Glass and glass ceramic for nonlinear optics: fundamentals to applications

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NonLinear Optical Materials

Nonlinear Parameters

Third order Nonlinearities

Second order Nonlinearities

Nonlinear Absorption
Nonlinear optical effects

\[ P = \varepsilon_0 \left( \chi^{(1)} E(\omega) + \chi^{(2)} E(\omega) E(\omega) + \chi^{(3)} E(\omega) E(\omega) E(\omega) + \ldots \right) \]

- \( P \): Polarisation
- \( E \): Electric Field
- \( \chi^{(n)} \): Linear and Nonlinear susceptibilities
- \( n_0 \): Refractive Index
- \( \chi^{(1)} \): Linear susceptibility
- \( \chi^{(2)} \): Second harmonic generation
- \( \chi^{(3)} \): Third harmonic generation

SHG (\( 2\omega \))
\( n \approx f(E) \)
\[ n = n_0 + \zeta E \]

THG (\( 3\omega \))
\( n \approx f(E^2) \)
\[ n = n_0 + n_2 I \]
Third order nonlinearity

- Four wave mixing
  \[ \chi^{(3)}(-\omega_4, \omega_1, -\omega_2, \omega_3) \]

- Kerr effect
  \[ \chi^{(3)}(-\omega, \omega, -\omega, \omega) \]
  Self focusing
  Self phase modulation
  Soliton Propagation
  Optical switching

- Third Harmonic generation
  \[ \chi^{(3)}(-3\omega, -\omega, \omega, \omega) \]

- Stimulated Raman
  \[ \chi^{(3)}(-\omega_s, \omega_p, -\omega_s, \omega_p) \]

- Two photon absorption
  \[ \chi^{(3)}(-\omega, -\omega, \omega, \omega) \]
The formalism of nonlinear optics

- **Polarization of the material** described by a perturbative development:

\[
\tilde{P}_i(\vec{r};t) = \tilde{P}_i^{(0)}(\vec{r};t) + \tilde{P}_i^{(1)}(\vec{r};t) + \tilde{P}_i^{(2)}(\vec{r};t) + \tilde{P}_i^{(3)}(\vec{r};t) + \ldots
\]

linear polarization nonlinea polarization

- **3rd-order polarization**:

\[
\tilde{P}_i^{(3)}(\vec{r};t) = \varepsilon_0 \int_{-\infty}^{t} \int_{-\infty}^{t} \int_{-\infty}^{t} R_{ijkl}^{(3)}(\vec{r};t-t_1,t-t_2,t-t_3)\vec{E}_j(\vec{r};t_1)\vec{E}_k(\vec{r};t_2)\vec{E}_l(\vec{r};t_3)dt_1dt_2dt_3
\]

- **3rd-order susceptibility** = Fourier transform of the 3rd-order response function. describes the nonlinearities of the glass.

\[
\chi_{ijkl}^{(3)}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \int_{-\infty}^{+\infty} R_{ijkl}^{(3)}(t_1,t_2,t_3)\exp[i(\omega_1t_1 + \omega_2t_2 + \omega_3t_3)]dt_1dt_2dt_3
\]

Polarization of the material described by a perturbative development:

\[
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linear polarization nonlinea polarization

3rd-order polarization:

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\]
The different contributions to the nonlinear response

- **Electronic polarization**: instantaneous nonlinear distortion of the electronic cloud around the nucleus (response time \(\sim 1\ \text{fs}\)).

- **Nuclear response**: rearrangement of the nucleus position in the new potential created by the electrons electric field (response time \(\sim 100\ \text{fs-1 ps}\)).

- **Electrostrictive response**: increase of the density, inducing an increase of the nonlinear response (response time \(\sim 1\ \text{ns}\)).

- **Thermal response**: absorption of the electric field followed by dissipation of the energy under the form of heat, inducing a variation of the nonlinear response (response time \(\sim 10\ \mu\text{s}\)).

\[
\chi^{(3)} = \chi_{\text{elec}}^{(3)} + \chi_{\text{nuc}}^{(3)} + \chi_{\text{str}}^{(3)} + \chi_{\text{th}}^{(3)}
\]

*With fs pulses*, electrostrictive and thermal contributions are neglected because their building-up time is too long compared to the pulse duration.
Third order nonlinearity

Measured at 1.5 μm

\[
\frac{n^2}{n^2_{SiO_2}}
\]

- Sulfide, Selenide
- Oxide
- Fluoride

Chalcogenide
Tellurite
\(d^0\) ions (Ti\(^{4+}\), Nb\(^{5+}\), W\(^{6+}\)) in silicate, borate, phosphate matrices
Silicates, borates, phosphates
Fluoride
Fused silica

**Raman Spectrum**

Nuclear contribution up to 6% to the $n_2$

**Vibrational Contribution**

\[ \sigma_{xxx}^{(3)} = 2.65 \times 10^{-22} \text{ m}^2 \text{. V}^{-2} \]

**Nuclear response functions (m^2 V^{-2} s^{-1})**

**Raman Spectrum**

- Depolarized VH
- Polarized VV

**Nuclear contribution (%)**

- Wave number (cm^{-1})
- FWHM pulse width (fs)

**Raman Spectrum**

- d_{xyxy}

**Nuclear response functions (m^2 V^{-2} s^{-1})**

- Time (fs)

**Raman Spectrum**

- Nuclear contribution (cm^2/(sr.cm^{-1}))

- Wave number (cm^{-1})

**Raman Spectrum**

- Raman cross-section (cm^{-1} / (sr.cm^{-1}))

**Raman Spectrum**

- Functional Glasses for Energy and Information

January 6-11, 2013
Niobium oxide containing Glasses

- Short Nb-O bond
- 1D Octahedra network
- 3D Octahedra network

Increase of Raman Intensity

$\lambda_{exc} = 514 \text{ nm}$

Relative Raman Intensity (a.u.)

Wavenumber (cm$^{-1}$)
Evolution of the Kerr effect

Measured at 800 nm

\[ \frac{\chi^{(3)}}{\chi^{(3)} \text{ SiO}_2} \]

- Borophosphate (niobium)
- Borophosphate (titanium)
- Silicate (titanium)
- Silicate (niobium)
- Electronic contribution

Ti or Nb concentration (10^3 mol/cm^3)

Graph showing the evolution of the Kerr effect measured at 800 nm.
Glass local structure

Low concentration < 10% Nb$_2$O$_5$

Intermediate concentration 10% < Nb$_2$O$_5$ < 35%

High concentration > 35% Nb$_2$O$_5$

From less than 10% of nuclear contribution to 60% to the n$_2$
Structural units of Tellurite network

Decrease of polarisability and hyperpolarisability

TeO$_2$ + 15% Al$_2$O$_3$

TeO$_2$

TeO$_4$ unit

TeO$_3$ unit

TeO$_3+1$ unit

TeO$_2$ unit

TeO$_2$

n$_2$/n$_2$ SiO$_2$

Chalcogenide

Tellurite

d$^0$ ions (Ti$^{4+}$, Nb$^{5+}$, W$^6$)

Silicates, borates, phosphates

Fluoride

Decrease of polarisability and hyperpolarisability
**Medium range order**

OKE: optical Kerr effect

<table>
<thead>
<tr>
<th>Tellurium-Thallium glass</th>
<th>50TeO$_2$-50Tl$_2$O</th>
<th>70TeO$_2$-30Tl$_2$O</th>
<th>75TeO$_2$-25Tl$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>THG susceptibility</td>
<td>1042.1</td>
<td>973.4</td>
<td>668.9</td>
</tr>
<tr>
<td>(×10$^{-22}$ m$^2$.V$^{-2}$) (± 30%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OKE susceptibility</td>
<td>29.4</td>
<td>47.6</td>
<td>48.2</td>
</tr>
<tr>
<td>(×10$^{-22}$ m$^2$.V$^{-2}$) (± 10%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Strong relation** between the glass network and the third order nonlinearity
Fiber Transmission

Raman gain

Telecommunications Window for Amplifiers

- **O** (being deployed)
- **E** (being deployed)
- **S** (widely deployed)
- **C**
- **L** (being deployed)
- **U**

Fiber Transmission Window

- **λ** (nm) range: 1260 to 1675

EDFA

January 6-11, 2013
Raman gain results from 4 waves mixing phenomena (3\textsuperscript{rd} order nonlinearity) combining excitation, signal and vibration mode.
Raman gain bandwidths are fixed by the bandwidth of the Raman active medium.
Raman Gain Spectrum

**SiO$_2$**

- **Relative Raman Intensity (a.u)**
  - Wavelength (nm)
  - 0 10 20 30 40
  - 1 1100 1150 1200 1250

**Borophosphate**

- **Relative Raman Gain Coefficient**
  - Frequency Shift (THz)
  - 0 10 20 30 40
  - 20 40 60 80 100

- **Relative Raman Intensity (a.u)**
  - Wavelength (nm)
  - 0 5 10 15 20 25 30 35 40

- **x TeO$_2$ - (100-x) TlO$_{0.5}$**
  - Frequency Shift (THz)
  - 0 5 10 15 20 25 30 35 40
  - 0 20 40 60 80 100

**Functional Glasses for Energy and Information**

January 6-11, 2013
Vibrational response

80TeO$_2$-(20-y)TaO$_{5/2}$-yZnO

Functional Glasses for Energy and Information
January 6-11, 2013
Drastic decrease of the hyperpolarizability during the ZnO introduction.
Hyperpolarizability and Raman Gain

- **Raman gain** linearly proportional to **hyperpolarizability** \( \chi^{(2)} \propto \chi^{(3)} \)

\[ \beta_{HRS} \]

- Relationship between a **local measurement** (hyperpolarizability) and a **macroscopic property** (Raman gain)
Supercontinuum generation

80TeO$_2$-10ZnO-10Na$_2$O

Theoretically up to 3000 nm if no Hydroxyls

I. Savelii et al., Optics Express, Vol. 20 Issue 24, pp.27083-27093 (2012)

Self phase modulation
Raman Gain
Four Wave Mixing
THG

M. Liao, Optics Express, 20, 26 (2012), p574
Supercontinuum generation

As$_2$S$_3$

I. Savelii et al., Optics Express, Vol. 20 Issue 24, pp.27083-27093 (2012)

Simulation without SH and OH groups
Quantum dots for NLO

\[ W = \frac{\Delta n_{\text{sat}}}{\alpha_0 \tau} \]

Finlayson et al.,

Glasses doped semiconductor quantum dots
PbS, PbSe, PbTe
- narrow band-gap,
- large optical nonlinearity
- fast response time

S. Ju,
Optics Express, 19, 3, (2011), p2599
metallic nanoparticles for NLO

Large aspect ratio metal nanoparticles

non-spherical silver nanoparticles

Enhancement of nonlinearity 2 order of magnitude

A. Stalmashonak, Optics Letters 35, 10, (2010), p1673
S. Mohan
Optics Express, 20, 27, (2012, p28655
Second order nonlinearity

Nonlinear optical effects

\[ P = \varepsilon_0 \left( \chi^{(1)} E(\omega) + \chi^{(2)} E(\omega) E(\omega) + \chi^{(3)} E(\omega) E(\omega) E(\omega) + \ldots \right) \]

SHG (2\(\omega\))

\[ n \approx f(E) \]

\[ n = n_0 + \zeta E \]

Applications

Variation of the refractive index

Modulation or switching of the light
Sample placed between two electrodes

anode (+)

Glass
cathode (-)

\[ P_{NL} (2\omega) = \chi^{(3)} E_{dc} E(\omega)E(\omega) \]

\[ \approx \chi^{(2)} \]
Material performance

\[ P^{NL} (2\omega) = \chi^{(3)} E_{dc} E(\omega)E(\omega) \approx \chi^{(2)} \]

Need for quasi phase matching

Structuration of SHG

Ag thin film (200 nm) :

**Anode**

Laser Ablation of Ag Lines

**Structured Anode**

Thermal poling

230 °C, t = 1 h, U = 1 kV, i ~ 0.5 mA
Analysis of µSHG signal

**Image MEB**

- Zone non ablatée
  - Flight intensity
  - $\chi^{(2)}_{xxx} \approx 0$

- Zone ablatée
  - $\chi^{(2)}_{xxx} \approx -600$

**μSHG Signal polarisations XXX**

- Incident field 1064nm
- Signal Field SHG 534nm

**Graphs**

- Intensity (u.a.) vs. Wavenumber (cm$^{-1}$)
- Number of wavelengths (cm$^{-1}$)

**Table**

<table>
<thead>
<tr>
<th>Zone</th>
<th>Intensity (u.a.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>0</td>
</tr>
<tr>
<td>1µm below</td>
<td>100</td>
</tr>
<tr>
<td>2µm below</td>
<td>200</td>
</tr>
<tr>
<td>3µm below</td>
<td>300</td>
</tr>
<tr>
<td>4µm below</td>
<td>400</td>
</tr>
</tbody>
</table>

**Equation**

$$\chi^{(2)}_{xxx} = [xxx \ yyy \ yyy \ yyy \ yyy \ yyy \ yyy \ zzz \ zzz \ yyy \ yyy \ zzz \ zzz \ yyy \ yyy \ zzz \ zzz \ yyy \ yyy \ zzz \ zzz \ yyy \ yyy \ zzz \ zzz]$$

**Images**

- Surface
- 1µm below Surface
- 2µm below Surface
- 3µm below Surface
- 4µm below surface

**Notes**

- Functional Glasses for Energy and Information
- January 6-11, 2013
Symmetry control

(a) Polarisation $C_{xy}$ (axis $z$)

$$\chi^{(2)} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & xxz & 0 & 0 \\ zxx & zxx & zxx & 0 & 0 & 0 \end{bmatrix}$$

(b) Ablation + Polarisation $C_\delta$ (plane $xz$)

$$\chi^{(2)} = \begin{bmatrix} xxx & xyy & xzz & 0 & xxz & 0 \\ 0 & 0 & 0 & yzy & 0 & yyx \\ zxx & zyy & zyy & 0 & zzz & 0 \\ zxx & zyy & zyy & 0 & zzz & 0 \end{bmatrix}$$
Pattern implementation

A. Lipovskii et al.,
Materials structure modification

M. Dussauze et al., The journal of physical chemistry. C
A glass-ceramic for frequency doubling

Before heat treatment
Centrosymmetric glass

After heat treatment
Non-Centrosymmetric crystallites

**Characteristics:**
Size and space control of μ-crystallites precipitation:

- Sub – micro or nano crystals for transparency or low refractive index difference between the matrix and the crystallites
- Homogenous bulk crystallization

Current material:

- Large-sized Monocristals
- Cut out with a specific way

Potassium Dihydrogen Phosphate

Nuclear simulation test

High Power Laser

Medical research

Electricity production?

NIF

Hyper

LMJ

Cost
Control of low refractive index difference between the crystalline phase and the glass

25La₂O₃-25B₂O₃-50GeO₂
Crystalline phase LaBGeO₅
(200 nm à 200 µm)

15K₂O- 15Nb₂O₅-68TeO₂-2MoO₃
Crystalline phase KNbO₃

Effect of Poling

15K₂O- 15Nb₂O₅-68TeO₂-2MoO₃, Crystallites KNbO₃
Second order NLO increase by a factor 6 to 20 [58].

In 0.7Na₂B₄O₇-0.3Nb₂O₅, Crystallites NaNbO₃ (30 nm)
SHG signal measured after poling
Spherulites distributed in the matrix with distances greater than the coherence length.

Total second harmonic intensity: Sum of the individual contributions (incoherent case).

Similar phenomenon in
25La$_2$O$_3$-25 B$_2$O$_3$-50GeO$_2$
Cristalline phase LaBGeO$_5$

H. Vigouroux
Nonlinear absorption

CdS$_x$Se$_{1-x}$  
CdTe  
InAs  
CuInS$_{2x}$Se$_{2(1-x)}$  
CuSe  
PbS (PbSe)

Q switching and mode locking of near-infrared solid-state lasers to obtain light pulses of high power and short/ultrashort duration

Key parameters:  
Ground-state absorption cross section,  
Residual non-saturable absorption,  
Bleaching relaxation absorption recovery time (ps)  
Saturation intensity

Size distribution: 5%–10% around their main diameter
**Dye Fluorescence in solution**

**Nonlinear absorption**

- **Nonlinear effect**
  - = multiphoton
  - Localized absorption

- **Linear effect**:
  - Absorption along the light propagation

**Short pulsed Lasers**

- \( P \)
- \( P_c \approx GW - TW \)
- \( 1/T \)

**Equation**:

\[
A^* \approx A
\]

\( l_1, l_2, l_4 \)
Nonlinear Absorption

Possible to implement local $\chi^{(2)}$ and $\chi^{(3)}$
Local THG in silver containing glass

THG microscopy

$3\omega$ resonant species induced by femtosecond laser irradiation

$\chi^{(3)}_{\text{non-resonant}}$  

$\chi^{(3)}_{\text{resonant}}$

$\lambda = 1030\text{ nm}$

Local Formation of Clusters

\[ \text{Ag}_m^{x+} \]

(formed of Ag$^0$ atoms and Ag$^+$ ions)

Induced Absorption

Wavelength (nm)
THG for data storage

Exaltation of the THG signal due to the resonance

THG imaging of the 3 layers

3D data recording and reading

Nonlinear optical process \leftrightarrow \text{Confocal per nature}

Local SHG in silver containing glass

Silver containing phosphate glass

\[ \text{Ag}^2+ \text{(hole)} \rightarrow \text{Ag}_x^{m+} \text{(e- trap)} \]

\[ E_{dc} \text{ (Space charge)} \]

Theoretical SHG | Measured (HH) SHG

\[ \chi^{(2)} \approx \chi^{(3)} E_{dc} E(\omega)E(\omega) \]

Laser:
- Wavelength: 1.04 µm
- Duration: 400 fs
- Repetition rate: 10 Mhz

Charge separation process
And thanks to the glass composition

Stabilization of the charge separation
Summary

- Understanding of the relation **glass structure / NLO properties**
  - resonant (**Raman gain**, **Nonlinear absorption**)
  - non-resonant (**Kerr effect**, **THG**)
  - **Nonlinear absorption**

- Impact of **glassceramics** (Loss issues)
  - **Second order nonlinearity**
  - **Metal** or **semiconductor**

- Control of **local phase separation** or **local crystallization**
  - **Third order** and **Second order nonlinearity**
Acknowledgments

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J.Y. Choi, C. Rivero, G. Stegeman, M. Richardson
CREOL, University of Central Florida, USA
(*co-tutelle de thèse-Univ. Bordeaux1)
Table 1. Various highly nonlinear fibers and their SC generations in picosecond regime. 10 dB bandwidths were obtained from the SC spectra in the publications. When determining the 10 dB bandwidth, the strong pump peak was excluded.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Pump wavelength (nm)</th>
<th>Nonlinear coefficient (km$^{-1}$W$^{-1}$)</th>
<th>Fiber length (m)</th>
<th>Pulse width (ps)</th>
<th>Peak power of pulse (W)</th>
<th>SC total bandwidth (nm)</th>
<th>10 dB bandwidth (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our tapered fiber</td>
<td>1064</td>
<td>800-5500</td>
<td>0.75</td>
<td>15</td>
<td>375</td>
<td>350-2000</td>
<td>780-1890</td>
</tr>
<tr>
<td>Silica tapered fiber [20]</td>
<td>1064</td>
<td>8-40</td>
<td>2</td>
<td>3-4</td>
<td>19608-32680</td>
<td>350-1750</td>
<td>380-1750</td>
</tr>
<tr>
<td>Silica microstructured fiber [21]</td>
<td>1064</td>
<td>-</td>
<td>2</td>
<td>21</td>
<td>24000</td>
<td>400-2250</td>
<td>420-1620</td>
</tr>
<tr>
<td>Silica microstructured fiber [22]</td>
<td>1064.5</td>
<td>8.5</td>
<td>100</td>
<td>600</td>
<td>4200</td>
<td>600-1750</td>
<td>650-1750</td>
</tr>
<tr>
<td>Silica microstructured fiber [5]</td>
<td>647.1</td>
<td>150</td>
<td>3</td>
<td>60</td>
<td>400</td>
<td>440-1130</td>
<td>480-940</td>
</tr>
<tr>
<td>Silica microstructured fiber [23]</td>
<td>1050</td>
<td>11</td>
<td>5</td>
<td>350</td>
<td>8893</td>
<td>400-1700</td>
<td>600-1700</td>
</tr>
</tbody>
</table>

*M. Liao*, *Optics Express*, 20, 26 (2012), p574
Material performance

![Graph showing material performance](image)

- LiNbO$_3$: 30
- NbO$_x$: 3
- SiO$_2$: 0.3

**Niobium Oxide Tellurite**
SHG efficiency can be connected to combination of third-order non-linearity with spatial modulation of linear polarizability.
Pump-probe experimental setup

Santran et al., JOSA B 21, 2180-2190 (2004).

- Absolute measurements.
- Measurement uncertainty ~10%.
- Appropriate technique to characterize bulk materials.
- Difficult to implement on structured materials (maintain of the polarization under microscope, small nonlinear interaction length, etc…).