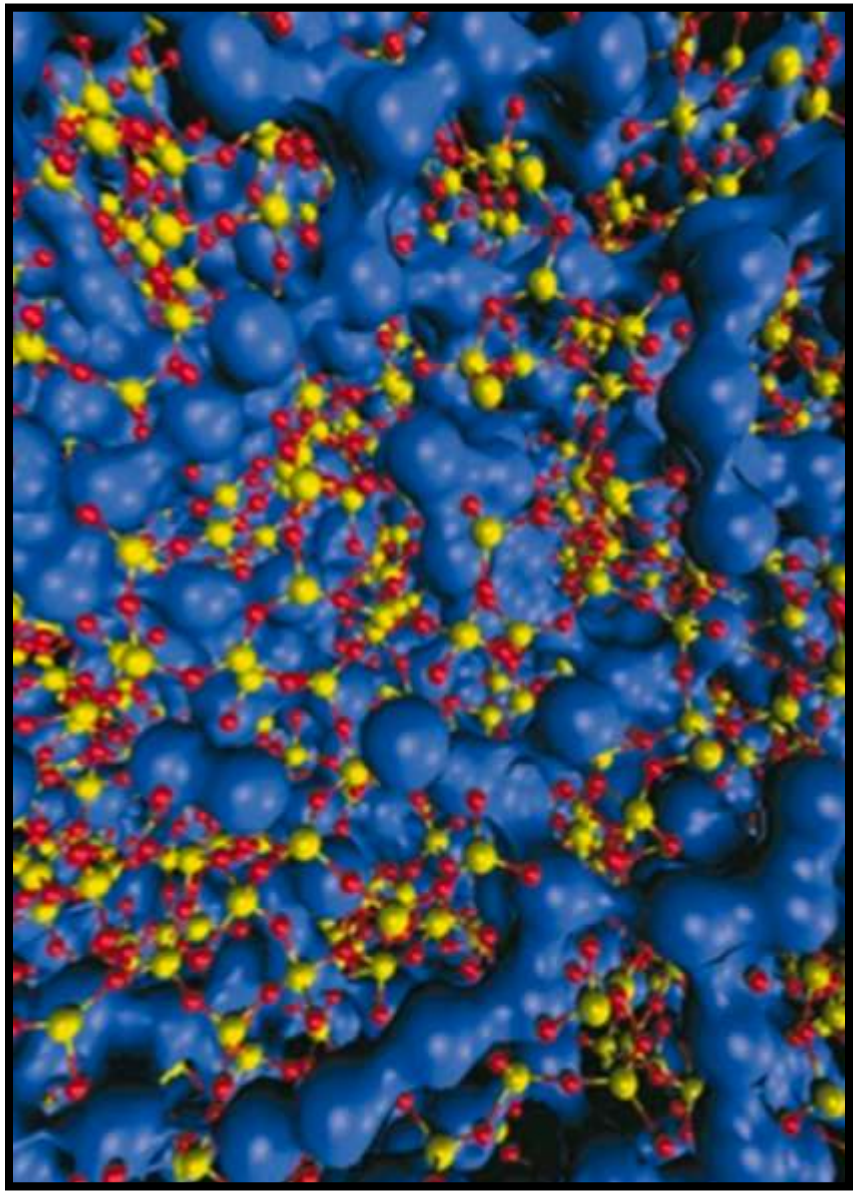
- Simulations provide explicit origin for modes
- Deformation can also be simulated
- Frequency-structure relationships may be developed
  e.g. Q^n, Si-O bond length, ring structures, etc.

In glasses:

- Q^n distribution
- Inter-tetrahedral angle (<Si-O-Si)
- Ring structures (3-, 4-member rings)

→ Should be tested by several methods: NMR, IR, XPS

Glass network: Connectivity and Polymerization



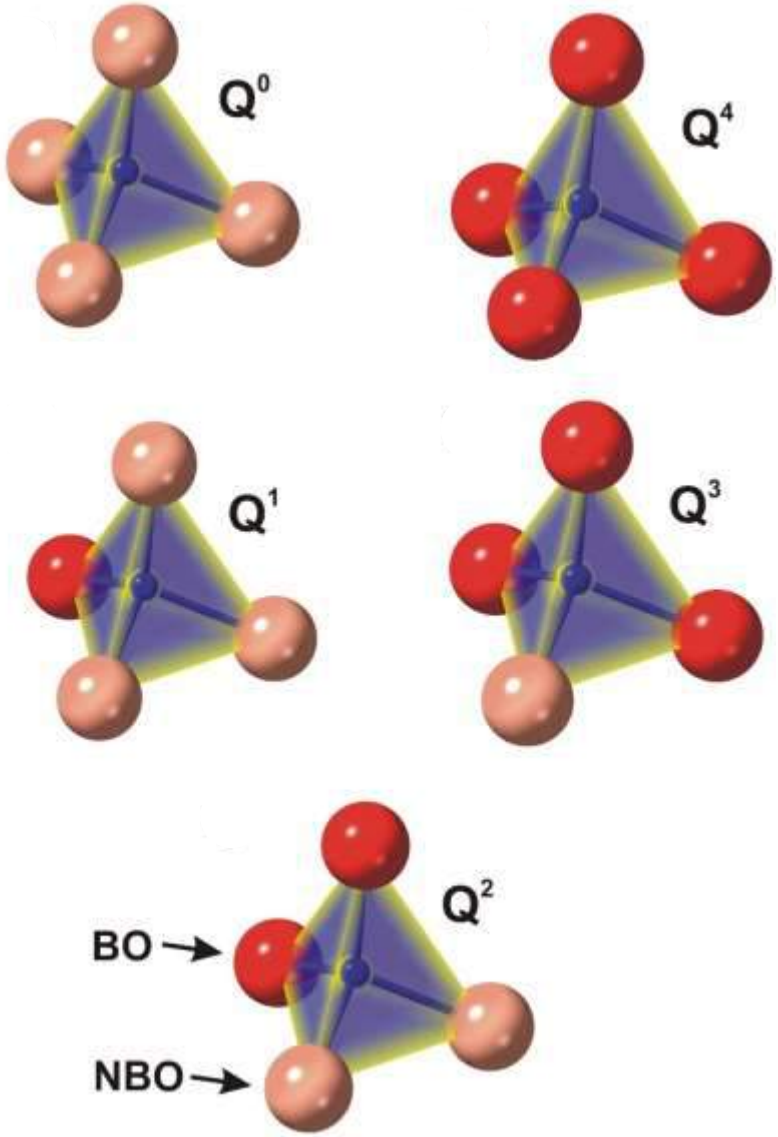
Meyer et al., 2004 Phys Rev B 93, 027801

Glass network has some **Q^n species distribution.**

Oxygens: **O^{2-}, BO & NBO**

Mean connectivity = NBO/T

Knowing the Q^n distribution & bulk composition… we can related these quantities.



We now use these concepts to quantify the glass structure.

Polymerization vs Disproportionation

(De-)polymerization

$$BO + O^{2-} \rightleftharpoons 2NBO^{-}$$

or

$$Q^n + BaO \leftrightarrow Ba^{2+} + 2Q^{n-1}$$

Adding BaO breaks Si-O-Si bridges to produce non-bridging oxygens (NBO).

O^{2-} = Free oxygen = Non-network oxygen …oxygen bound only to modifiers.

Disproportionation

$$2Q^n \leftrightarrow Q^{n-1} + Q^{n+1}$$

For example

$$2Q^3 \leftrightarrow Q^4 + Q^2$$

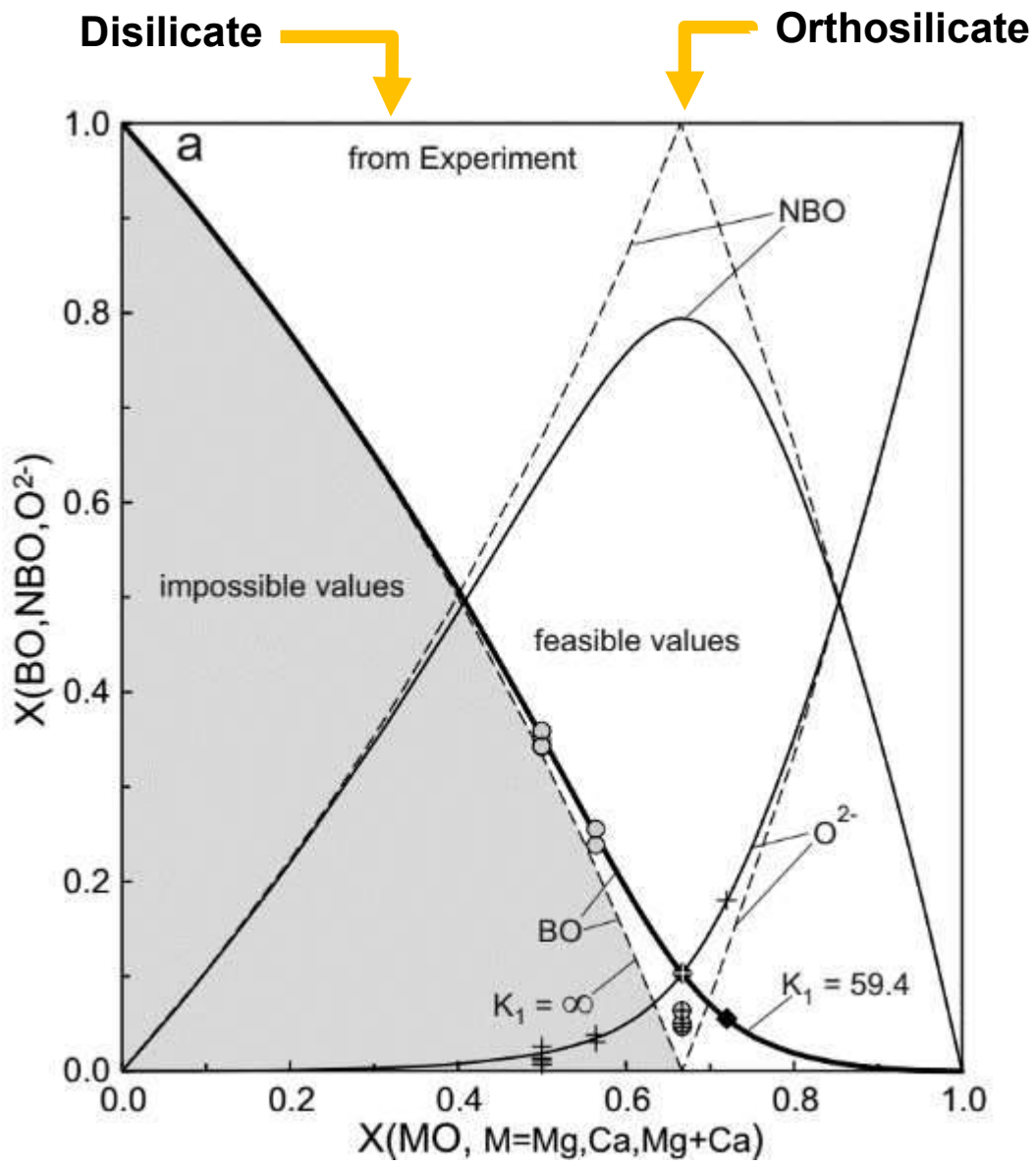
$$2Q^2 \leftrightarrow Q^3 + Q^1$$

Disproportionation can NOT change the BO:NBO ratio.

It can change the Q^n population.

How is oxygen distributed in the glass network?

Fincham & Richardson, 1954



$$BO + O^{2-} \leftrightarrow 2NBO^{-}$$

The mass action equation for this reaction is:

$$K_1 = (NBO^{-})^2/[(BO)(O^{2-})]$$

If K_1 goes to infinity (all BO are reacted to form NBO) than at the orthosilicate composition (SiO_2 = 66 mol. %) there should be no more BO.

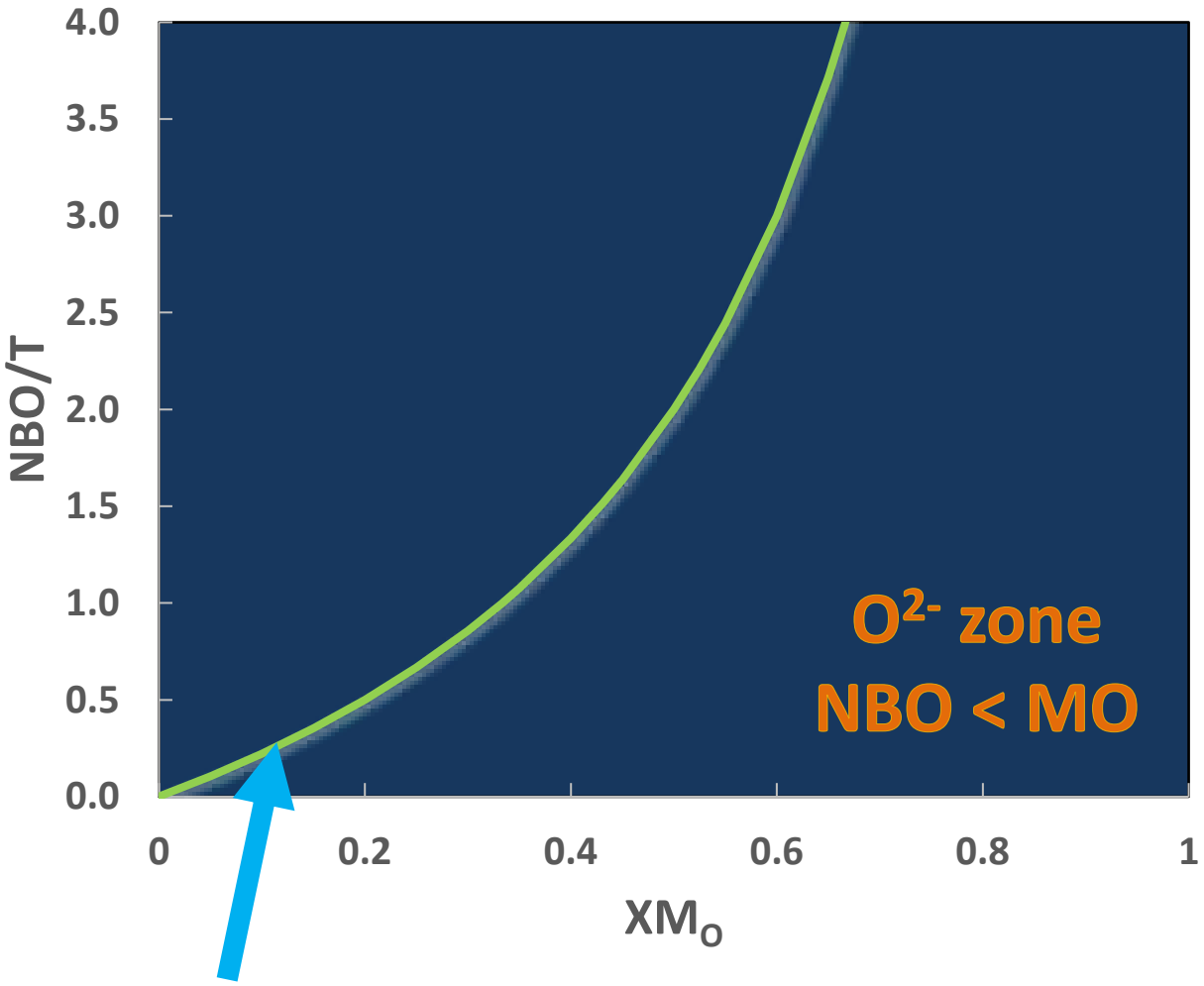
$$2Q^n \leftrightarrow Q^{n-1} + Q^{n+1}$$

If K_1 goes to infinity ≈ "*disproportionation goes to completion*"…
is the assumption of 99% of studies until ~2010.

Nesbitt, Bancroft, Henderson, Sawyer, Secco (2015) Am Min. 100:2566-2578.

Polymerization: Plausible vs. Implausible

3 possible solutions for how NBO are distributed on tetrahedral network formers (T):



On this line % MO = % NBO.

Situation #1: Assuming $K_1 = \infty$

Q^n = NBO

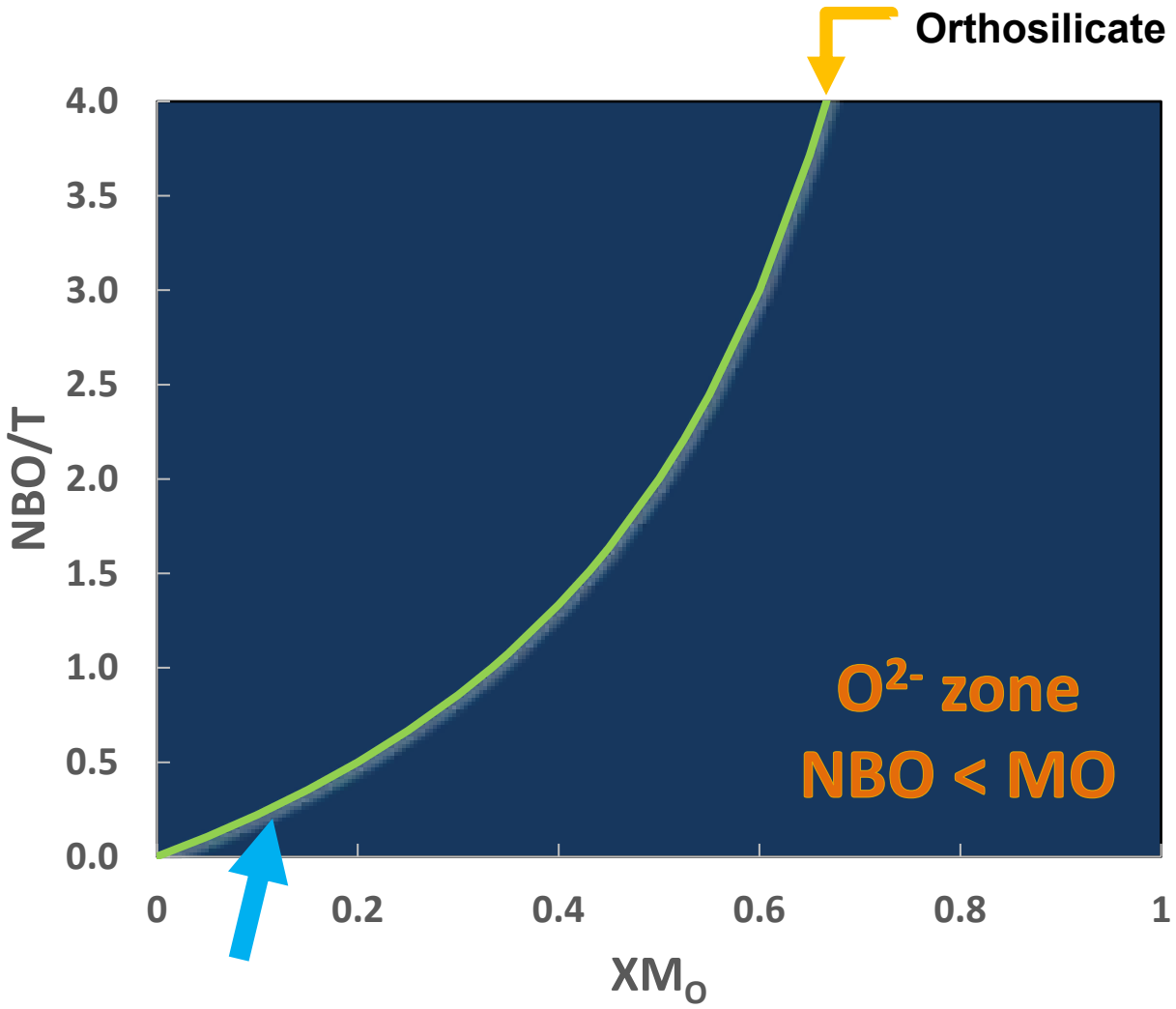
- Polymerization has gone to completion
- All O^{2-} is used to form NBO

$$BO + O^{2-} \rightarrow 2NBO^-$$

If this case is assumed *a priori*…
Interpretations suffer from:

- **in consistent data treatment.**
- **conflicting interpretations.**

Polymerization: Plausible vs. Implausible



On this line % MO = % NBO.

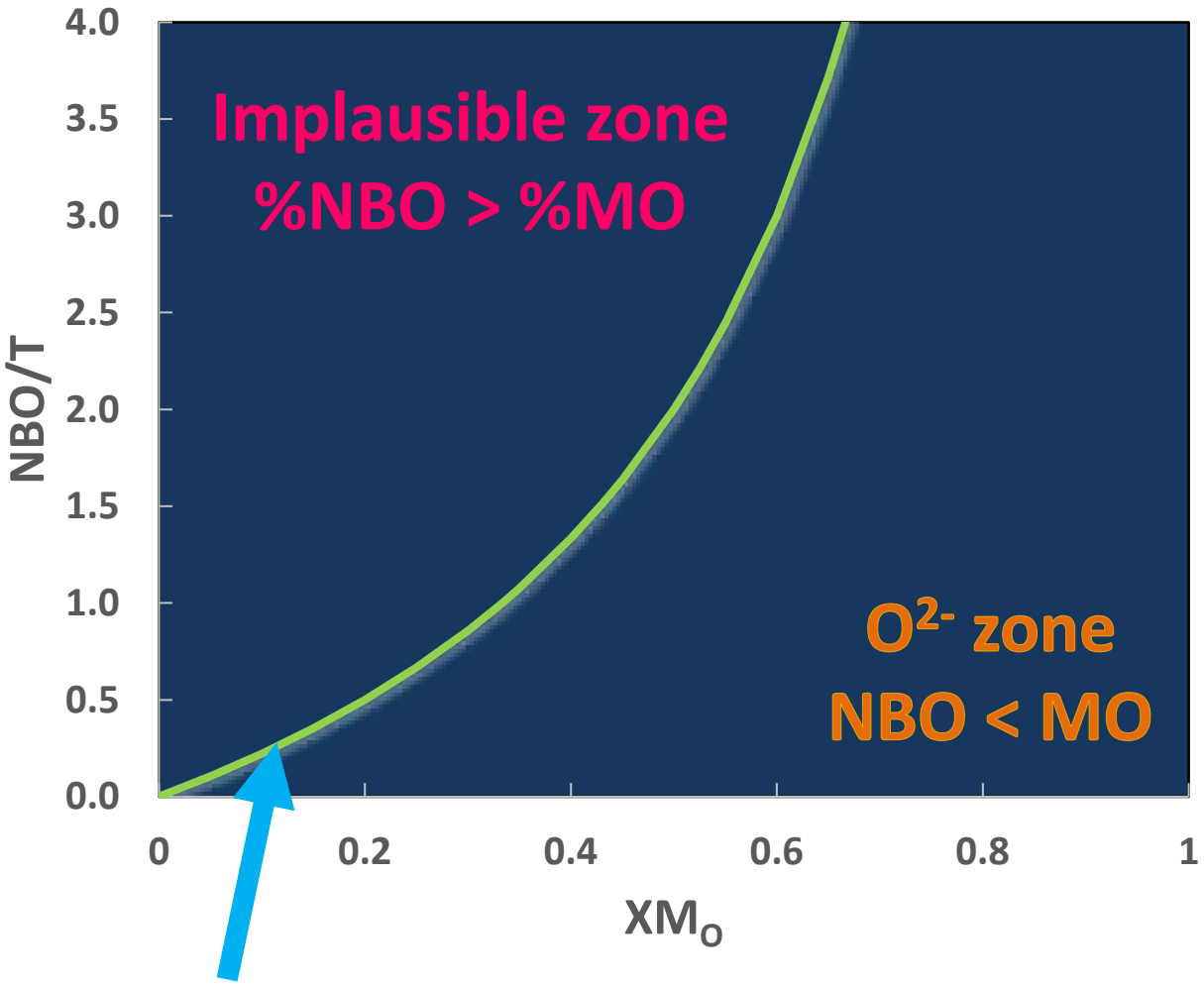
Situation #2

Q^n < NBO

- the glass is MORE polymerized than expected
- there MUST be some O^{2-} in the glass.

$$BO + O^{2-} \Leftarrow 2NBO^-$$

Polymerization: Plausible vs. Implausible



On this line % MO = % NBO.

Situation #3

Q^n > NBO

- the glass is LESS polymerized than expected
- There is more NBO produced than MO added

???

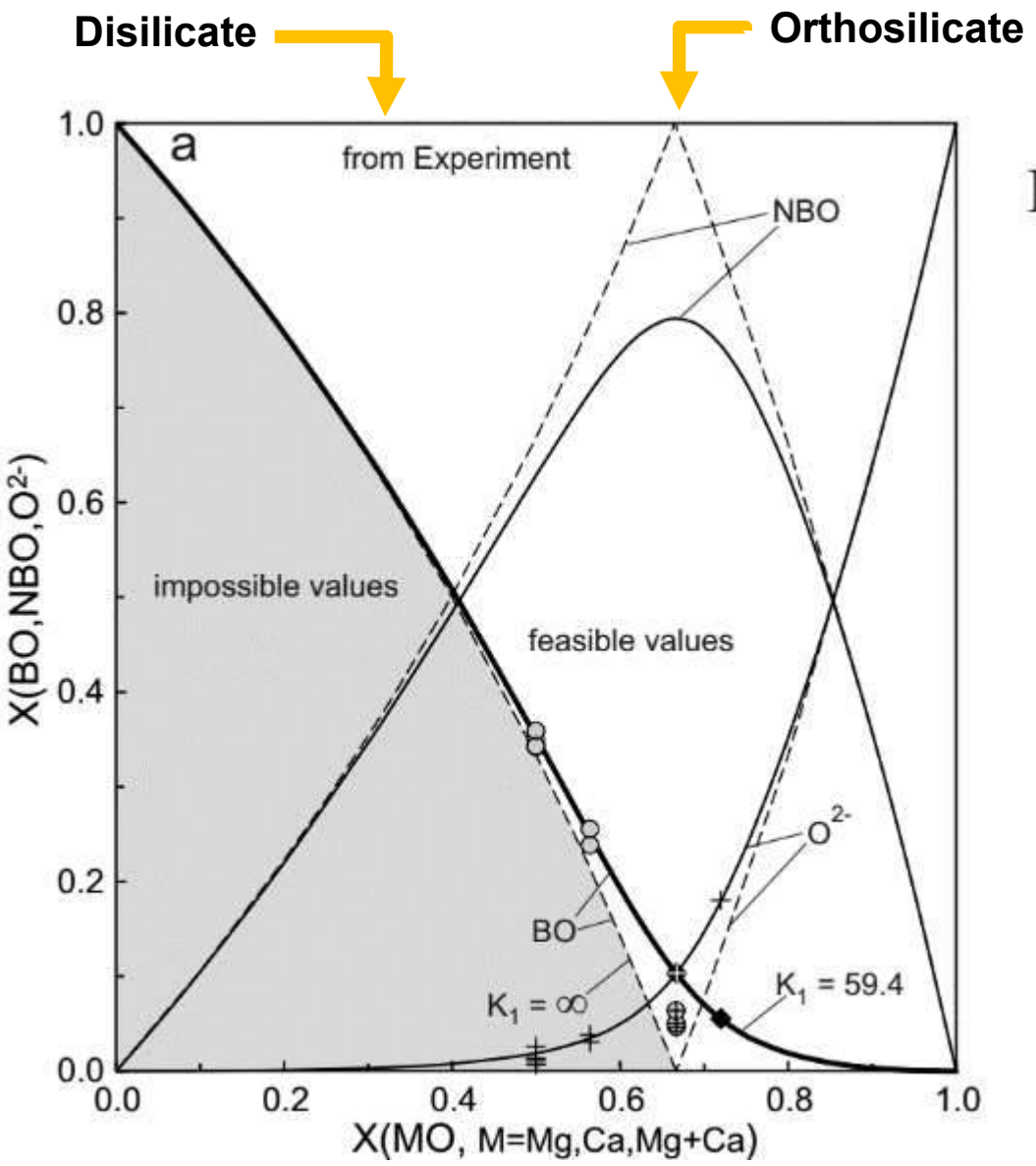
CN_{Si} > 4?

$$BO + O^{2-} \not\rightleftharpoons 2NBO^-$$

The consequences…

If $K_1 < \infty$ than:

- BO will persist to higher MO concentrations
- BO:NBO ratio will be higher than expected as MO increases above disilicate.



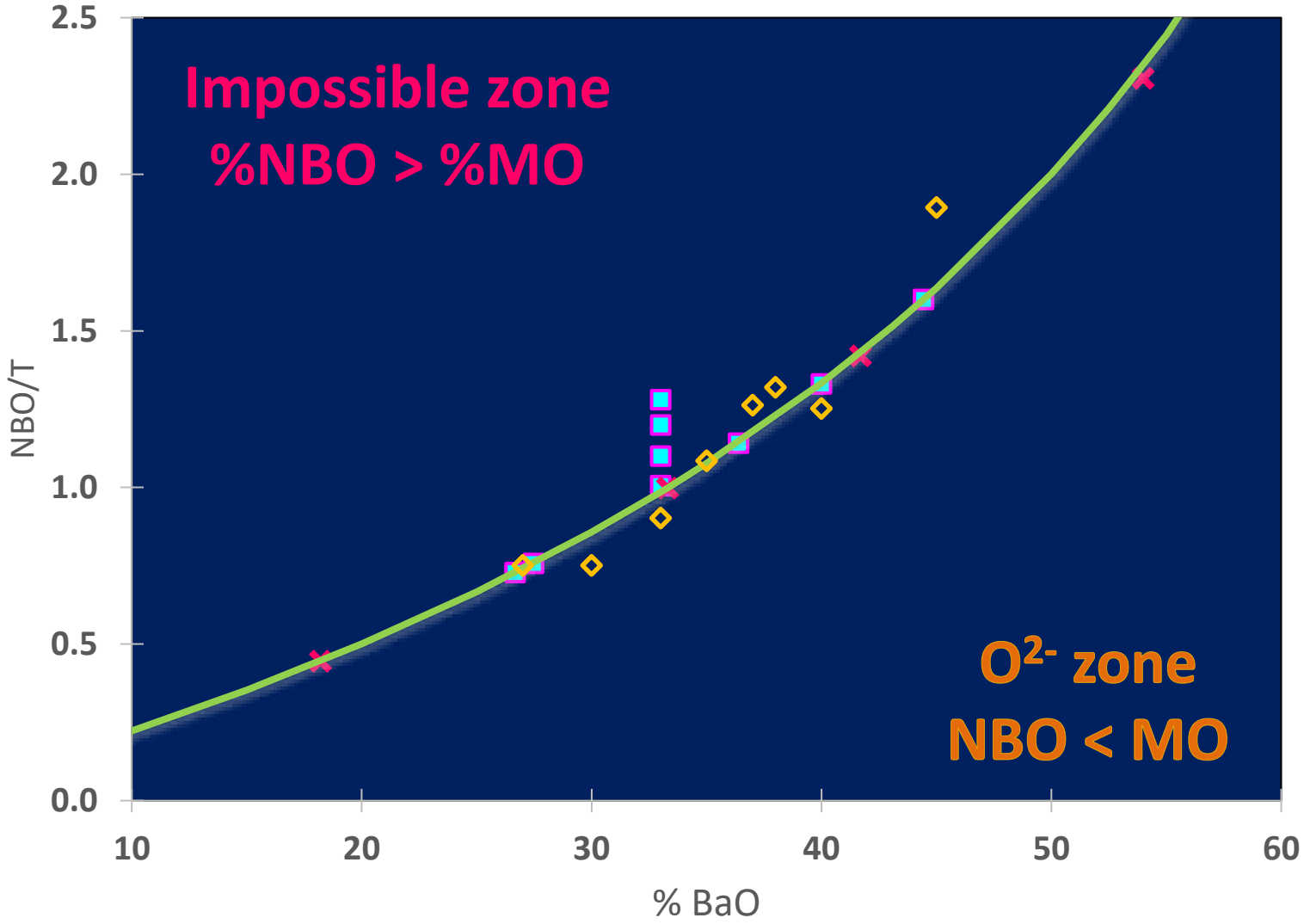
$$K_1 = (NBO^-)^2/[(BO)(O^{2-})]$$

If $K_1 < \infty$ than:

- Q^n will be expected to be more polymerized = higher mean Q^n.

Nesbitt, Bancroft, Henderson, Sawyer, Secco (2015) Am Min. 100:2566-2578.

Polymerization: A test example in the $BaO-SiO_2$ system.

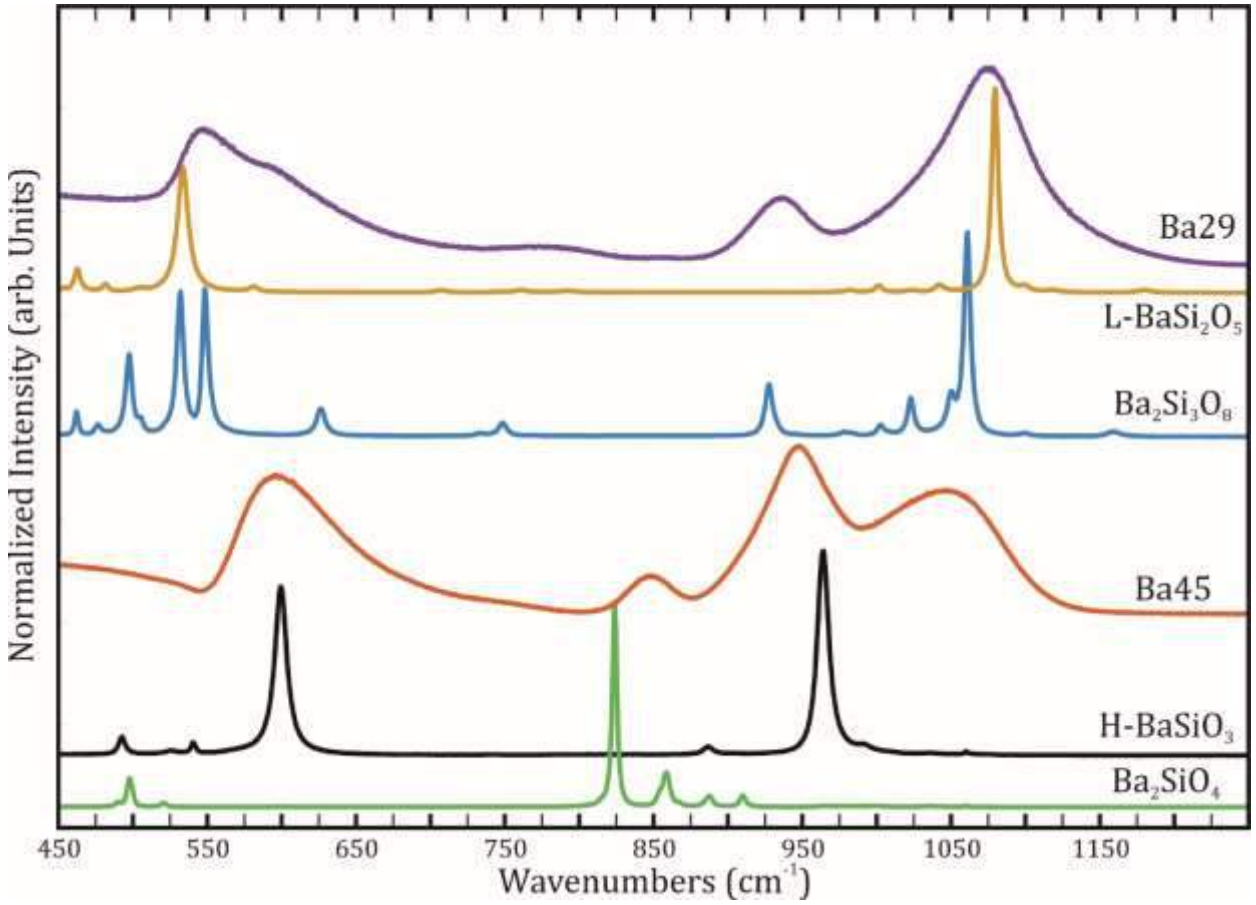


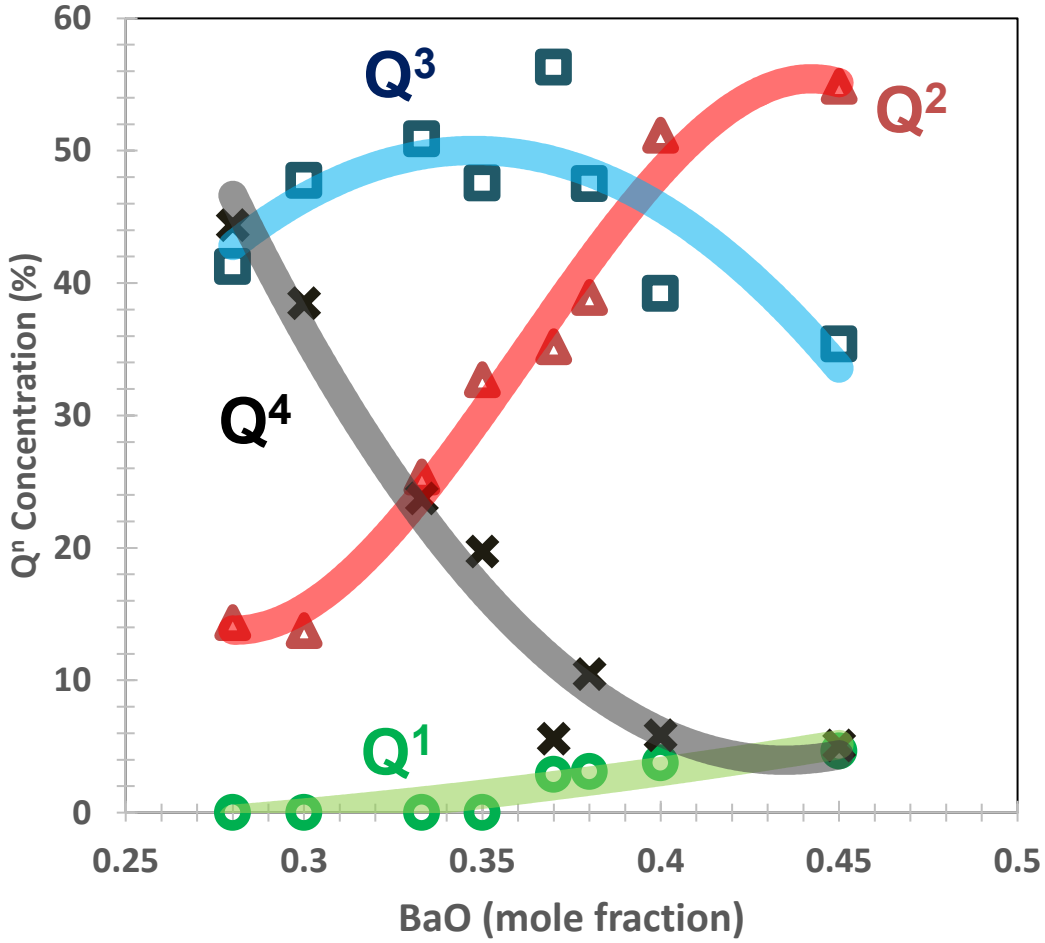
When evaluating the quality of an interpretation it is important to identify (& report) what assumptions were used & evaluate whether they produce a reasonable model?

3 Trends are Observed:

1. Data lying perfectly on the NBO/T theoretical curve. (X & □) → assumed *a priori*.
2. Data at 33% which scatters to higher NBO/T → unconstrained model give unrealistic structural models.
3. Data that scatters around the NBO/T curve. (Orange) → Fit using 'reasonable' parameters scatter within some error about the 'ideal' trend.

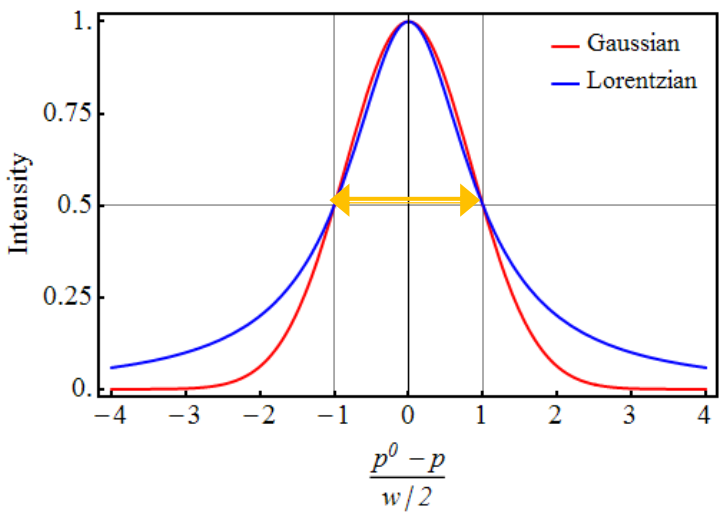
How do we quantify a spectrum?





Moulton, unpublished data.

Peak Parameters: FWHM, Position, Intensity, Area

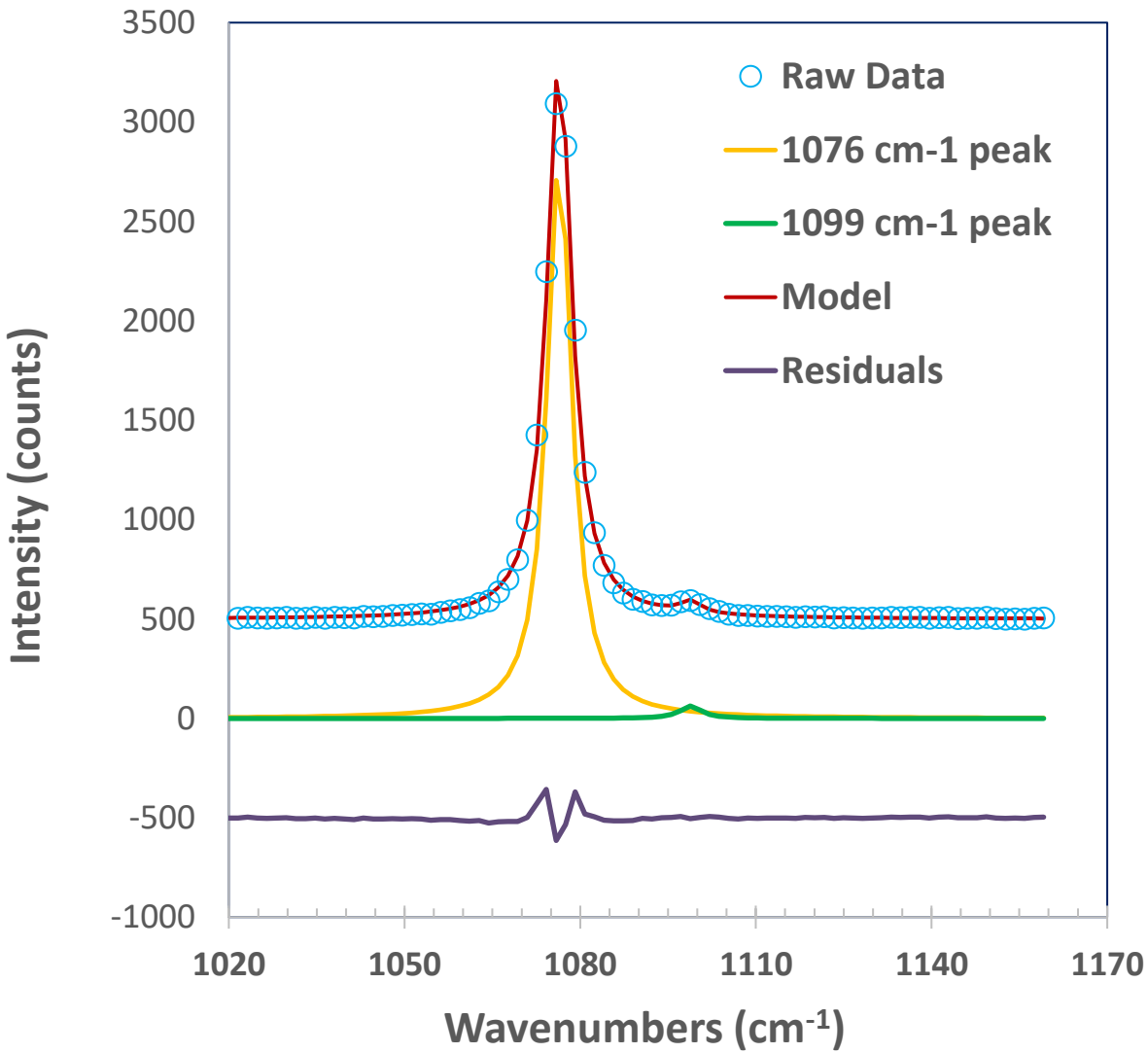


P_0 – center = 0

FWHM = Full-width at half-maximum

$$\xi = \frac{p^0 - p}{FWHM/2}$$

$$I_{Lorentz} = \frac{1}{1+\xi^2} \qquad I_{Gauss} = e^{-Log_e 2 * \xi^2}$$



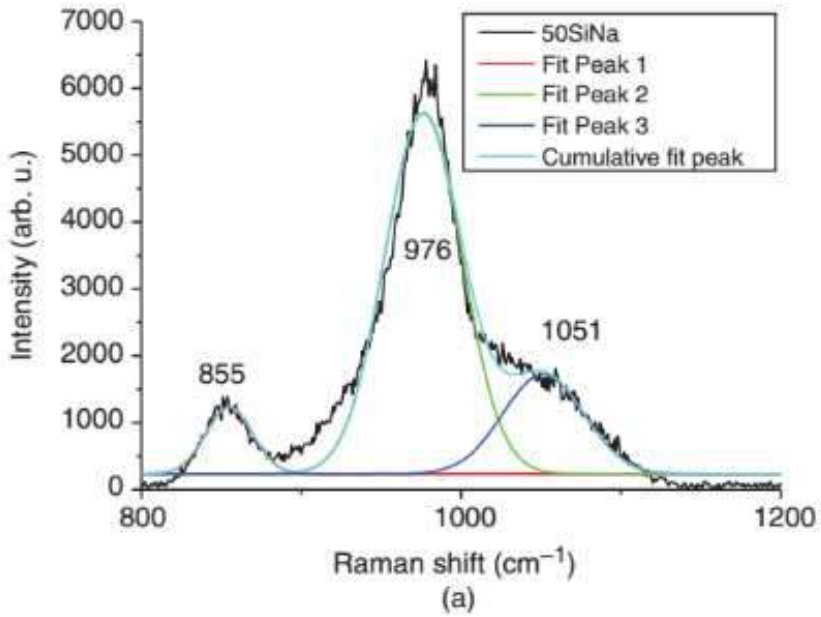
Lorentzian is the nature lineshape for a vibrational mode.

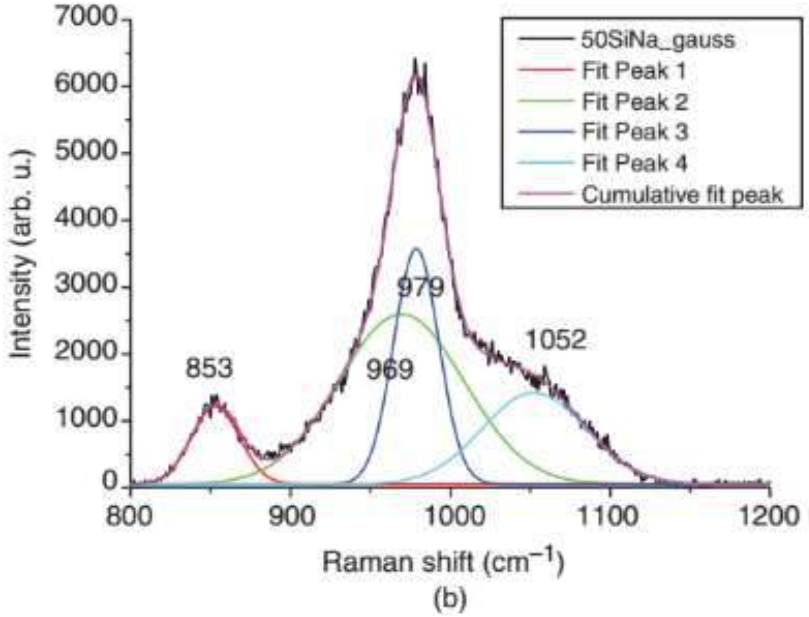
Gaussian is the expected lineshape for a random distribution of sites.

Pseudo-voigt is a combination of Gaussian & Lorentzian → introduces extra fit parameter.

Lineshapes in curve fitting:

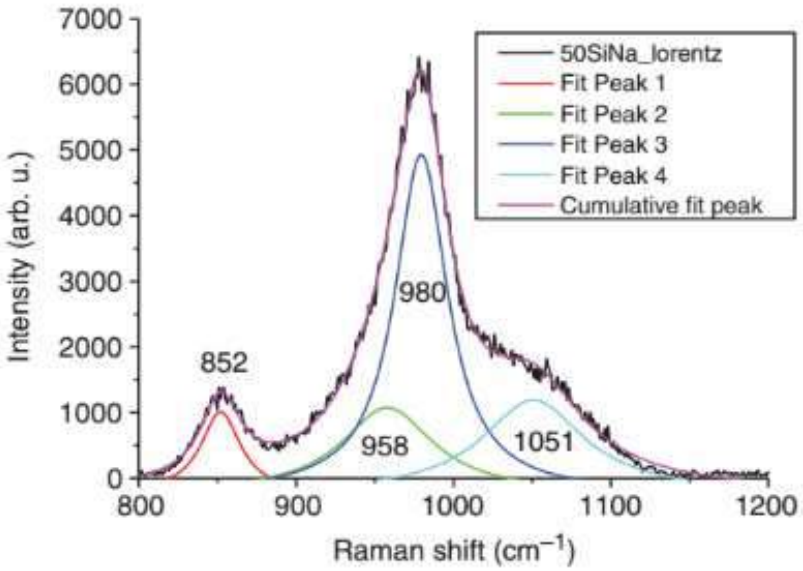
3 contributions
Does not reproduce the spectrum.

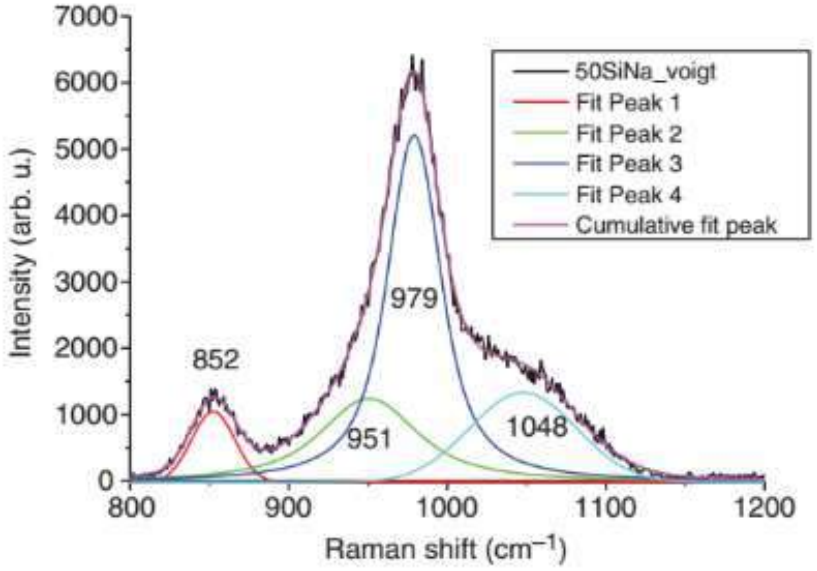




Gaussian, unconstrained peaks are broad, overlap highly, biggest peak is not most intense.

Lorentzian
→ Curve follow envelope = BEST FIT



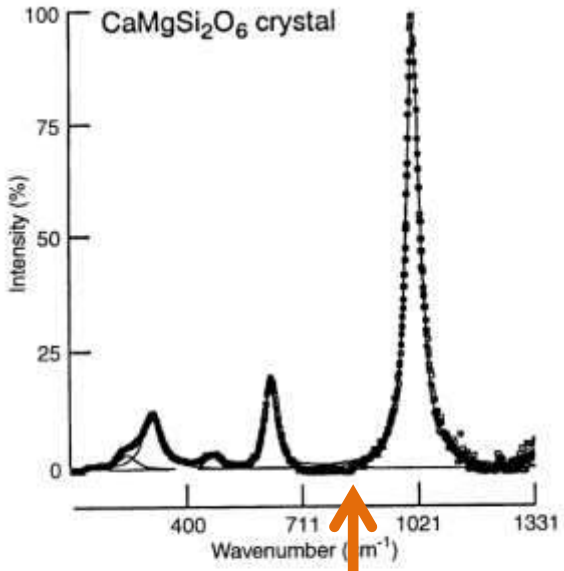


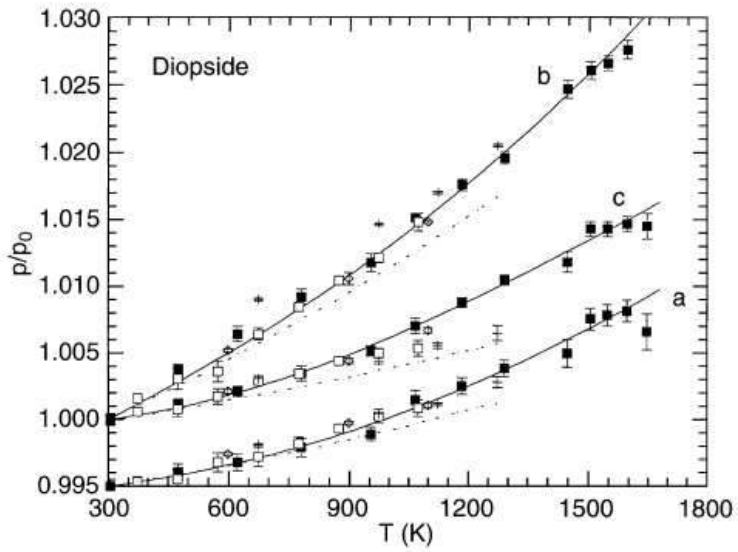
Pseudo-voigt

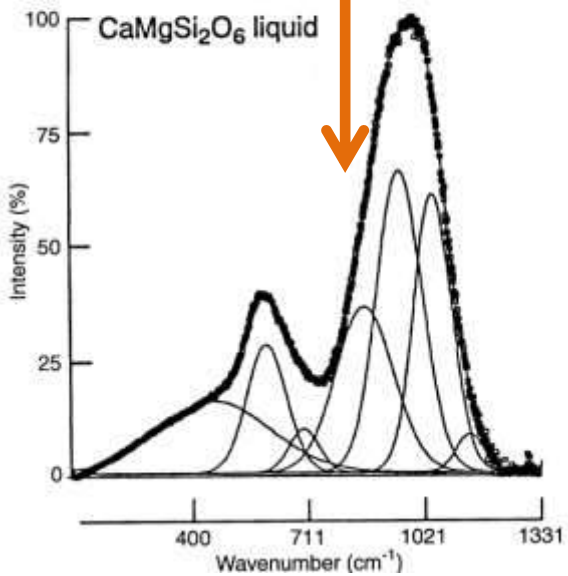
→ Curve follow envelope but broad bands & added fit parameter.

Almiedo & Santos, 2015

What is a physically reasonable constraint?







XRD diffraction can determine crystal lattice parameters.

These parameters can be used to make empirical structural models of Raman bands.

Q^n band position remains from crystal to liquid.

On heating there are 2 effects:

→ Thermal (**homogeneous**) broadening due to lifetime of excitation.

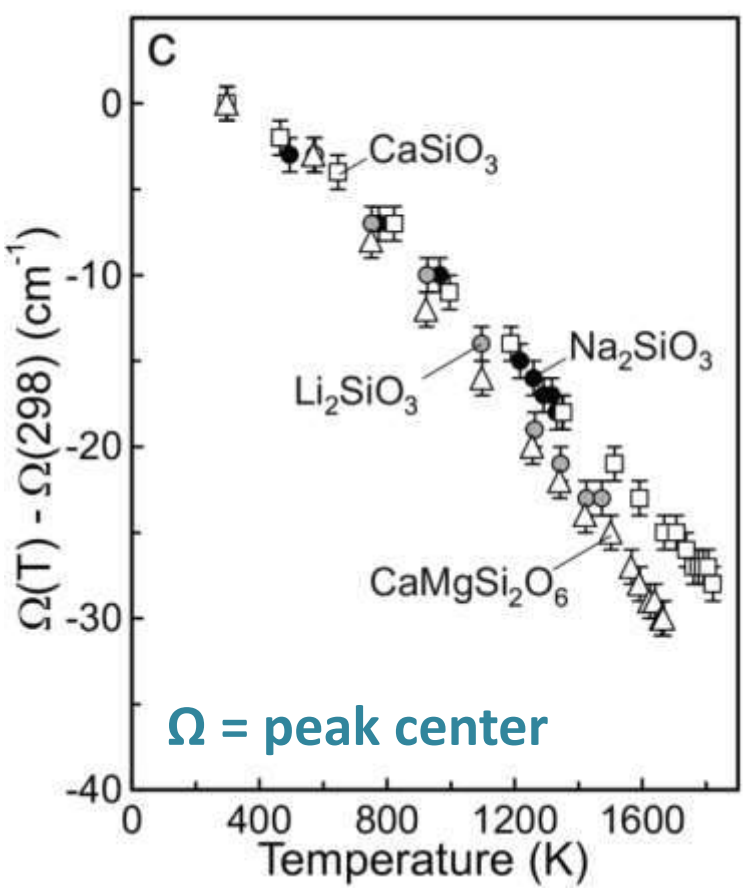
→ **Heterogeneous broadening due to new *sites* or *geometries*.**

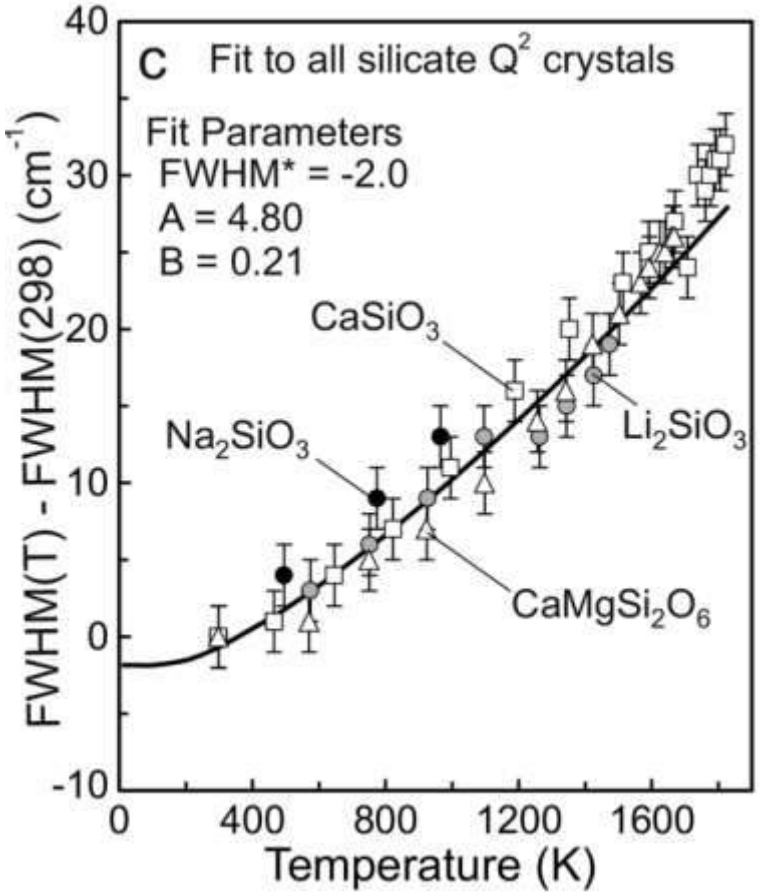
New bands appear just before melting.

May explain anomalous thermal expansion, Cp, density…

Richet, Mysen, Ingrin (1998) Phys Chem Minerals 25:401-414.

What is a physically reasonable constraint? E.g. Q^2 crystals





For Q^2 phases:

- The **center** and **FWHM** have a well defined temperature dependence.
- This is true, regardless of the counter-ion (e.g. Li, Ca, etc.)

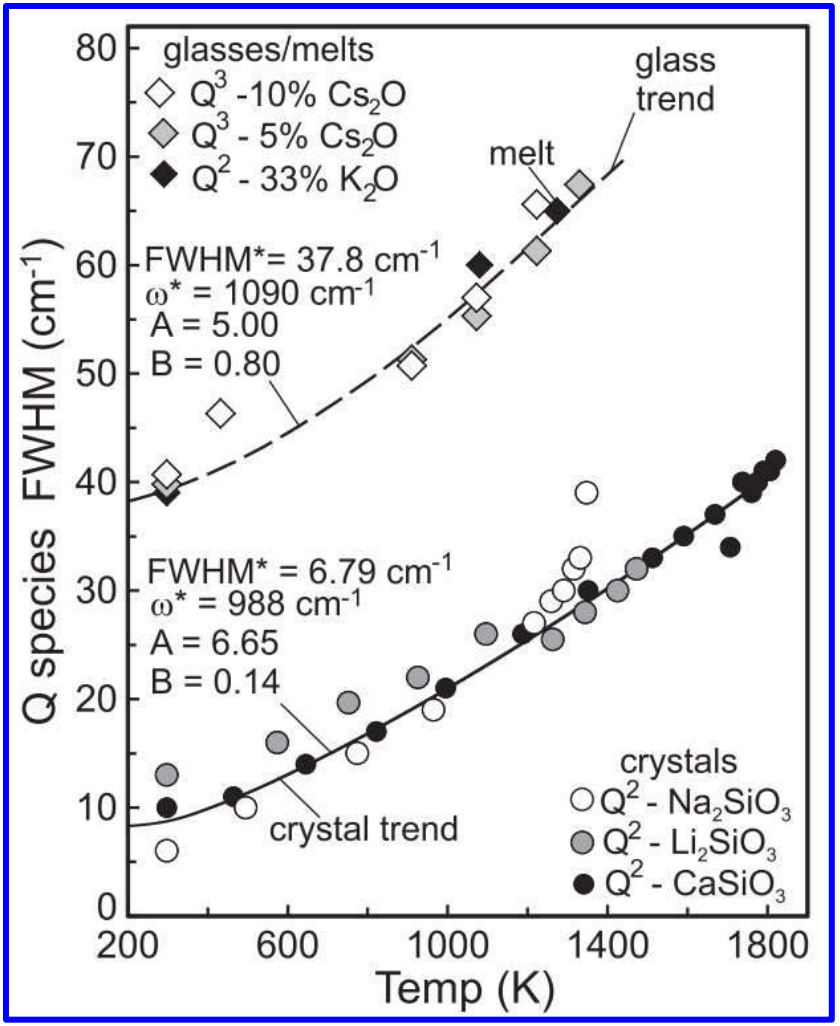
These parameters are transferrable across crystals with known Q^n species.

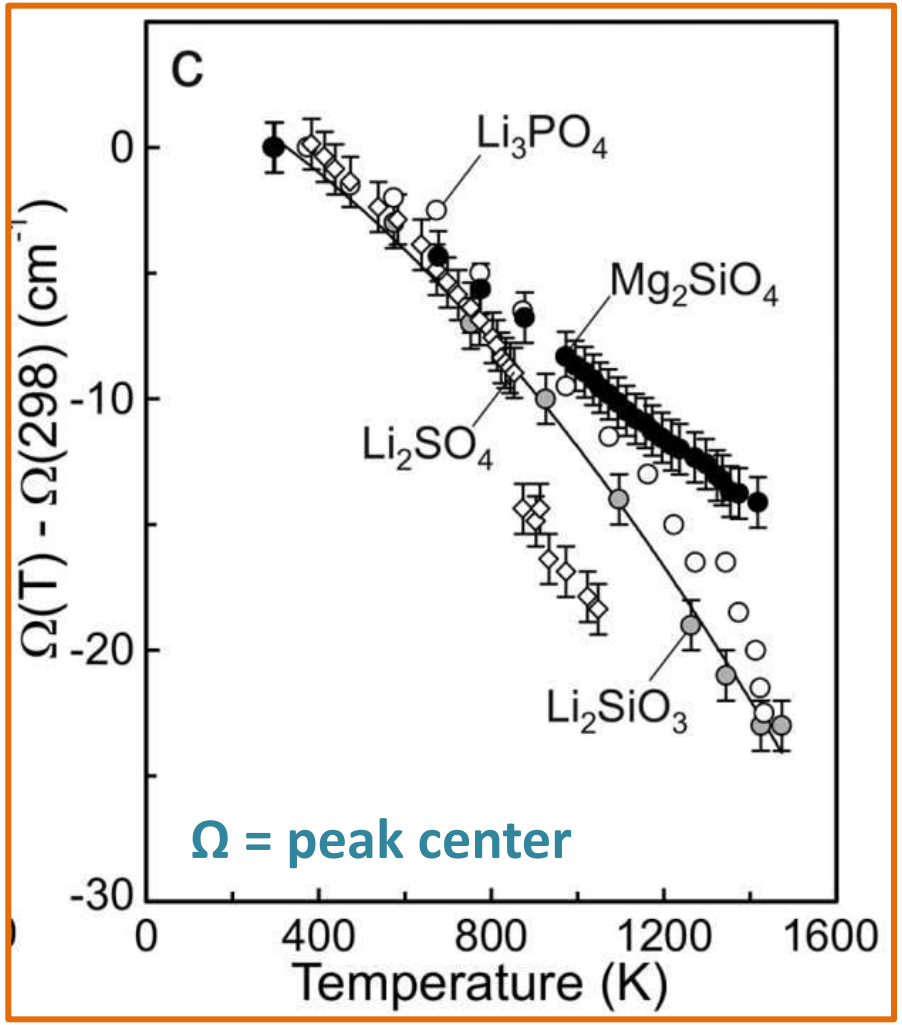
$$\Omega(T) = \Omega^* + C[2/(e^x - 1)] + D[3/(e^y - 1) + 3/(e^y - 1)^2]$$

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

Nesbitt et al., 2018
Am Min. 103:966-976
10.2138/am-2018-6314

Transferability of fit parameters… Phosphates? Sulfates?





For Q^0 phases:

- The **peak shift** and **FWHM** have a well-defined temperature dependence.
- Glass trend follows crystals trend except broadened by ~30 cm^{-1} → $FWHM_{(crystal, Tm)}$

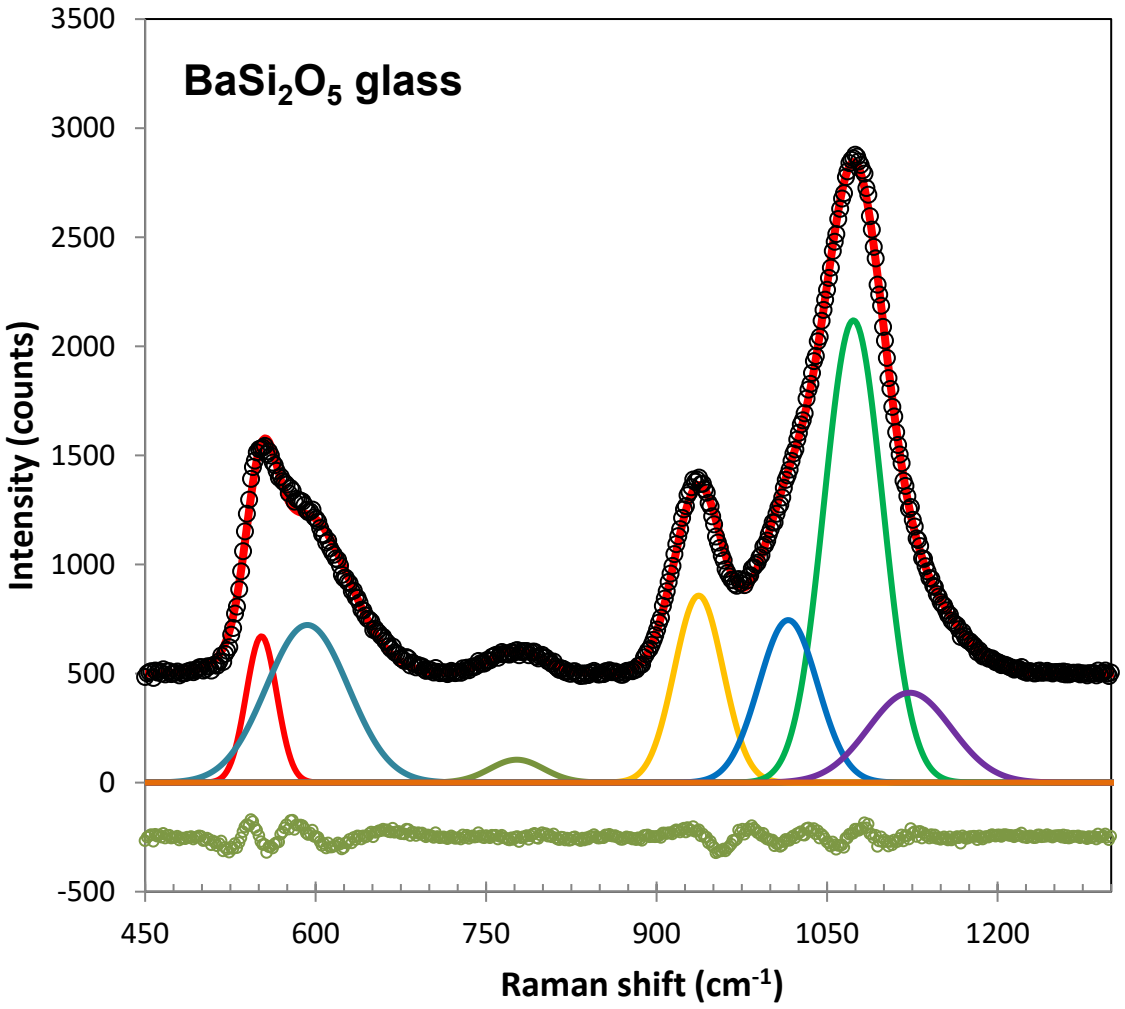
This is also true for phosphates & sulphates!

This needs confirmation for a broader variety of systems & compositions… But:

Nesbitt et al., 2018
Am Min. 103:966-976
10.2138/am-2018-6314

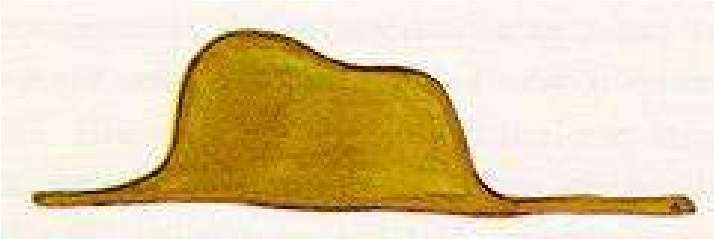
No just any value of peak parameters are '*reasonable*'!
e.g. FWHM >>60 cm^{-1} are unrealistic in all known cases.

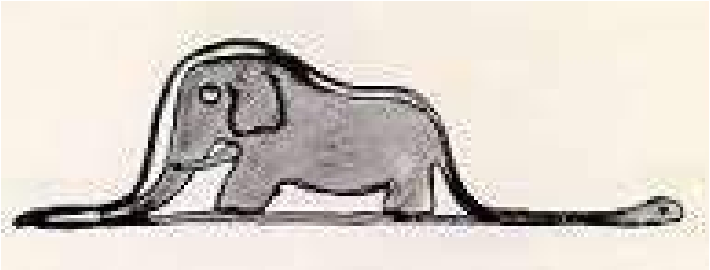
Final thoughts:



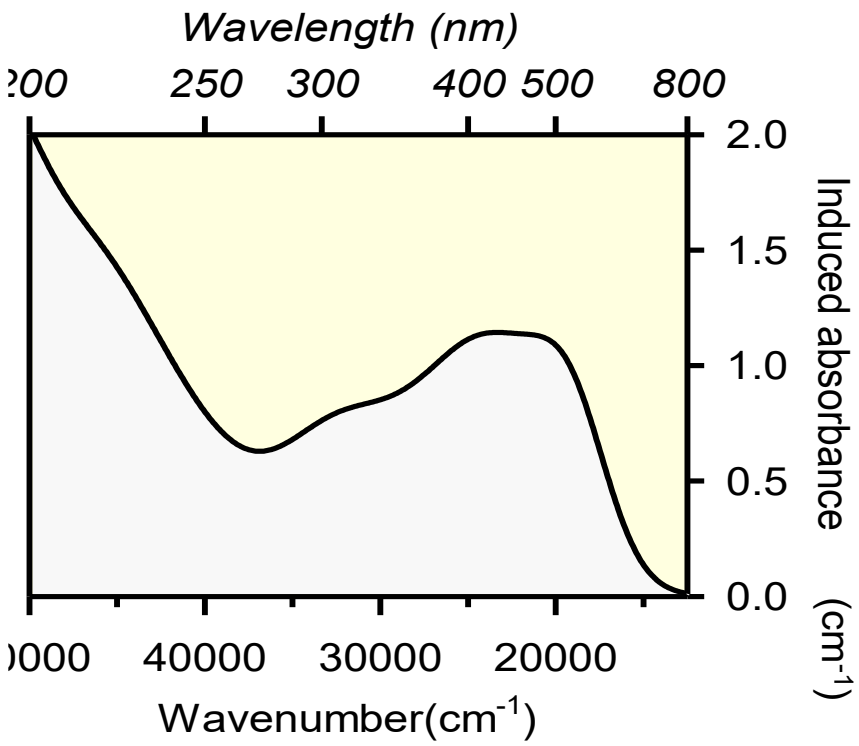
1. **Peak intensities should follow the spectral envelope**
2. Minimum number of peaks should be used **unless there is an explanation** for the extra peaks.
3. **Use a X-P-T-t suite** to characterize the peak behaviors.
4. Test physically realistic peak parameters!

Be humble…





“The little prince”
Antoine de Saint-Exupéry

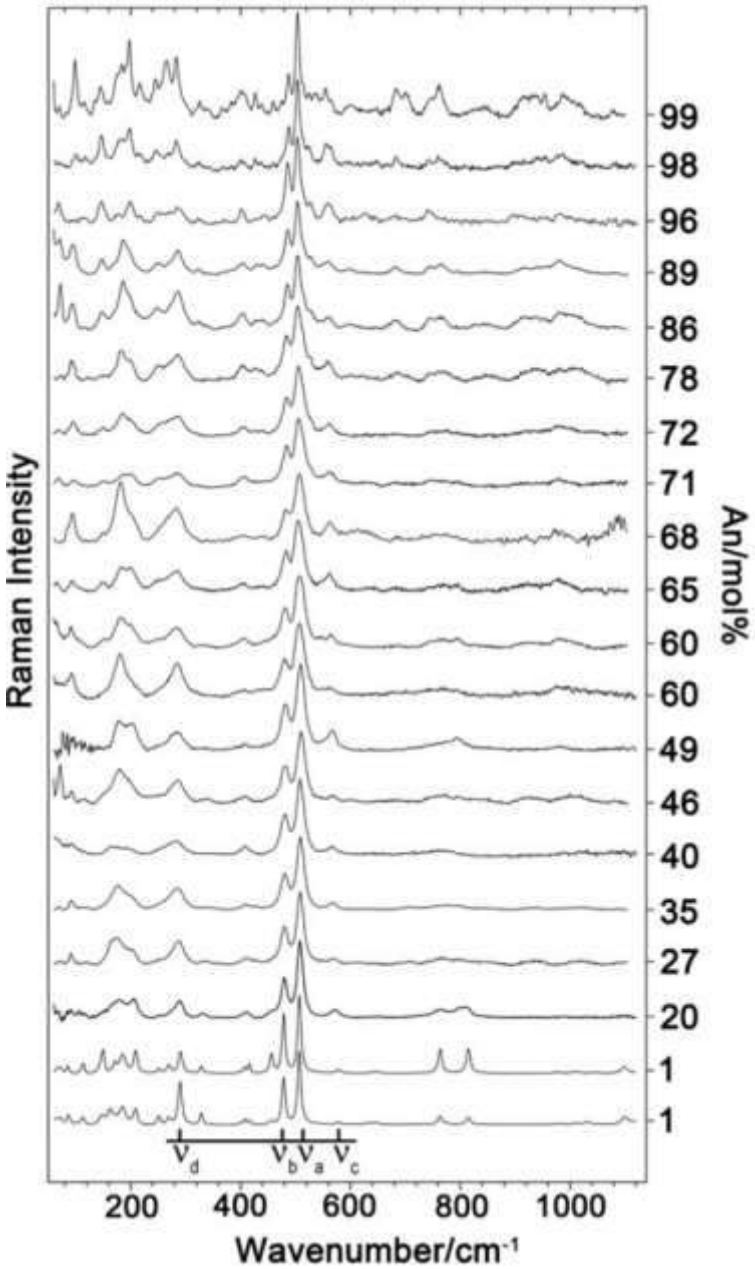


Overview for today:

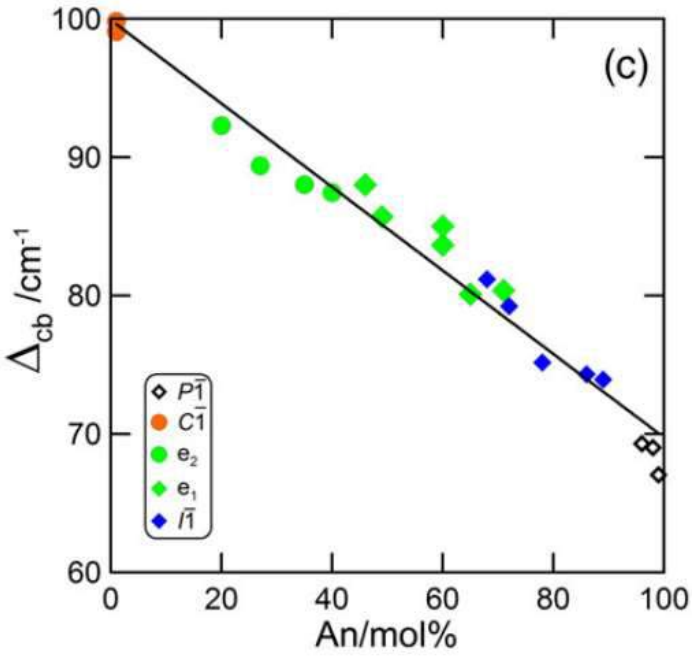
1. Glass versus Crystal structure
2. What is Raman scattering?
3. Glass spectra and how we determine glass structure?
4. Exemplar studies

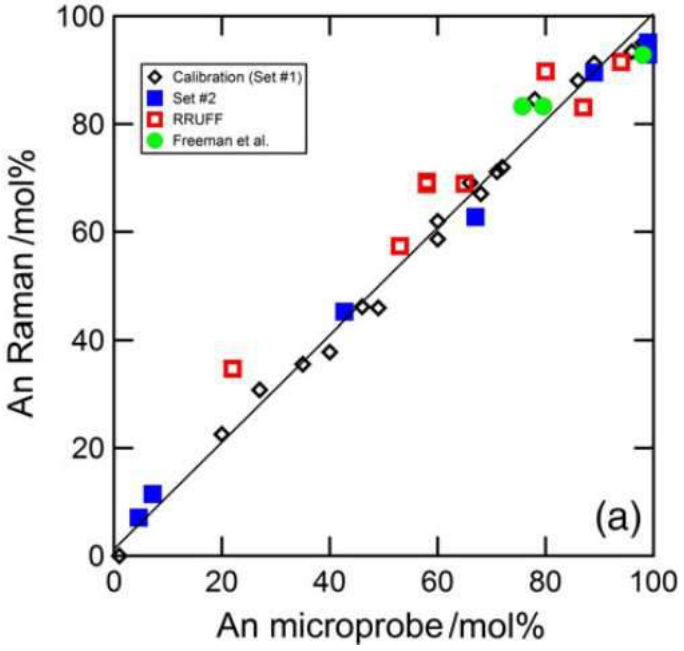
Raman for compositional determination:

Bersani, Aliatis, Tribaudino, et al. (2018)
J Raman Spec. 49:684-698. DOI: 10.1002/jrs.5340



$NaAlSi_3O_8$ (0%) → $CaAl_2Si_2O_8$ (100%)





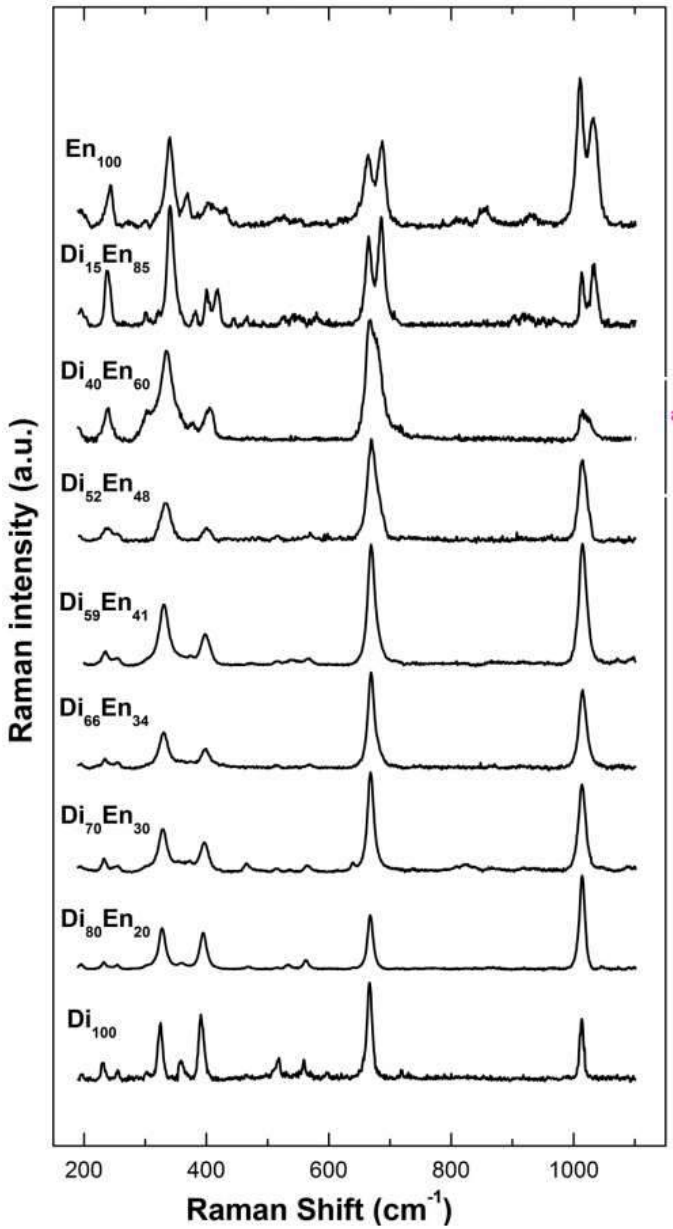
The aluminosilicate *plagioclase* can be determined within <5 mol. % in minutes!

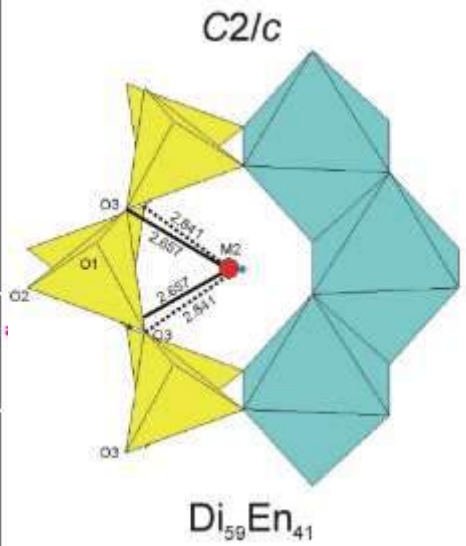
Moreover, the authors report sensitivity to Al-Si ordering, exsolution, incommensurate modulations, and phase transitions are also possible!

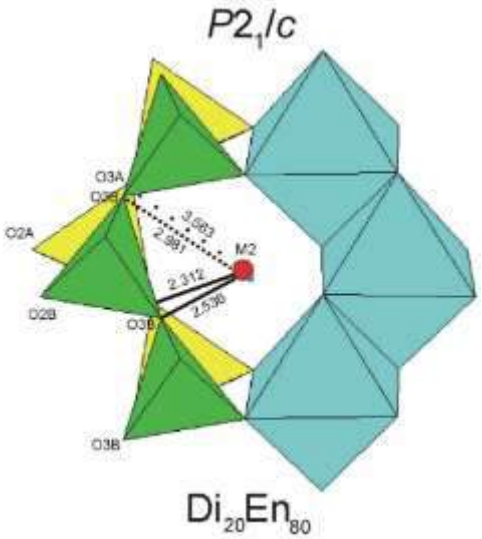
Phase transformation & composition:

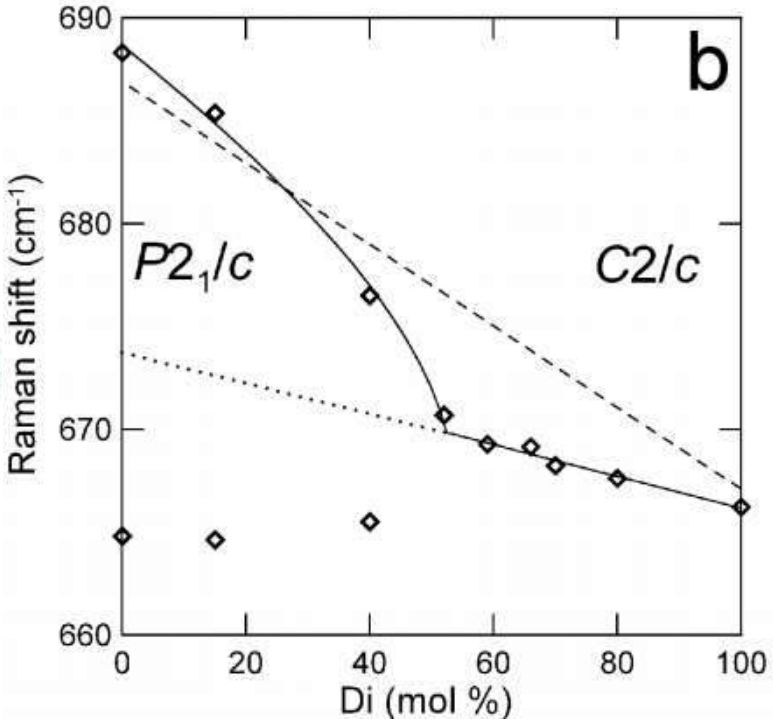
Tribaudino, Mantovani, et al., 2012
Am Min. 97:1339-1347. Doi:10.2138/am.2012.4057

$CaMgSi_2O_6$ → $Mg_2Si_2O_6$









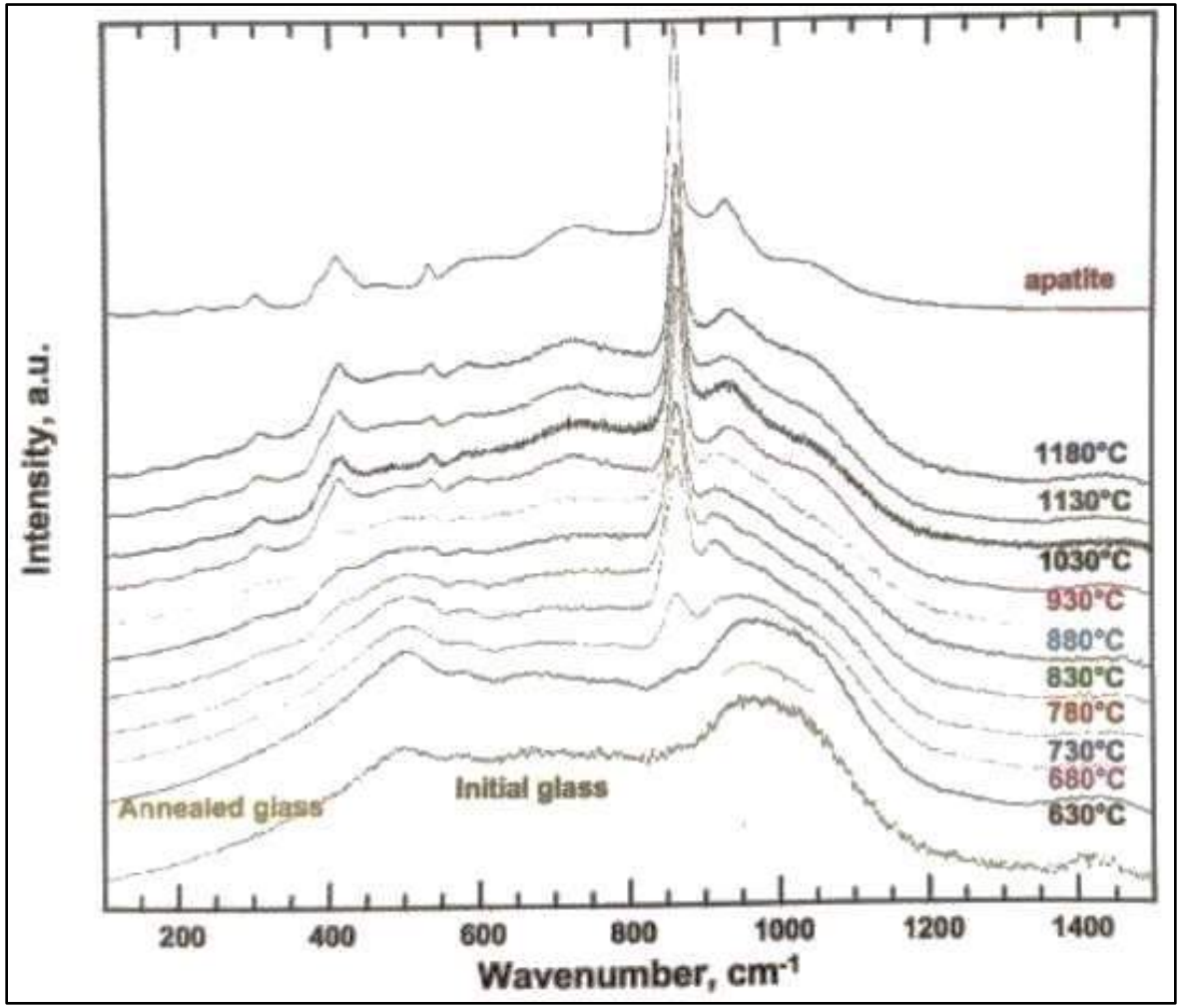
The diopside content of $CaMgSi_2O_6$ vs. $Mg_2Si_2O_6$ can easily be determined (<5 mol. %)!

With phase changes easily identified by new bands or change in shift.

Many compositional suites have already been calibrated… more phases coming each year!

GC: Apatite growth in borosilicate glass

Spectra after 2 h annealing at temperature:



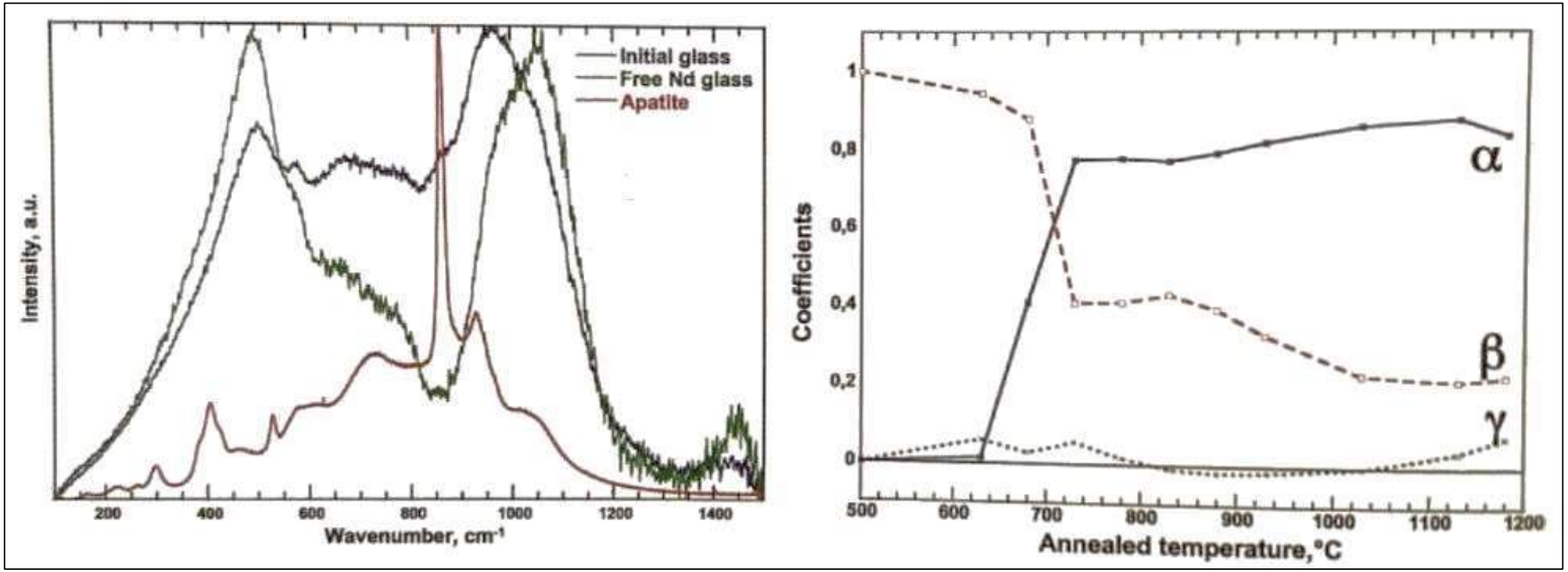
Glass-ceramic as a host for nuclear waste

- Nd is used as a “model” fission product.
- If the fission products can be concentrated in a crystalline phase (e.g. apatite) the GC may be used to safely store this waste material.
- Can Nd been removed from the glass (stored safely)?

De Ligny & Neuville, 2017 Chapter 12 in From Glass to Crystal

GC: Nuclear waste apatite in borosilicate glass

$$I = \alpha I_{apatite} + \beta I_{initialglass} + \gamma I_{glasswithoutNd}$$



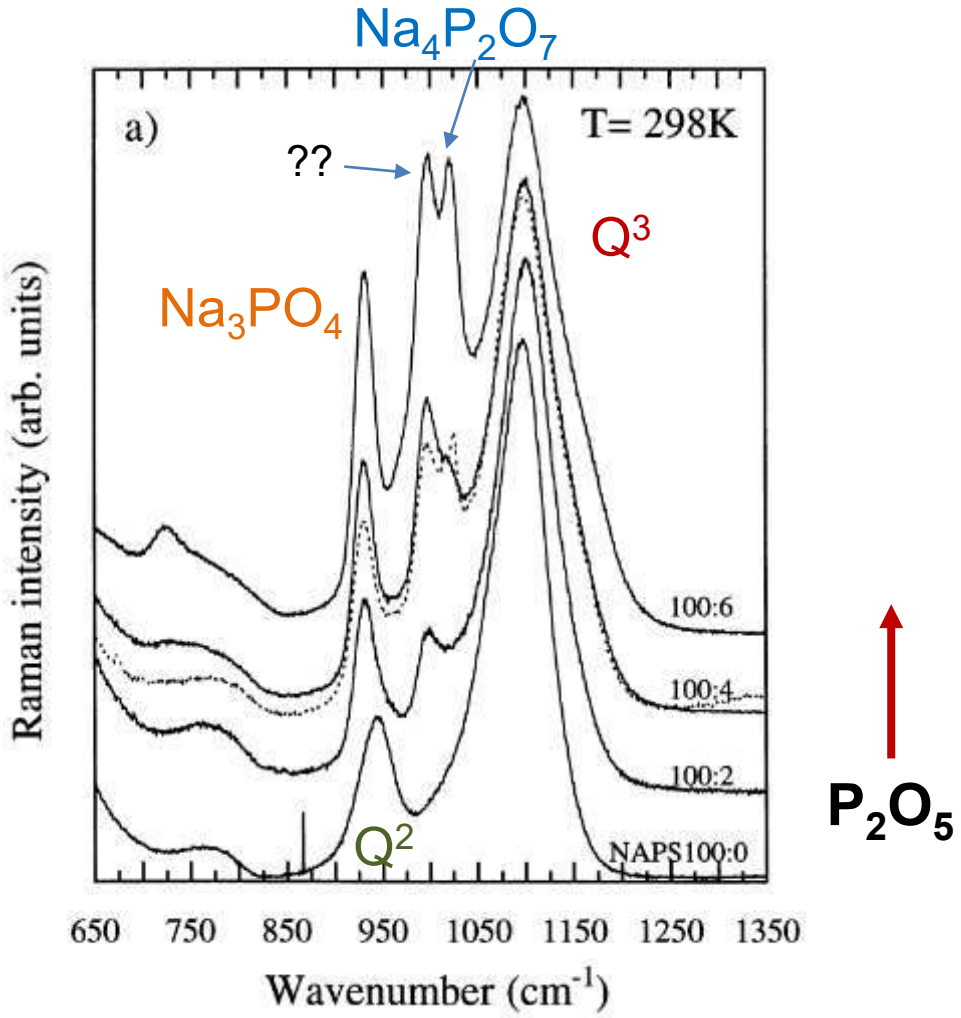
Yes, apatite was stabilized but Nd was not partitioned into apatite suggesting this would not be a good nuclear waste glass.

De Ligny & Neuville, 2017 Chapter 12 in From Glass to Crystal

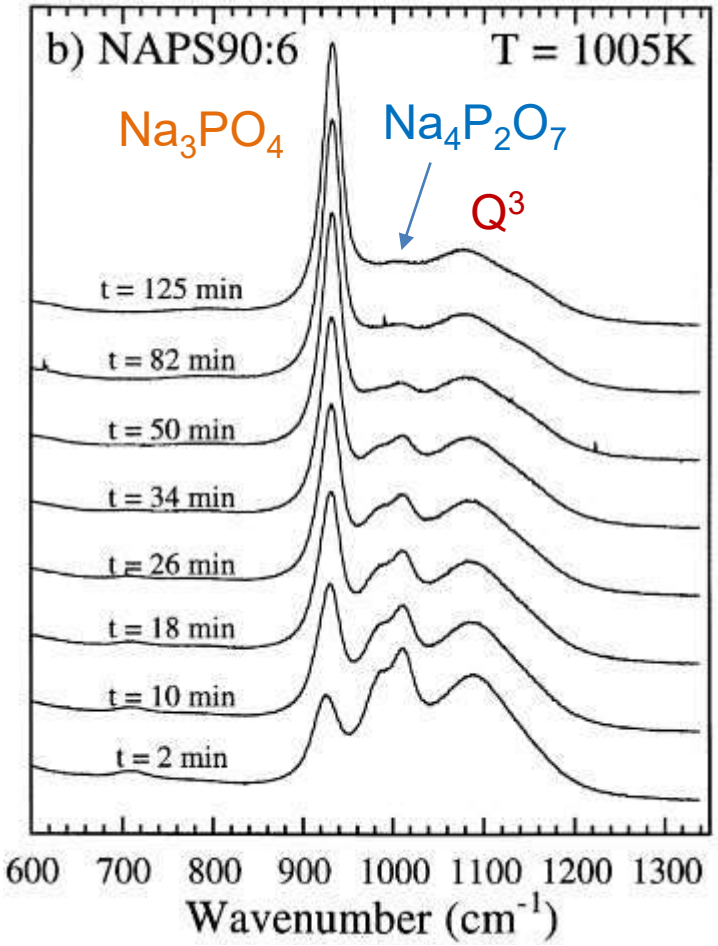
Phase separation in P-doped NAPS glass

Toplis M, Reynard B (2000)
JNCS. 263&264: 123-131

$0.9Na_2O\text{-}0.01Al_2O_3\text{-}2SiO_2{:}xP_2O_5$

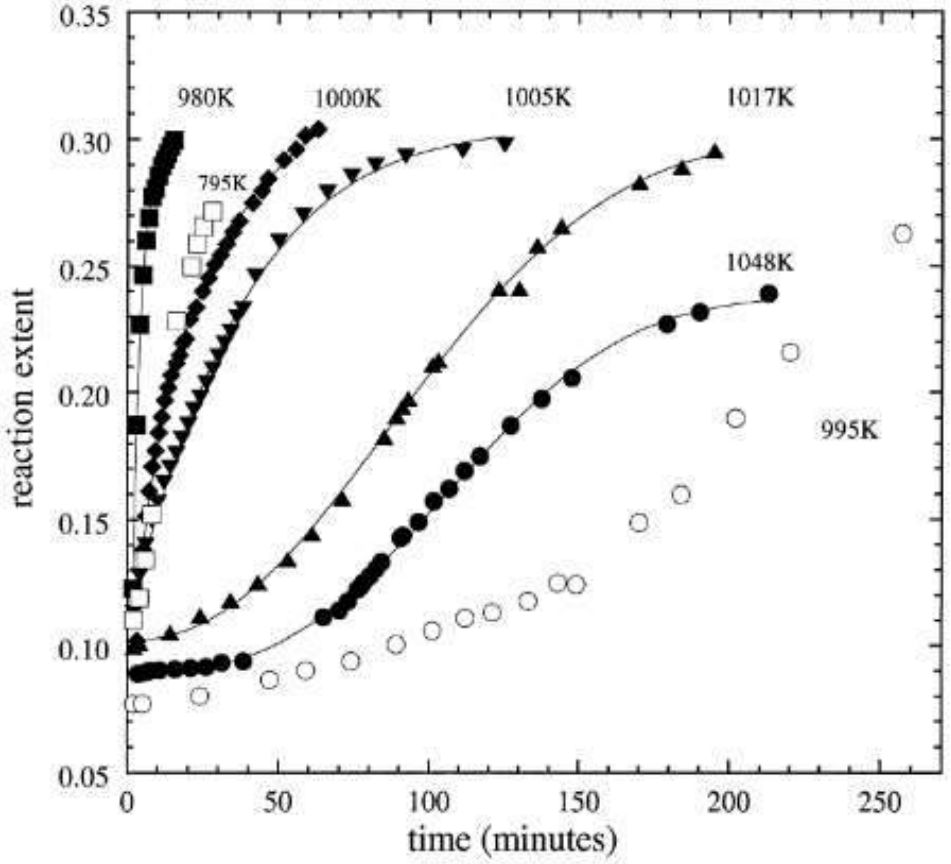


Noticed structural changes with P-dopant concentration & quench-rate



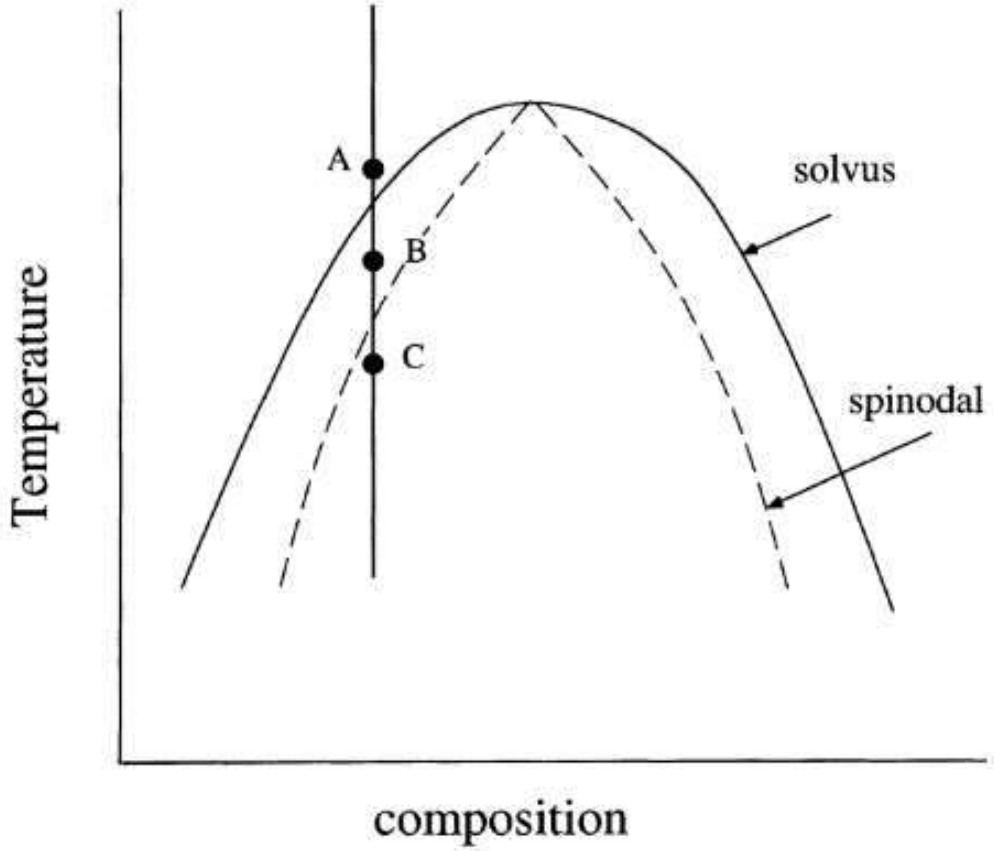
Phase separation in P-doped NAPS glass

Toplis M, Reynard B (2000)
JNCS. 263&264: 123-131



At high T → crystallization

At low T → spinodal decomposition

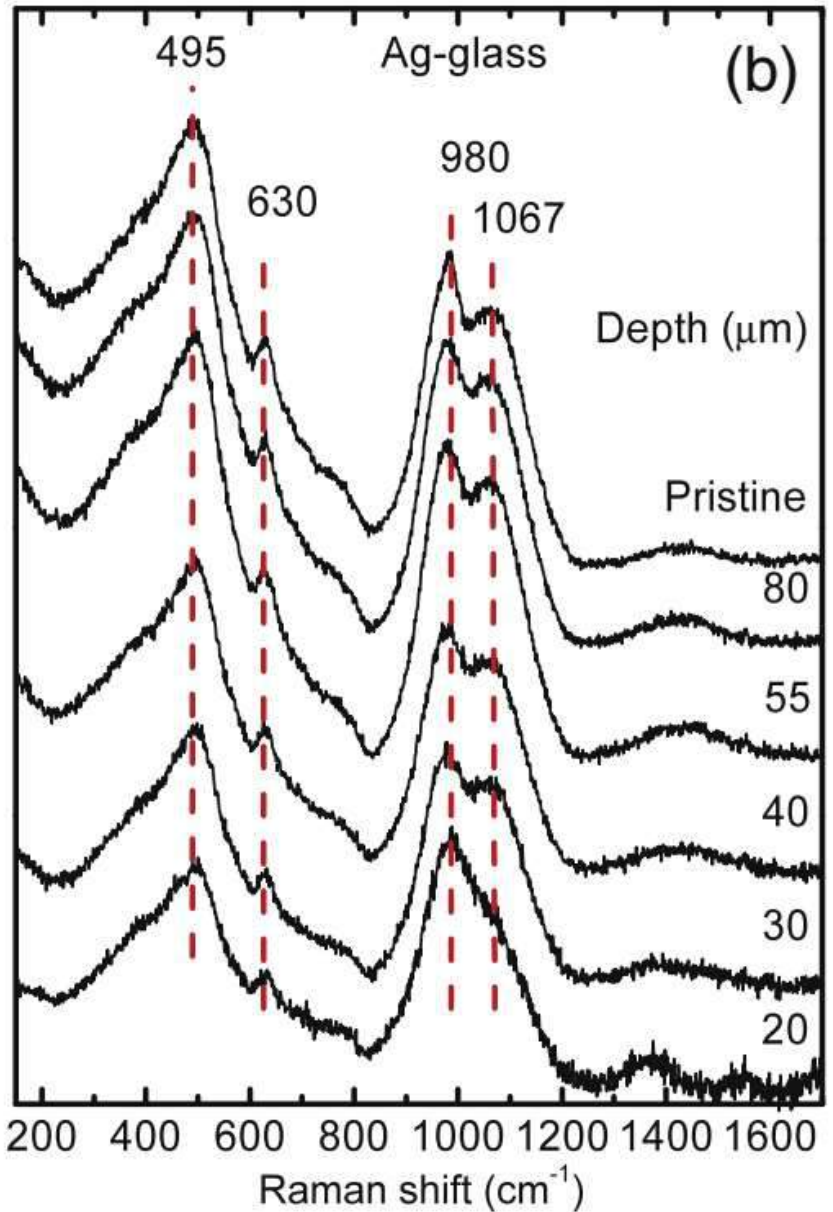


The Avrami eq. $$X = 1 - \exp(-kt^n),$$

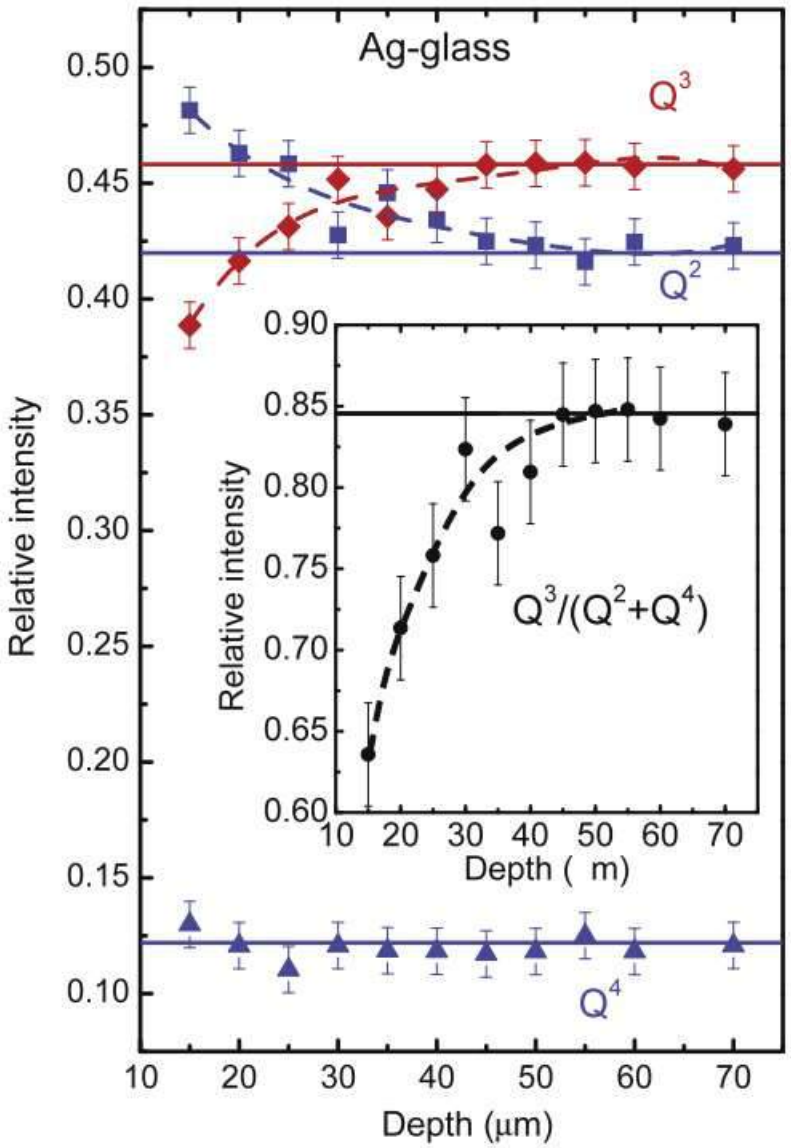
X = extent of reaction
K = the rate constant
n = the 'Avrami' exponent
When n is >2 it suggests crystallization; n = 1 for spinoidal decomposition

Ion exchange effects in $(SiO_2)_{60}(B_2O_3)_{10}(Al_2O_3)_6(Na_2O)_{20.2}(ZrO_2)_{3.7}(Sb_2O_3)_{0.1}$

Glass in a bath of 5 mol. % $AgNO_3$ at 340°C for 3 hrs.



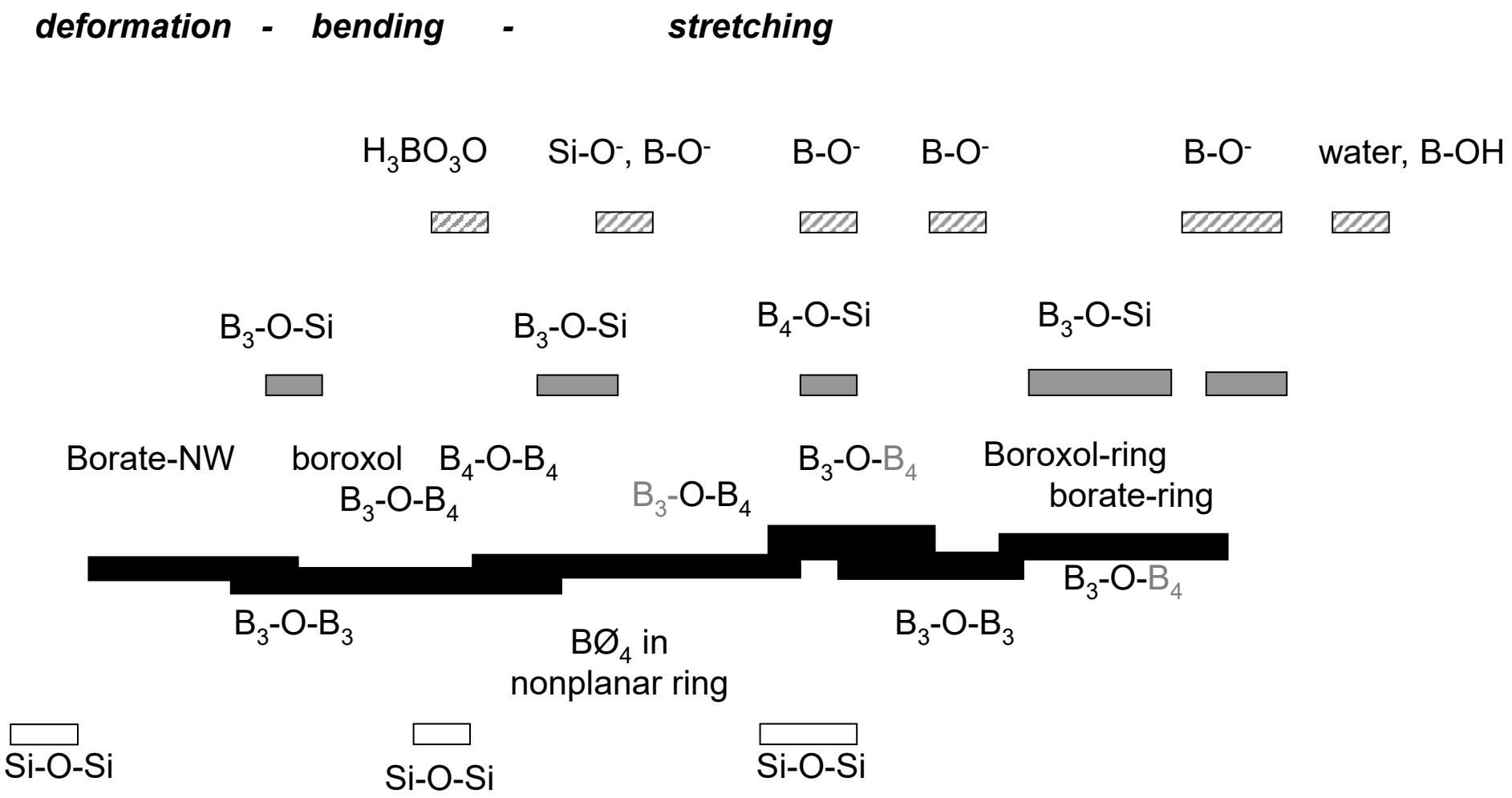
Exchange of Ag^+ ions for Na^+ ions in the glass causes not only replacement but also polymerization!



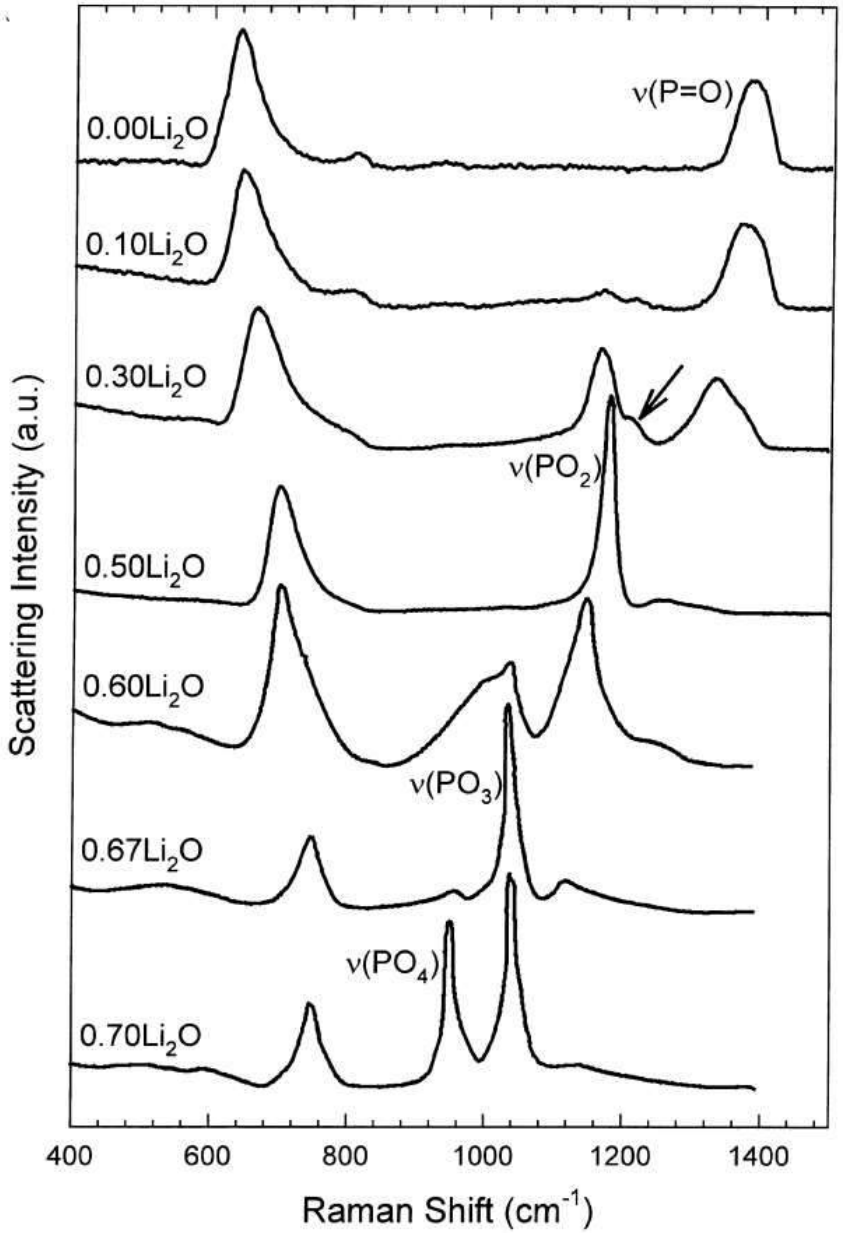
Stavrou, Palles, Kamitsos, et al., (2014) JNCS. 401:232-236.

Raman bands in Na-B-2Si

Problems with band overlaps:



How do silicates compare to phosphates?



P^{5+} in tetrahedron has an double bond O → does not form P-O-P bonds.

P=O prevents Q^4 species from forming. **Only Q^0-Q^3**

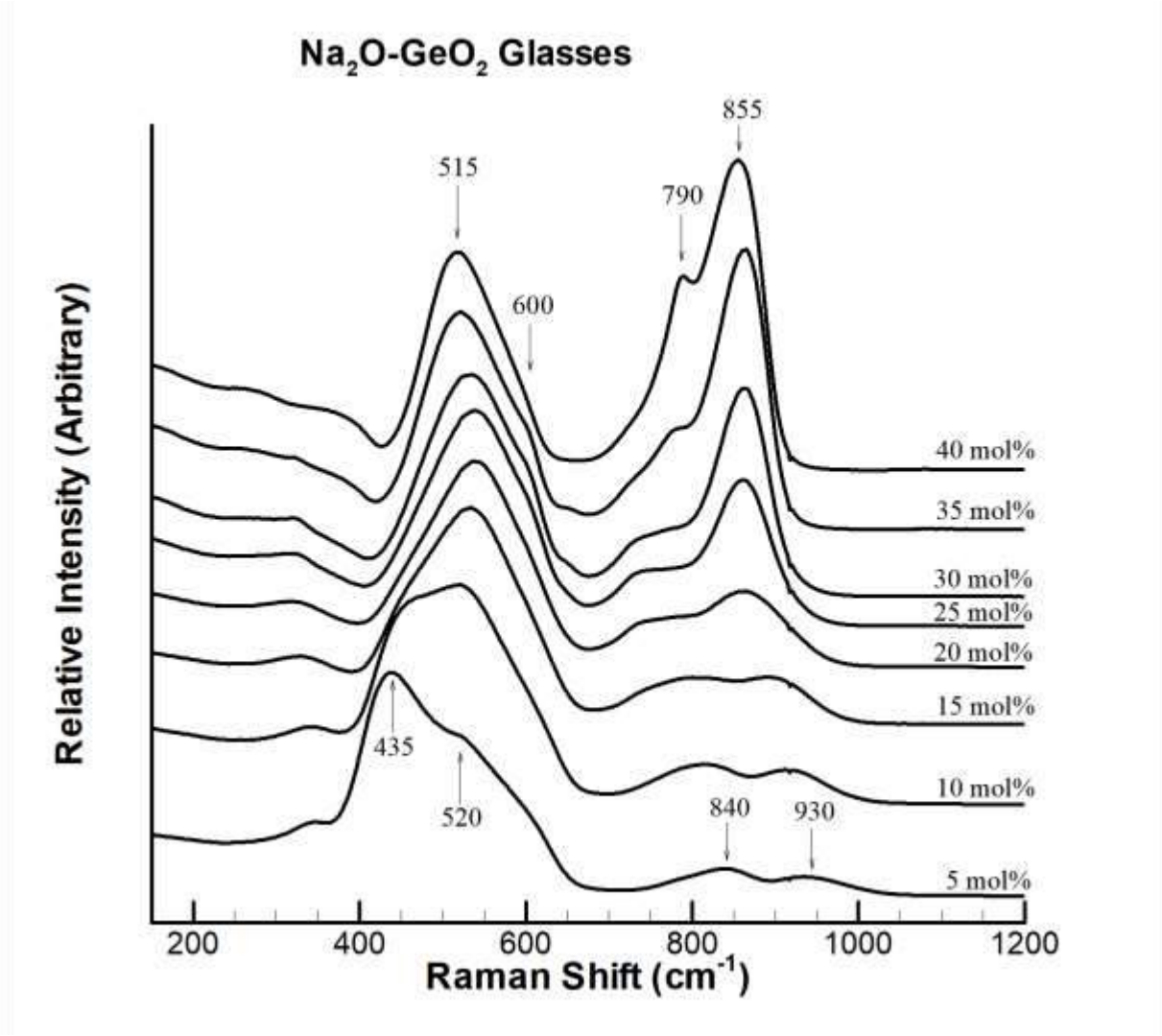
Unlike silicates, phosphates readily form glasses over a wide range of compositions from orthophosphate to pure P_2O_5.

Otherwise, the trends for silicates are found for phosphate glasses.

All the concepts above are transferrable broadly to tetrahedral-based glasses!

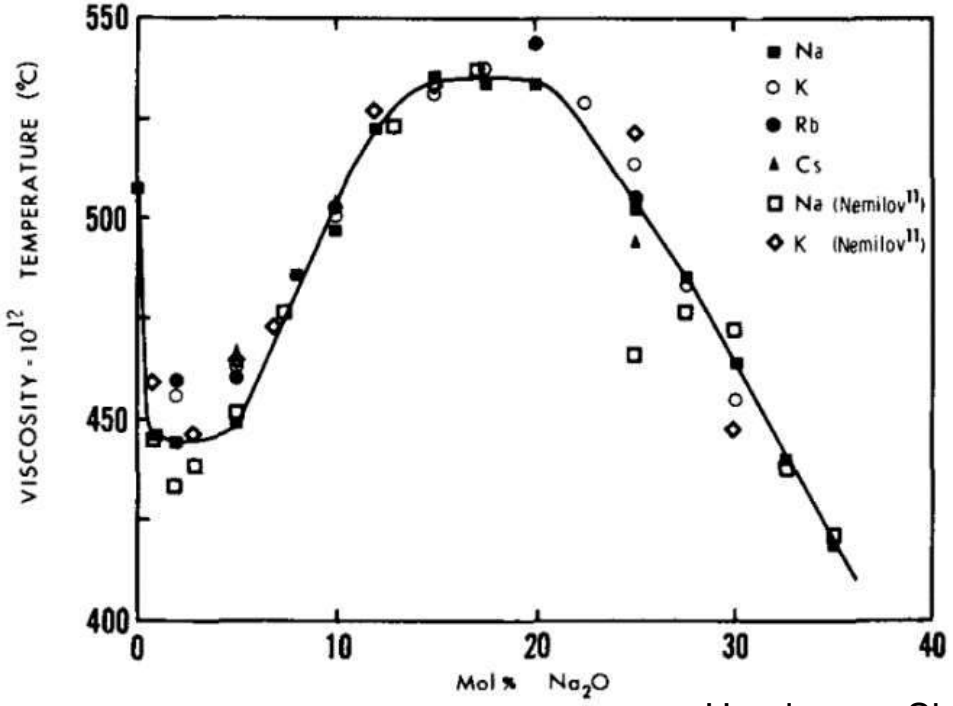
Brow RK (2000) Review: The structure of simple phosphate glasses. JNCS. 263&264:1-28

Na_2O-GeO_2 Glasses: Also analogous to Si but $CN_{Ge} > 4$



Spectral changes correlate with density, T_g, viscosity, etc…

- Low Na2O <20 mol. %, Ge CN changes.
- Q^3 formation at ~20 mol. %
- Q^2 formation ~35 mol. %
- Changes correlate with viscosity changes:



Henderson; Shelby, 1974

Summary

1. Raman scattering involves a frequency change in the scattered light corresponding to the vibrational frequency of the atom(s).
2. The application to any solid, liquid, glass, even *in situ* during reactions / extreme conditions.
3. Excellent probe of amorphous solids / SCL.
4. **Current Goal: Test structural models (generated form curve fitting) to produce predictive structure-property models.**

Acknowledgements

Some slides were inspired and borrowed from other teachers:

Grant Henderson, University of Toronto, Canada

Doris Möncke, Alfred University, USA

Daniel Neuville, IPGP-CRNS, France

J. Dubessy, University of Lorraine, France

Many figures are from my work, published or under-review.

Whenever figures and photographs, from either literature or internet, where used I have tried to acknowledge the respective sources on the slides – though older slides might still lack full references.

سپاس از شما! Thank-you! Obrigado!

FAPESP

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ufscar

References

Databases for Raman spectra:

RRUFF - **Lafuente** B., Downs R. T., Yang H. and Stone N. (2015) *The power of databases: the RRUFF project.* eds. T. Armbruster and R. M. Danisi, W. De Gruyter.

Glass (Definition & Structural overview):

Definition: **Zanotto** ED, Mauro JC (2017) The glassy state of matter: Its definition and ultimate fate. J. Non-Crystalline Solids. 471:490-495.

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