Contribution of infrared spectroscopy to the analysis of the glass structure

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- Infrared spectroscopy
- Retrieval of the optical functions
- Dielectric function models
- Focus software
- Origin of the vibrational modes
- Silicates glasses
- Aluminosilicate glasses
- Iron in silicate glasses and melts
Experimental observables

Parallel plate sufficiently thick to avoid the observation of interferences

Reflectivity \( \rho = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \)

Reflectance \( R_M = \rho \left[ 1 + \frac{(1 - \rho)^2 \tau^2}{1 - \rho^2 \tau^2} \right] \)

Transmittance \( T_M = \tau \frac{1 - \rho}{1 + \rho} \frac{1 - \rho^2}{1 - \rho^2 \tau^2} \)

Absorbance and Emittance

\( E = A = 1 - R_M - T_M = \frac{(1 - \rho)(1 - \tau)}{1 - \rho \tau} \)

* Measurement at near-normal incidence
Emittance measurement

Directional spectral emittance measurement
Ratio of the intensities emitted by the sample and a blackbody in the same conditions

\[ E(\omega, \hat{T}, \theta) = \frac{L(\omega, \hat{T}, \theta)}{L_{BB}(\omega, \hat{T})} \]

\( \hat{T} \): temperature

Blackbody
Ideal radiator whose spectral intensity is given by the Planck’s law

\[ L_{BB}(\omega, \hat{T}) = \frac{C_1 \omega^3}{\exp\left(\frac{C_2 \omega}{\hat{T}}\right) - 1} \]

\( C_1 = 1.191043 \times 10^{-16} \text{ W.m}^2.\text{Sr}^{-1} \)
\( C_2 = 0.01438777 \text{ mK} \)

Kirchhoff’s law
At LTE, spectral absorptance \( A \) and emittance are equal

\[ A(\omega) = E(\omega) \]
Bruker Vertex 80v and Vertex 70
Spectral range: [20-20 000 cm\(^{-1}\)](500-0.5 \mu m)

\[ \text{CO}_2 \text{ laser (500W)} \]
[400 - 3000 K]

**Measurements**
- Reflection \( R \)
- Transmission \( T \)
- Emission \( E \)

D. De Sousa Meneses, P. Melin, L. del Campo, L. Cosson, P. Ecchegut
Infrared Physics & Technology 69 96–101 2015
Infrared spectroscopy

SiO$_2$

Reflectivity - $\rho$

From experimental observables to physical properties

Glass

Isotropic infrared response.
The complexity of the glass structure is revealed by its polar vibrational dynamics.

Single crystal

Anisotropic infrared response.
Activity of normal modes (phonons) fixed by crystal symmetry and infrared spectroscopy selection rules
Complex refractive index extraction – inversion methods

IR-Visible-UV spectroscopies  Ellipsometry

<table>
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<th>$R_s$</th>
<th>$\rho$</th>
<th>$R_M$</th>
<th>$T_M$</th>
<th>$E$</th>
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Several inversion methods necessitates the knowledge of two experimental quantities.

Under certain conditions, 1 measure may be sufficient to determine the indices.

**Inversion method using the Kramers-Kronig relations**

\[
\delta(\omega_a) = \frac{1}{2\pi} \int_{0}^{\infty} \ln \left( \frac{\omega - \omega_a}{\omega + \omega_a} \right) \frac{d}{d\omega} \ln[\rho(\omega)] \, d\omega
\]

\[
\begin{align*}
\rho(\omega) &= \frac{1 + \rho(\omega) + \sqrt{1 + 4\rho(\omega) - (\rho(\omega) - 1)^2 k(\omega)^2}}{1 - \rho(\omega)} \\
k(\omega) &= -\frac{\ln(\tau(\omega))}{4\pi \omega d}
\end{align*}
\]

\[
\begin{align*}
n(\omega) &= \frac{1 + \rho(\omega)}{1 - \rho(\omega) - 2\sqrt{\rho(\omega)} \cdot \cos[\delta(\omega)]} \\
k(\omega) &= \frac{2\sqrt{\rho(\omega)} \cdot \sin[\delta(\omega)]}{1 + \rho(\omega) - 2\sqrt{\rho(\omega)} \cdot \cos[\delta(\omega)]}
\end{align*}
\]

$\theta_0$ : angle of incidence

Complex refractive index extraction – inversion methods

\[
\delta(\omega_a) = \frac{1}{2\pi} \int_0^\infty \ln \left| \frac{\omega - \omega_a}{\omega + \omega_a} \right| \frac{d}{d\omega} \ln[\rho(\omega)] d\omega
\]

\[
n(\omega) = \frac{1 - \rho(\omega)}{1 + \rho(\omega) - 2\sqrt{\rho(\omega)} \cdot \cos[\delta(\omega)]}
\]

\[
k(\omega) = \frac{2\sqrt{\rho(\omega)} \cdot \sin[\delta(\omega)]}{1 + \rho(\omega) - 2\sqrt{\rho(\omega)} \cdot \cos[\delta(\omega)]}
\]

\[
\rho = \frac{R_M(R_M - 2) - T_M^2}{1 + \sqrt{1 + T_M^2 - R_M(R_M - 2)^2} + 4R_M(R_M - 2)}
\]

\[
\tau = \frac{1}{T_M} \left( \frac{R_M}{\rho} - 1 \right)
\]

\[
n(\omega) = \frac{1 + \rho(\omega) + \sqrt{4\rho(\omega) - (\rho(\omega) - 1)^2 k(\omega)^2}}{1 - \rho(\omega)}
\]

\[
k(\omega) = -\frac{\ln(\tau(\omega))}{4\pi\omega d}
\]
Causal Voigt model

Allows to account for a Gaussian (G) broadening of a Lorentzian absorption profile (L).

\[ \varepsilon_V(\omega) = \varepsilon_\infty + \sum_j \hat{V}_j(\omega) = \varepsilon_\infty + \sum_j \hat{V}(\omega; A_j, \omega_j, \gamma_j, \sigma_j) \]

\[ \hat{V}_j(\omega) = V_j(x, y) \]

\[ = A_j \left[ -3 \frac{w(x-x_j + iy) + w(x+x_j + iy)}{\Re(w(iy))} + i \frac{w(x-x_j + iy) - w(x+x_j + iy)}{\Re(w(iy))} \right] \]

\[ x = \frac{2\sqrt{\ln 2}}{\sigma_j \omega_j} \quad x_j = \frac{2\sqrt{\ln 2}}{\sigma_j \omega_j} \quad y = \frac{\gamma_j}{\sigma_j \sqrt{\ln 2}} \]

Faddeeva function:

\[ w(z) = \frac{i}{\pi} \int_{-\infty}^{+\infty} \frac{e^{-t^2}}{z-t} \, dt = K(x, y) + i J(x, y) \]

Dielectric function models – disordered media

**Convolution model**
Expression based on a Gaussian distribution of damped harmonic oscillators

\[ \varepsilon(\omega) = \varepsilon_\infty + \sum_j \frac{S_j}{\sqrt{2\pi}\sigma_j} \int_{-\infty}^{+\infty} \exp \left[ -\frac{1}{2} \left( \frac{x - \omega_j}{\sigma_j} \right)^2 \right] \frac{dx}{x^2 - \omega^2 - i\gamma J} \]


The Voigt and convolution models have close absorption profiles for high frequency modes with low inhomogeneous broadening. The difference can be large at low frequency.

**Causal Gaussian model**
Allows to take into account several components having a Gaussian absorption profile respecting the causality principle.

\[ \varepsilon(\omega) = \varepsilon_\infty + \sum_j \frac{2A_j}{\sqrt{\pi}} \left[ D \left( 2\sqrt{ln2} \frac{\omega J + \omega_j}{\sigma_j} \right) - D \left( 2\sqrt{ln2} \frac{\omega - \omega_j}{\sigma_j} \right) \right] + i A_j \left[ \exp \left( -4ln2 \left( \frac{\omega - \omega_j}{\sigma_j} \right)^2 \right) - \exp \left( -4ln2 \left( \frac{\omega + \omega_j}{\sigma_j} \right)^2 \right) \right] \]

Dawson function: \[ D(x) = \exp(-x^2) \int_0^x \exp(t^2) \, dt \]

Temperature measurement at the Christiansen point \( \bigcirc \) \( n = 1, k \ll 1 \rightarrow E \approx 1 \)

Retrieval of the complex refractive index \( N(\omega) = n(\omega) + i \ k(\omega) \)

Fit of the data with the following parallel plate model of emittance \( (E) \):

\[
E = \frac{(1 - \rho)(1 - \tau)}{1 - \rho\tau} \quad \rho = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \quad \tau = \exp(-4\pi k\omega d) \]

\( d \) : sample thickness
**Dielectric function**: \( \varepsilon(\omega) = [N(\omega)]^2 \)

Causal Gaussian dielectric function model for glasses

\[
\varepsilon(\omega) = \varepsilon_\infty + \sum_j \frac{2A_j}{\sqrt{\pi}} \left[ D \left( 2\sqrt{\ln 2} \frac{\omega + \omega_j}{\sigma_j} \right) - D \left( 2\sqrt{\ln 2} \frac{\omega - \omega_j}{\sigma_j} \right) \right] + i A_j \left[ \exp \left( -4ln2 \left( \frac{\omega - \omega_j}{\sigma_j} \right)^2 \right) - \exp \left( -4ln2 \left( \frac{\omega + \omega_j}{\sigma_j} \right)^2 \right) \right]
\]

\( D \) is the Dawson function

Examples of fit of emittance spectra of a silica glass

SiO\(_2\) Thickness = 2mm

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**USTV SCHOOL ON THE CHARACTERIZATION OF GLASS STRUCTURE/ November 18-22 2019**
Complex refractive index of the silica sample

![Graph showing complex refractive index and extinction coefficient for different wavenumbers and temperatures.](image-url)
The causal Gaussian dielectric function model represents a good compromise in terms of quality of fit and simplicity for the analysis of the infrared response of most of glasses.
Fits of reflectivity with a Gaussian dielectric function model

Silica glass

Germania glass

Boria glass

SiO₂

GeO₂

B₂O₃
Fits of reflectivity with a Gaussian dielectric function model

**Aluminate glass**

(CaO)_{0.6}(Al_{2}O_{3})_{0.4}

**Aluminosilicate glass**

Ca_{2}Al_{2}SiO_{7}

**Chalcogenide glass**

Ge_{0.25}Se_{0.75}
Borate glass: 

\[(\text{Na}_2\text{O})_{0.2}(\text{B}_2\text{O}_3)_{0.8}\] 

Borosilicate glass: 

Borofloat®: 

\[(\text{BaO})_{0.29}(\text{SiO}_2)_{0.71}\] 

Silicate glass: 

Fits of reflectivity with a Gaussian dielectric function model
Infrared response of silicate glasses

Silicate glasses

Non-homogeneous broadening due to the glass disorder.

Coexistence of narrow, intermediate and wide distributions of vibrational modes.

Why such a high number of Gaussian components? Do they have a physical meaning? What about the fidelity of the dielectric function model? Does it include information on the glass network? Can I probe cation modifiers? ...

(BaO)_{0.29}-(SiO_2)_{0.71}
Site occupation disorder

Al/Mg disorder

\((\text{Mg}_{1-x}\text{Al}_x)[\text{Mg}_x\text{Al}_{2-x}]\text{O}_4\)

Coexistence of allowed modes and modes forbidden by symmetry.

Intensity of the widest absorption component linked to the inversion rate \(x\).
Dynamics and phase transitions of crystalline SiO$_2$

Emissivity

Wavenumber (cm$^{-1}$)

Temperature (K)

Emissivity

Wavenumber (cm$^{-1}$)

Temperature (K)

Wavelength (µm)

Temperature (K)

Dynamic disorder

Floppy modes

A single mode allowed by the average symmetry of β cristobalite. 4 modes are visible.
Dynamics of a silica glass versus temperature

Normal spectral emittance

\[ \text{v-SiO}_2 \]

Thickness = 500 µm

1-R-T

\[ \text{Wavenumber (cm}^{-1}) \]

\[ \text{Temperature (K)} \]

\[ T_{\alpha\beta}, \quad T_g, \quad T_m \]

\[ \text{Area} \]

\[ \text{Imaginary dielectric function} \]

\[ \text{Wavenumber (cm}^{-1}) \]
Gaussian components give information on the silicate network dynamics, cation motions, network connectivity, short and medium range order....

**Infrared response of silicate glasses**

- Local oscillators
- Medium range order
- Mode activation due to dynamic disorder
- Tetrahedral connectivity
- bridging oxygen
- non bridging oxygen
- local oscillators
- modifiers
- short range order
- dynamic disorder

\[(\text{BaO})_{0.29}(\text{SiO}_2)_{0.71}\]

- \(\text{Q}_4\)
- \(\text{Q}_3\)
- \(\text{Q}_2\)
- \(\text{NBO}\)
Strong evolution of the reflection spectrum with the increase of the K₂O content.

Below 200 cm⁻¹, vibrational modes are due to potassium motions.

Above 200 cm⁻¹, modes are induced by vibrations of the silicate network.

Possibility of extracting information on the glass microstructure at short and medium distances.

D. De Sousa Meneses et al Vibrational Spectroscopy 65 50-57 2013
\[ \varepsilon(\omega) = \varepsilon_{\infty} + \sum_j \frac{2A_j}{\sqrt{\pi}} \left[ D \left( 2\sqrt{\ln 2 \frac{\omega - \omega_j}{\sigma_j}} \right) - D \left( 2\sqrt{\ln 2 \frac{\omega + \omega_j}{\sigma_j}} \right) \right] + i A_j \left[ \exp \left( -4\ln 2 \left( \frac{\omega - \omega_j}{\sigma_j} \right)^2 \right) - \exp \left( -4\ln 2 \left( \frac{\omega + \omega_j}{\sigma_j} \right)^2 \right) \right] \]

Dawson function: \( D(x) = \exp\left( -x^2 \right) \int_0^x \exp(t^2) dt \)
**K₂O - SiO₂ glass system: short range order**

- **Imaginary dielectric function**
- **Wavenumber (cm⁻¹)**
- **Occupation site K**
  - \( K = K_1 + K_2 \)
- **Sites of potassium cations**
  - \( Q_n \): tetrahedra with \( n \) bridging oxygens
- **Species**
  - **Occupation site K**
  - **Occupation site K**
  - **Occupation site K**
  - **Occupation site K**
- **Bridging and non-bridging oxygen**
  - \( \frac{n(BO)}{n(O)} = \frac{2-3x}{2-x} \)
  - \( \frac{n(NBO)}{n(O)} = \frac{2x}{2-x} \)

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[BM] Binary model
Random Connectivity Model does not explain the glass structure. Depolymerization follows a specific path.
SiO₂ thin film implanted with Krypton

Krypton implantation
220 KeV
510^{16} Kr/cm²

Static relative permittivity versus annealing temperature

- After implantation
- After annealing 900°C
- After annealing 750°C
- After annealing 400°C

IR : infrared reflectivity
CV : capacitance measurement

Strong decrease of the static relative permittivity of the SiO₂ thin film after implantation.
Material healing after annealing at 900 °C
SiO$_2$ thin film implanted with Krypton

After implantation

K$_2$O – SiO$_2$
13.2% (K$_2$O)

2 $Q_4$ → $Q_3 + E'$
1-2x

Implantation mechanism
Damage of the silicate network by creating $E'$ centers and $Q_3$ structural units.
Loss of 50% of the $Q_4$ structural units inducing a diminution of the vibrational contribution to the static permittivity.

Non bridging oxygen
Structural relaxation of a silicate glass

\((\text{Na}_2\text{O})_{0.27} \text{(SiO}_2\text{)}_{0.73}\) silicate glass

 Thermal heat treatment

Glass transition temperature \((T_g)\): \(\approx 730K\)

Continuous acquisition of spectra during annealing at 870 K and 925K
Annealing at 870 K does not lead to crystallization of the glass. \(2Q_3 \rightleftharpoons Q_2 + Q_4\)

First step, small shift of the chemical equilibrium to the right.

After \(t_c\), structural relaxation \((\tau \approx 10 \text{ mn})\) and shift to the left of the chemical equilibrium.

\[
Q_n(t) = c_n \exp \left( -\frac{t - t_c}{\tau} \right) + d_n
\]

At 925 K crystallization is evidenced after 20 mn.
Infrared response of aluminosilicate glasses

Ca$_2$Al$_2$SiO$_7$ glass

BaAl$_2$Si$_2$O$_8$ glass

ZnAl$_2$Si$_2$O$_8$ glass
Infrared response of aluminosilicate glasses

Crystal structure of gehlenite

Yellow tetrahedra: Wyckoff site 2a labelled $T_1$ is fully occupied by Al atoms

Blue tetrahedra: Wyckoff site 4e, labelled $T_2$ is filled with a mix of Al (50%) and Si (50%) atoms

Access to structural information

$Q_{nAl}^m$ structural units

SiO$_4$ with a non bridging oxygen

Nature of AlO$_4$ tetrahedra
Crystal structure of BaAl$_2$Si$_2$O$_8$ (paracelsian)

Blue tetrahedra: Al atoms (AlO$_4$) surrounded by 4 Al atoms.
Gray tetrahedra: Si atoms (SiO$_4$) surrounded by 4 Al atoms.

BaAl$_2$Si$_2$O$_8$ glass

$Q^n_{4Al}$ structural units

100% of $Q^4_{4Al}$

Broad distribution of $Q^m_{4Al}$ structural units.
Al-O-Al bonds
Infrared response of aluminosilicate glasses

**ZnAl$_2$Si$_2$O$_8$ glass**

Asymmetric distribution of $Q_n^{mAl}$ structural units for ZnAl$_2$Si$_2$O$_8$.

**$Q_n^{mAl}$ structural units**

- **BaAl$_2$Si$_2$O$_8**
- **SrAl$_2$Si$_2$O$_8**
- **ZnAl$_2$Si$_2$O$_8**
Infrared response of aluminosilicate glasses

$\text{Ca}_2\text{Al}_2\text{Si}_7\quad \text{SiO}_4$

$\text{BaAl}_2\text{Si}_2\text{O}_8$

$\text{ZnAl}_2\text{Si}_2\text{O}_8$

$Q_n^{m\text{Al}}$ structural units

Absorption band position (cm$^{-1}$)

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<th>$\approx 860$</th>
<th>$\approx 900$</th>
<th>$\approx 950$</th>
<th>$\approx 1010$</th>
<th>$\approx 1060$</th>
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<tr>
<td>$Q_3^{3\text{Al}}$</td>
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<td>$Q_3^{0\text{Al}}$</td>
<td>$Q_2^{0\text{Al}}$</td>
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</tbody>
</table>
Silicate glass containing iron

75.5 SiO$_2$-14 Na$_2$O-10 CaO-$0.5$Fe$_2$O$_3$
Silicate glass containing iron

75.5 SiO$_2$-14 Na$_2$O-10 CaO-0.5Fe$_2$O$_3$

Iron absorption bands

Iron redox = \[ \frac{[Fe^{2+}]}{[Fe^{2+}] + [Fe^{3+}]} \] = 27.8%

Literature result at room temperature

Fe$^{2+}$

Vincent Vercamer. [REF-Vercamer]

Spectroscopic and Structural Properties of Iron in Silicate Glasses.
Material chemistry. Université Pierre et Marie Curie - Paris VI, 2016
Silicate glasses containing iron

High temperature dependence of the absorption coefficient

$75.5 \text{ SiO}_2 - 14 \text{ Na}_2\text{O} - 10 \text{ CaO} - 0.5\text{Fe}_2\text{O}_3$
Silicate glasses containing iron

75.5 SiO$_2$-14 Na$_2$O-10 CaO-0.5Fe$_2$O$_3$

Intervalence Charge Transfer (IVCT)
Transfer of an electron between two adjacent Fe$^{2+}$-Fe$^{3+}$ ions.
Strong increase at high temperature in the melt.

Figure 5.15 – Molar absorption coefficient of Fe$^{3+}$ in the soda-lime oxidized glass (NCS05Ox) after UV-edge removal. Example of Fe$^{3+}$ bands fitted with 6 Gaussians.

Table: Fit of Fe$^{2+}$ bands with 3 Gaussian functions for NCS05Red

<table>
<thead>
<tr>
<th>#</th>
<th>Position (cm$^{-1}$)</th>
<th>σ (cm$^{-1}$)</th>
<th>FWHM (cm$^{-1}$)</th>
<th>Intensity (L/mol/cm$^2$)</th>
<th>ε$^{2+}$ (L/mol/cm$^2$)</th>
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</table>
Silicate glasses containing iron

75.5 SiO$_2$-14 Na$_2$O-10 CaO-0.5Fe$_2$O$_3$
Infrared spectroscopy is a powerful tool to investigate the structural and optical properties of glasses and melts at high temperature.

Thank you for your attention