

Source

- All the manufacturers use a **heated ceramic source**.
- The composition of the ceramic and the method of heating vary but the idea is always the same, the production of a heated emitter operating at as high a temperature as with a very long life.
- The manufacturers tend to go for either a conducting ceramic or a wire heater coated with ceramic.

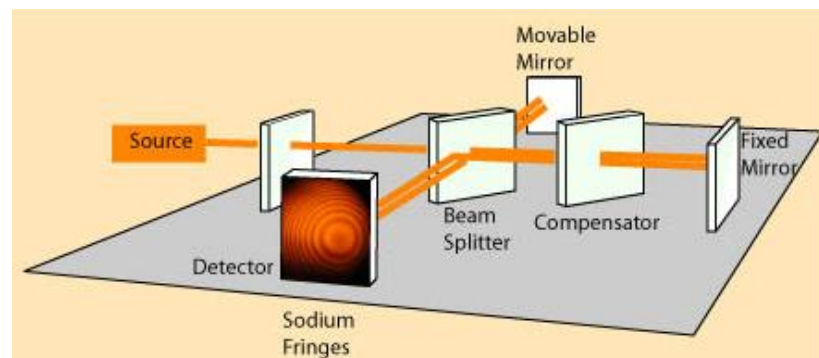
Interferometer: heart of the instrument

- This device splits and recombines a beam of light such that the recombined beam produces a wavelength-dependent interference pattern or an **interferogram**. The Michelson interferometer is most commonly used.

The Michelson interferometer produces interference fringes by splitting a beam of monochromatic light

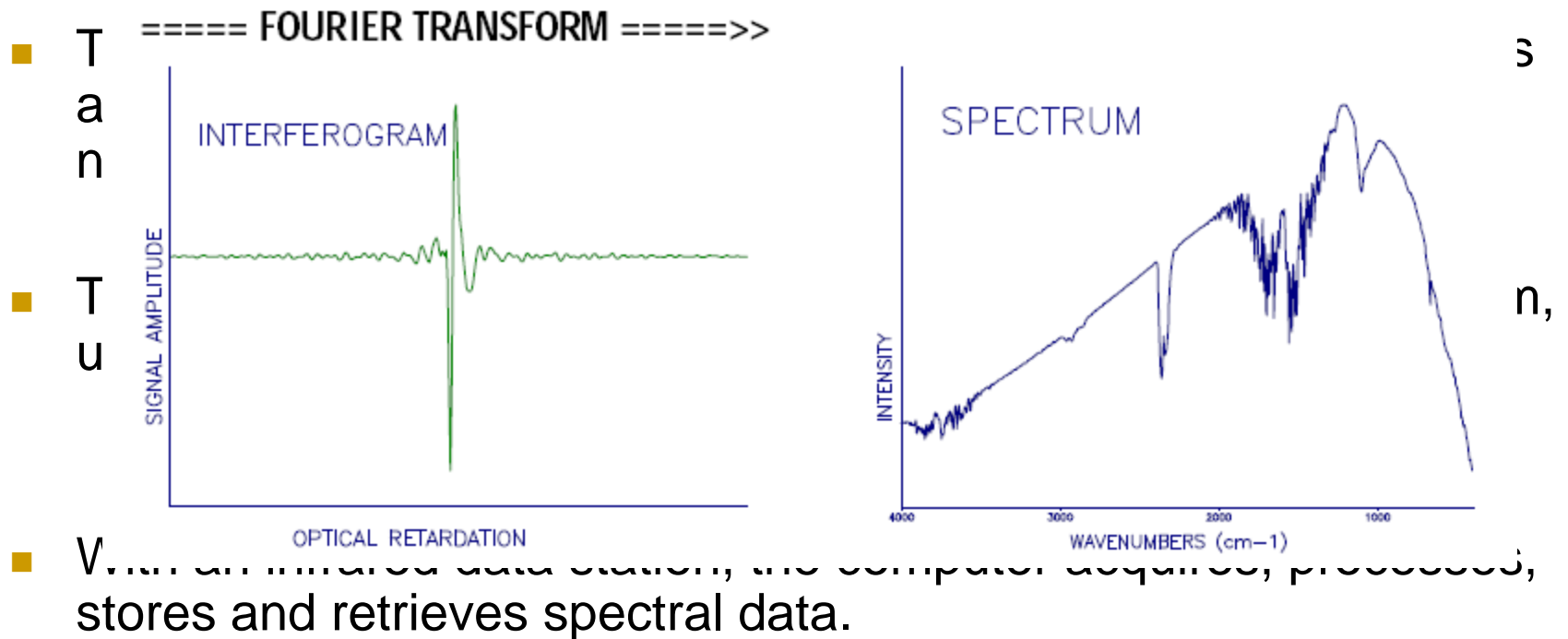
- one beam strikes a fixed mirror
- the other a movable mirror.

When the reflected beams are brought back together, an interference pattern results.



Interferometer: Michelson Interferometer

- The signal is recorded as a function of the optical path difference between the fixed and the movable mirror.



Infrared Detector

- It is a device which measured the infrared energy of the source which has passed through the spectrometer. *These devices change radiation energy into electrical energy which can be processed to generate a spectrum.*
- 2 basic types:
 - **Thermal detectors** which measure the heating effect of radiation and respond equally well to all wavelengths
 - **Selective detectors** whose response is markedly dependent on the wavelength

Infrared detectors

- Examples of thermal detectors:

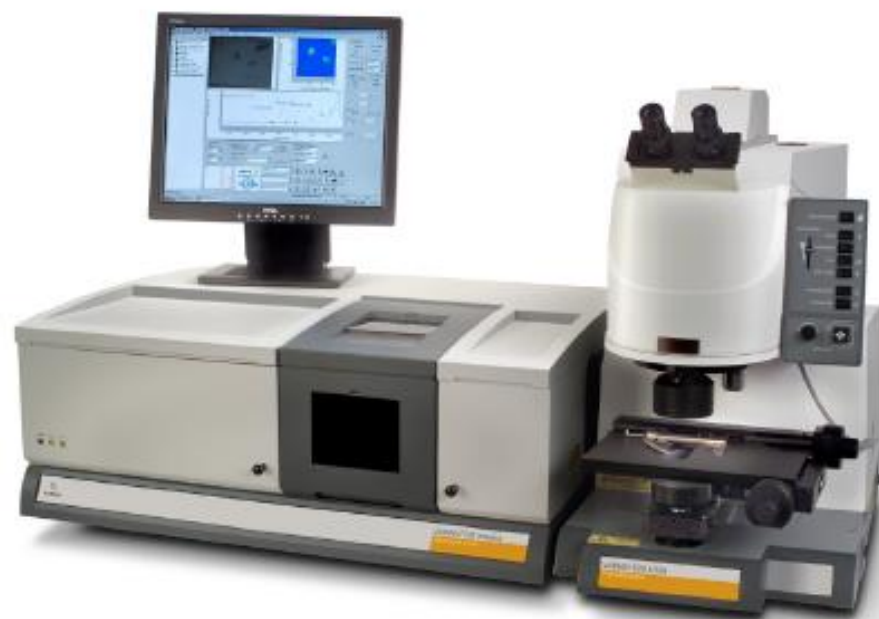
Thermocouples: when incident radiation is absorbed at the junction, the temperature rise causes an increase in the electromotive potential developed across the junction leads

Bolometers: detecting device which depends on a change of resistance with temperature

Pyroelectric: it consists of a thin pyroelectric crystal. If it is electrically polarized in an electric field, it retains a residual electric polarization after the field is removed.

Nicolet Continuum Infrared Microscope

- Acquisition of mid-IR spectra from very small ($>10\ \mu\text{m}$) samples with diffraction limited spatial resolution.
- Material science applications including:
 - Forensic analysis
 - Surface analysis
 - Art conservation
 - Mineralogy
 - Biochemistry



Varian 7000 FT-IR imaging system

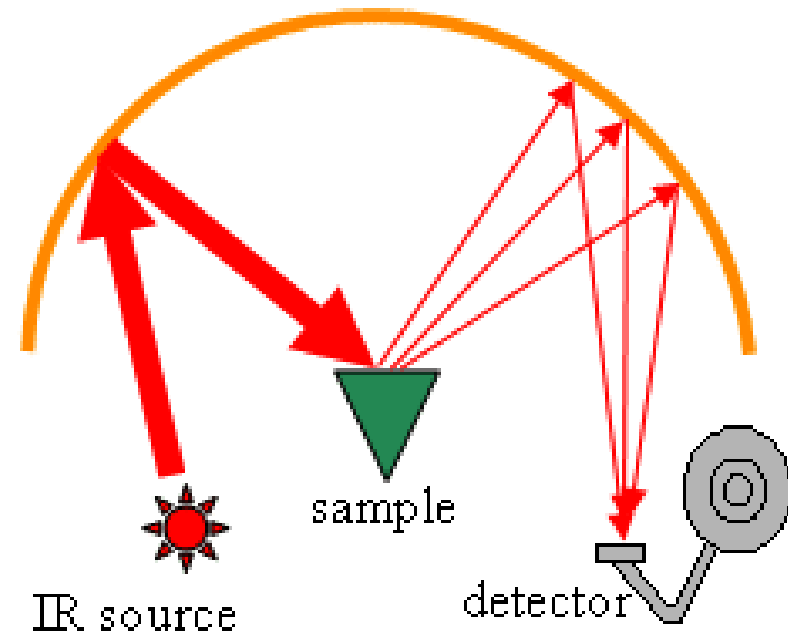
Diffuse Reflectance Spectroscopy



- Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is a technique that **collects and analyzes scattered IR energy**. It is used for measurement of fine particles and powders, as well as rough surface (e.g., the interaction of a surfactant with the inner particle, the adsorption of molecules on the particle surface). Sampling is fast and easy because little or no sample preparation is required.

Diffuse Reflectance Spectroscopy

- When the IR beam enters the sample, it can either be reflected off the surface of a particle or be transmitted through a particle.
- The IR beam that passes through a particle can either reflect off the next particle or be transmitted through the next particle.
- This transmission-reflectance event can occur many times in the sample.
- Finally, such scattered IR energy is collected by a **spherical mirror that is focused onto the detector**. The detected IR light is partially absorbed by particles of the sample, bringing the sample information



Preparation of the samples

- There are three ways to prepare samples for DRIFTS measurement:
 - 1) Fill the micro-cup with the powder (or the mixture of the powder and KBr).
 - 2) Scratch the sample surface with a piece of abrasive (SiC) paper and then measuring the particles adhering to the paper.
 - 3) Place drops of solution on a substrate. If colloids or powders are dissolved or suspended in a volatile solvent, you can place a few drops of the solution on a substrate, and then evaporate the solvent, subsequently analyze the remaining particles on the substrate.

Other techniques:

- Attenuated Total Reflectance (ATR)



required for analysis is that the sample of interest be brought into contact with the ATR crystal. Under this condition total internal reflection of the beam occurs

- Specular Reflectance (SR)



Occurs from bulk samples with a glossy surface such as crystal faces, glasses, and monolithic polymers.

Other techniques:



- Reflection-Absorption (RA)

Occurs when thin films are present on a reflective substrate.

- Photoacoustic (PA)

Quite complex and difficult to perform.



The photoacoustic signal is generated when the infrared radiation absorbed by a sample is converted to heat within the sample. This heat diffuses to the sample surface and into the adjacent gas atmosphere. The thermal expansion of this gas produces the photoacoustic signal. Assuming a suitable signal level is attainable, the PAS spectrum of almost any sample can be obtained without preparation.

Furnace and high-temperature measurements

- High-temperature spectra recorded by heating samples in a furnace.
- Sample pellets are positioned within a cylindrical platinum-wound furnace with a recycle-water-cooling system.
- The cooling system is used to prevent the outside of the furnace from becoming too hot. Two thermocouples are used in the furnace. The temperature of the furnace is controlled by using a Pt/PtRh thermocouple located close to the heating platinum wires in the furnace and a Eurotherm 815 temperature controller, which allows a temperature variation of less than $\pm 1\text{K}$. A heating rate of 8-15 K/min is recommended for most experiments.

■ Water diffusivity in rhyolitic glasses as determined by in situ IR spectroscopy

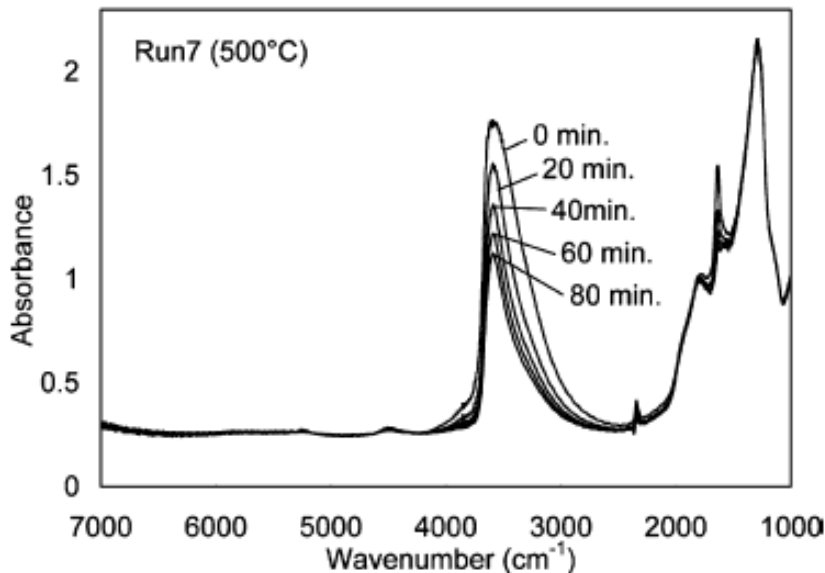


Fig. 2 Successive infrared (IR) spectra obtained by in situ heating experiments for a synthetic water-containing obsidian of 2.8 wt% total water (*Run7 sample*) at 500 °C. The spectra after 0, 20, 40, 60 and 80 min are shown

Rhyolitic glass:
mainly SiO_2 with Al_2O_3 , Na_2O , K_2O

Goal: Determination of the diffusion coefficients of total water in rhyolitic glasses at high temperatures.

Dehydration experiments

The absorption bands of water species at 5200, 4500, 3550 and 1630 cm^{-1} , corresponding to H_2O , OH , $\text{OH} + \text{H}_2\text{O}$ and H_2O , respectively

- Er³⁺-doped SiO₂-GeO₂-Al₂O₃ prepared by sol-gel.
- Film deposited on Silicon using spin coating

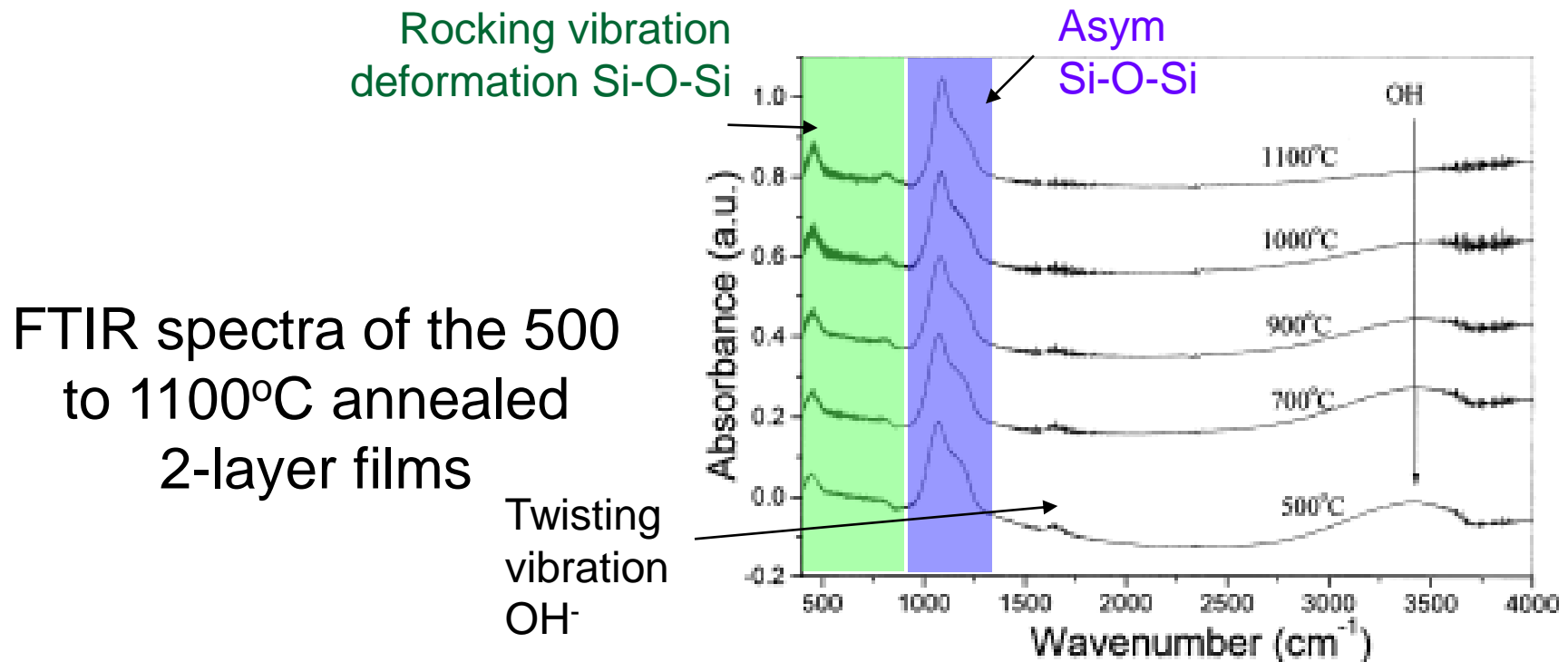
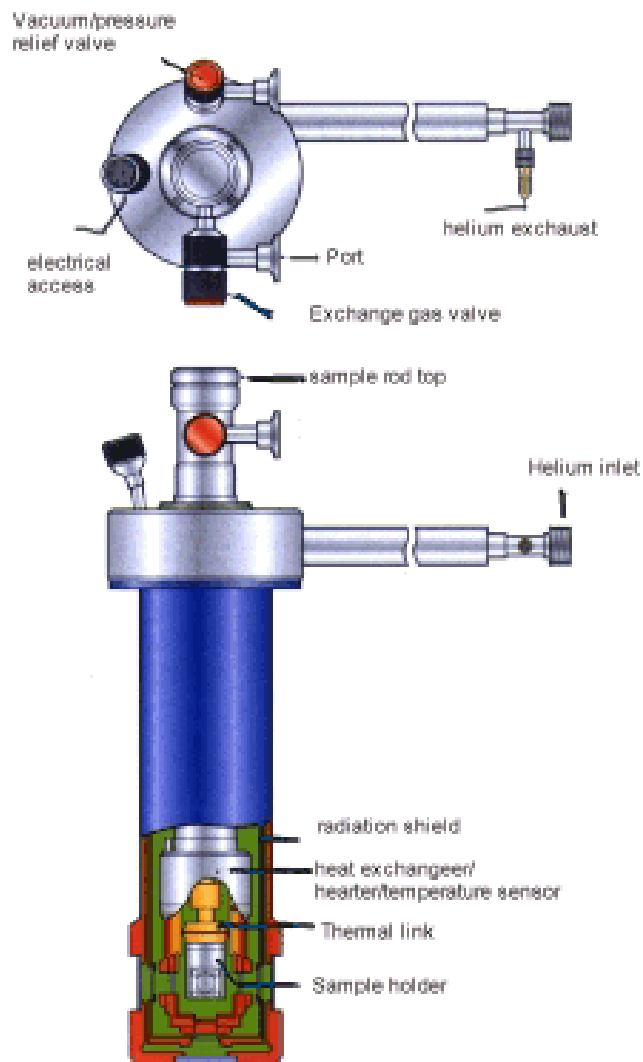


Fig. 3. FTIR spectra of the Er³⁺-doped SiO₂-GeO₂-Al₂O₃ thin films annealed at different temperatures.

Cryostats and low-temperature measurements

- Temperature range of 20-310 K is used for most low-temperature measurements.
- A sample holder is made from high-thermal-conductivity oxygen-free copper. A gold-coated lattice made from oxygen-free copper is installed at the sample position to improve the thermal contact between the sample and the sample holder. One temperature sensor, positioned near the heating unit, is used to control the temperature of the cryostat while another calibrated Si-diode temperature sensor is glued on the centre of the sample holder for measuring the sample temperature.



Ordered low-temperature structure in K_4C_{60} detected by infrared spectroscopy

- Infrared spectra of a K_4C_{60} single-phase thin film measured between room temperature and 20 K.
- At low temperatures, the two high-frequency $T1u$ modes appear as triplets, indicating a static $D2h$ crystal-field stabilized Jahn-Teller distortion of the C_{60} 42 anions. The $T1u(4)$ mode changes into a known doublet above 250 K, a pattern which could have three origins:
 - a dynamic Jahn-Teller effect,
 - static disorder between ‘staggered’ anions,
 - a phase transition from an orientationally ordered phase to one where molecular motion is significant.

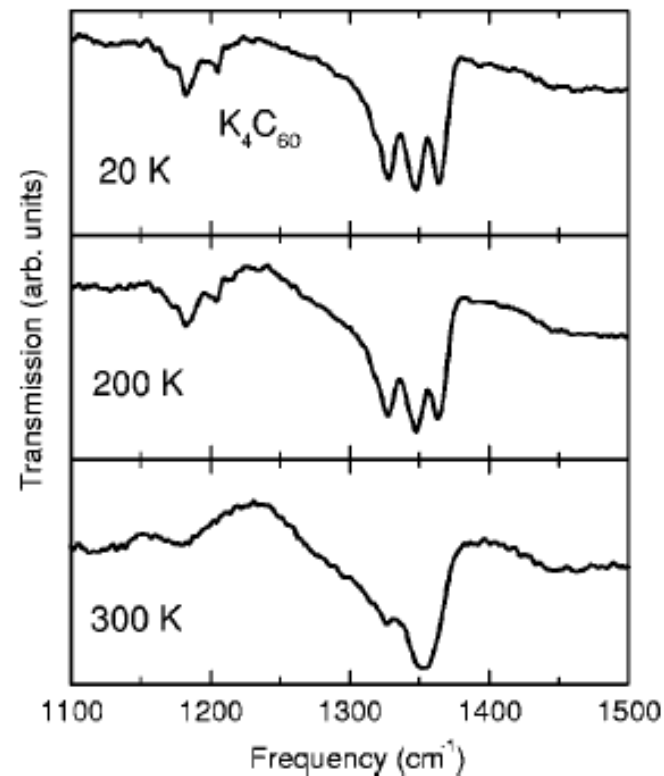
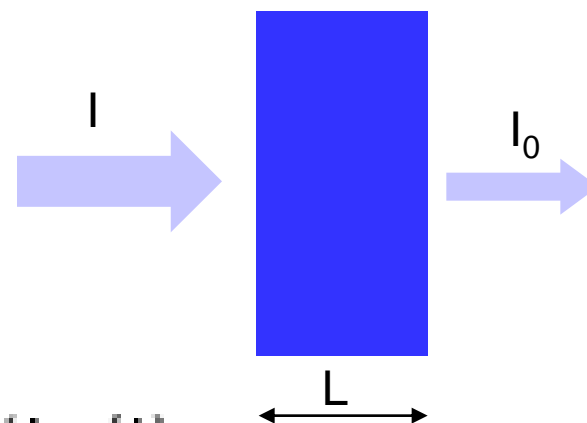


FIG. 2. Infrared spectra of K_4C_{60} in the region of the high-frequency C_{60} molecular vibrations, at three different temperatures.

Quantitative analysis

Transmittance $T = I/I_0$

Absorbance $A = \log(1/T) = \log(I_0/I)$



I_0 = Intensity of incident radiation

I = Intensity of transmitted radiation

e = molar extinction coefficient

c = concentration (mole/l)

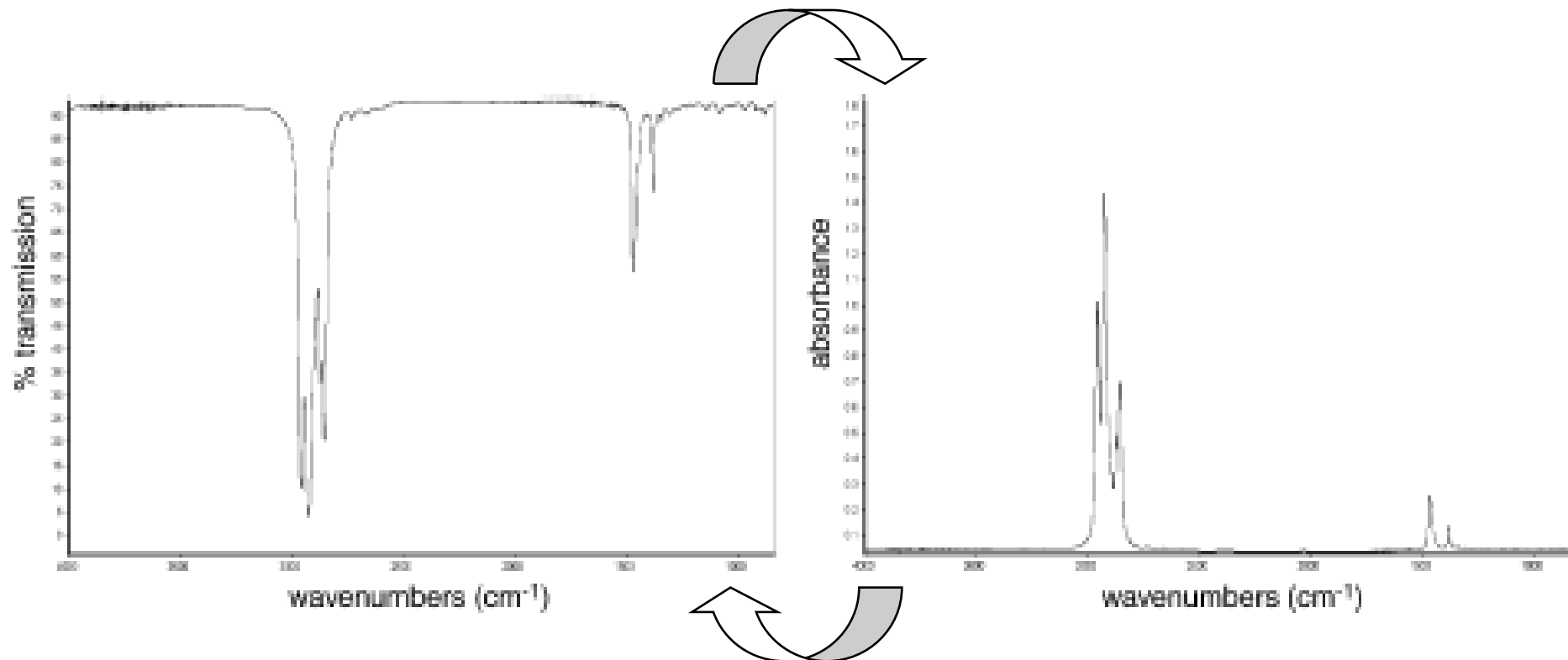
L = sample pathlength (cm)

$$T = \frac{I}{I_0} = 10^{-ecL}$$

Example of transmittance and absorbance spectra

Band intensities can also be expressed as absorbance (A).

$$A = \log_{10} (1/T)$$

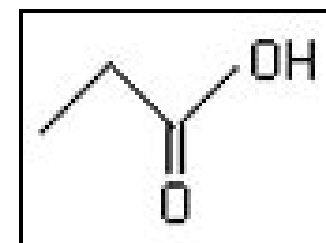


Infrared Absorption due to vibrational transitions

- 3 absorptions:
 - **Impurity absorption due to gases or bound hydrogen isotopes** (dissolved $\text{CO}_2 \Rightarrow$ IR absorption band @ $4.26\mu\text{m}$)
 - **The IR cutoff or multiphonon edge due to IR absorption due to stretching & bending of glass structure bonds.**
 - **Fundamental structural vibrations such as water bands**
 - are problems when designing fiber optic systems
 - Si—OH stretching frequencies @ $2.7\mu\text{m}$ etc.

The following is a list of frequency regions (in cm^{-1}) and associated functional groups for organic compounds.*

3,700 - 3,100:	OH, NH and $\equiv\text{CH}$
3,180 - 2,980:	aryl, olefinic, and three-membered ring CH
3,000 - 2,700:	aliphatic CH
3,100 - 2,400:	acidic and strongly bonded hydrogens
2,300 - 1,900:	$\text{C}\equiv\text{C}$ and $\text{C}=\text{C}=\text{C}$
2,000 - 1,700:	aryl and olefinic overtones
1,900 - 1,550:	$\text{C}=\text{O}$
1,700 - 1,550:	$\text{C}=\text{C}$ and $\text{C}=\text{N}$
1,660 - 1,450:	$\text{N}=\text{O}$
1,660 - 1,500:	NH_2 , CNH
1,620 - 1,420:	aromatic and heteroaromatic rings
1,500 - 1,250:	CH_3 and CH_2
1,350 - 1,150:	CH_2 and CH wag
1,300 - 1,000:	$\text{C}-\text{O}$
1,000 - 600:	olefinic and acetylenic wag
900 - 700:	aromatic wag
900 - 500:	OH, NH and NH_2 wag
830 - 500:	CCl , CBr and Cl



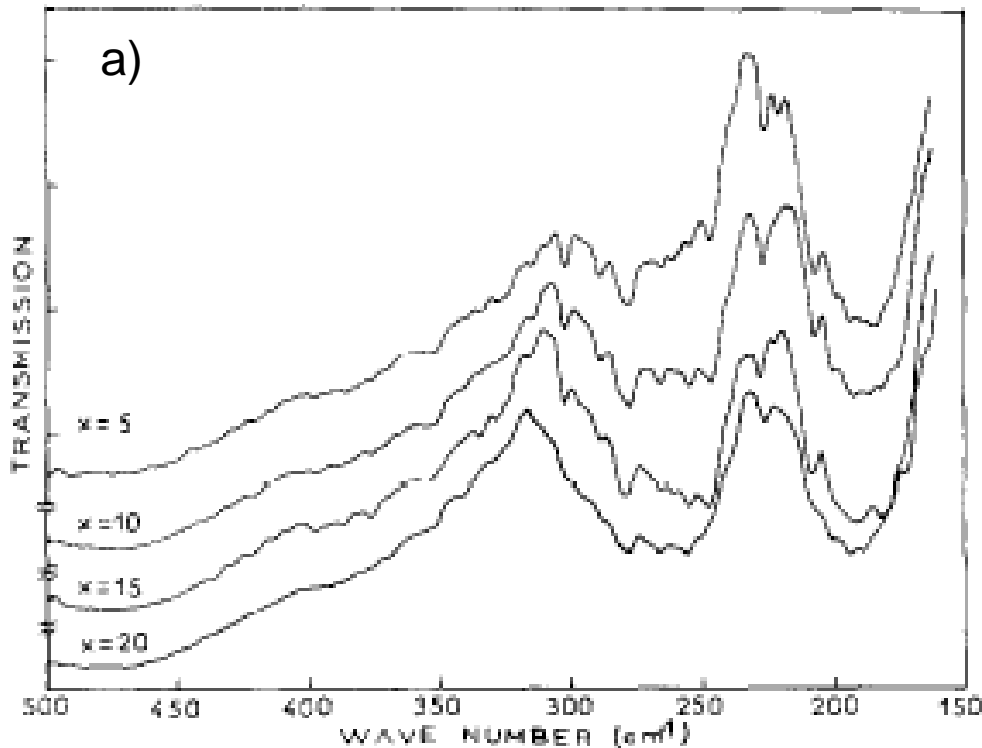
*Colthup, N. B.; Daly, L. H.; Wiberley, S. E., *Introduction to Infrared and Raman Spectroscopy*, 3rd edition, Academic Press, Boston, 1990, Chapter 13.

Strong absorption at just over 1710 cm^{-1} and a medium absorption at $2500\text{-}3300\text{ cm}^{-1}$. (Formula $\text{C}_3\text{H}_6\text{O}_2$)

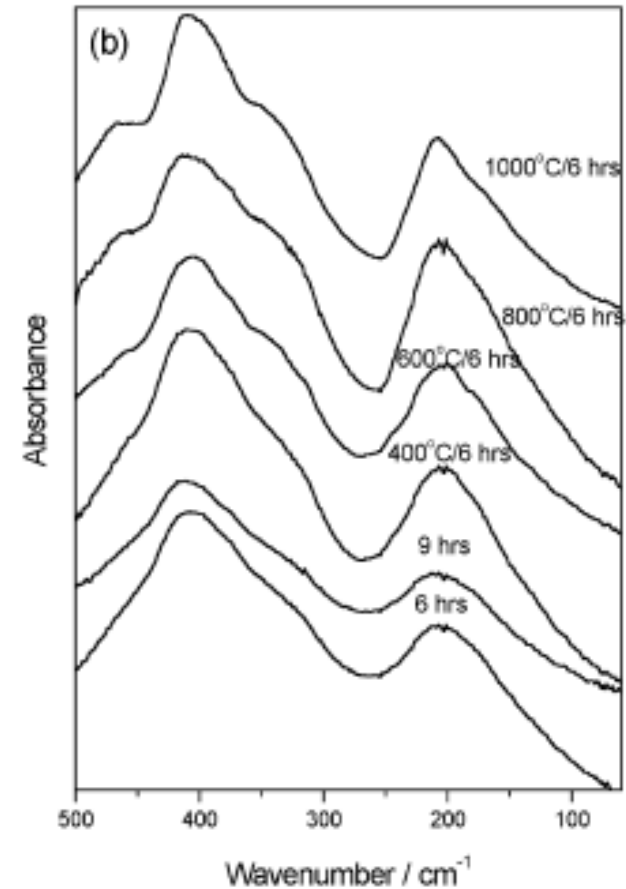
Looking at the table, these bonds correspond to the $\text{C}=\text{O}$ and $\text{O}-\text{H}$ groups found in a carboxylic acid.

Few examples:

- IR spectrum of GeSe_2 and GeO_2 based glasses?



GeSe_2 based glass

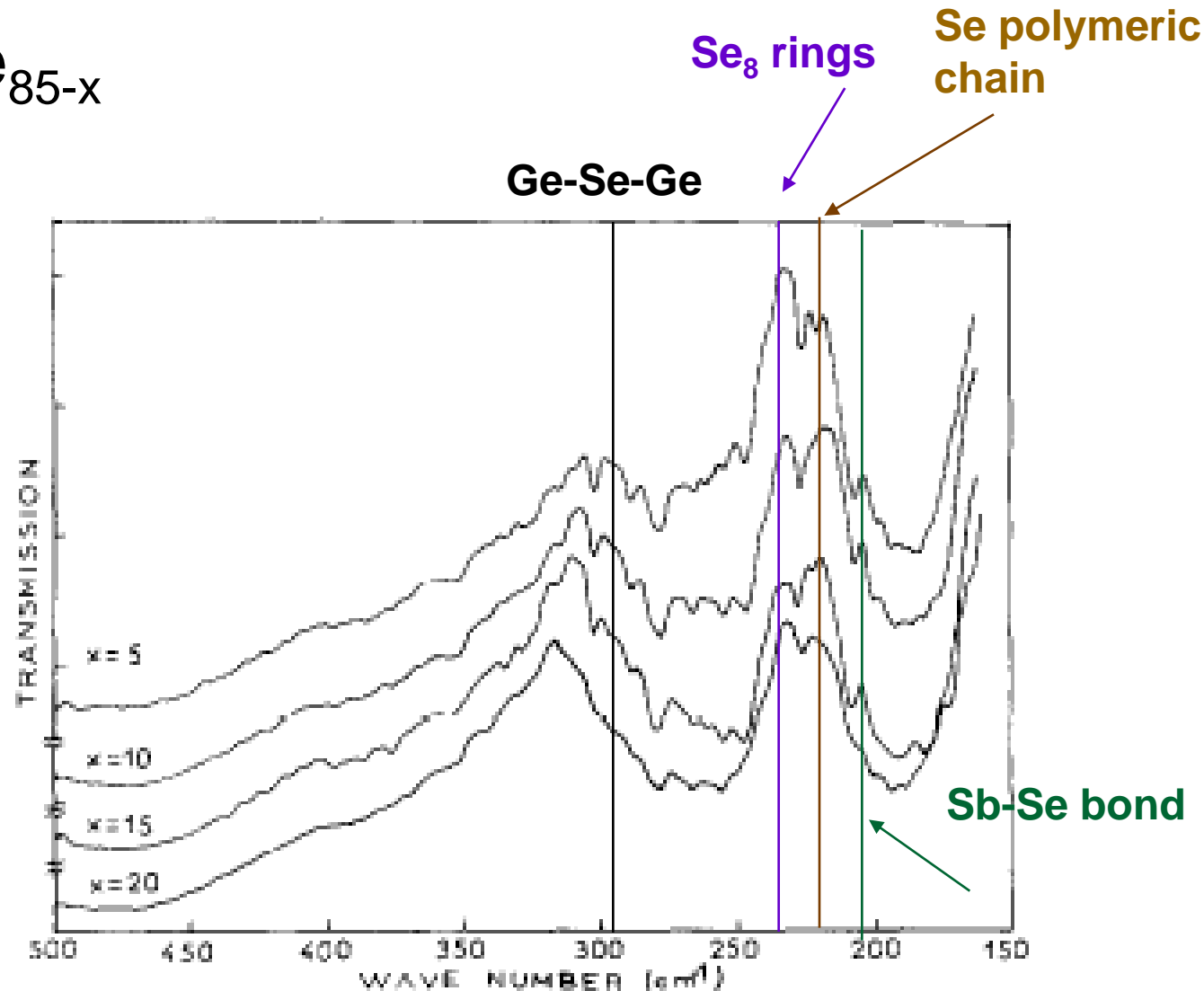


GeO_2 based glass

D.R. Goyal, AS. Maan/Journal of Non-Crystalline Solids 183 (1995) 182-185



Presence of much fewer modes than expected because frequency difference between some modes is small and bandwidth so large that the corresponding bands are not resolved in the spectra measured for powder samples.



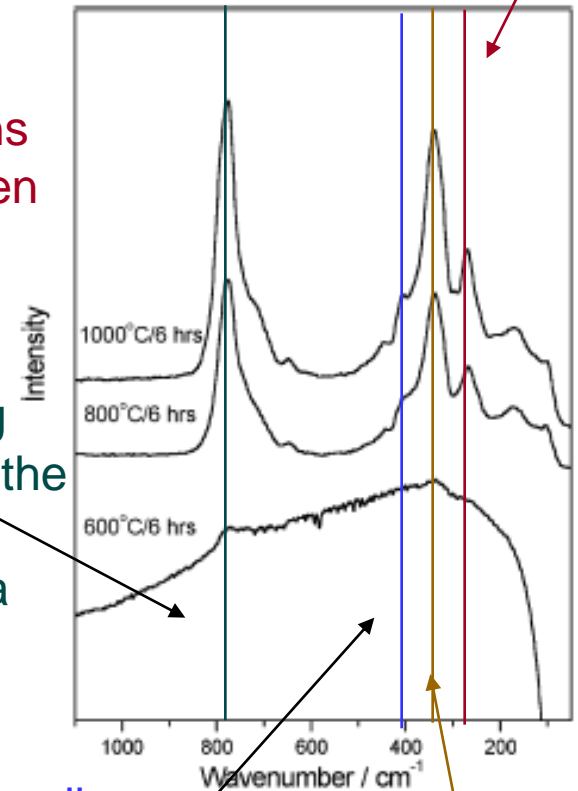
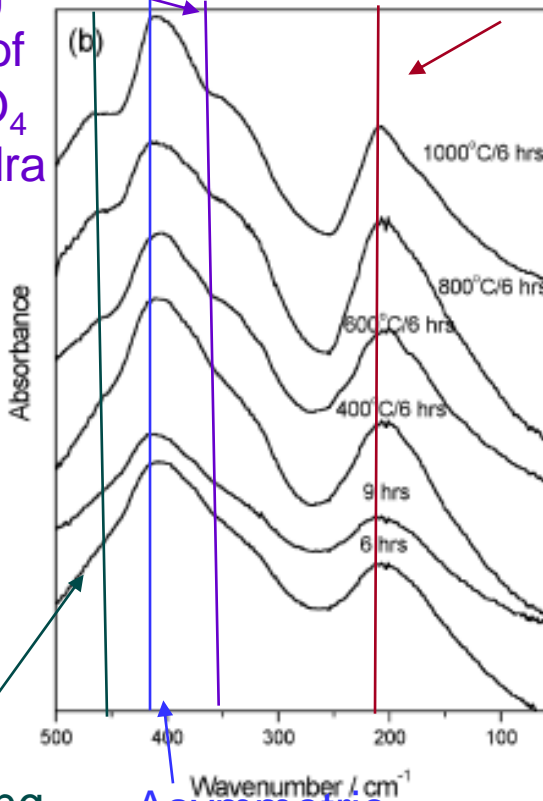
IR and Raman spectra of $\text{La}_2\text{O}_3\text{-GeO}_2$ based glasses

La-O bond vibration

IR spectrum

La-O bond vibration & Coupled translational motions of germanate ions and vibration of the oxygen atoms located inside the hexagonal channels

Raman spectrum



Bending modes of the GeO_4 tetrahedra

Stretching modes of the GeO_4 tetrahedra.

Asymmetric Bending modes of the GeO_4 tetrahedra.

Sym. Stretching modes of the GeO_4 tetrahedra

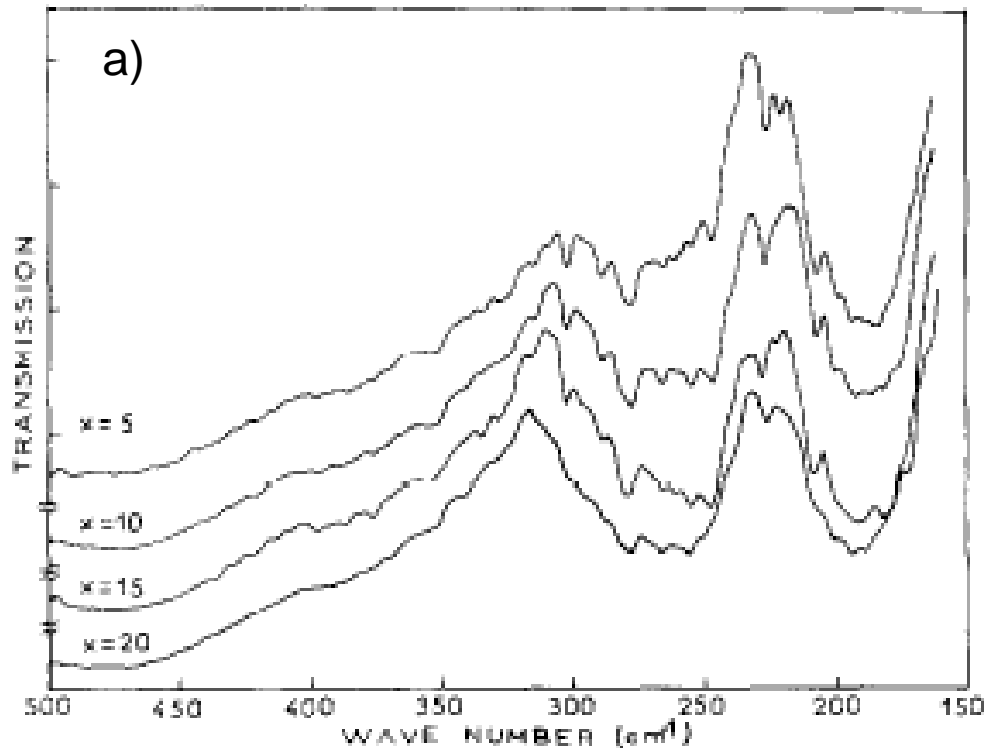
Asymmetric Bending modes of the GeO_4 tetrahedra.

Asym. Stretching modes of the GeO_4 tetrahedra

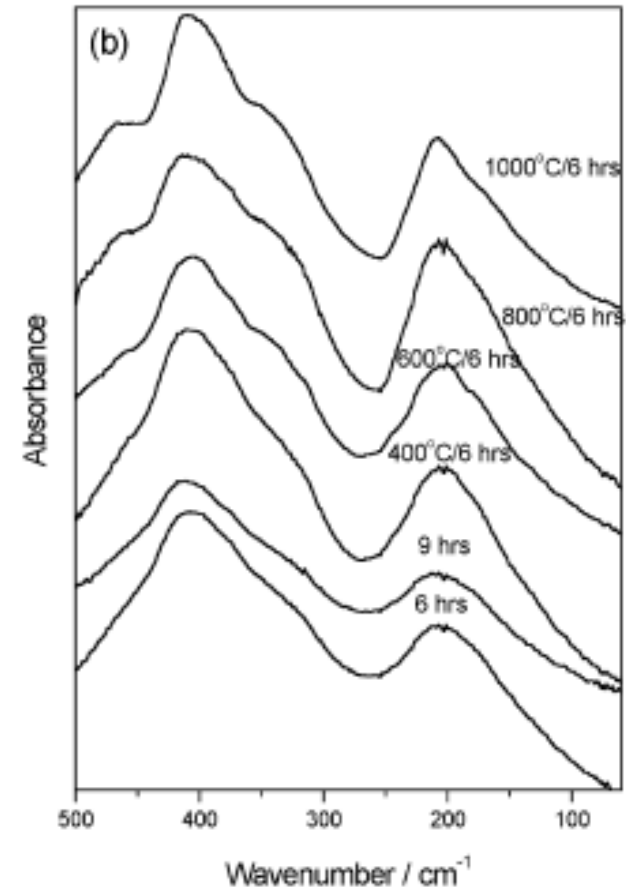
E. Rodríguez-Reyna et al. / Solid State Sciences 8 (2006) 168–177

Few examples:

- IR spectrum of GeSe_2 and GeO_2 based glasses?



GeSe_2 based glass



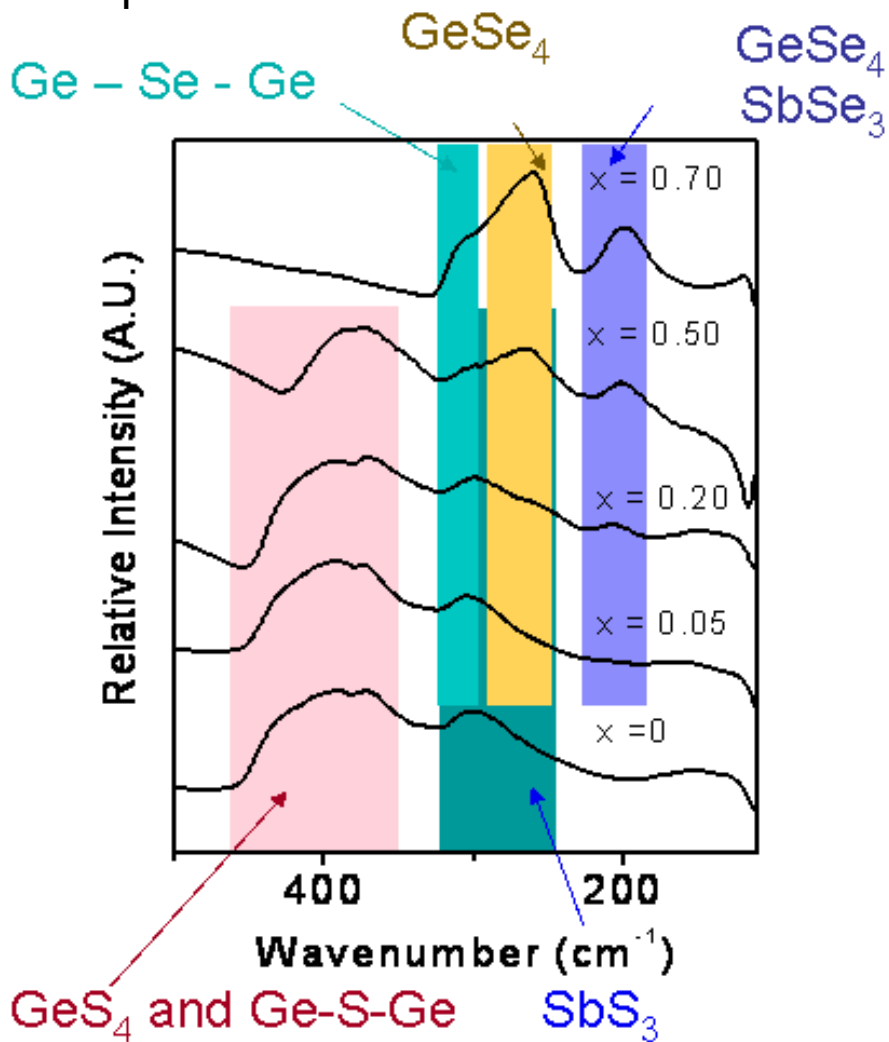
GeO_2 based glass

Anion Exchange: Sulfoselenide glasses

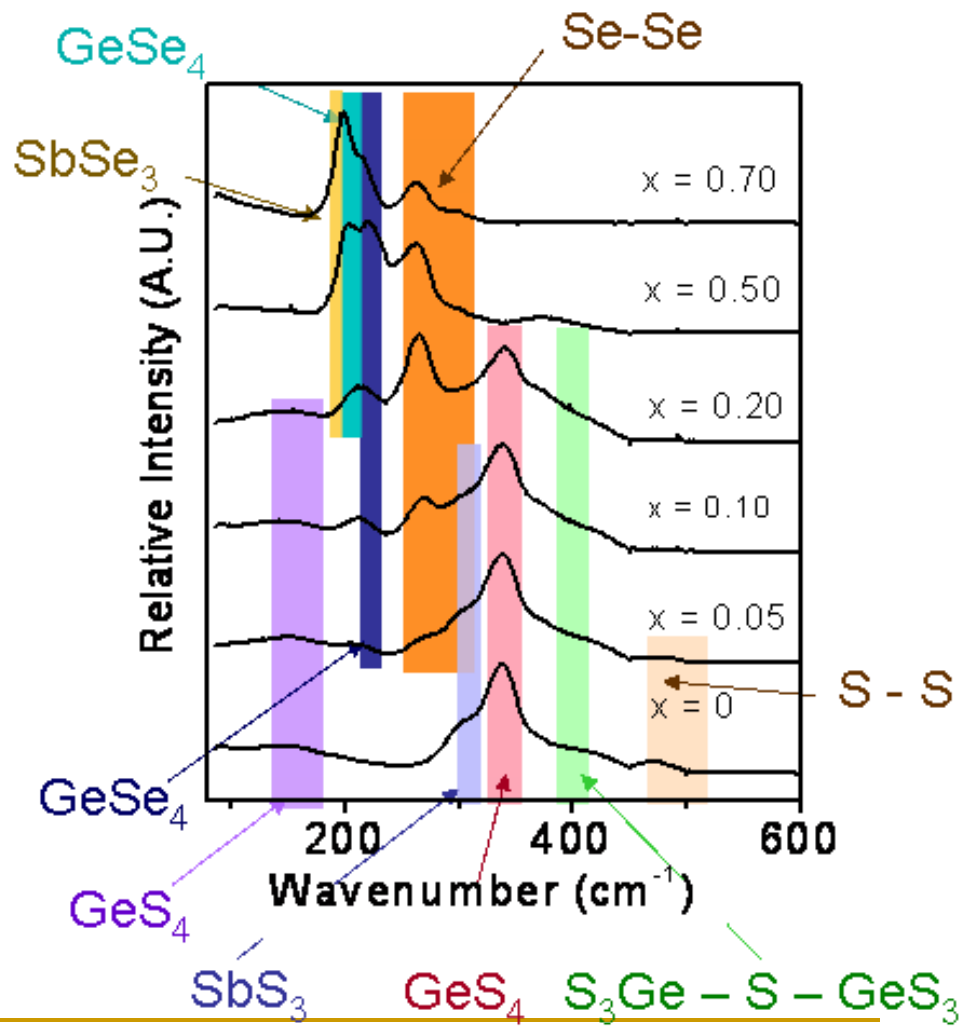
J. Phys. and Chem. of Solids, 66 (2005) 1788-1794

Glass Systems: $Ge_{0.23-y}Sb_{0.07}S_{0.70-x}Se_x$

IR spectra



Micro Raman spectra ($\lambda_{exc}=752\text{ nm}$)



Infrared spectroscopy is one of the best methods to examine the results of sulfination of oxide gel films: : Exchange of O by S

J. Xu, R.M. Almeida, Materials Science in Semiconductor Processing 3 (2000) 339-344

■ Sulfination of GeO₂ Films prepared by sol-gel.

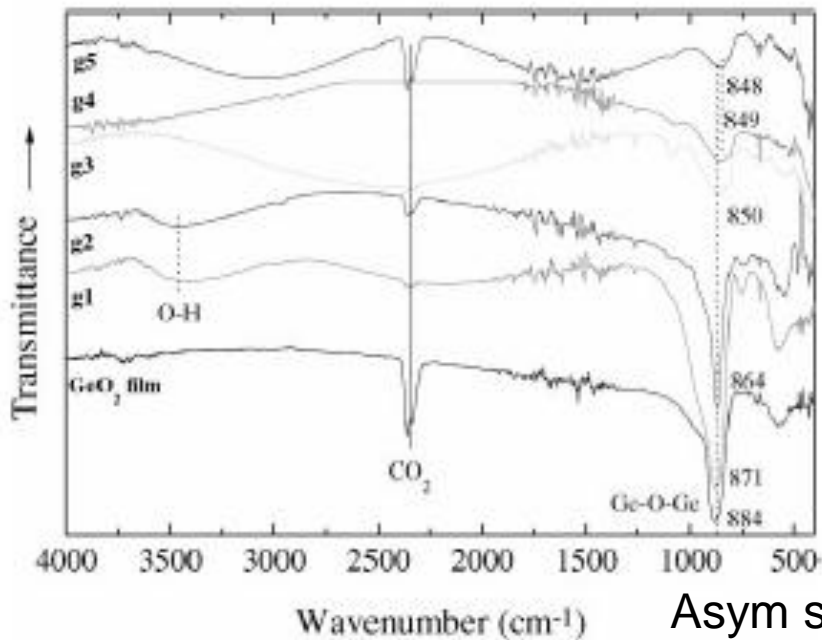


Fig. 2. Mid-IR spectra of gel films, after heat treatments in H₂S gas.

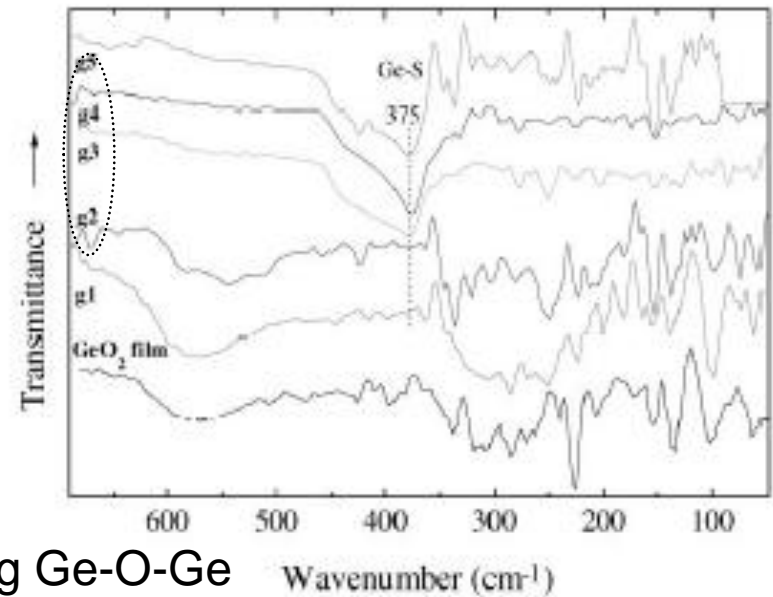


Fig. 3. Far IR spectra of gel films, after heat treatments in H₂S gas.

H₂S heat treatment @ near

160 (g1), 260 (g2), 320 (g3), 360 (g4) and 400°C (g5), for 4 days, using a hot plate.

Infrared spectroscopy is one of the best methods to examine the results of sulfination of oxide gel films: Exchange of O by S

J. Xu, R.M. Almeida, *Materials Science in Semiconductor Processing* 3 (2000) 339-344

Using IR and Raman spectroscopies:
successful preparation of
Ge-O-S films

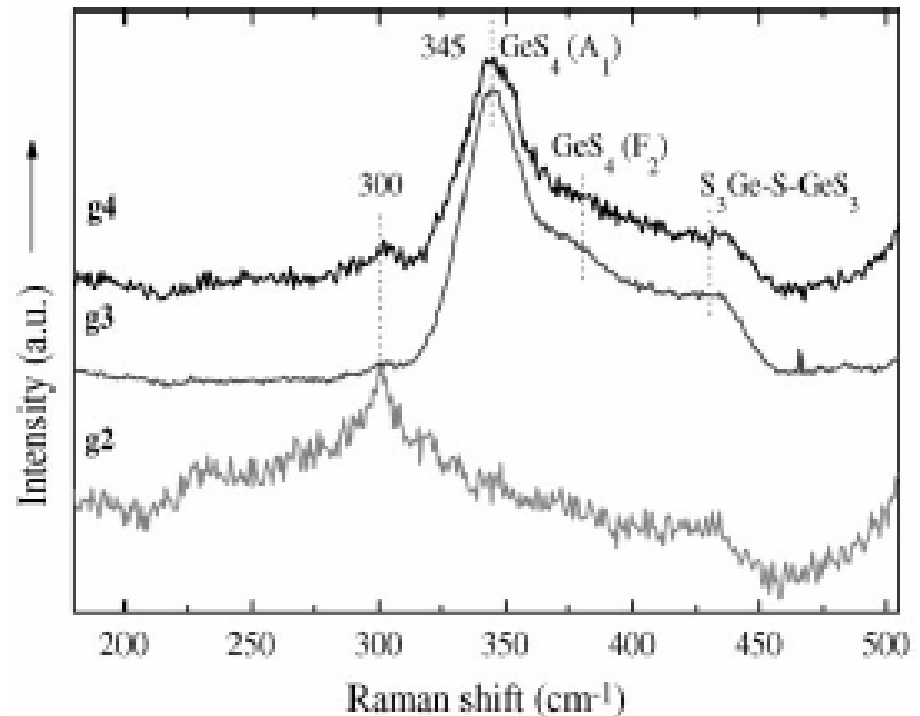


Fig. 4. Micro-Raman spectra of sulfide films, after heat treatment in H₂S gas.

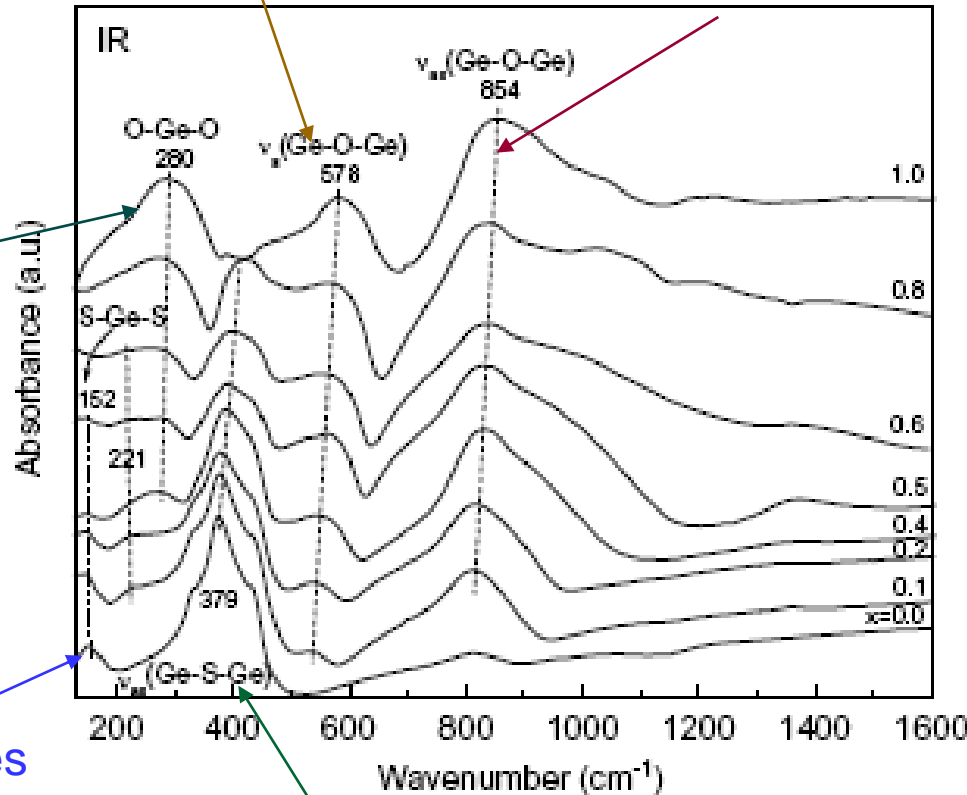
Anion exchange: Oxysulfide bulk glasses

Y. Kim et al. / Journal of Non-Crystalline Solids 351 (2005) 1973–1979

symmetric stretching
modes of bridging Ge–O–Ge

asymmetric stretching modes of
bridging Ge–O–Ge bonds

bending modes
of O–Ge–O bonds



bending modes

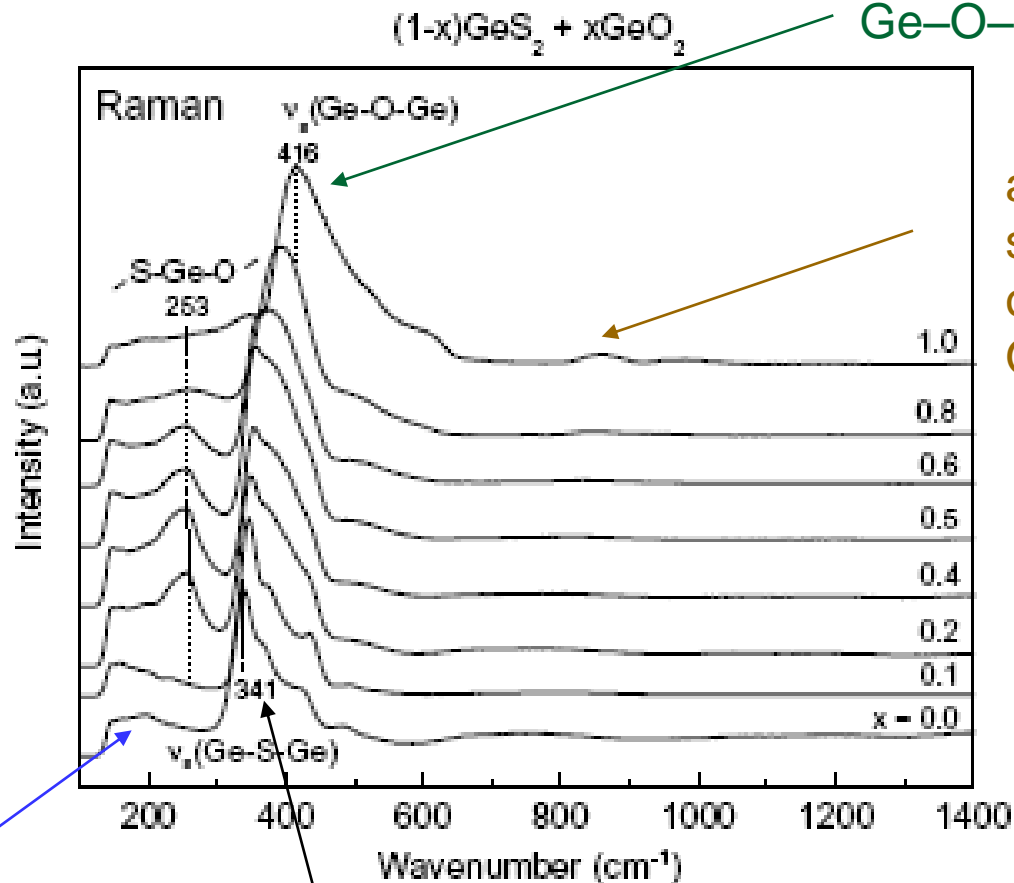
asymmetric stretching
modes of the bridging Ge–S–Ge bonds

Anion exchange: Oxysulfide bulk glasses

Y. Kim et al. / Journal of Non-Crystalline Solids 351 (2005) 1973–1979

$\lambda_{exc} = 488\text{nm}$

symmetric stretching
modes of bridging
Ge–O–Ge

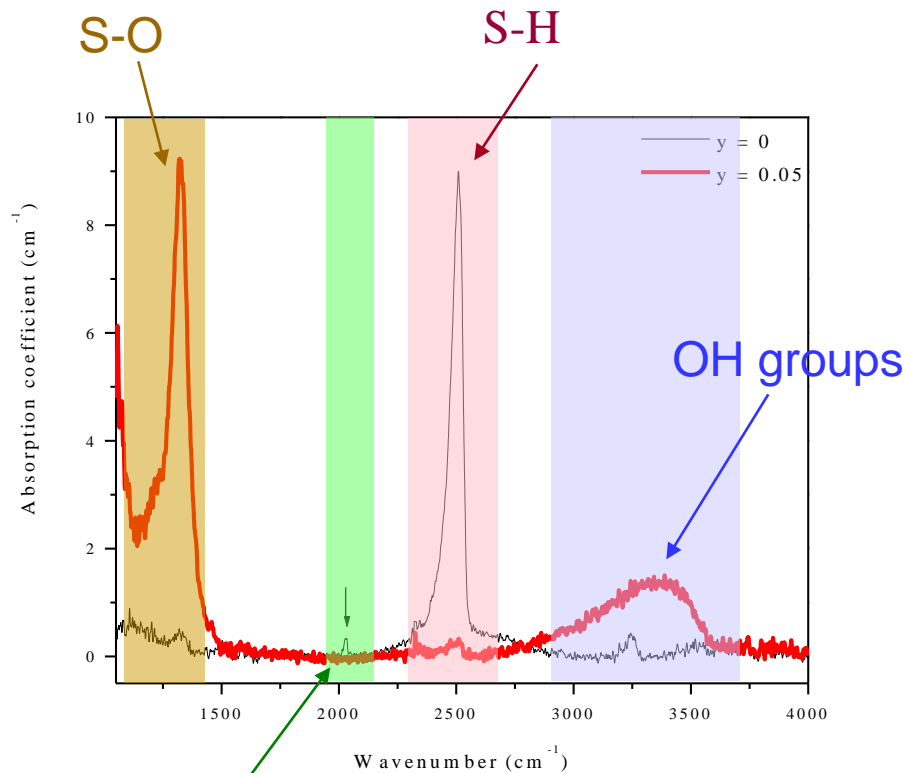


asymmetric
stretching modes
of bridging Ge–
O–Ge

bending
modes of Ge–S–Ge bonds

symmetric
stretching mode of bridging Ge–S–Ge
bonds.

Replacement of Ge by Ga: $\text{Ge}_{0.23-y}\text{Ga}_y\text{Sb}_{0.07}\text{S}_{0.70}$: IR spectra

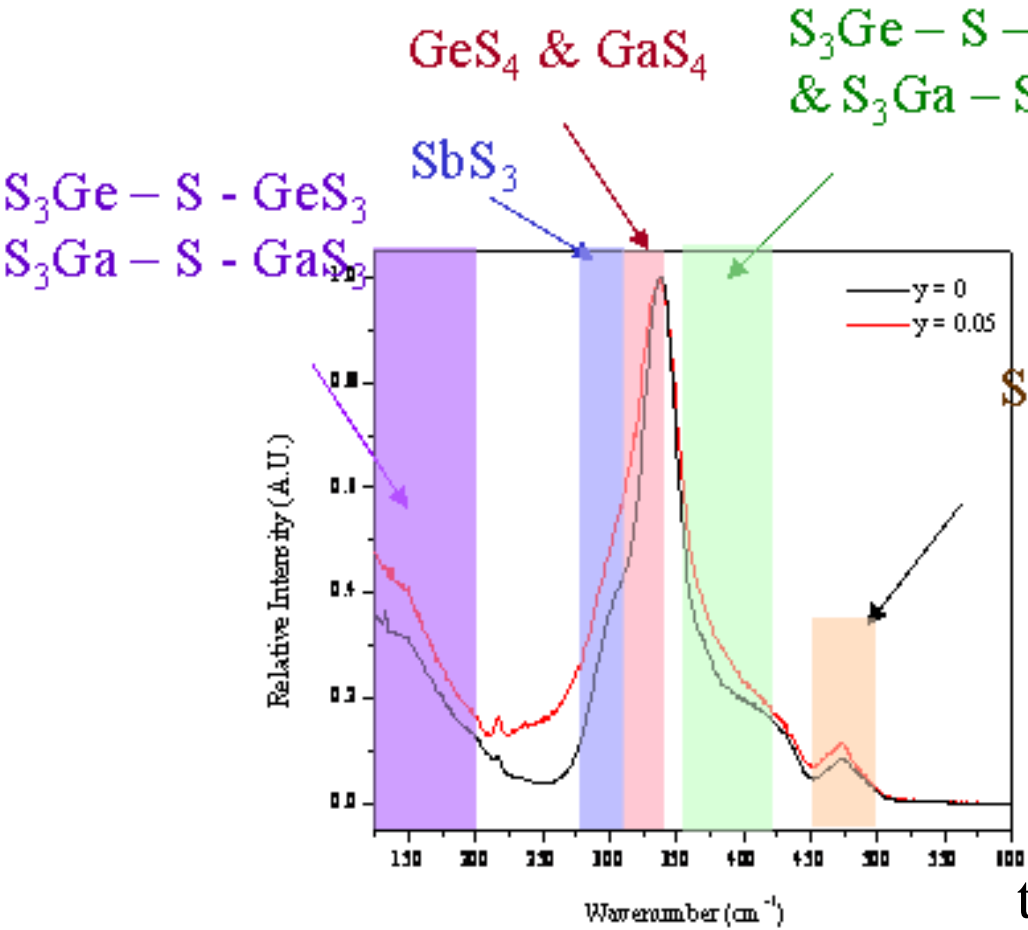


C-O-S (pollution of ChG especially Ge)

Addition of Ga

⇒ more O contamination (S-O and OH groups)

Replacement of Ge by Ga: $\text{Ge}_{0.23-y}\text{Ga}_y\text{Sb}_{0.07}\text{S}_{0.70}$: Raman spectra ($\lambda_{\text{exc}}=752 \text{ nm}$)

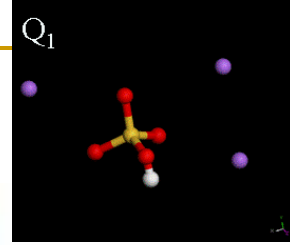


Raman spectrum larger when addition of Ga

⇒ Related to the presence of GaS_4

the glass network more open and so more hygroscopic

Examples: $(100-x) \text{NaPO}_3 - x \text{Nb}_2\text{O}_5$



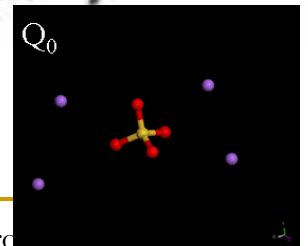
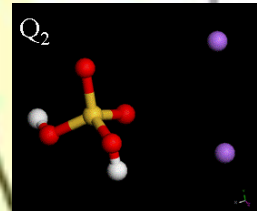
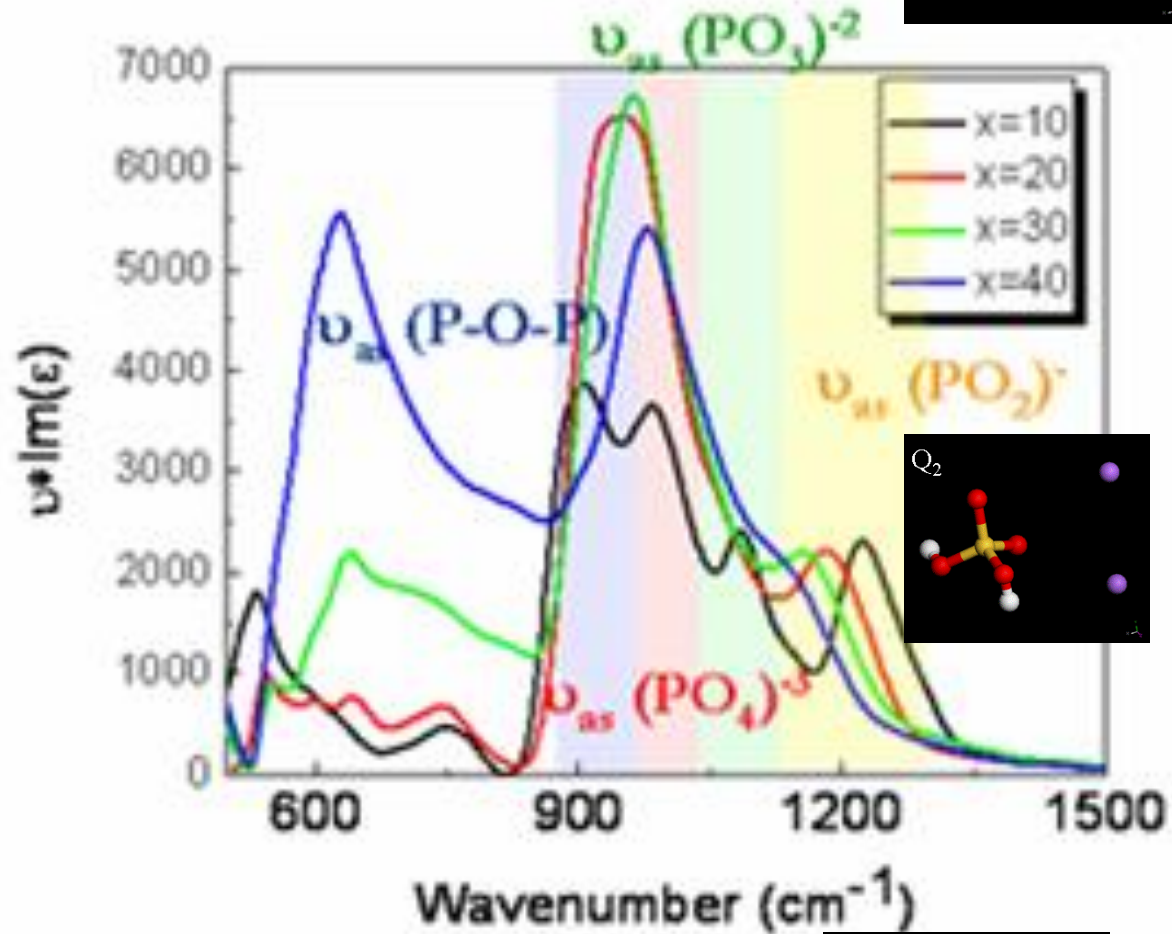
$x = 10$

IR spectrum = signature of a Phosphate network

When x increases

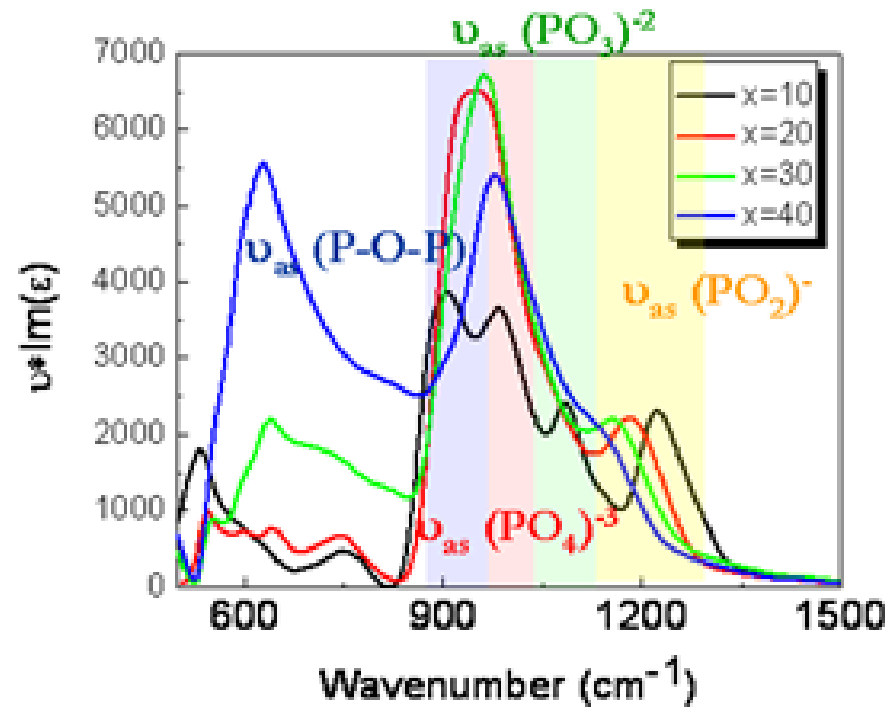
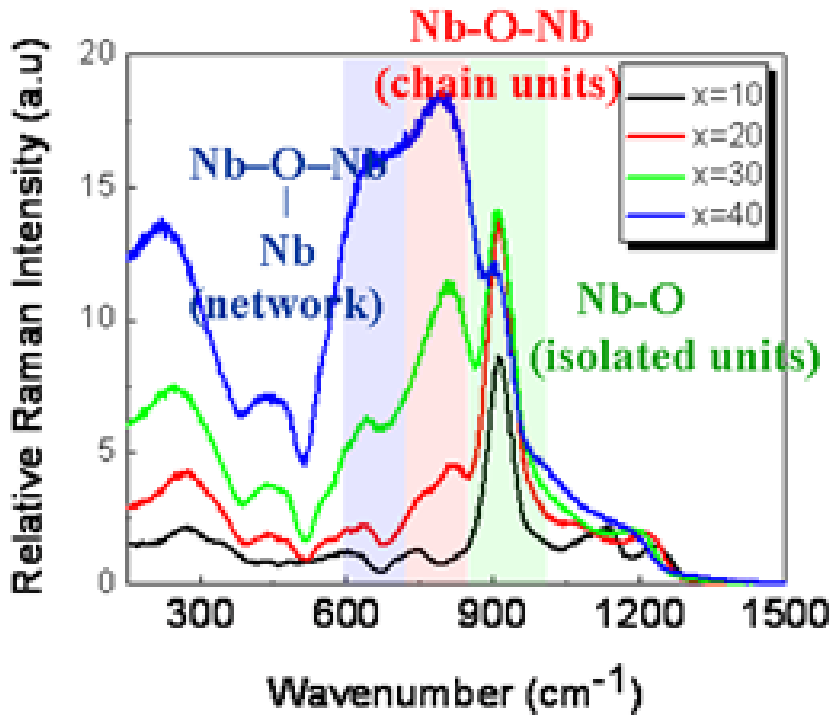
Diminution of the IR bands related to P-O-P, Q^2 and Q^1

more isolated PO_4 units



C. Rivero, PhD thesis, CREOL/College of Optics (UCF), 2005

Examples: $(100-x) \text{NaPO}_3 - x \text{Nb}_2\text{O}_5$



Raman & IR Spectroscopies:

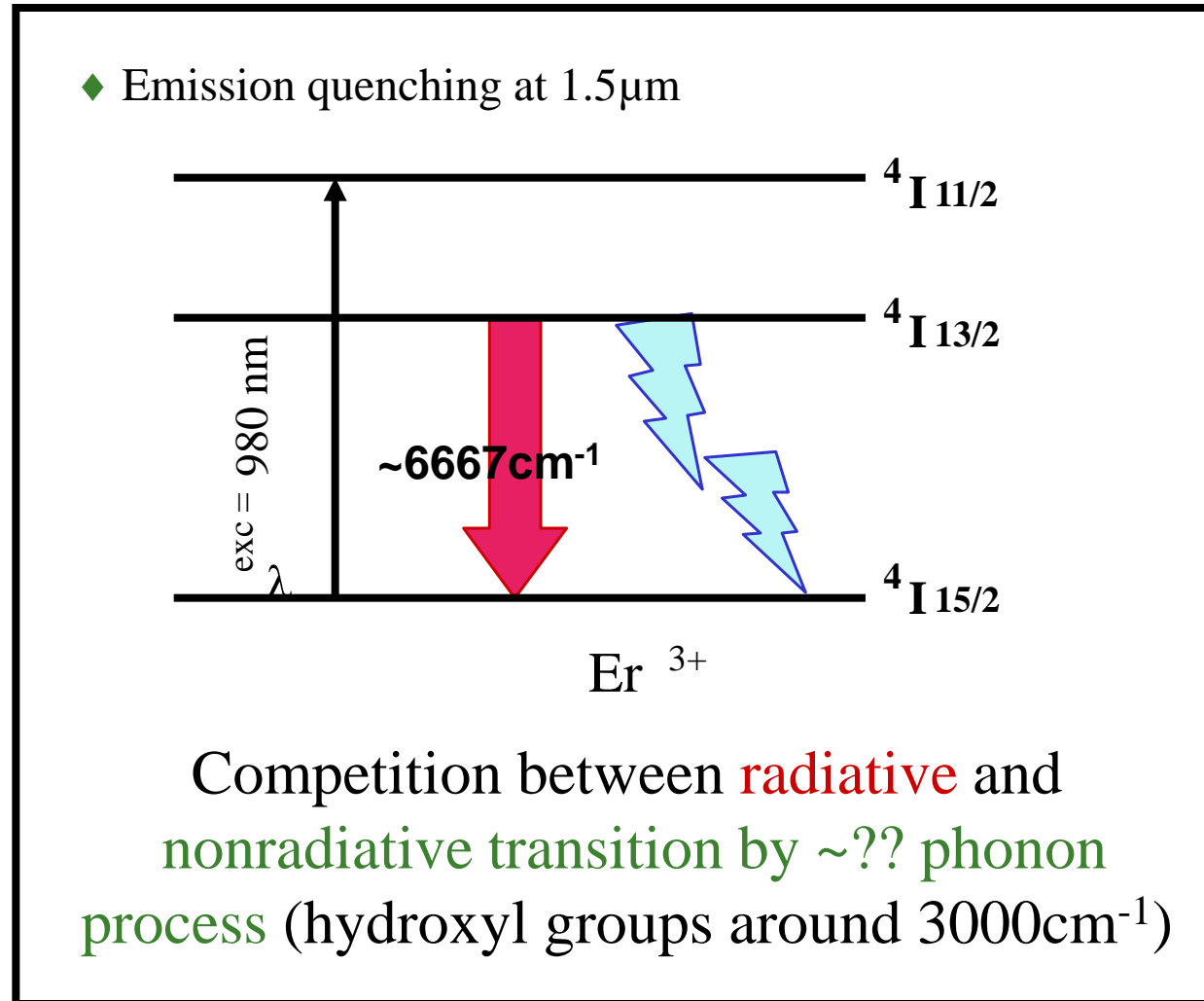
→ Complementary Techniques

→ Allow full characterization of vibrational spectrum of material

C. Rivero, PhD thesis, CREOL/College of Optics (UCF), 2005

Why is that important to measure OH groups?

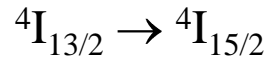
- Telecommunication applications



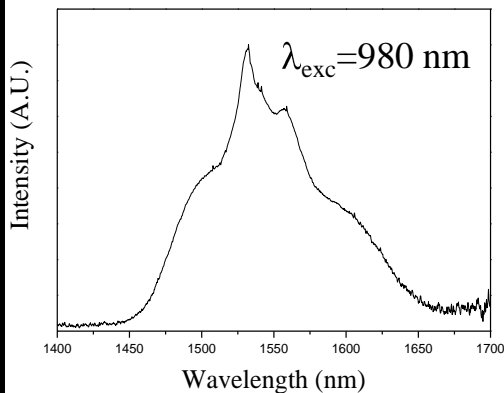
Why is that important to measure OH groups?

■ Example: $(1-x)\text{TeO}_2 - x\text{Na}_2\text{B}_4\text{O}_7$

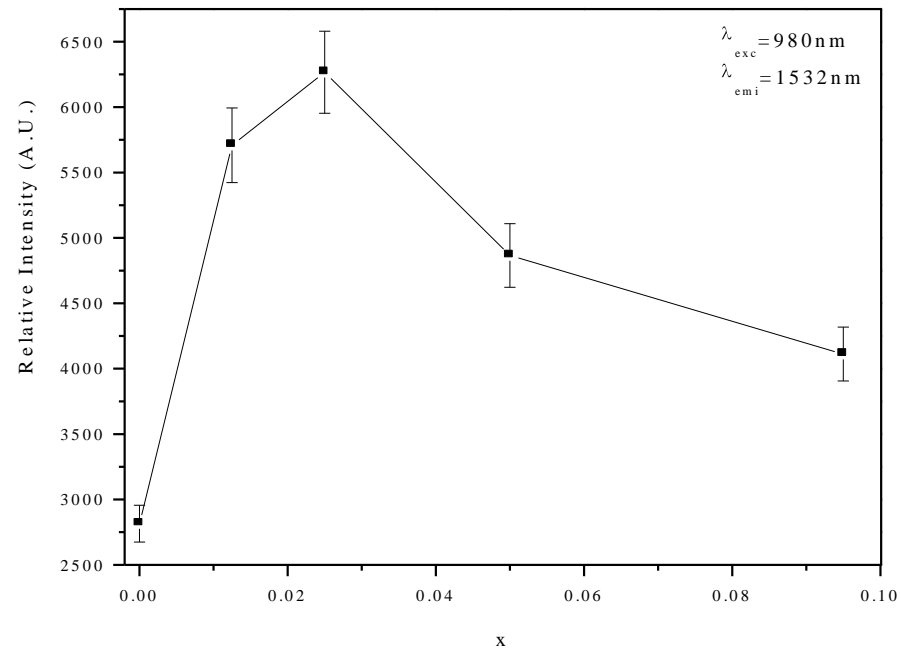
- ◆ Emission spectrum corresponding to



$x=0.025$



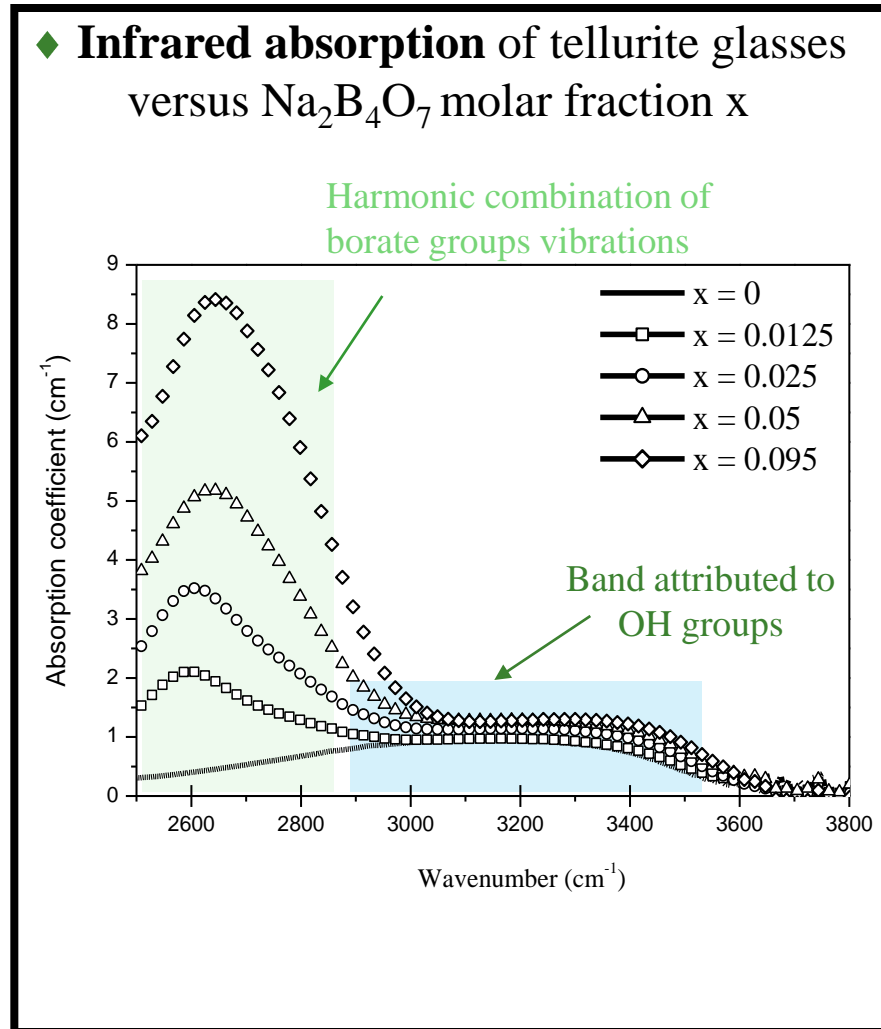
- ◆ Intensity of emission at 1.5 μm versus $\text{Na}_2\text{B}_4\text{O}_7$ molar fraction x



High emission at 1534 nm for $x=0.025$

Why is that important to measure OH groups?

- Example: $(1-x)\text{TeO}_2 - x\text{Na}_2\text{B}_4\text{O}_7$

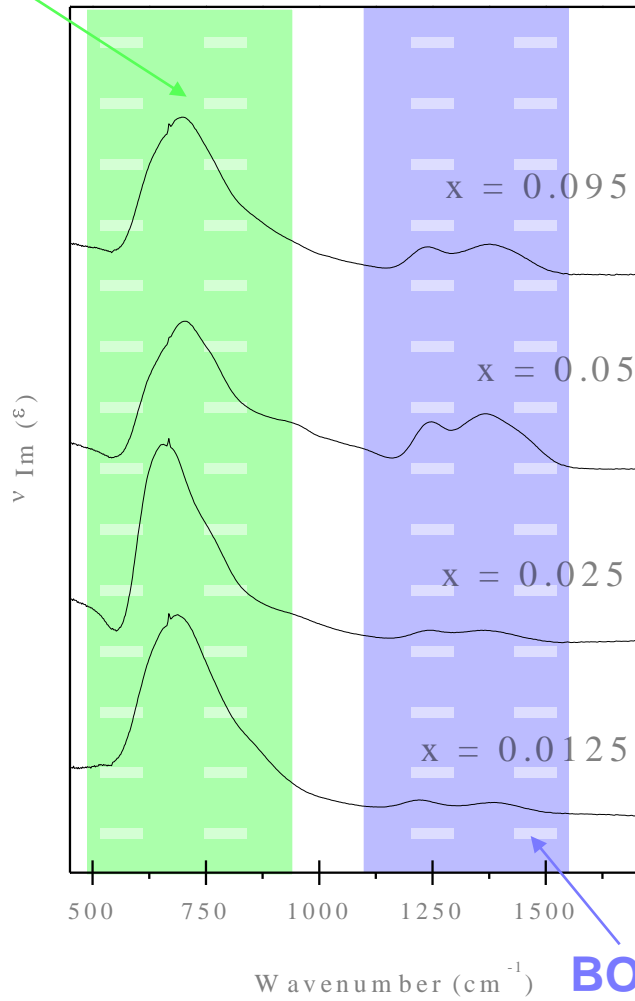


J. Non-Cryst. Solids, 298 (1)
(2001) 76-88

Why is that important to measure OH groups?

Infrared spectra

TeO₄ units

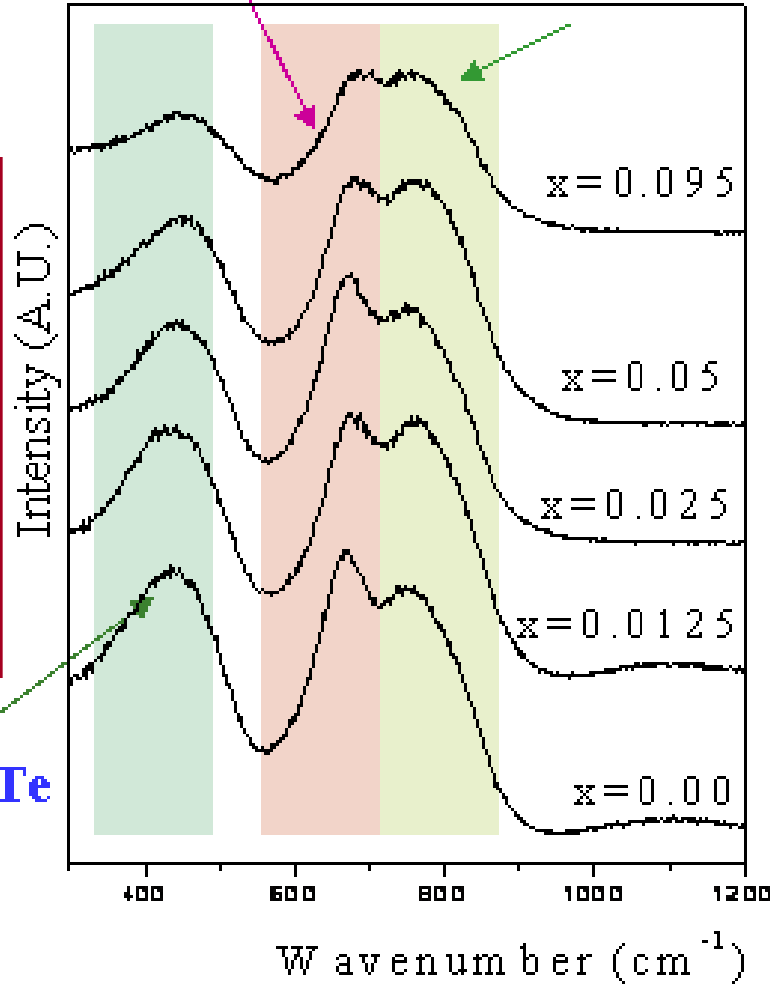


Increase of Na₂B₄O₇ content
 → More distorted TeO₄ called TeO₃₊₁
 → Formation of BO₃ groups

Raman spectra

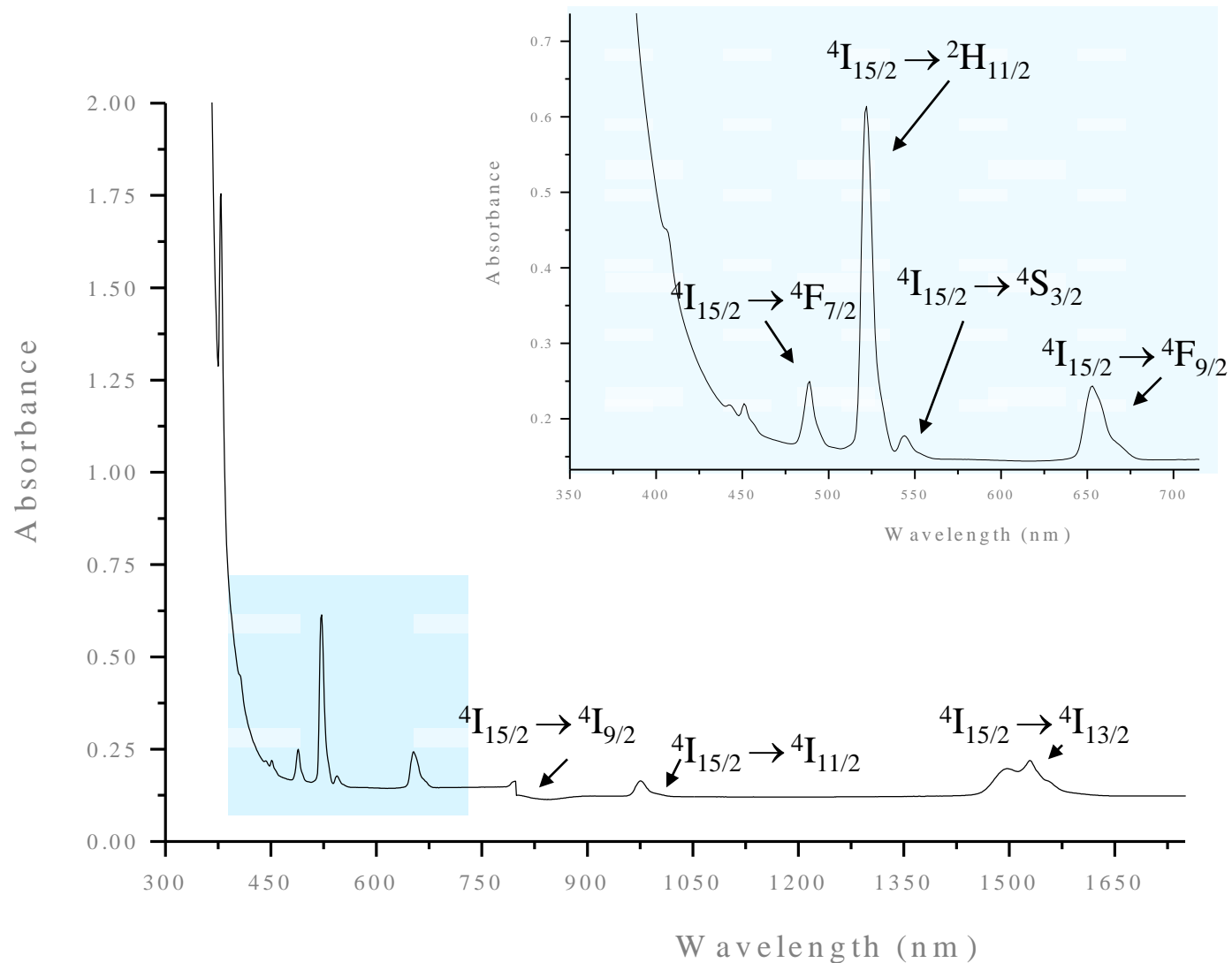
TeO₄

TeO₃

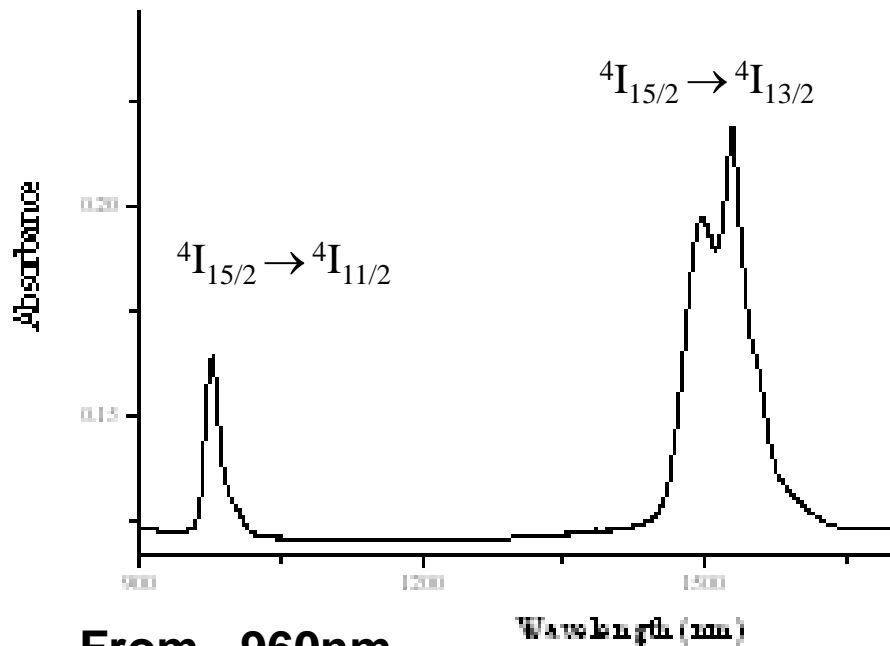


Te-O-Te

Absorption spectrum: $(1-x)\text{TeO}_2 - x\text{Na}_2\text{B}_4\text{O}_7$ with $x = 0.025$



Absorption spectrum: $(1-x)\text{TeO}_2 - x\text{Na}_2\text{B}_4\text{O}_7$ with $x = 0.025$

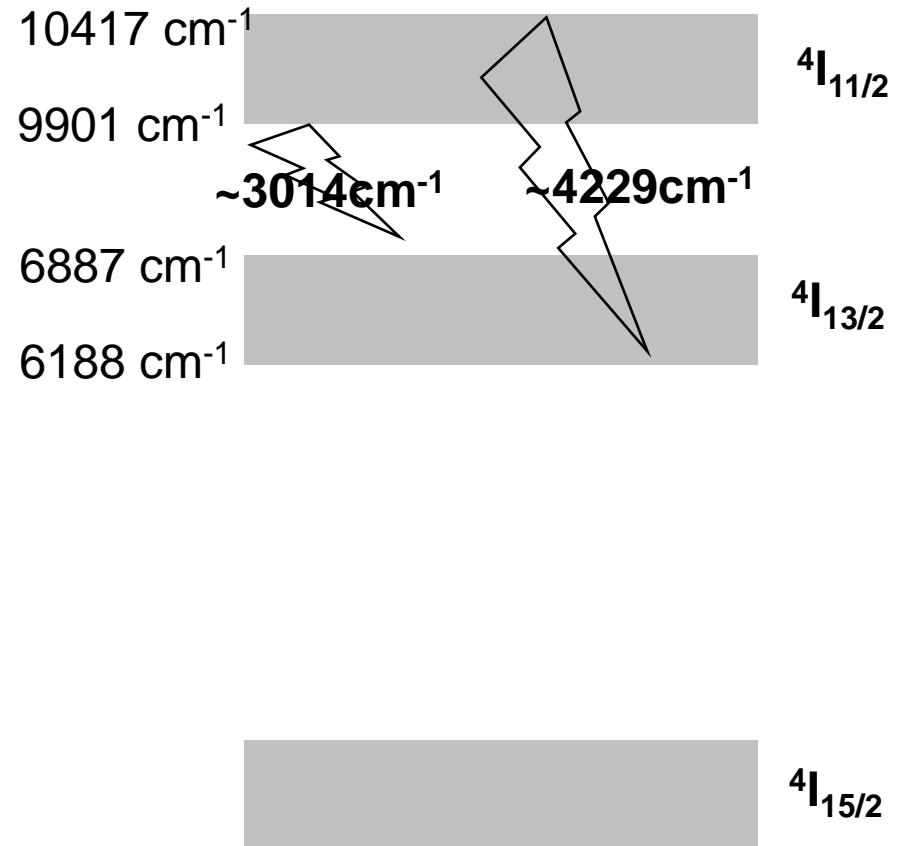


From ~960nm
to ~1010nm

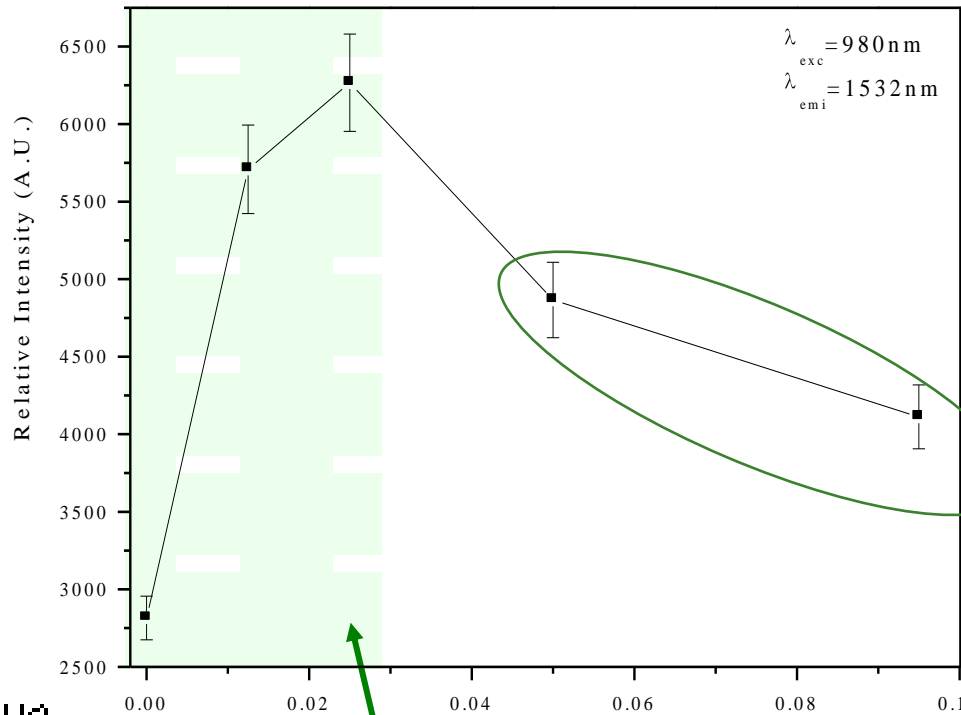
Wavelength (nm)

From ~1452nm
to ~1616nm

Frequency of non-radiative transition?



Example: $(1-x)\text{TeO}_2 - x\text{Na}_2\text{B}_4\text{O}_7$

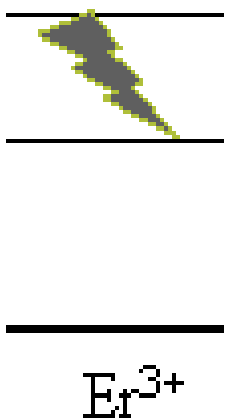


x Decrease due to high OH⁻ content

Vibration of BO₃ groups ($\nu_{\text{BO}_3} = 1450 \text{ cm}^{-1}$)

$\Rightarrow \uparrow$ multiphonon relaxations ${}^4\text{I}_{11/2} \rightarrow {}^4\text{I}_{13/2}$

Better population inversion on the ${}^4\text{I}_{13/2}$ excited level of Er³⁺



Conclusion

- IR spectroscopy is simple, fast and non destructive
- IR spectroscopy is used to analyze the structure and check the presence of impurities of
 - Bulk
 - Film
 - Powder

References

- <http://www.organicworldwide.net/indexnew.html?infrared.html&boven.html&onder.html>
- <http://sis.bris.ac.uk/~sd9319/spec/IR.htm>
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