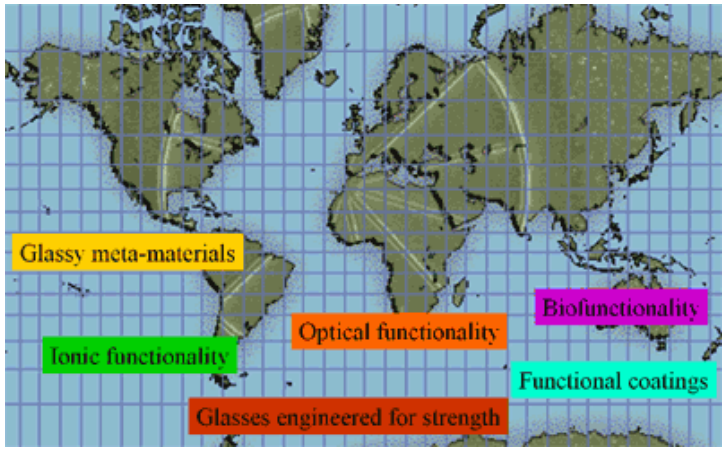


June 2005

International Materials Institute for
NEW FUNCTIONALITY IN GLASSES
Glass Tutorial

Glass structure by infrared reflectance spectroscopy

E.I. Kamitsos

Theoretical and Physical Chemistry Institute
National Hellenic Research Foundation, Athens, Greece

Glass Tutorial Series: prepared for and produce
International Material Institute for New Functional
An NSF sponsored program – material herein no
Available at www.lehigh.edu/imi

Outline of presentation

1. Basic principles of vibrational spectroscopy

- Comparison of infrared / Raman: common characteristics & differences in mechanism and selection rules

2. Sampling methods in infrared spectroscopy

- Advantages of infrared reflectance spectroscopy

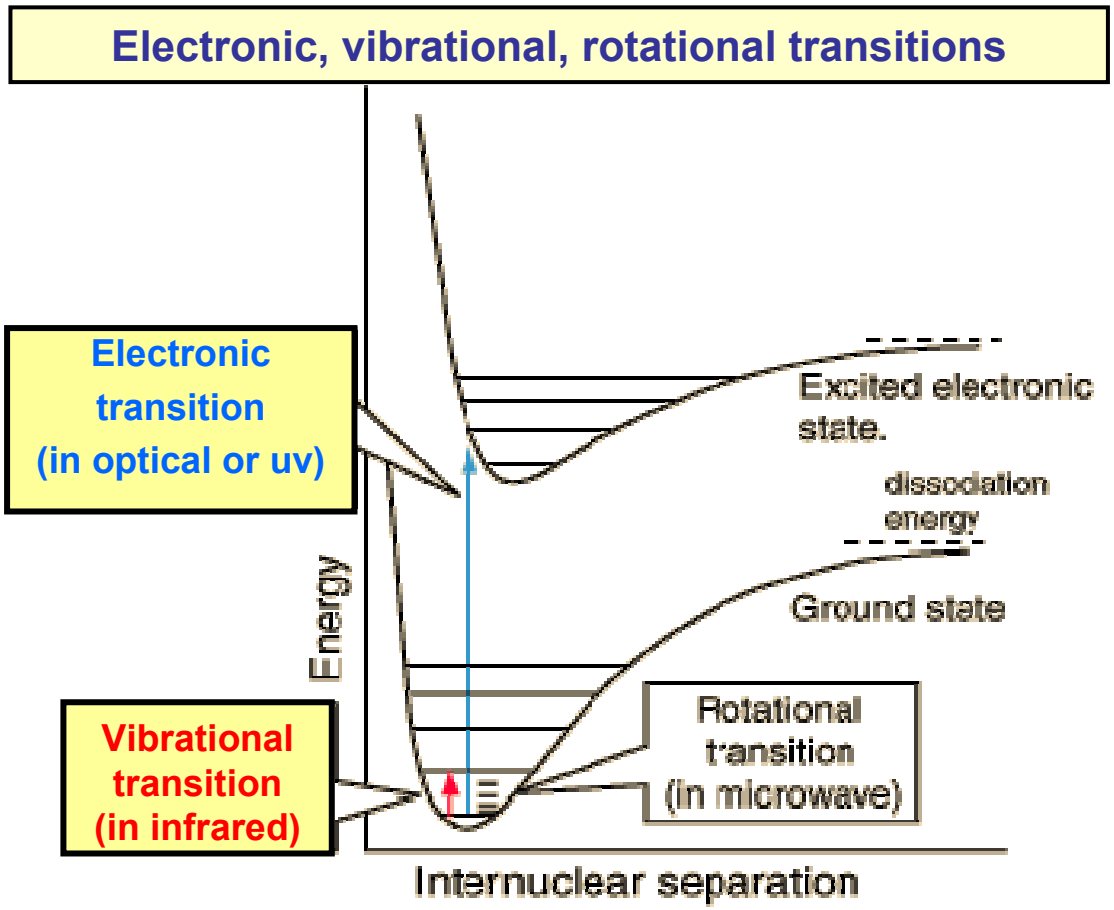
3. Methods of analysis of infrared reflectance spectra

- Fitting of reflectivity using classical dispersion theory
- Kramers-Kronig (K-K) transformation
- Comparison of K-K and reflectivity fitting results

4. Examples of IR reflectance spectroscopy in glass structural studies

- Single alkali & alkaline earth borate glasses: structure of glass network & metal ions sites
- Dependence of Na-borate glass structure on depth from the glass surface.

Basic principles of vibrational spectroscopy



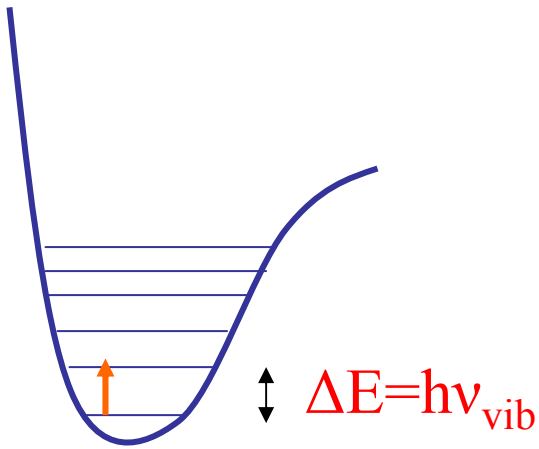
Infrared & Raman spectroscopy in materials science

Common characteristics:

- Probe structure and bonding through molecular vibrations
- Can probe both crystalline and amorphous phases (no long-range order required)
- Widely used in materials science

Infrared & Raman spectroscopy:
differences in mechanism & selection rules

INFRARED



Infrared:

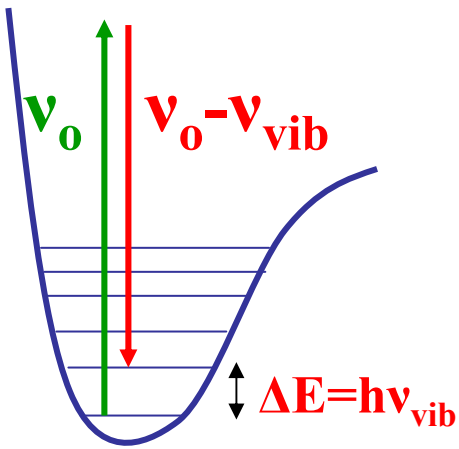
- **Resonance phenomenon:** $E=h\nu_0=\Delta E=h\nu_{vib}$
- **Selection rules (harmonic oscillator):**

$\Rightarrow$ **$\Delta n=\pm 1$, n: quantum number**

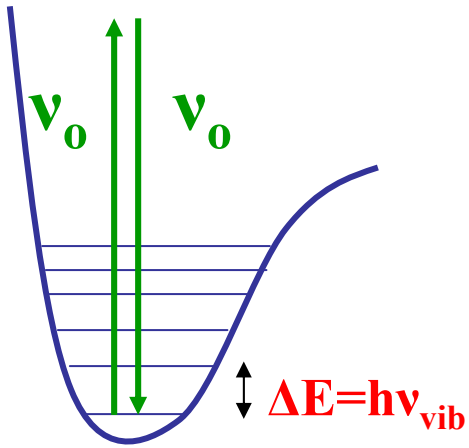
$\Rightarrow$ **$(\partial\mu/\partial x)_0 \neq 0$, μ: dipole moment**

Infrared & Raman spectroscopy:
differences in mechanism & selection rules, cont.

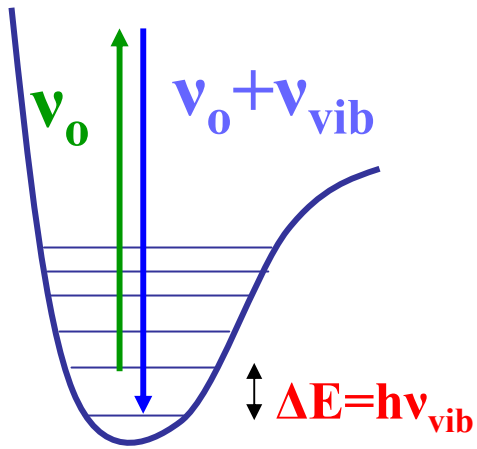
RAMAN



inelastic
Stokes Raman
<<0.01%



elastic
Rayleigh
>>99.99%



inelastic
anti-Stokes Raman
<<0.01%

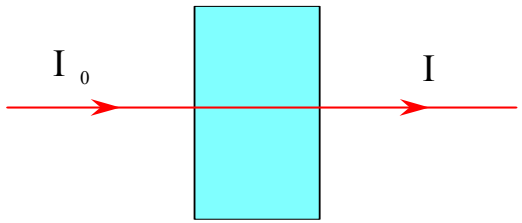
Raman:

- Scattering phenomenon: $E=h\nu_0 >> \Delta E=h\nu_{vib}$
- Selection rules (harmonic oscillator):

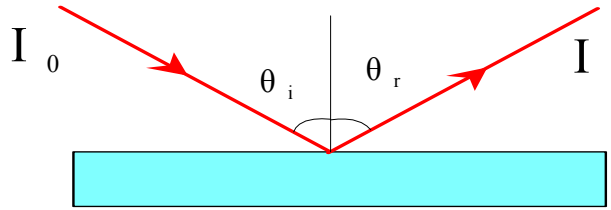
$\Rightarrow \Delta n=\pm 1$, n: quantum number

$\Rightarrow (\partial\alpha/\partial x)_0 \neq 0$, α: polarizability ($\mu_{ind}=\alpha E$)

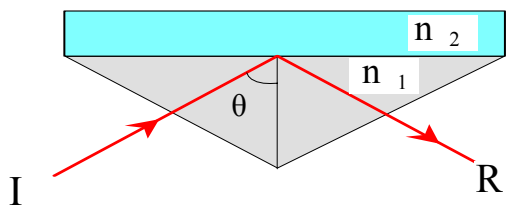
Sampling methods for measuring infrared spectra



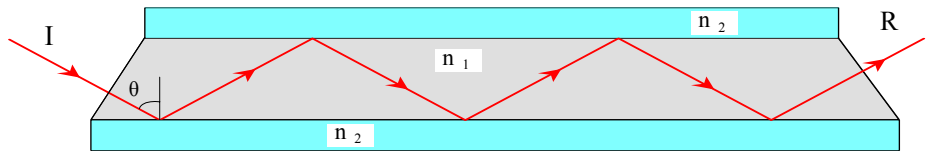
Transmission



Specular Reflection

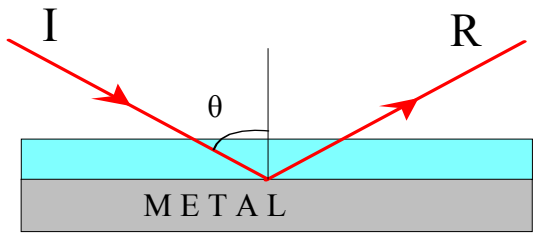


Attenuated Total Reflectance (ATR) – single reflection

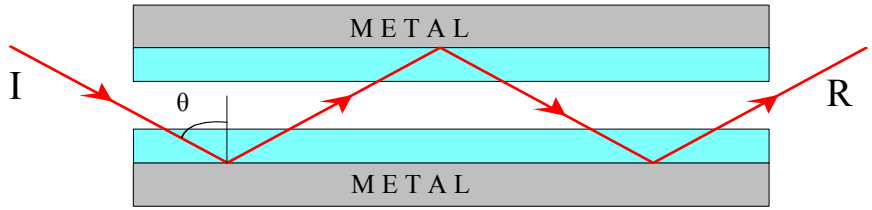


ATR – multiple reflection

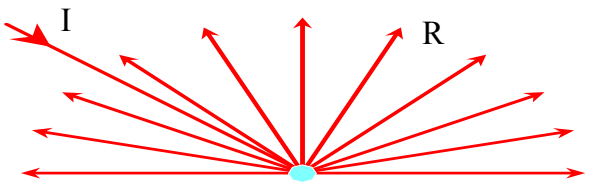
Sampling methods for measuring infrared spectra , cont.



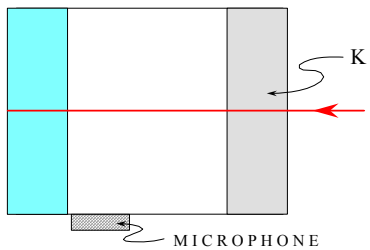
Reflection-Absorption Spectroscopy (RAS) – single reflection



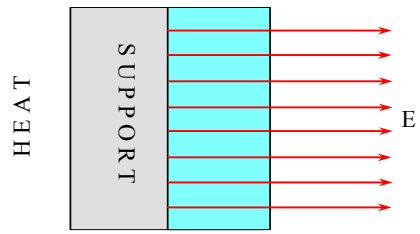
RAS – multiple reflection



Diffuse Reflectance Spectroscopy



Photoacoustic Spectroscopy



Emission Spectroscopy

Advantages of infrared reflectance spectroscopy

- True band shapes:

- no band distortion and hydrolysis effects associated with the use of alkali halide salts as matrix materials in traditional transmission measurements,

-no saturation effects and background interference patterns encountered in transmission measurements on films.

- Use the same samples for data acquisition in a broad frequency range covering both the mid- and far-infrared (ca. 20 – 5000 cm^{-1}).

- Combined with the use of modern Fourier-transform spectrometers and the availability of software, infrared reflectance leads to the quantitative determination of the frequency-dependent optical and dielectric properties of materials.

$\Rightarrow$ **Infrared reflectance spectroscopy is a powerful tool in materials science.**

ANALYSIS OF REFLECTIVITY SPECTRA

$$R(\nu) = \frac{[n(\nu)-1]^2 + k^2(\nu)}{[n(\nu)+1]^2 + k^2(\nu)}$$

R(ν): measured reflectivity

n(ν): refractive index

k(ν): exctinction coefficient

$\tilde{n}(\nu)$=n(ν)+ik(ν) complex refractive index

Analysis methods:

- Reflectance curve fitting
- Kramers-Kronig transformation

REFLECTANCE CURVE FITTING

Use a model for the dielectric function, $\tilde{\varepsilon}(\nu)$, to fit the reflectivity spectrum.

$\tilde{n}(\nu) \equiv n(\nu) + ik(\nu) = \sqrt{\tilde{\varepsilon}(\nu)}$. Classical dispersion theory:

$$\tilde{\varepsilon}(\nu) = \varepsilon'(\nu) + i\varepsilon''(\nu) = \varepsilon_\infty + \sum_j \frac{\Delta\varepsilon_j \, \nu_j^2}{\nu_j^2 - \nu^2 - i\nu\Gamma_j}$$

Lorentzian oscillators:

ν_j = resonance frequency; Γ_j = bandwidth; $\Delta\varepsilon_j$ = dielectric strength

ε_∞ = high frequency dielectric constant

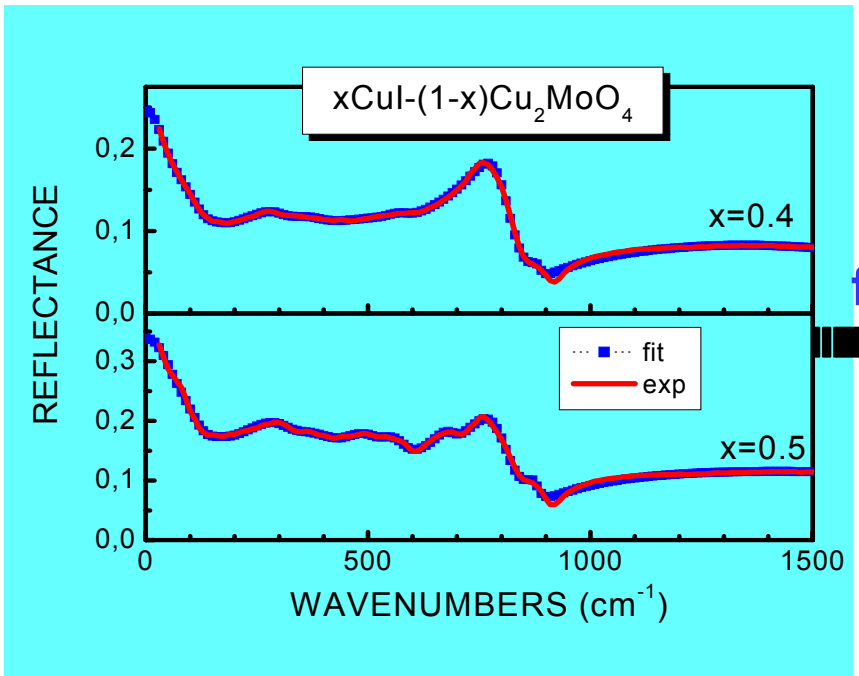
$$\varepsilon'(\nu) = n^2(\nu) - k^2(\nu) = \varepsilon_\infty + \sum_j \frac{\Delta\varepsilon_j \, \nu_j^2(\nu_j^2 - \nu^2)}{(\nu_j^2 - \nu^2)^2 + \Gamma_j^2\nu^2}$$

$$\varepsilon''(\nu) = 2n(\nu)k(\nu) = \sum_j \frac{\Delta\varepsilon_j \nu_j^2 \Gamma_j \nu}{(\nu_j^2 - \nu^2)^2 + \Gamma_j^2\nu^2}$$

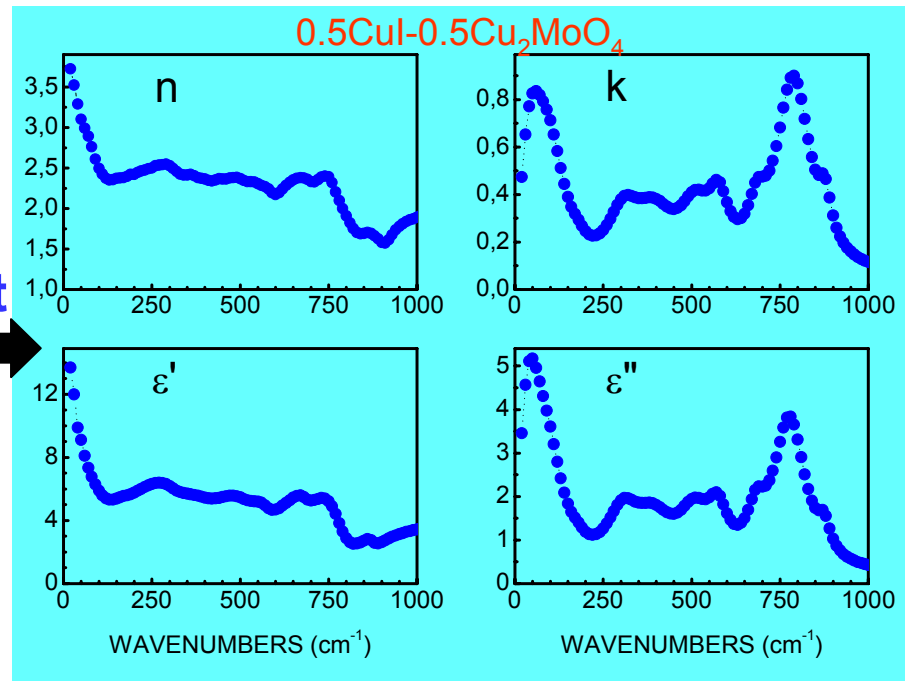
Example of Reflectance Curve Fitting

$$R(\nu) = \frac{[n(\nu) - 1]^2 + k^2(\nu)}{[n(\nu) + 1]^2 + k^2(\nu)} = f[\varepsilon'(\nu), \varepsilon''(\nu)]$$

The adjustable parameters (ν_j, Γ_j, $\Delta\varepsilon_j$, ε_∞) are determined by best fitting the calculated R(ν) spectrum to the experimental reflectivity spectrum.



fit



Dispersion parameters obtained by fitting the reflectivity data of $xCuI\text{-}(1\text{-}x)Cu_2MoO_4$ glasses

	$0.4CuI\text{-}0.6Cu_2MoO_4$			$0.5CuI\text{-}0.5Cu_2MoO_4$		
j	ν_j (cm^{-1})	Γ_j (cm^{-1})	$\Delta\varepsilon_j$	ν_j (cm^{-1})	Γ_j (cm^{-1})	$\Delta\varepsilon_j$
1	58.0	110.0	3.422	62.8	110.0	6.254
2	113.8	115.0	1.029	110.0	112.1	1.662
3	175.0	50.0	0.025	180.0	50.0	0.043
4	301.0	90.0	0.109	310.0	113.7	0.430
5	390.0	144.6	0.161	399.4	145.2	0.394
6	490.0	100.0	0.048	501.9	91.2	0.167
7	579.2	79.9	0.034	570.3	88.3	0.192
8	670.0	70.0	0.010	684.4	58.2	0.077
9	782.5	104.8	0.441	779.0	110.7	0.500
10	881.5	30.3	0.011	875.1	40.0	0.027
	ε_∞=3.4			ε_∞=4.4		

KRAMERS-KRONIG TRANSFORMATION

Measured quantity: Reflectivity, $R(\nu)=I_r(\nu)/I_i(\nu)$

$I_r(\nu)$ = Intensity of the reflected beam

$I_i(\nu)$ = Intensity of the incident beam

$$\rho(\nu)=r(\nu)\exp[i\theta(\nu)]$$

$\rho(\nu)$ = complex reflectivity coefficient

$r(\nu)$ = amplitude = $[R(\nu)]^{1/2}$

$\theta(\nu)$ = phase difference between reflected and incidence beam

$$\theta(\nu)=\frac{2\nu}{\pi}\,P\int_0^{\infty}\frac{\ln r(\nu_i)-\ln r(\nu)}{\nu^2-\nu_i^2}\,d\nu_i$$

Kramers-Kronig (K-K) transformation: measure $R(\nu) \Rightarrow$ calculate $\theta(\nu)$

Kramers-Kronig transformation, cont.

⇒ Optical response functions for normal incidence (Fresnel relations):

$$n(\nu) = \frac{1 - r^2(\nu)}{1 + r^2(\nu) - 2\, r(\nu)\, \cos\theta(\nu)}$$

$$k(\nu) = \frac{2\, r(\nu)\, \sin\theta(\nu)}{1 + r^2(\nu) - 2\, r(\nu)\, \cos\theta(\nu)}$$

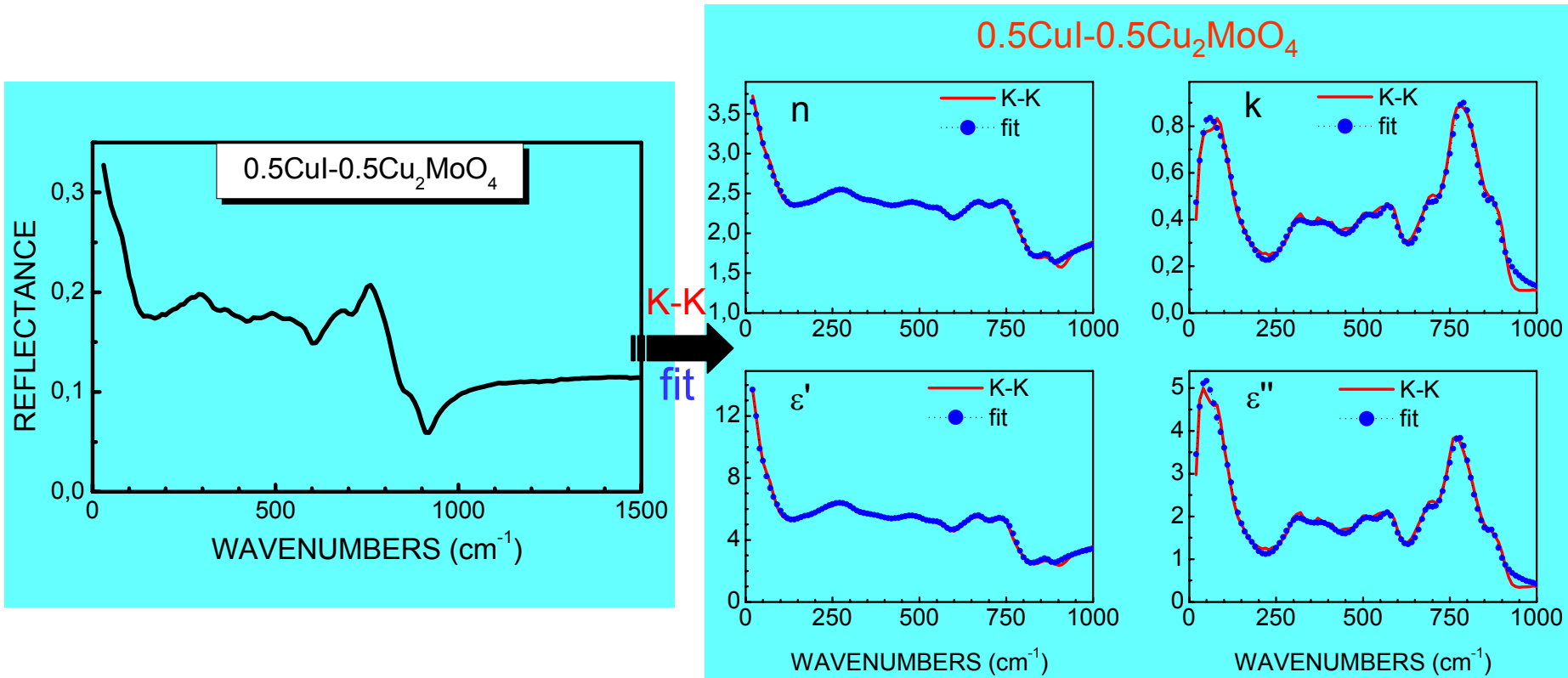
⇒ Dielectric functions: $\varepsilon'(\nu) = n^2(\nu) - k^2(\nu)$

$$\varepsilon''(\nu) = 2\, n(\nu)\, k(\nu)$$

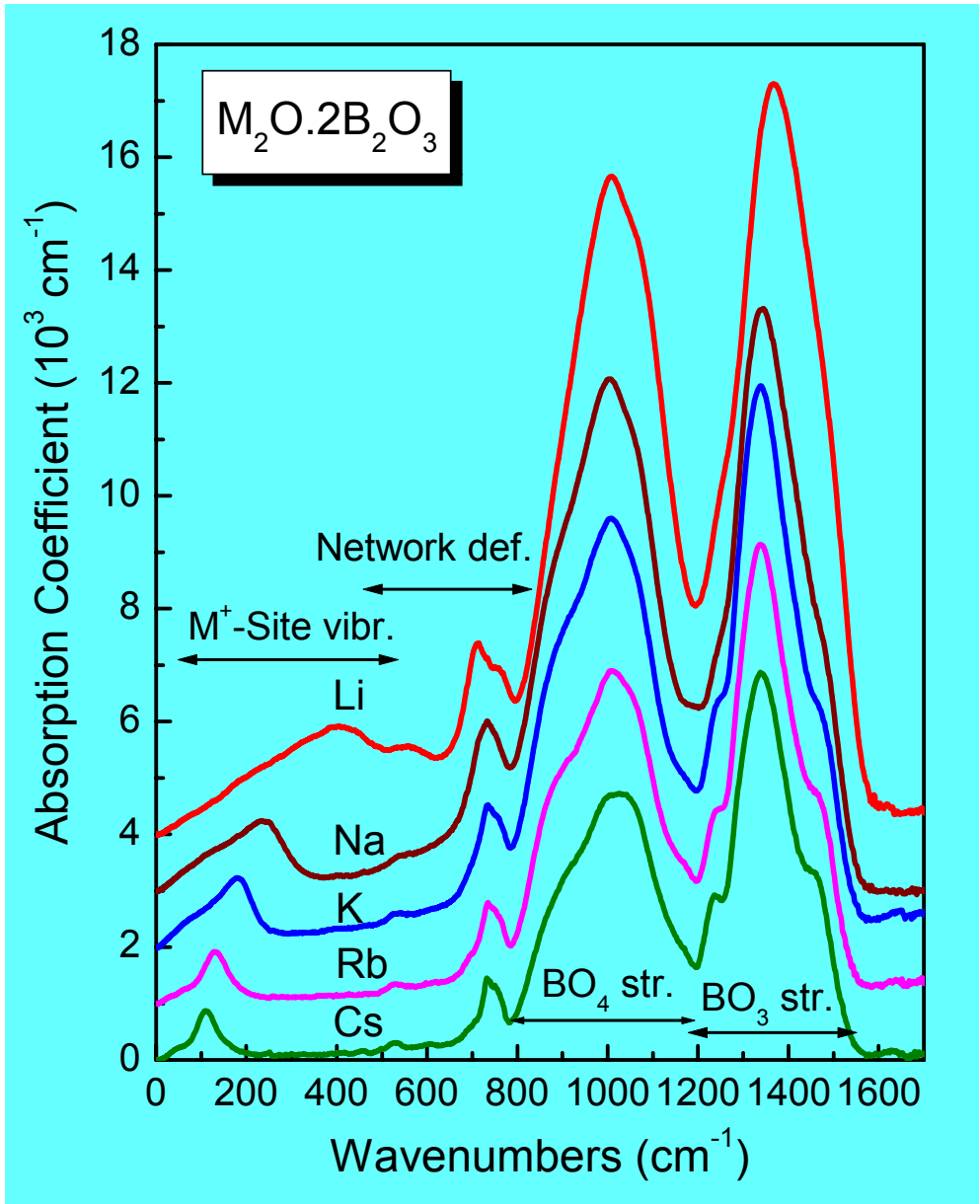
⇒ Absorption coefficient: $\alpha(\nu) = 4\pi\nu k(\nu)$

⇒ Optical conductivity: $\sigma(\nu) = (2\pi c\varepsilon_0)\nu\varepsilon''(\nu)$

Optical (n, k) and dielectric (ε′, ε″) properties of the 0.5CuI-0.5Cu_2MoO_4 glass obtained by K-K analysis and fitting of reflectivity spectra



Infrared absorption spectra of alkali diborate glasses obtained by K-K analysis of the reflectance spectra



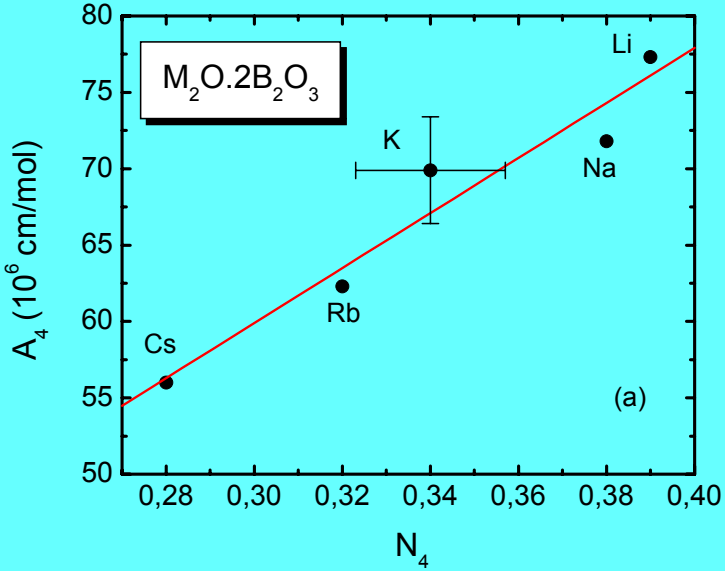
Mid-Infrared
(above ca. 500 cm^{-1})

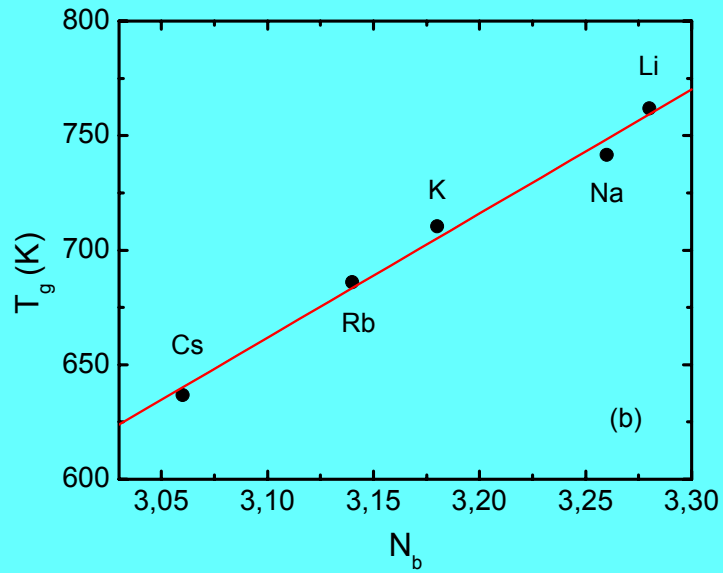
⇒ Vibrations of Short Range Order (SRO) borate network units

Far-Infrared
(below ca. 500 cm^{-1})

⇒ Metal ion–site (M-O) vibrations

Normalized infrared intensity A_4 versus the fraction of four-fold coordinated boron atoms, N_4, determined from NMR





$A_4 = \langle A_4 \rangle V_{mol}$

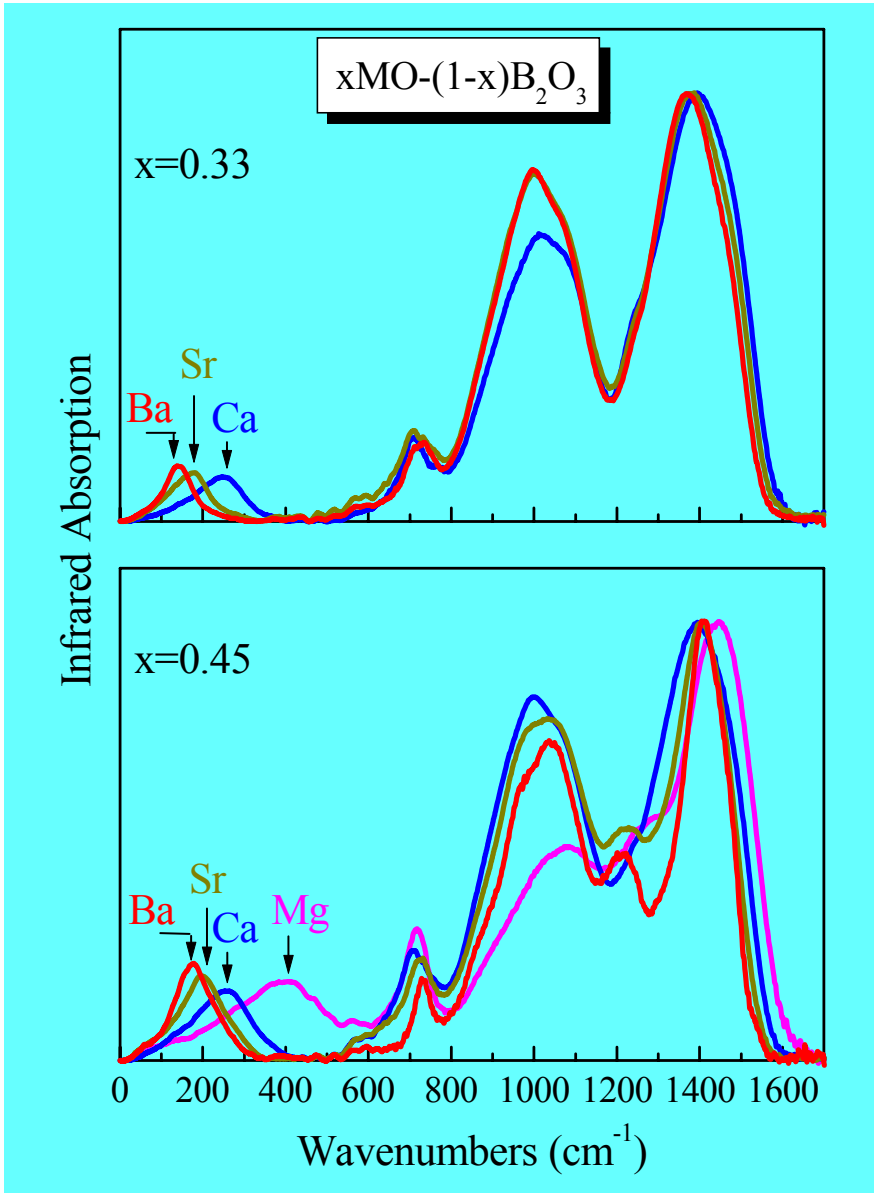
$\langle A_4 \rangle$ = integrated intensity of the 800-1200 cm^{-1} region

V_{mol} = glass molar volume

Glass transition temperature, T_g, versus number of bridging B-O bonds per boron atom, N_b.

$N_b = 2.5 + 2N_4$

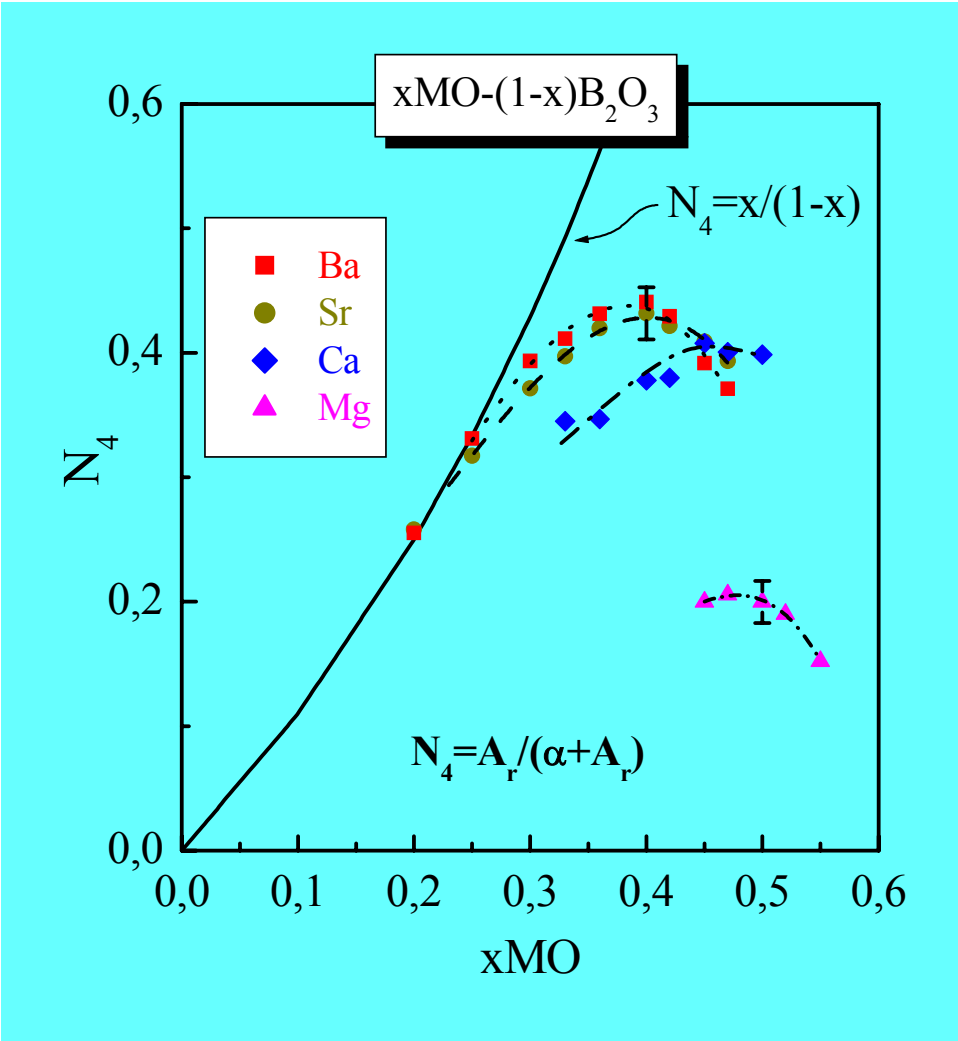
Infrared absorption spectra of alkaline earth borate glasses obtained by K-K analysis of the reflectance spectra



Mid-Infrared:

⇒ SRO structure depends on both MO content and type

Fraction of four-fold coordinated boron atoms, N_4, in alkaline earth borate glasses obtained from analysis of the infrared spectra



$N_4 = A_r/(\alpha+A_r)$

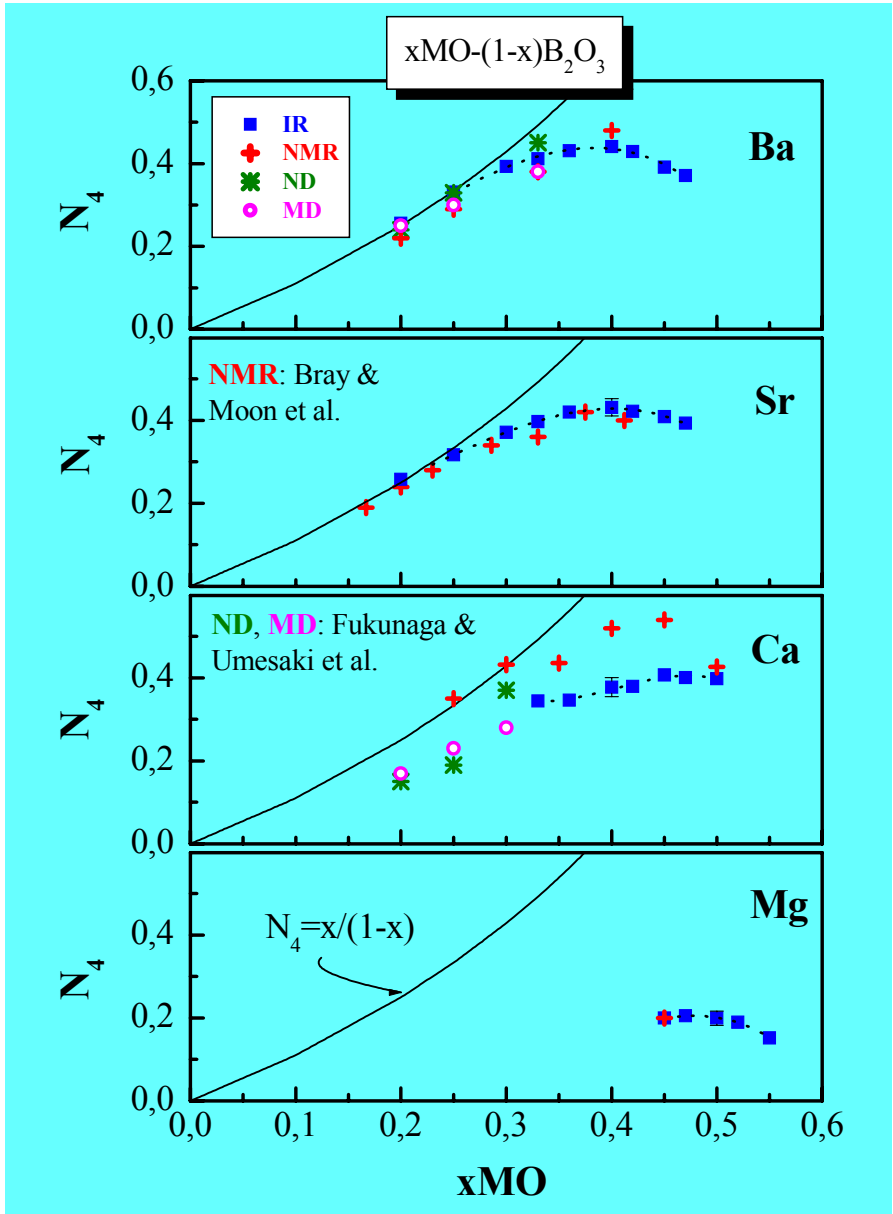
$A_r = \langle A_4\rangle/\langle A_3\rangle$

$\langle A_4\rangle$ = integrated intensity of the 800-1150 cm^{-1} region

$\langle A_3\rangle$ = integrated intensity of the 1150-1550 cm^{-1} region

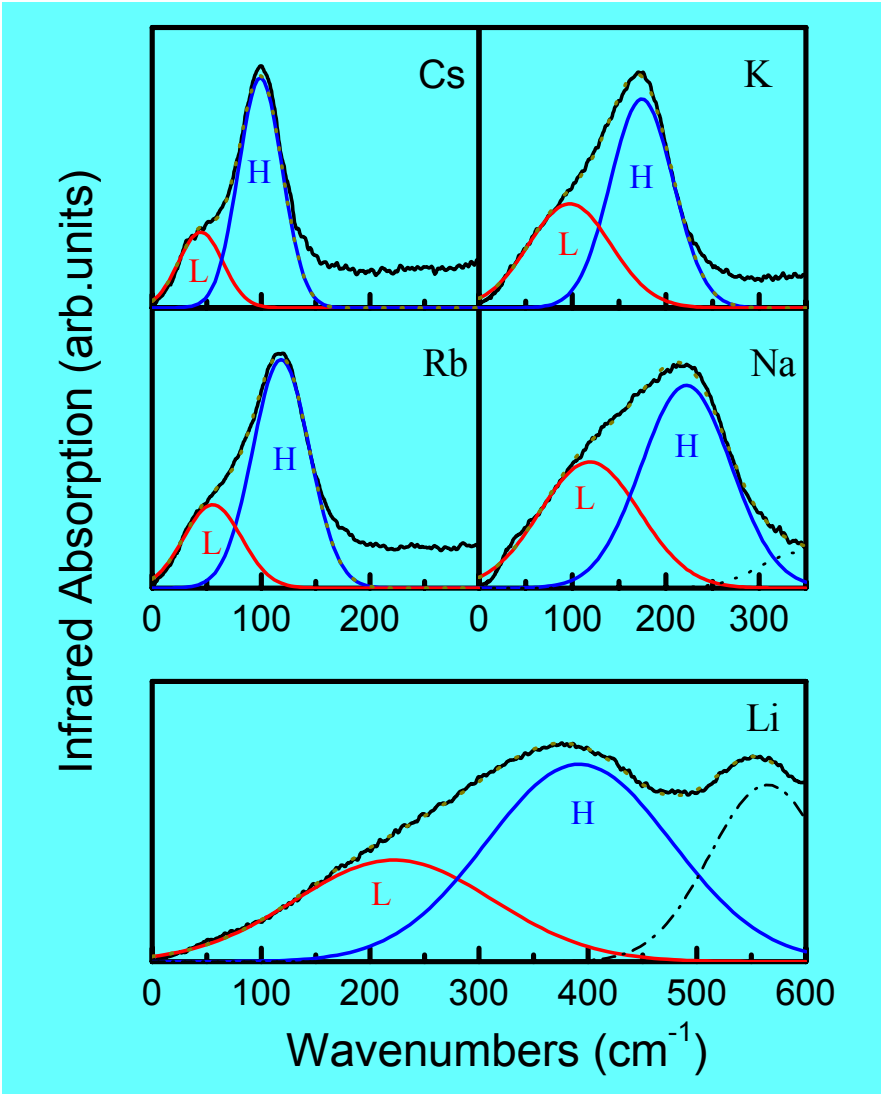
α =relative absorption coefficient of borate tetrahedral units (α=1.3)

Comparison of N_4 values of alkaline earth borate glasses obtained from IR, NMR, neutron diffraction (ND) and molecular dynamics (MD) studies

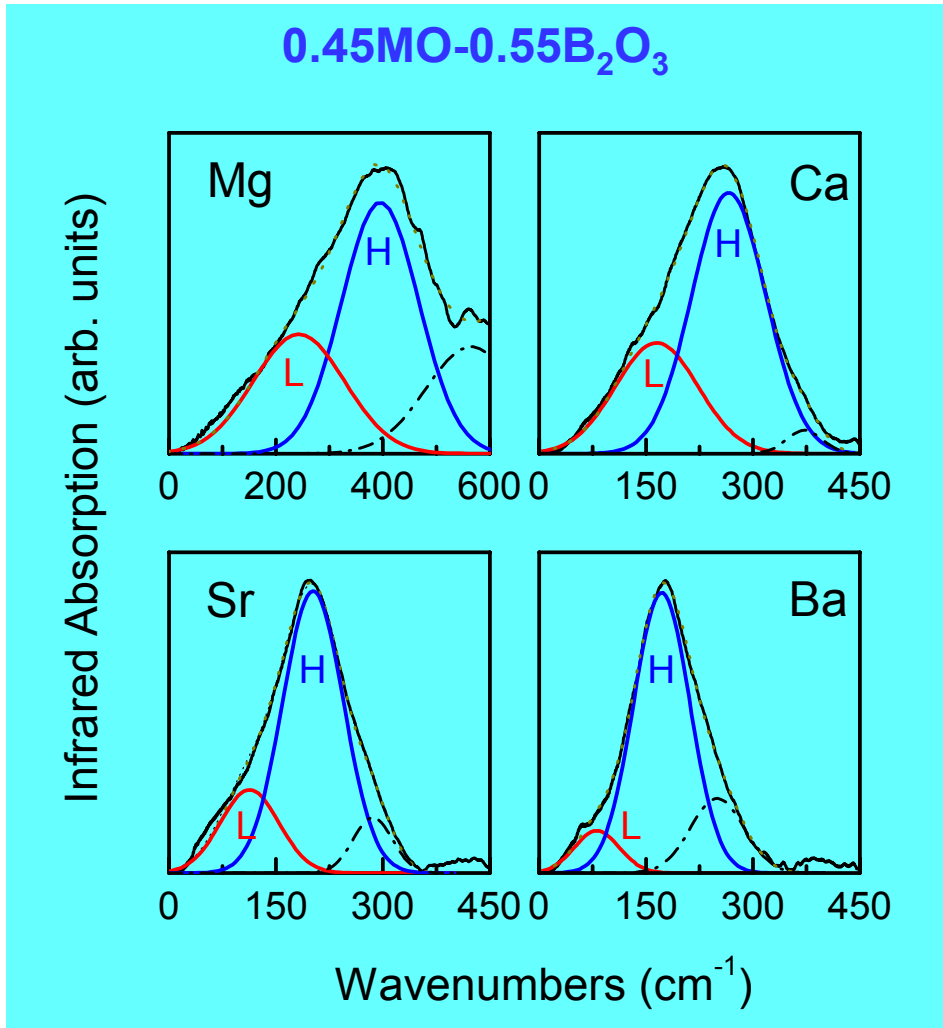


Proper analysis of infrared reflectance spectra can lead to the quantitative determination of the short-range order borate structure

Far-Infrared absorption spectra of alkali triborate glasses, M_2O-$3B_2O_3$, resulted from K-K analysis of the reflectance spectra

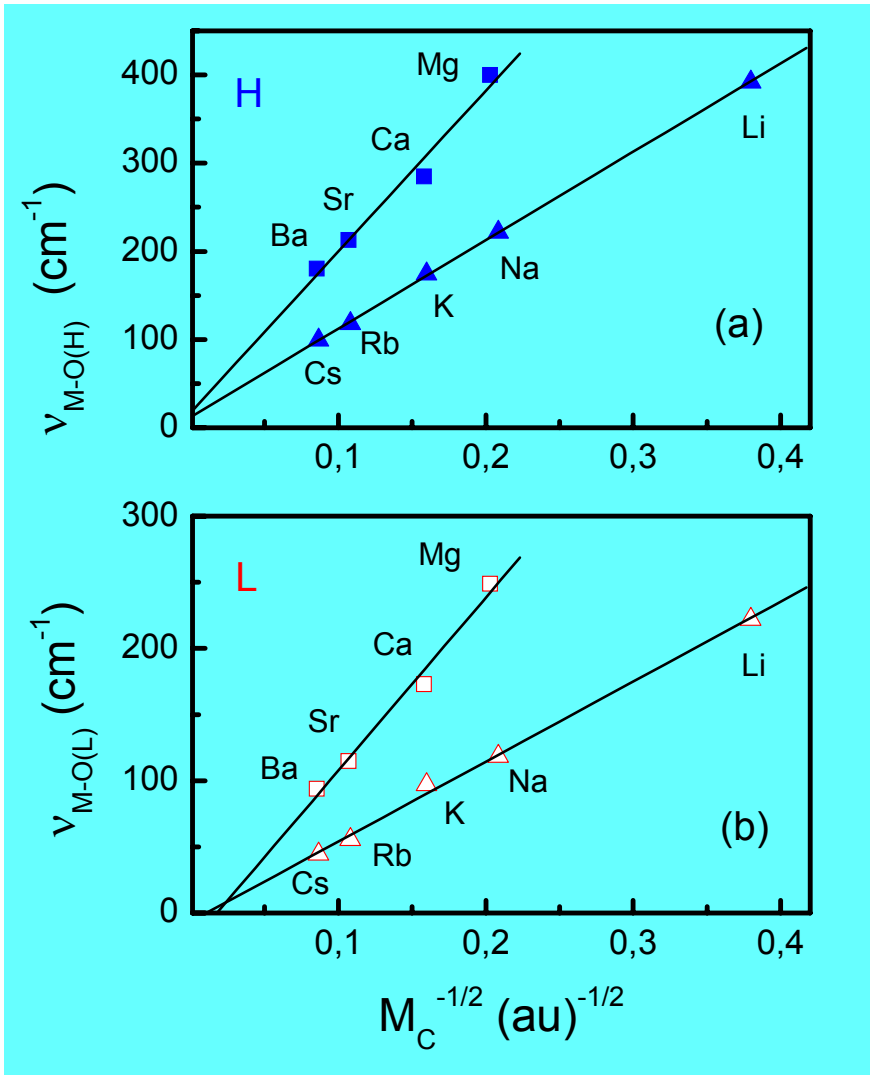


Far-Infrared absorption spectra of alkaline earth borate glasses resulted from K-K analysis of the reflectance spectra



Meta-ion site vibration frequencies, $\nu_{M\text{-}O}$, versus the square root of the inverse metal ion mass, $M_c^{-1/2}$

M_2O-$3B_2O_3$ (M=Li–Cs) & 0.45MO-0.55B_2O_3 (M=Mg-Ba)



$$\nu_{M\text{-}O} = (1/2\pi c)\,[f_{M\text{-}O} / \mu_{M\text{-}O}]^{1/2}$$

$f_{M\text{-}O}$ & $\mu_{M\text{-}O}$: the force constant and reduced mass of the metal ion – site vibration

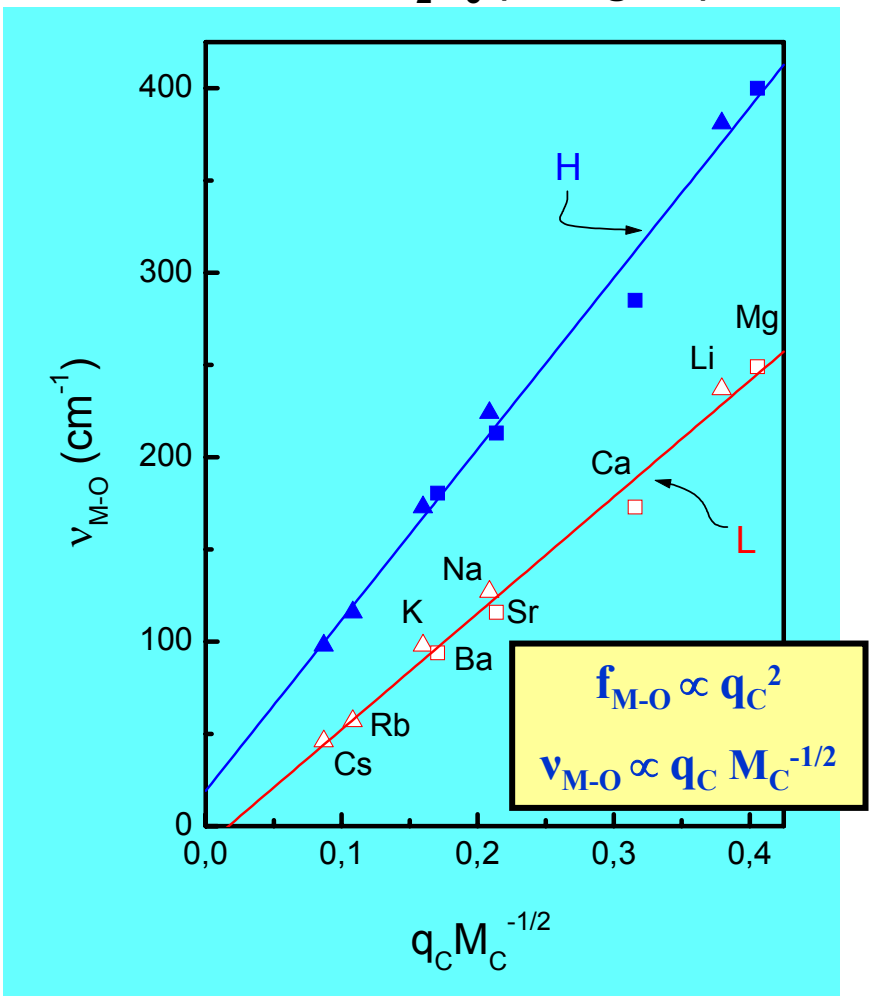
$$\mu_{M\text{-}O} \approx M_C$$

Meta-ion site vibration frequencies, ν_{M-O}, versus $q_C M_C^{-1/2}$

where q_C and M_C are the charge and mass of metal ion

M_2O-3B_2O_3 (M=Li–Cs)

0.45MO-0.55B_2O_3 (M=Mg-Ba)



Far-IR spectra:

- presence of two type of sites where M-O vibrations give rise to bands H & L

MD simulations on Li-borate glasses:

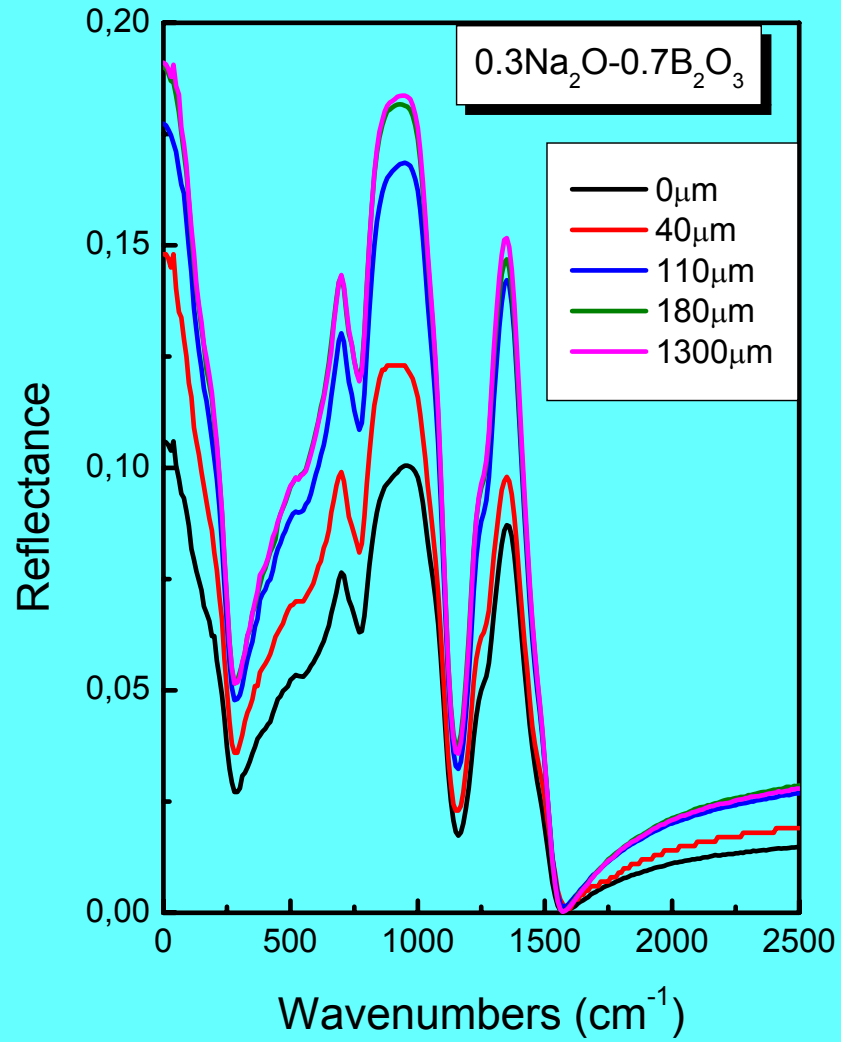
- H band: M-O vibrations in nb-type sites (non-bridging & bridging oxygen atoms)
- L band: M-O vibrations in b-type sites (bridging oxygen atoms)

Dependence of Na-borate glass structure on depth from the glass surface

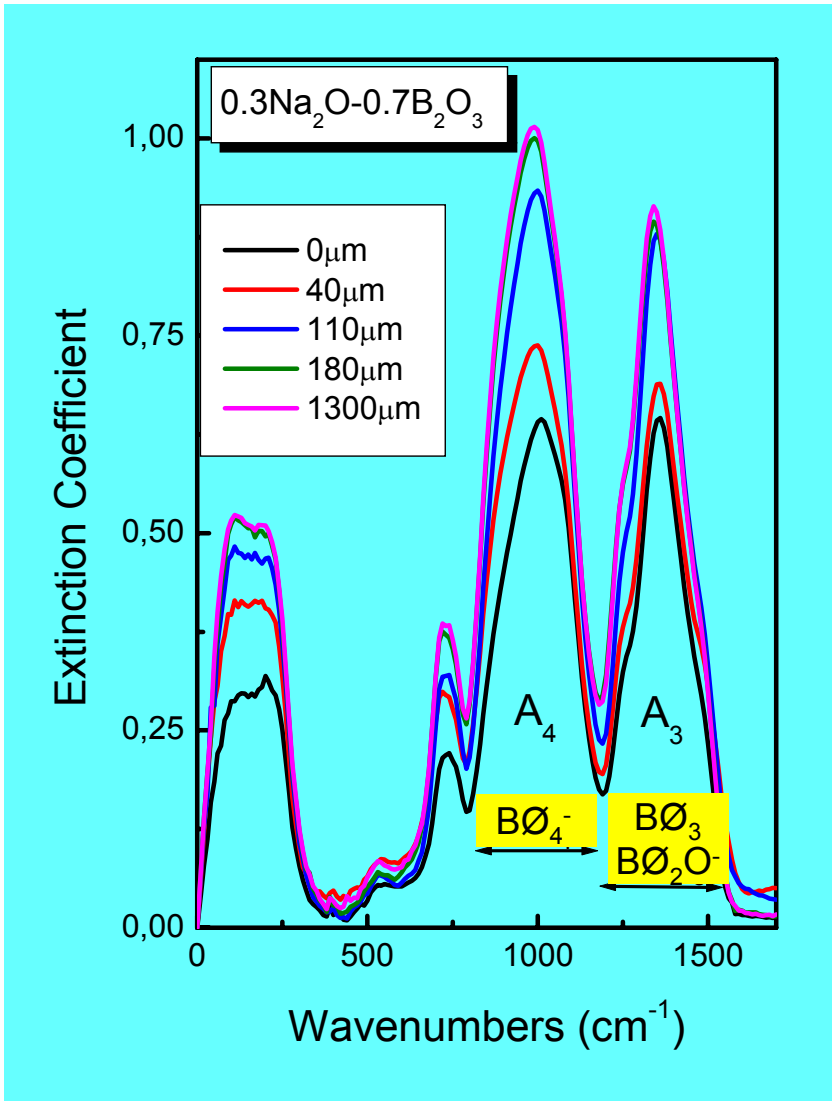
⇒ Glass disks were prepared by quenching from the melt, with diameter: 15mm, thickness: 2mm

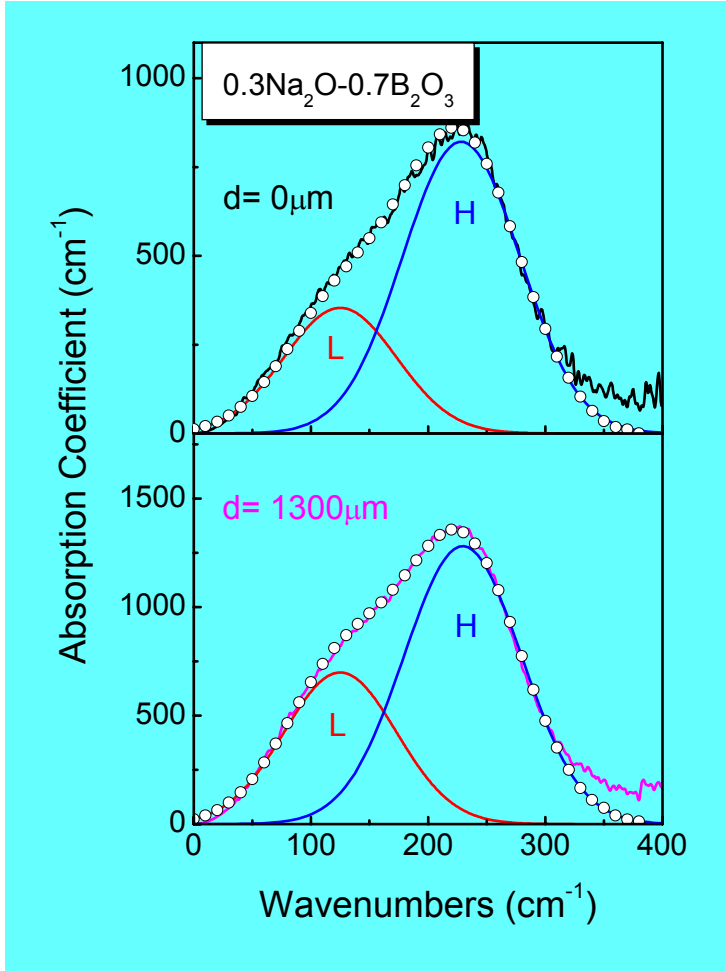
⇒ Controlled removal of glass layers by grinding & polishing the same specimen on an automatic polishing machine

⇒ Recording infrared reflectance spectra at various depths from the original glass surface



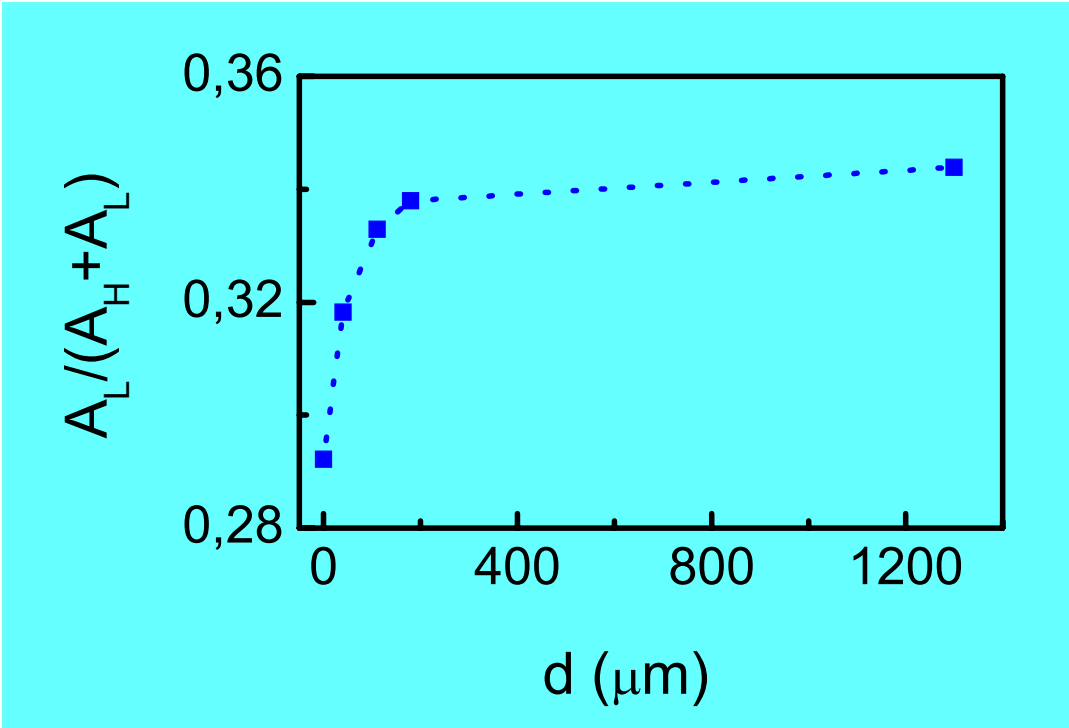
Infrared absorption spectra calculated from the reflectance spectra measured at different depths from the surface of the $0.3Na_2O$-$0.7B_2O_3$ glass





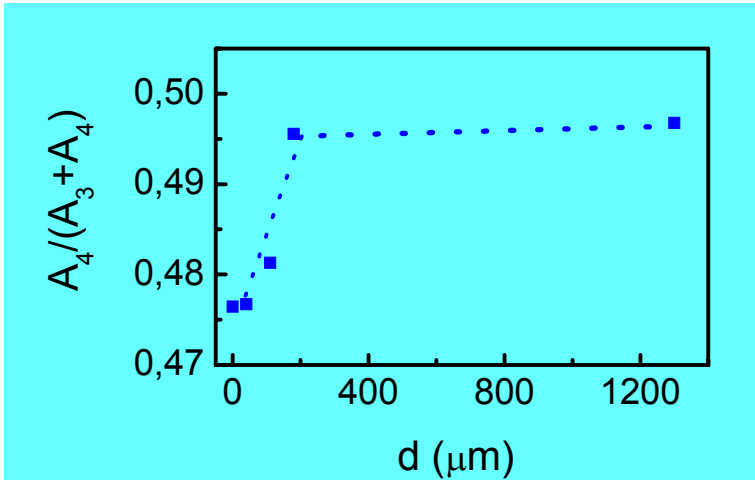
$0.3Na_2O$-$0.7B_2O_3$ Glass: Na Ion – Site Vibrations

Deconvolution of far infrared absorption spectra into Gaussian component bands



L-component band (b-type) of the Na-O (site) vibration gains relative intensity up to ca. 200 μm

$0.3Na_2O$-$0.7B_2O_3$ glass: Short-Range Order (SRO) Borate Structure



Borate SRO structure:

- Tetrahedral units: $B\emptyset_4^-$ (intensity A_4, mole fraction X_4)
- Trigonal units: $B\emptyset_3$ & $B\emptyset_2O^-$ (intensity A_3, mole fractions X_3 & X_2)

mass balance: $X_4+X_3+X_2=1$ $\Rightarrow X_3 = [B\emptyset_3]=0.57$

charge balance: $X_4+X_2=0.3/0.7=0.43$

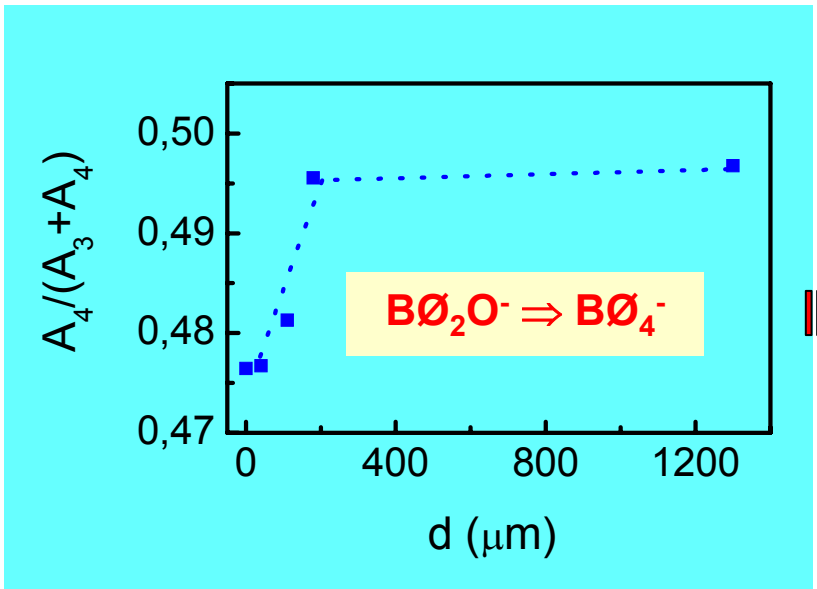
$B\emptyset_2O^- \Rightarrow B\emptyset_4^-$

Cooling rate gradient from the surface to the core of the glass sample

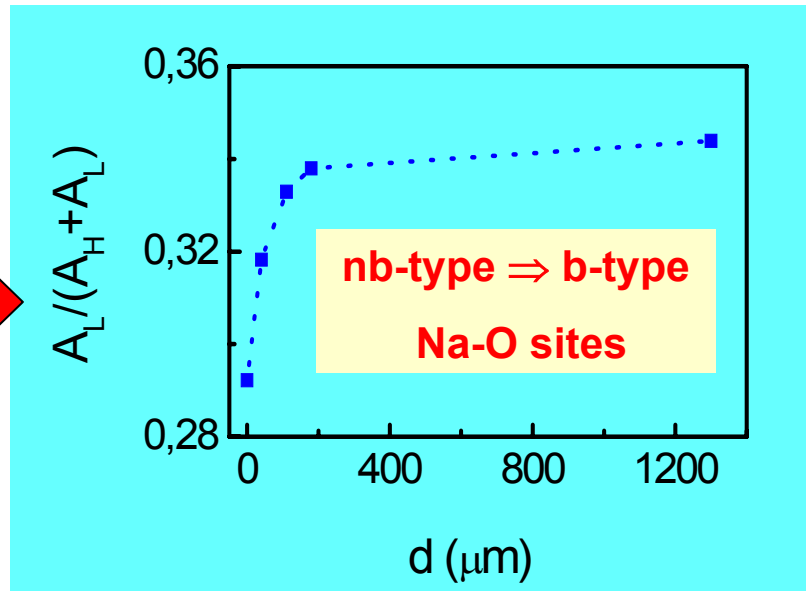
$0.3Na_2O$-$0.7B_2O_3$ Glass: Mid-IR & Far-IR correlations

Mid-Infrared: Short-Range Order (SRO)

Borate Structure



Far-Infrared: Na Ion – Site Vibrations



Infrared reflectance spectroscopy facilitates the simultaneous study of the SRO borate structures (mid-IR) and their effect on the relative population of the network sites hosting metal ions (far-IR)

ACKNOWLEDGMENT

Thanks to:

- Colleagues at NHRF, Athens, for original infrared spectral data.

- IMI – New Functionality in Glass, for support.