Scintillating silica fibers: microscopical material properties and \textit{in vivo} dosimetry applications

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SOL-GEL

SOL

HYDROLISIS, CONDENSATION

GEL

LIQUID/SOLID

DRYING (T ~ 40°C)

XEROGEL

SOLID, POROUS

SINTERING (T_d= 450...1050°C)

GLASS

SOLID

RTT

SOLVENT:
H_2O - Etanol

TEOS

PRECURSORs

\( \text{TEOS} \)

\( \text{PRECURSORs} \)

\( \text{Si(OR)}_4 + \text{H}_2\text{O} \rightarrow \text{Si(OR)}_3(\text{OH}) + \text{ROH} \)

\( (\text{OR})_3\text{Si-OH} + \text{HO-Si(OR)}_3 \rightarrow (\text{OR})_3\text{Si-O-Si(OR)}_3 + \text{H}_2\text{O} \)

\( (\text{OR})_3\text{Si-OR} + \text{HO-Si(OR)}_3 \rightarrow (\text{OR})_3\text{Si-O-Si(OR)}_3 + \text{ROH} \)

\( \text{SiO}_2: \text{RE} \)

\( \text{H}_2\text{O} - \text{ROH} \)
Effect of OH content on RL signal

Strong increase of RL signal upon increase of sintering temperature

A. Baraldi et al., NIM A 486, 408 (2002)
N. Chiodini et al, APL 81, 4374 (2002)
Rapid Thermal Treatment RTT

Temperature during RTT

- Temperature vs. Time
  - Temperature range: 0°C to 1800°C
  - Time range: 0 s to 70 s
  - Peak temperature duration: ≈10 s
  - 

Radio-Luminescence

- Energy vs. RL Intensity
  - Energy range: 2 eV to 4 eV
  - RL intensity range: 0 to 1200 arb. un.
  - Materials: Ce 0.05% mol, Bi4Ge3O12, Ce 0.05% mol 1050 °C

- Energy and RL Intensity for different materials and conditions
Factors limiting RL emission
(Ce concentrations higher than 0.1 mol%):

- **Self-absorption**: Ce-related o.a. band at 2.5 eV, due to Ce dimers *(removed by RTT)*

- **CeO\(_2\) aggregate formation** *(size increase by RTT)*

- **Concentration quenching or energy transfer towards defects** *(partially removed by RTT)*

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Composite scintillating fibres

- A prototype detector for “in vivo” dosimetry has been obtained coupling (by splicing) a piece of scintillating fibre with a commercial optical fibre.

- This real-time dosimetric system has been tested, by low energy x-rays and conventional radiotherapy apparatuses (6 e 15 MeV photons and from 6 to 18 MeV electrons).

Fibre response to 6 MeV photons

Reproducibility: 1.7%

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Doping with different rare earth ions

Goals

• to investigate the incorporation of other rare earth ions (Tb$^{3+}$, Gd$^{3+}$, Eu$^{3+}$, Yb$^{3+}$) in SiO$_2$ and to compare with Ce$^{3+}$ doping (luminescence efficiency, RE dispersion, clustering)

• To provide emission centers which can be separated from Cerenkov emission by filtering

• To evaluate the use of Gd$^{3+}$ as luminescent activator, or as a tool of energy transfer towards Ce$^{3+}$ in co-doped samples, like already evidenced in crystalline and amorphous matrices.
Sol-gel SiO$_2$:Tb

Set of Tb-doped silica samples sinterized in oxidizing atmosphere up to 1050 °C.
Concentration range: **0.001 - 10 mol%**

Tb$^{3+}$ energy level diagram and cross relaxation process

Absorption spectra

Radio-luminescence
Radio-luminescence Intensity evaluated integrating the spectra over the whole emission range (1.77-3.54 eV).

The post-densification rapid thermal treatment (RTT) enhances the RL efficiency (up to two order of magnitude in sample with Tb concentration higher than 3 mol%).

**PL and RL spectra comparison**

PL - Before RTT: evidence of cross-relaxation  
After RTT: increase of $R \rightarrow$ better Tb dispersion (dissolution of small aggregates-dimers)

RL – Before RTT: spatial correlation with defects, like oxygen vacancies (formation of Tb$^{4+}$ ?)  
After RTT: removal of such defects – similarity with PL pattern
**Sol-gel SiO$_2$:Gd**

Spectra display only Gd$^{3+}$ $^6P_J$ - $^8S$ transitions.

Emission line position and shape depend on densification temperature.

RL Intensity increases by increasing T$_d$ particularly after RTT. RL Intensity does not depend significantly on Gd concentration.

**SiO$_2$:Gd 0.5 mol% RL spectra at different densification temperatures (T$_d$)**

![Graph showing RL intensity vs T$_d$ (°C) and integral between 3.7 and 4.13 eV]

**SiO$_2$:Gd 0.5 mol% RL intensity vs Gd concentration**

![Graph showing RL intensity vs Gd Concentration (mol%) at 1050°C and RTT]
RL of mixed Gd- and Ce- doping

No improvement of Ce emission intensity with Gd co-doping
(lack of an efficient energy transfer process in the amorphous structure)
Low Temperature RL (10-320 K)

Gd$^{3+}$ emission high energy shoulder and $^6P_{5/2}$ strongly dependent on T

High energy shoulder due to Crystal Field (CF) splitting of $^6P_{7/2}$ state

F. Moretti et al., J. of Lumin. 126, 759 (2007)
TEM and EDS measurements

TEM measurements on SiO$_2$:Gd 3 mol%

A) $T_d=1050^\circ$C, cluster mean diameter
   $\approx 13\pm4$nm

B) After RTT, cluster mean diameter
   $\approx 54\pm10$nm

No crystalline structure was observed

EDS measurements on SiO$_2$:Gd 3 mol%

Matrix contain only traces of gadolinium, clusters are Gd-rich phases

Cluster larger dimensions can explain the decrease of Gd decay time
Time resolved PL data

- 1050 °C densified samples: single exponential decay. Decay time slightly increases by increasing Gd concentration.
- After RTT: shorter time decays, faster component visible for all concentration especially for 3 mol% Gd, complex time decay dependence with Gd concentration.

Fast initial component at high Gd levels →

Presence of killer centers within aggregates.

Blue – before RTT

Red – after RTT
FTIR measurements

Vibration at ~880 cm\(^{-1}\) → O-Gd-O stretching mode
possible contribution of GSO in amorphous clusters
FTIR measurements

Vibrational mode at 4250 cm\(^{-1}\)

- Present only in Gd-doped samples
- Quadratic dependence vs Gd concentration
- It disappears after RTT
- Attribution to Gd dimer-OH
Presence of isolated Gd ions after RTT!
CONCLUSIONS

- Satisfactory incorporation of Tb$^{3+}$ in sol gel silica (maximum RL efficiency at $10^{-2} - 10^{-1}$ mol%) Strong RL increase after RTT
- Evidence of cross-relaxation effects in PL
- Complex dependence of $R = \sum J I(5D_3^{-7}F_J) / S J I(5D_4^{-7}F_J)$ upon concentration → influence of defects (oxygen vacancies?) close to Tb ions (removed by RTT) and possible valence modifications during irradiation.

- Gd emission: strong RL increase after RTT too
  - Dissolvement of Gd dimers close to OH (IR data)
  - Formation of Gd-rich clusters (possible GSO structure) (TEM, EDS and IR data)
  - Formation of a small concentration of isolated Gd ions (EPR data)
  - Removal of non-radiative channels (similarly to Ce doping)

Role of RTT in Gd-doped silica:
Figure. 4. Decay curves of the $^5$D$_{4}$-$^7$F$_{5}$ (λem=546 nm, λexc=225 nm) emissions of three silica samples doped with different Tb concentration: (a) 0.003, (b) 0.1 and (c) 3 mol% before (open circles) and after (filled circles) RTT. The curves are shifted on the ordinate scale for better clarity.
**Optical Absorption (OA)**

Spectra display Gd$^{3+}$ $^8$S - $^6$P$_J$, $^6$I$_J$, $^6$D$_J$ optical transitions.

Scattering contribution decreases by increasing densification temperature, and increases after RTT Absorption lines undergo low energy shift by densification temperature increasing. RTT causes further low energy shift

F. Moretti et al, *J. Lumin*. In press
Photo-Luminescence Time Decay

• 1050 °C densified samples: single exponential decay. $\tau$ slightly increase by increasing Gd concentration

• After RTT: shorter time decays, faster component visible for all concentration especially for 3mol% Gd, complex time decay dependence with Gd concentration

$E_{\text{exc}} = 4.5 \text{ eV}$  $E_{\text{em}} = 3.96 \text{ eV}$

PL Time decay of SiO$_2$:Gd 0.05 and 3 mol% before (black symbols) and after RTT (blue symbols)

$\tau$ of SiO$_2$:Gd versus Gd concentration before (black symbols) and after RTT (blue symbols)
Low Temperature PL Time Decay

\[ \tau \text{ of SiO}_2\text{-Gd 3 mol\% versus T before (black symbols) and after RTT (blue symbols)} \]

Gd\(^{3+}\) emission decay time components depend on temperature both for 1050°C \(T_d\) and after RTT

1050°C sample: decay dominated by the slow decay component for all the temperatures

After RTT: similar weight of short and long time decay components, slow decay component weight increase with temperature
Composite scintillating fibres

Dependence on total dose (6 MeV photons)

- Good reproducibility (1.7%)
- Linear dependence on dose rate and total dose over a clinically relevant dose range (~1cGy – 10 Gy)
- Stem effect due to Cherenkov radiation

Stem effect due to Cherenkov radiation
RL INTENSITY VERSUS Ce CONCENTRATION AND RAPID THERMAL TREATMENT

Need of a microscopic investigation on:
- Ce incorporation in silica matrix
- Role of defects in Ce RL efficiency

Doping with other rare earth ions: Gd, Tb, Eu
RTT does not cause further OH desorption (FTIR data)

Stars: 0.5 mol%Ce
Circles: 0.05 mol%Ce

a) and c) before RTT
b) and d) after RTT

Si-OH combination mode (stretching + bending)
Self-absorption of emitted light by 2.4 eV band, which is suppressed by RTT
Quadratic dependence of 2.4 eV band upon Ce Concentration $\rightarrow$ Ce dimers (dissolved by RTT)

A. Vedda et al. Chem of Mat. 18, 6178 (2006)
High Cerium concentrations: CeO$_2$ aggregate formation

5 mol% Ce after RTT

Raman Intensity (arb. units)

Raman shift (cm$^{-1}$)

ω$_1$

ω$_3$

D1

D2

ω$_3$

440

490

458

464

CeO$_2$ powder

5 mol% Ce before RTT

5 mol% Ce after RTT

CeO$_2$

undoped

undoped

5 mol% Ce

5 mol% Ce

5 mol% Ce

High Cerium concentrations: CeO$_2$ aggregate formation
Time resolved Photo Luminescence – non radiative centers

- RTT removes very fast decay component except for the highest Ce concentrations (above 1 mol%).

$\lambda_{\text{Exc}} = 315 \text{ nm}$  $\lambda_{\text{Em}} = 520 \text{ nm}$

- RTT removes very fast decay component except for the highest Ce concentrations (above 1 mol%).
Ce concentrations higher than 0.1 mol%:

- Self-absorption: Ce-related o.a. band at 2.5 eV (removed by RTT)
- CeO₂ aggregate formation
- Concentration quenching or energy transfer towards defects (partially removed by RTT)

A. Vedda et al., JNCS 351, 3699 (2005)