CSIC Instituto de Cerámica y Vidrio

LASES

Oxyfluoride nano-glass-ceramics doped with rare-earth ions: bulk and fibers

G. Gorni[1], J.J. Velázquez[1], M. Kochanowicz[2], J. Zmojda[2], J. Dorosz[2], D. Dorosz[3],

L. Pascual[4], Y. Castro[1], I. Iparraguirre[5], R. Balda[5], J. Fernández[5], M.J Pascual[1], A. Durán[1]

[1]Ceramics and Glass Institute, ICV-CSIC, Madrid, Spain
[2]Faculty of Electrical Engineering, Bialystok University of Technology, Bialystok, Poland
[3]Department of Silicate Chemistry, AGH University of Science and Technology, Krakow, Poland
[4]Catalysis and Petrochemistry Institute, ICP-CSIC, Madrid, Spain
[4]Applied Physics Department I, Superior school of Engineering, Basque Country University, UPV-EHU, Bilbao, Spain

Introduction

ICG
International Commission on Glass

Technical Commitee 07: Crystallisation & GCs

Glass-ceramics are polycrystalline solids obtained from the **CONTROLLED** crystallization of glasses.

REMARK

According to the definition, the crystal fraction is not important, whether it is 1 % or 99% we can still talk about glass-ceramics!

S. D. Stookey

FOTOCERAM®

Glass-ceramics are defined by the PROCESSING!

CSIC
Instituto de Cerámica y Vidrio

Introduction

Why oxyfluoride glass-ceramics ?

- 1993 Wang & Ohwaki:

  Pb_xCd_2-xF_2 nano-crystals within the **aluminosilicate glass matrix**

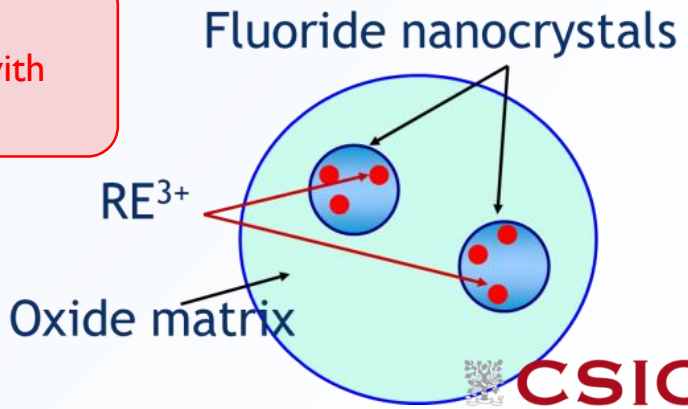
  Optically active GCs with improved properties as compared to glass

Oxyfluoride glass-ceramics offer better alternatives

- ✓ Low phonon energy, optical transparency and rare-earth ion of fluoride glasses
- ✓ Good mechanical, thermal and chemical properties of oxide glasses

Material	Phonon Energy (cm^{-1})
Phosphate	1200
Silicate	1100
Fluoride	500
LaF_3	350
$NaLaF_4$	300

Transparency condition:
uniformly dispersed nano-crystals with size less than 50 nm



* Y. Wang, J. Ohwaki, *Appl. Phys. Lett.* 63 (24) 3268 (1993)

A. de Pablos-Martín et al., *Int. Mater. Rev.* 57 [3], 165-186 (2012)

P.P. Fedorov et al. *J. Fluorine Chem.* 172, 22-50, (2015)

Materials Preparation

Bulk samples

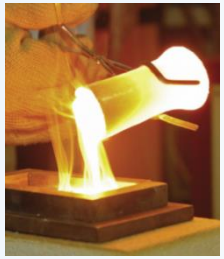
Glass composition (mol %) 55Si-10La*:

55 SiO_2 (% mol)
20 Al_2O_3
15 Na_2O
10 LaF_3
0.1, 0.2, 0.5, 1, 2 NdF_3
0.5 ErF_3, 0.5ErF_3-2YbF_3

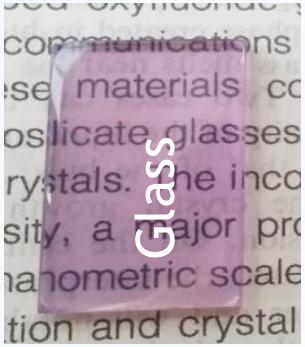
Crystallisation at Tg + (20-100 ºC)
Tg ~ 580ºC

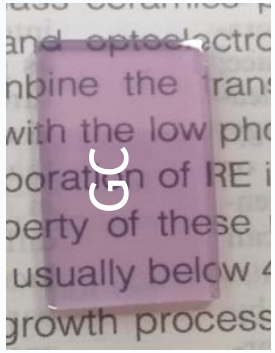
Raw materials

Melting
1650°C - 1.5h

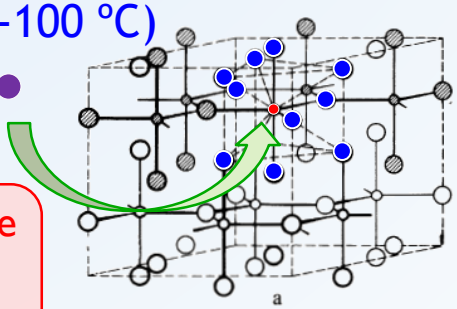


Heat treatment
GCs 620ºC, 660ºC





Nd



F
La

Space group $P\bar{3}C1$

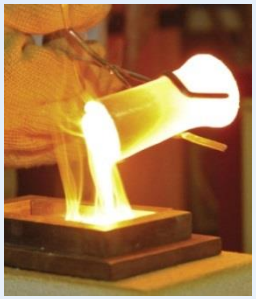
High solubility of RE^{3+} ions inside LaF_3 crystals
$La^{3+} \rightleftarrows Nd^{3+}$

*A. de Pablos-Martín *J. Am. Ceram. Soc.*, 94, 2420–2428 (2011)

Materials Preparation

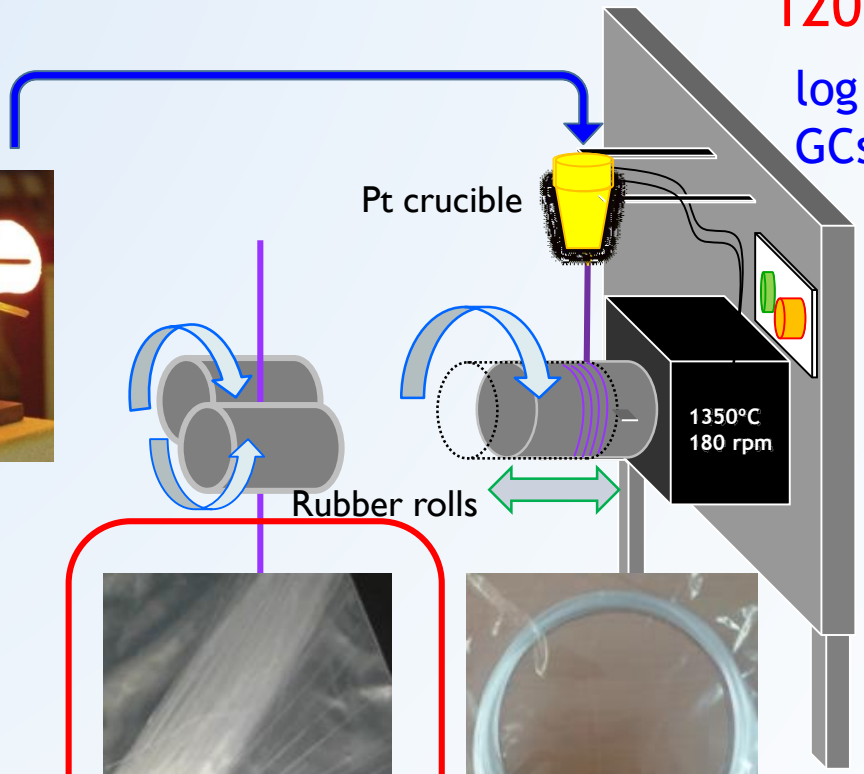
Fibers

Bulk glass specimens are heatead up and drawn into fibres



1200-1400 °C

log η ~ 3.2-5.8 dPa.s
GCs 640-660ºC



Doping with

0.1 and 2 NdF_3 (mol %)

200 μm fibres used for structural characterisation and for optical measurements

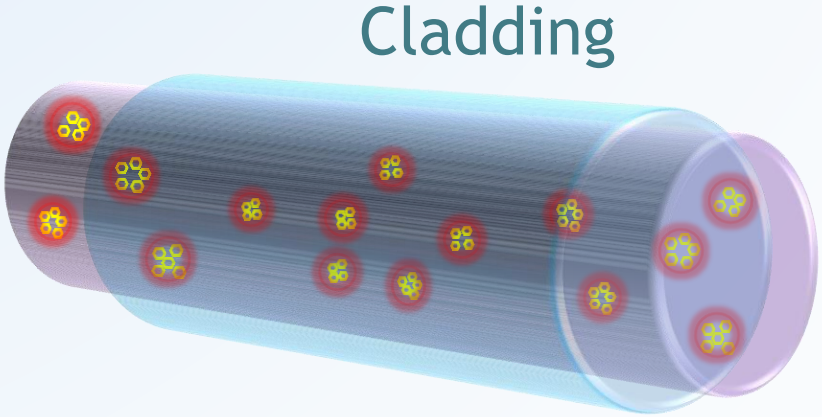
150-500 μm fibres

20-80 μm fibres

Materials Preparation

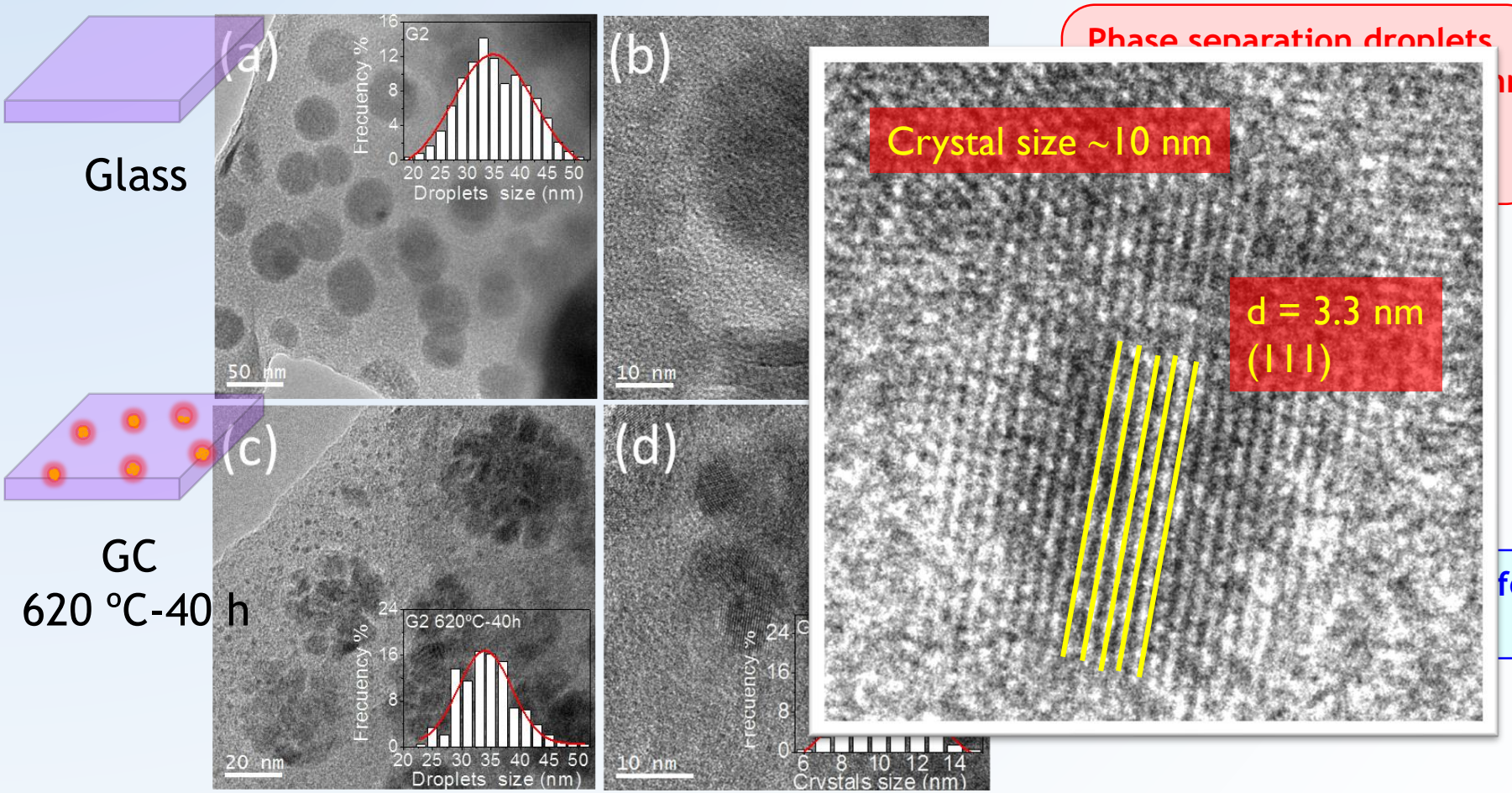
Cladding of glass-ceramic fibers

- Glass fibers (250 μm core size) heat treated at 640 ºC-40h to obtain GC core containing LaF_3 NCs
- SiO_2 cladding (3 μm) deposition using sol-gel (TEOS-MTES-LUDOX) and sintered at 450 ºC-1h



HR-TEM and Microstructure

Bulk doped with 2Nd



Phase separation droplets

nm

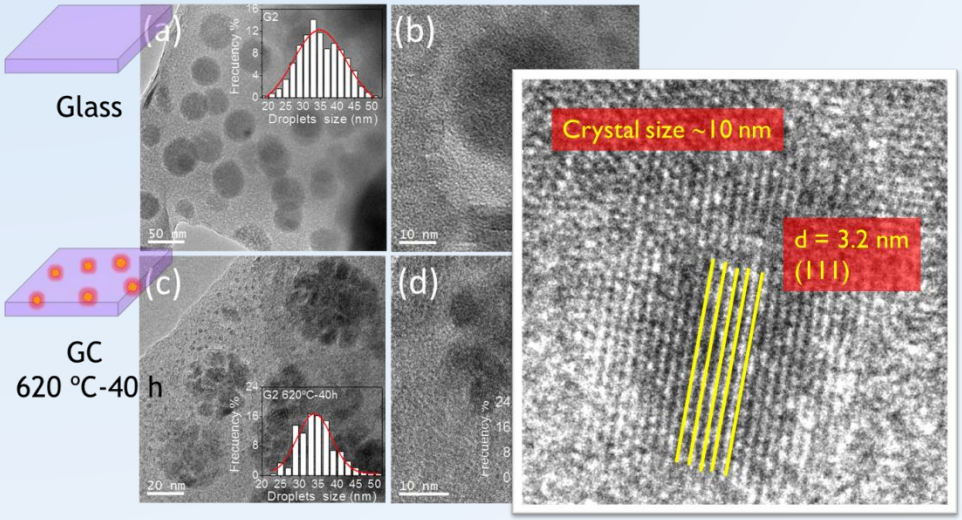
for

CSIC
Instituto de Cerámica y Vidrio

HR-TEM and Microstructure

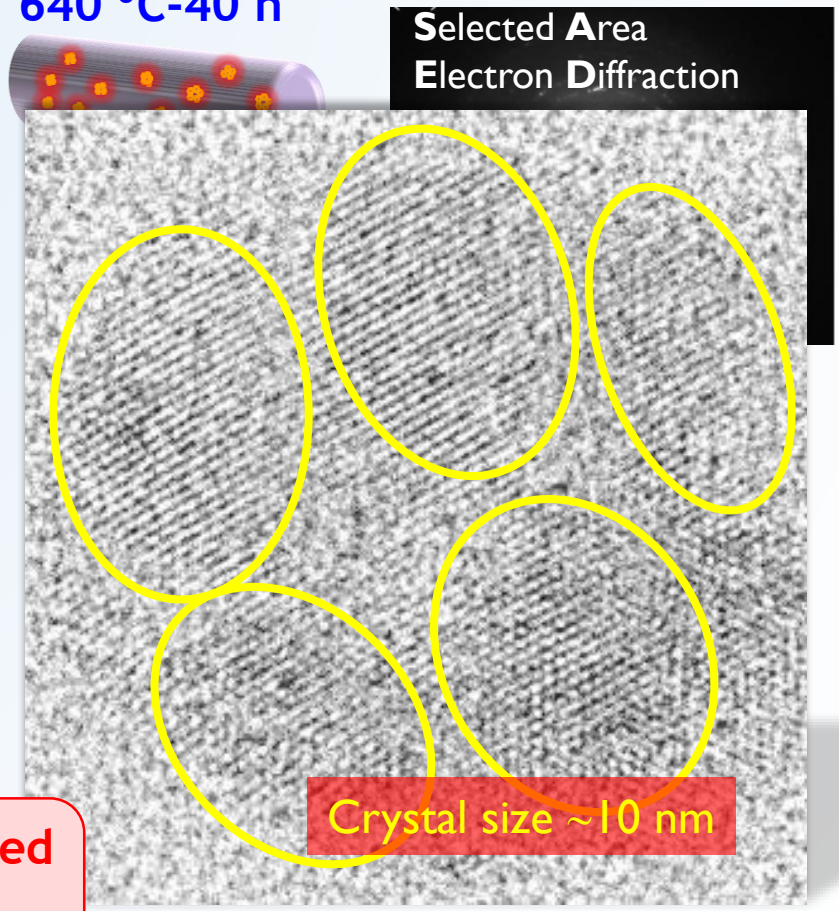
Bulk 2Nd

GC bulk
620 ºC-40 h



Fibers 2Nd

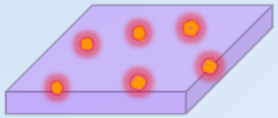
GC fibre
640 ºC-40 h



The same structure is observed for GC fibres but for slightly higher treatment temperature

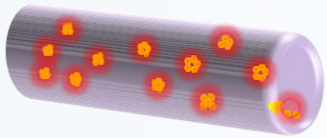
EDXS and RE distribution

Where are RE ions ?

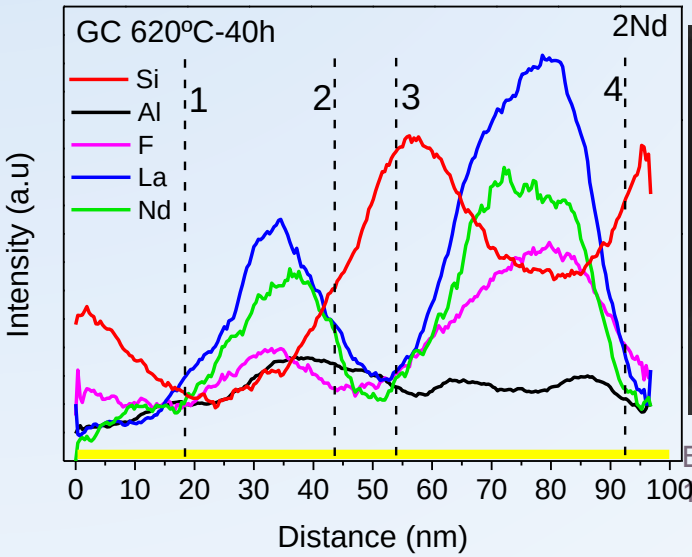


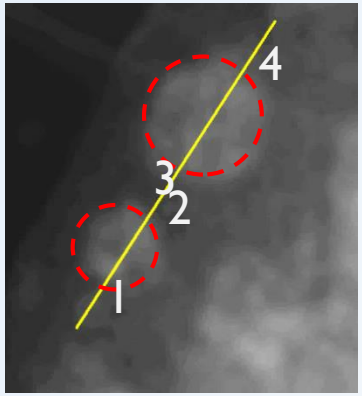
GC Bulk 620 °C-40h

Best optical efficiency when RE ions are in crystals

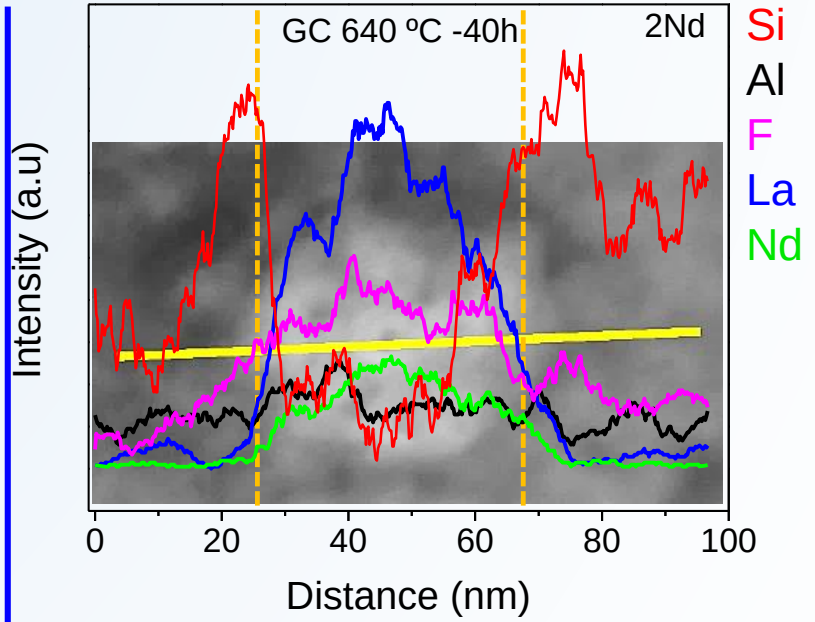


GC Fibers 640 °C–40 h

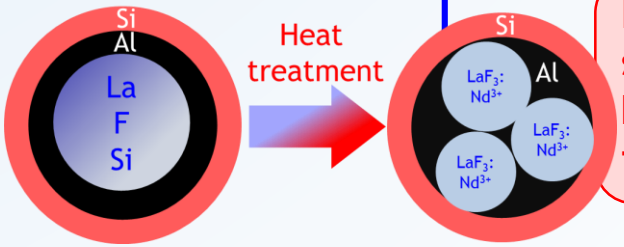




EDX in STEM mode along 100 nm

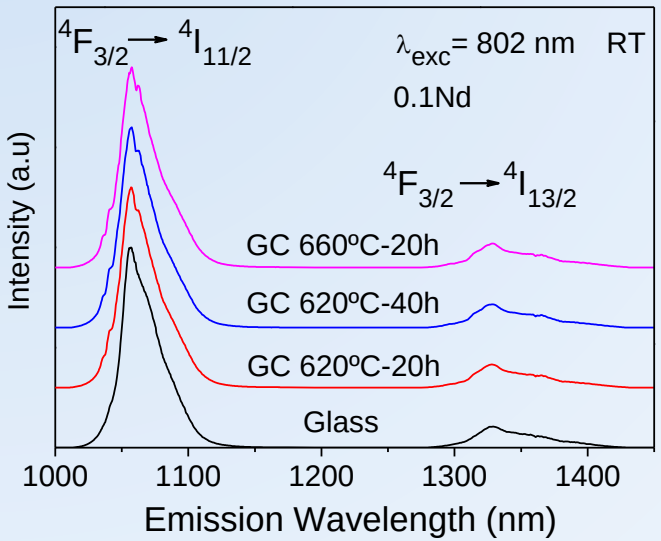


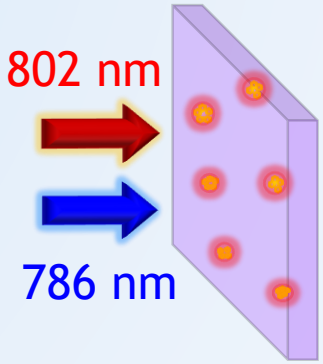
A viscous barrier enriched in Si surrounds the droplets.
Droplets are clearly enriched in La, Nd and F.



From TEM and EDXS the same structure and crystallisation behaviour as for bulk samples is observed.

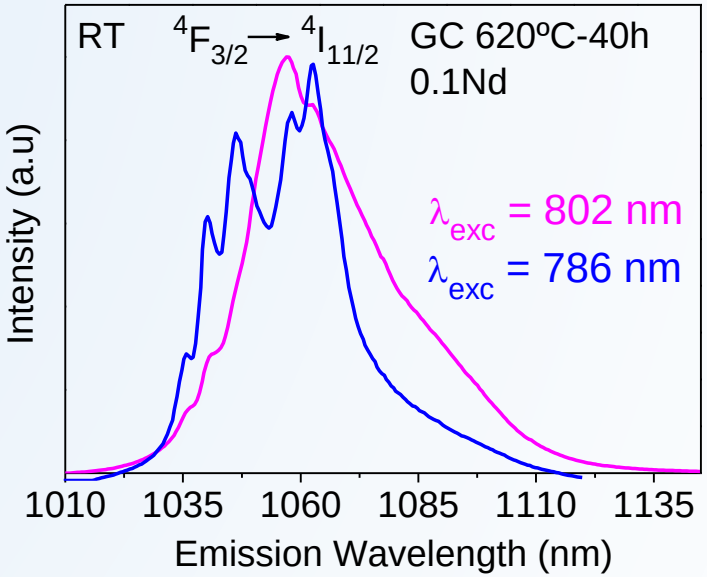
PL and lifetime

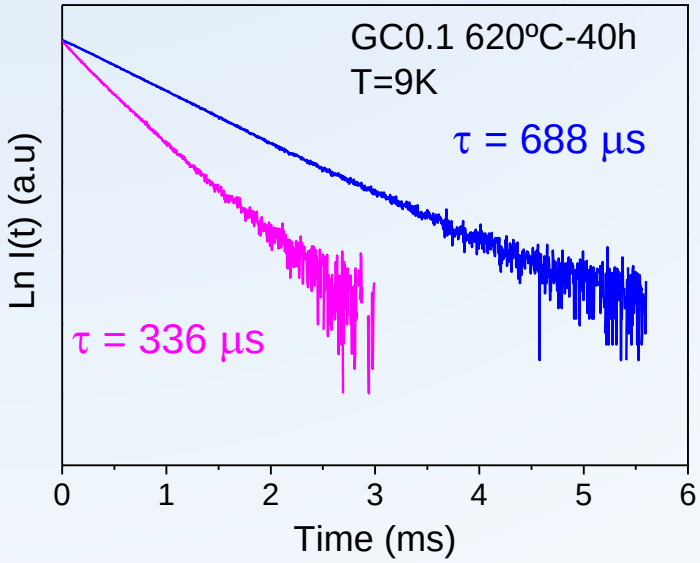


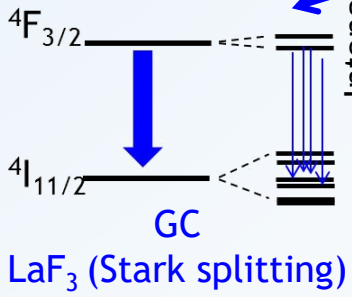


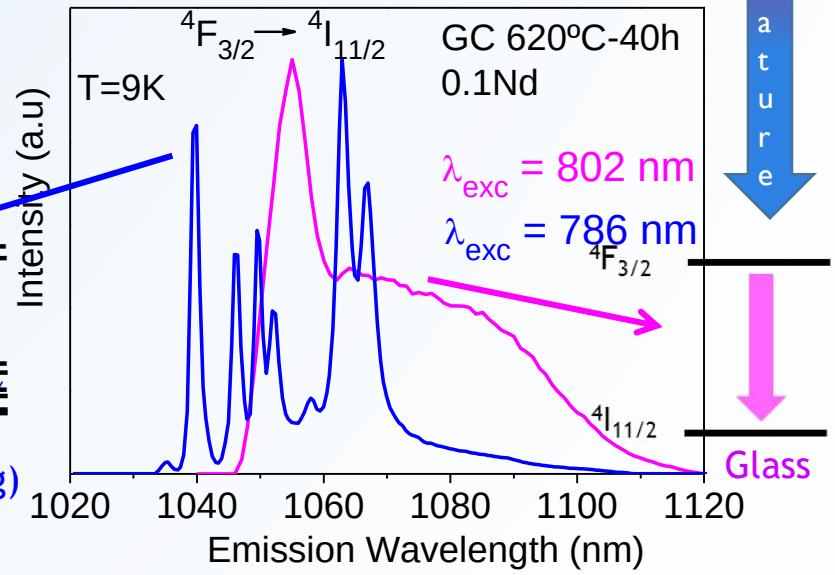
GC Bulk
620°C-40h

Selective excitation







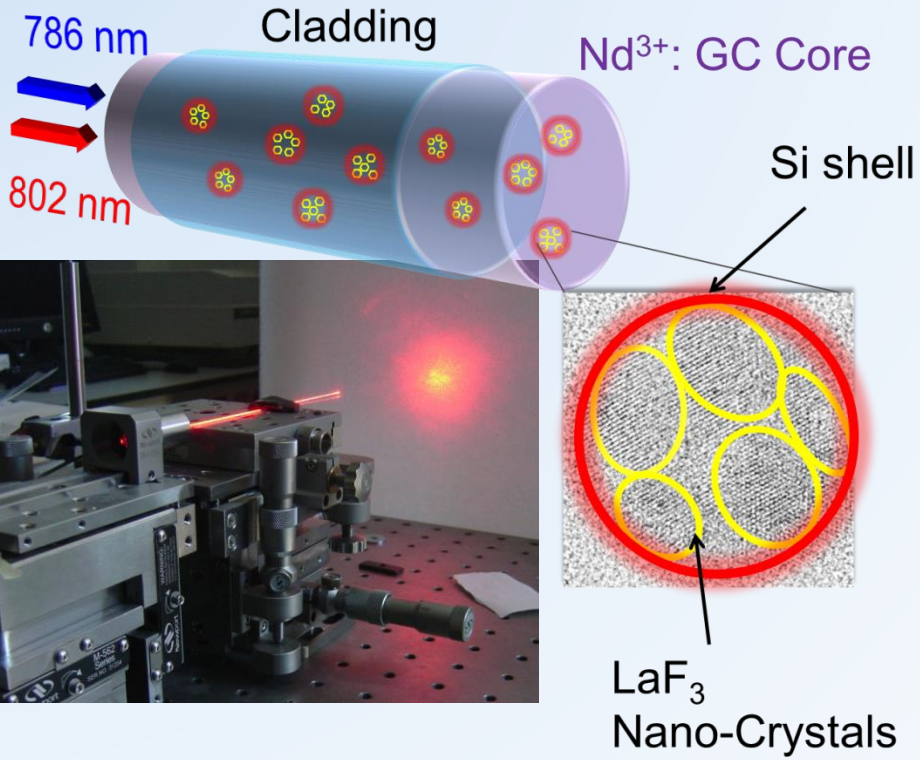


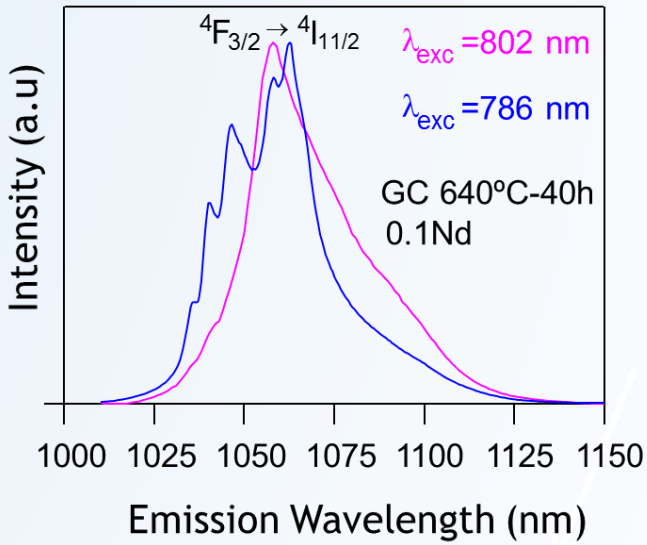
G. Gorni et al. *J. Eur. Ceram. Soc.* 37 (2017) 1695-1706

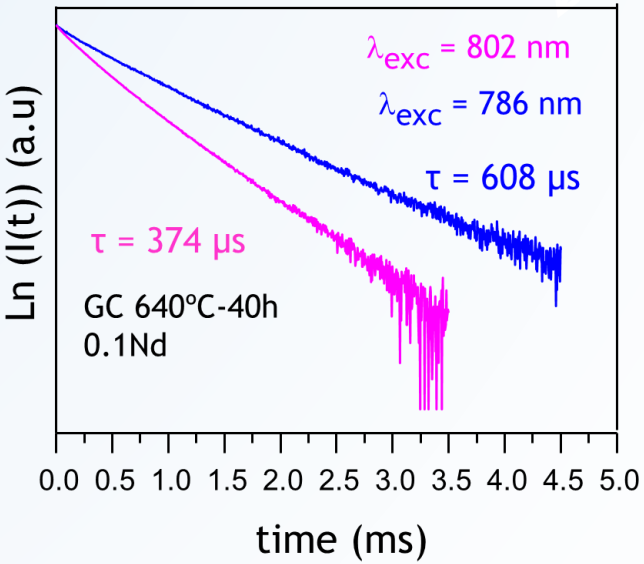
CSIC
Instituto de Cerámica y Vidrio

PL and lifetime

GC fibre 640°C-40h







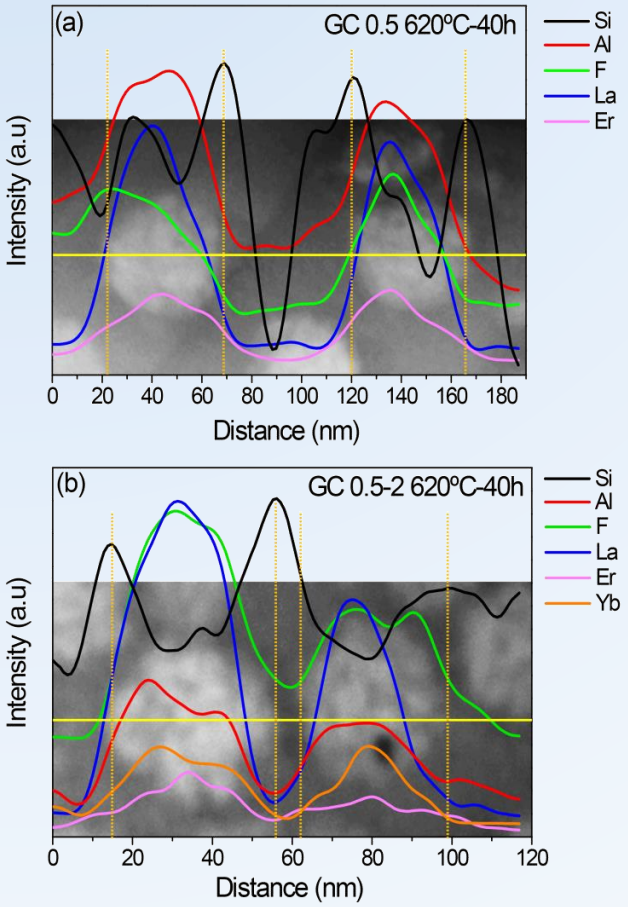
We demonstrated the possibility to obtain crystal-like optical properties in oxyfluoride glass-ceramic fibers!

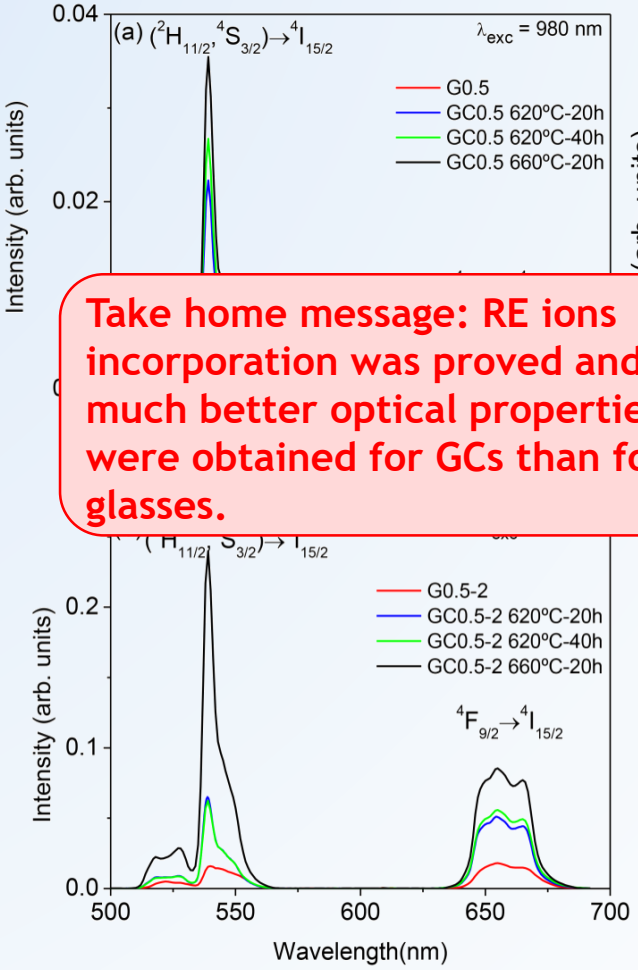
* G. Gorni et al. *CrystEngComm* (submitted) July 2017

CSIC
Instituto de Cerámica y Vidrio

Microstructure/PL and lifetime

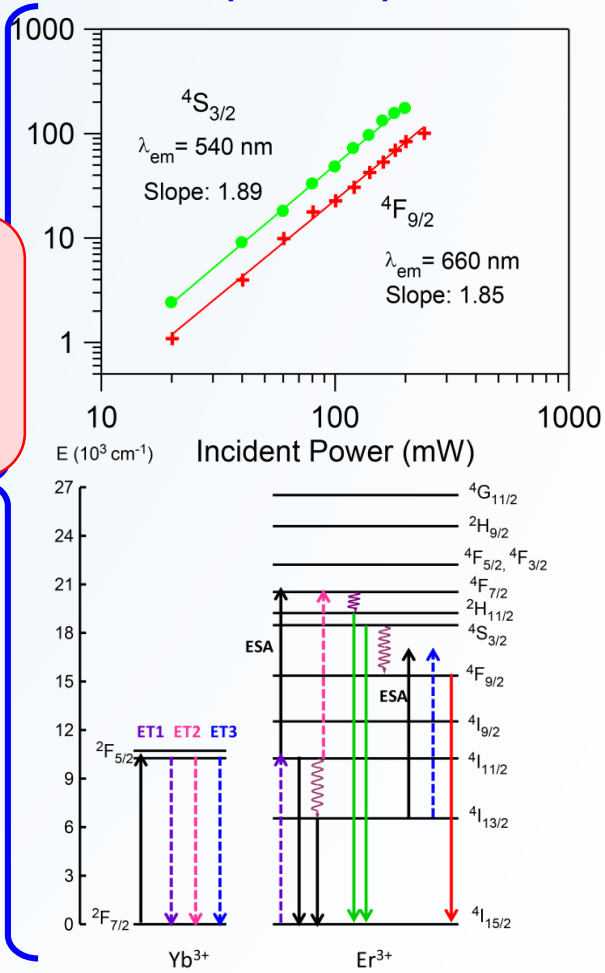
Er- Er/Yb doped bulk samples





Take home message: RE ions incorporation was proved and much better optical properties were obtained for GCs than for glasses.

Two photon process



G. Gorni et al. *J. Lumin* (2017) in press

CSIC
Instituto de Cerámica y Vidrio

STSM-MP1401

Laboratory of Optical Fiber Technology

7th Nov-9th Dec 2016 Bialystok, Poland

CSIC
Instituto de Cerámica y Vidrio

STSM-MP1401

Composition (%mol)	55Si-10La	70Si-7Gd
SiO_2	55	70
Al_2O_3	20	7
Na_2O	15	8
K_2O	0	8
LaF_3 /YF_3/ LuF_3/GdF_3	10	7
$(Na_2O + K_2O)/(SiO_2+Al_2O_3)$	0.20	0.21
$(Na_2O+K_2O)/Al_2O_3$	0.75	2.28
$LnF_3/(Al_2O_3+Na_2O+K_2O)$	0.28	0.30
T_g (ºC) (Dilatometry)	598 ± 2	510 ± 2
Crystalline phase	**LaF_3**	**$NaGdF_4$**

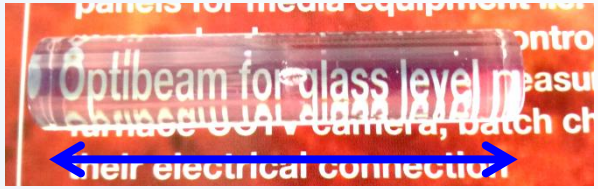
- Different crystalline phases doped with Nd^{3+}

Results 55Si10La

$55SiO_2$-$20Al_2O_3$-$15Na_2O$-$10LaF_3$-$0.1NdF_3$

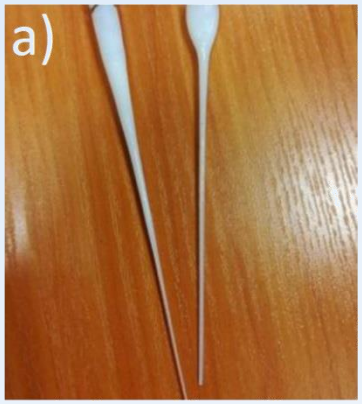
Rod-in-tube method
(AR GLAS® cladding)

Polished glass rod

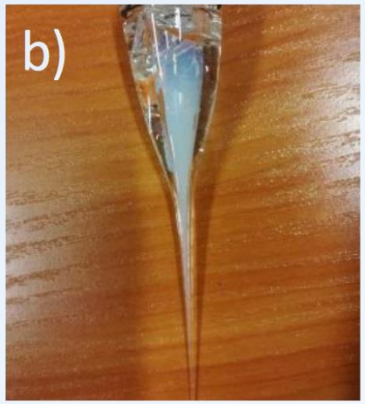


5 cm

Drawing at 1000 °C



Core drawing



Preform drawing

Crystallized

High glass tendency to crystallization. Strong crystallization peak (DTA) and low (100°C) thermal stability.

Higher T? Preform deforms under its own weight
Solution: to find suitable cladding

Results 55Si10La

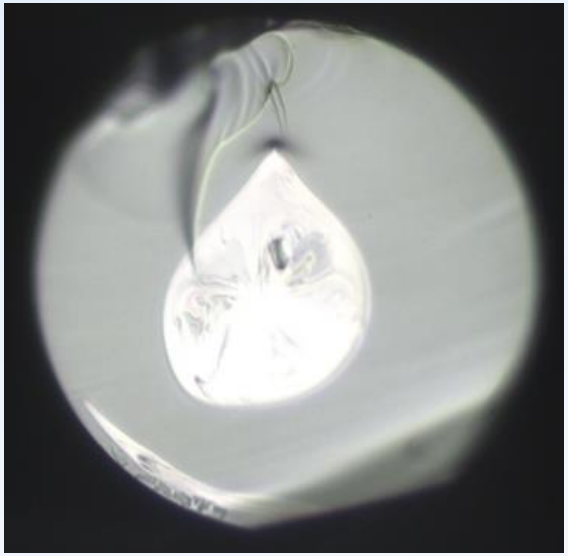
$55SiO_2$-$20Al_2O_3$-$15Na_2O$-$10LaF_3$-$0.1NdF_3$

Double crucible method
(AR GLAS® cladding)

Drawing T. 1200-1300 °C

Transparent fibers but unstable process ⟶ completely deformed core

AR-Glass cladding was flowing, while this T was good for 55Si10La glass drawing



We are working on suitable glass for the cladding with CTE and Tg similar to glass core.

Results 70Si7Gd

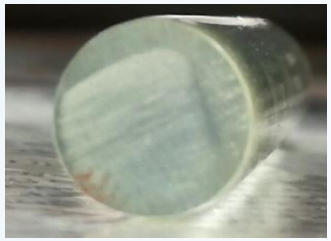
$70SiO_2$-$7Al_2O_3$-$8Na_2O$-$8K_2O$-$7GdF_3$-$0.1NdF_3$

Rod-in-tube method
(AR GLAS® cladding)

Drawing at 1000 °C

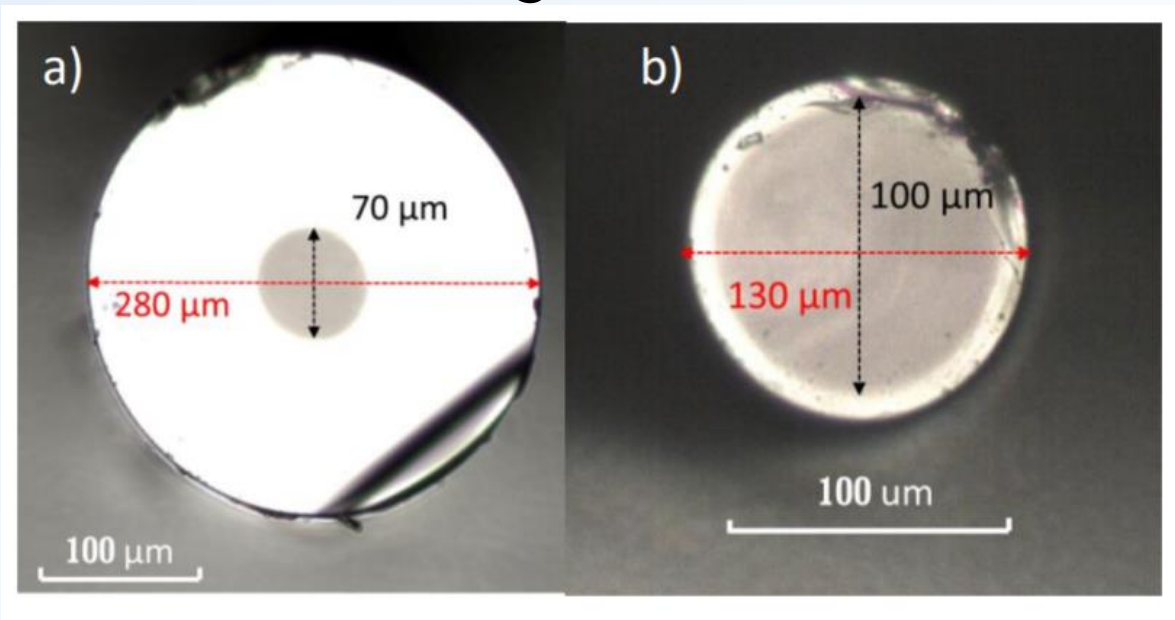
Transparent fibers and stable process

Polished glass rod

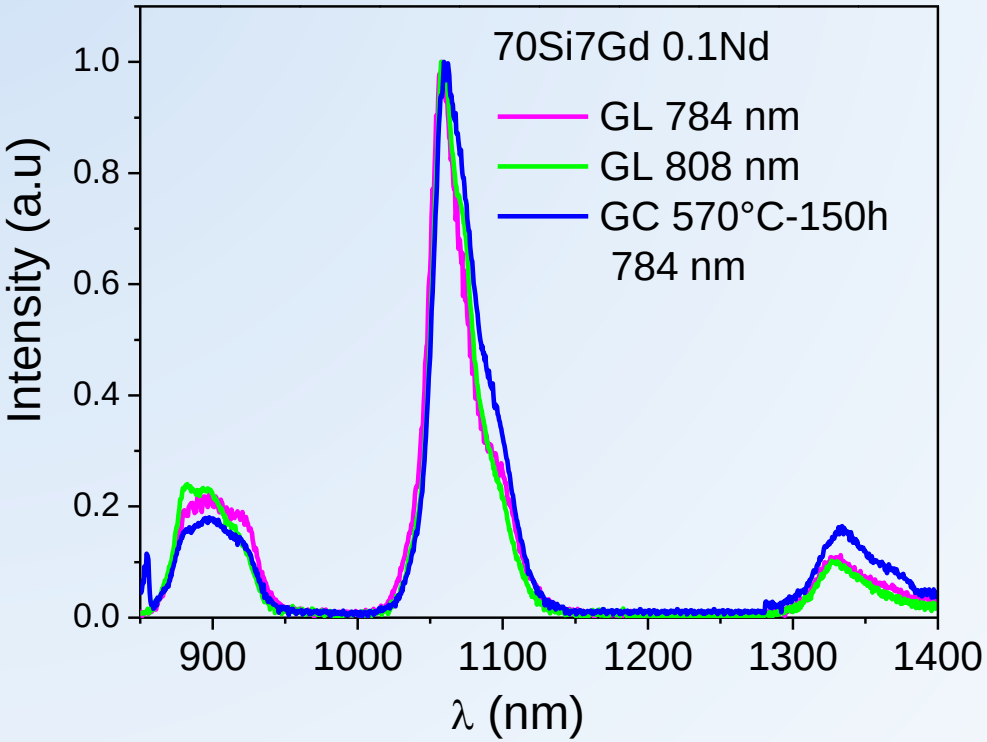


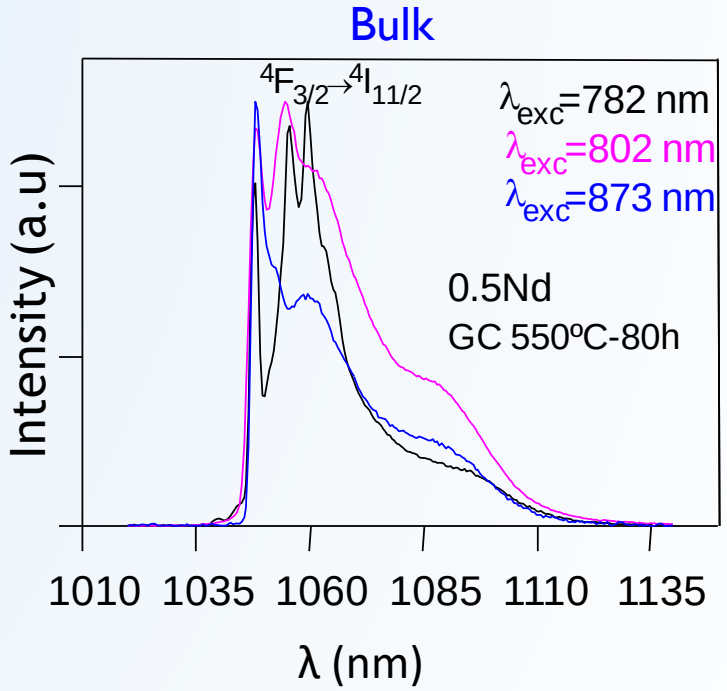
Core drawing

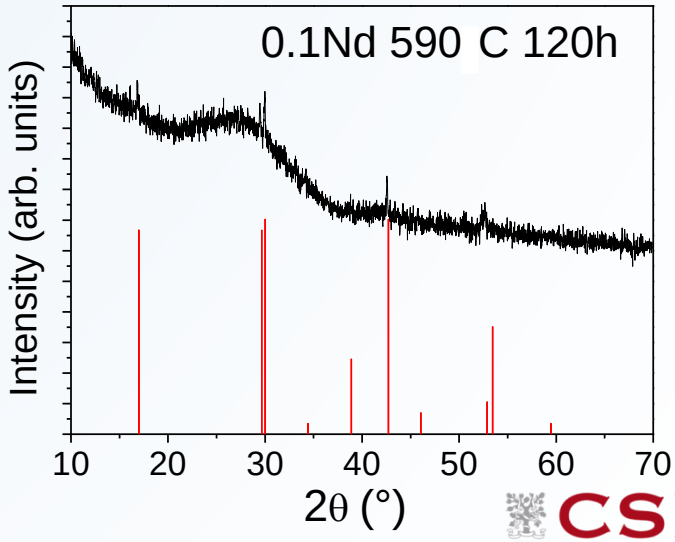
2 geometries



Results 70Si7Gd







No relevant differences in PL for treated and un-treated fibers:

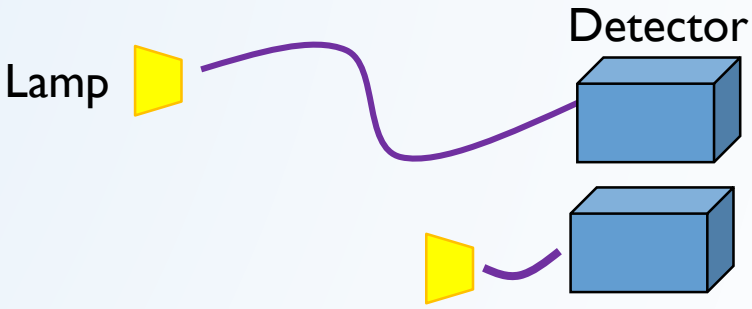
1. Wrong exc. λ ??
2. Wrong heat treatment ??

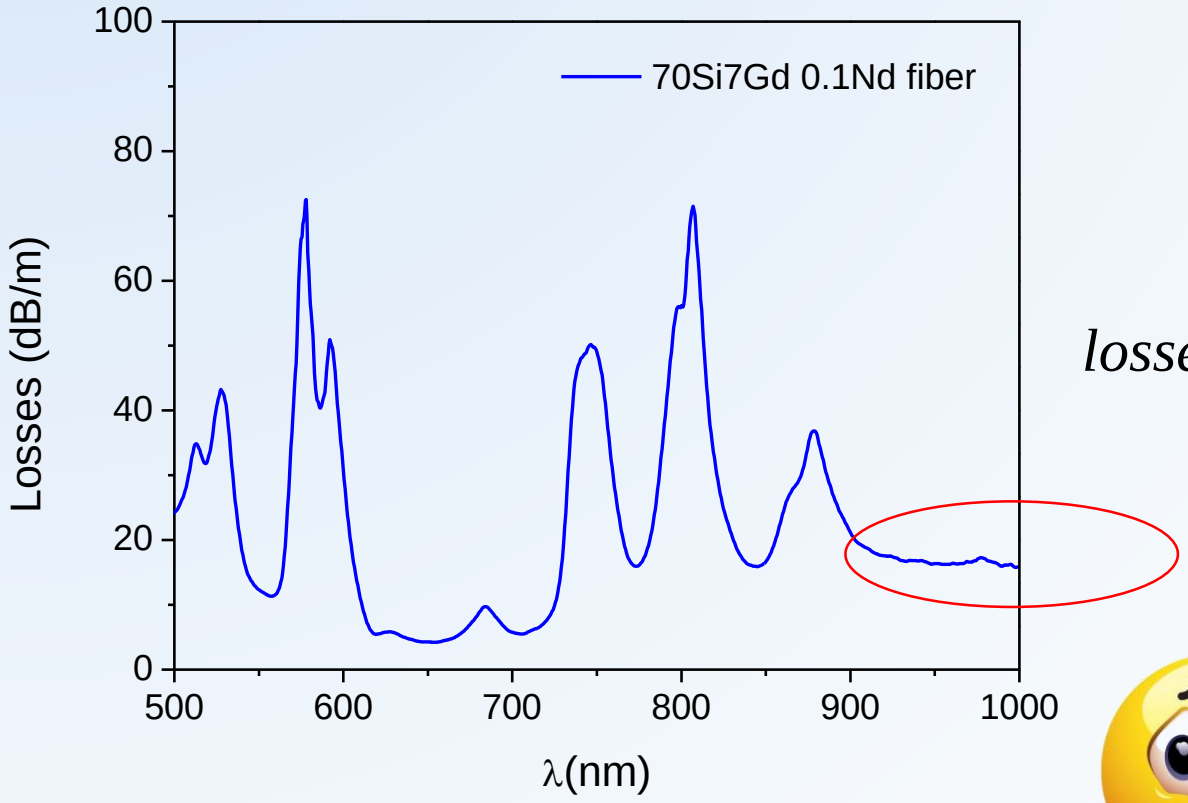
CSIC
Instituto de Cerámica y Vidrio

Results 70Si7Gd

Cut-back method

Spectral losses using Xe lamp





$$losses(dB/m) = \frac{10}{L}\log_{10}\left(\frac{P_{in}}{P_{out}}\right)$$

16 dB/m in the NIR region around 1 μm

Conclusions

- Transparent nano-glass-ceramics bulk and fibres containing only LaF_3 crystals were successfully obtained. Optical fibers were obtained by a SiO_2 cladding deposition using sol-gel method.

- Crystallisation mechanisms controlled by diffusion with constant number of nuclei is similar in bulk and fibers and phase separation is precursor for crystallization.

- A Si enriched viscous barrier prevents further crystals growth and limits the crystal size to the nanometric range (9-15 nm). RE ions are incorporated into the NCs

- Site-selective excitation spectra allowed isolating Nd^{3+} ions emission in LaF_3 nanocrystals reproducing the optical properties of pure Nd^{3+}:LaF_3 crystals in both bulk and fibers. Better optical properties for GCs than for glasses.

- Fiber drawing using a drawing tower showed the possibility to obtain good quality optical fibers but a specific cladding it is necessary (maybe another STSM !!).

Acknowledgements

Funding: National projects

MAT2013-48246-C2-1-P
MAT2013-48246-C2-2-P

GOBIERNO DE ESPAÑA
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

CSIC
Consejo Superior de Investigaciones Científicas

LASES
Universidad del País Vasco
Euskal Herriko Unibertsitatea

cost
EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY

Action MP1401

POLITECHNIKA BIAŁOSTOCKA

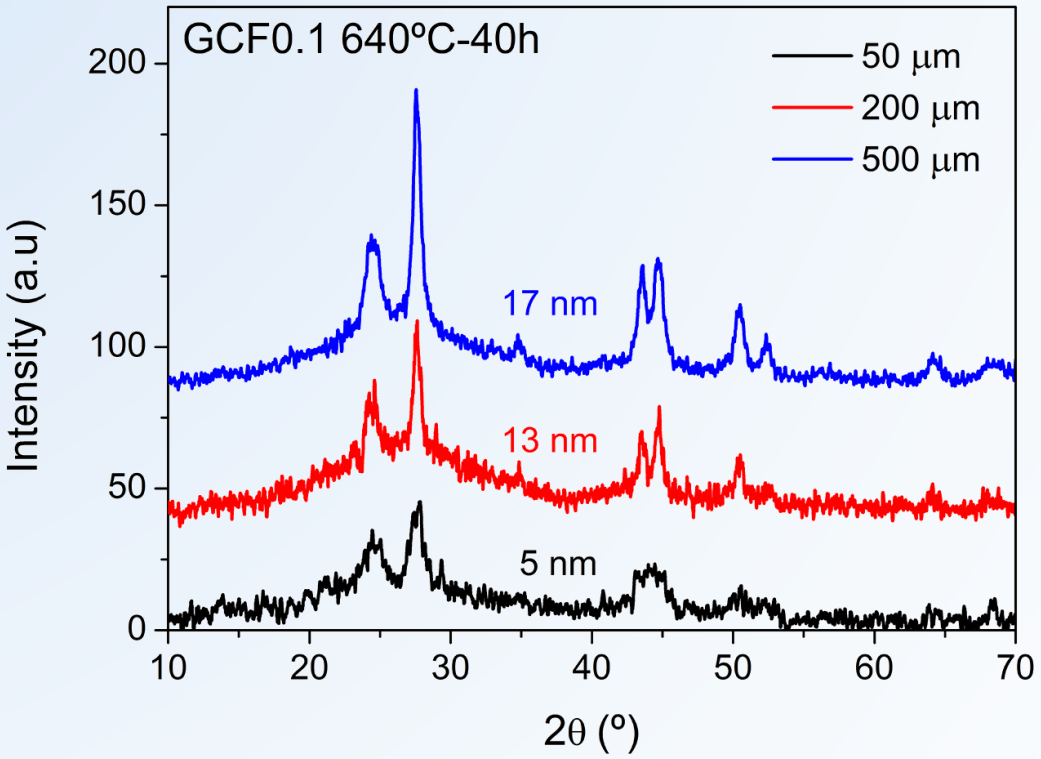
Faculty of Electrical Engineering

Leibniz ipht
LEIBNIZ INSTITUTE of PHOTONIC TECHNOLOGY

Thank you!

Crystal phase and crystal size

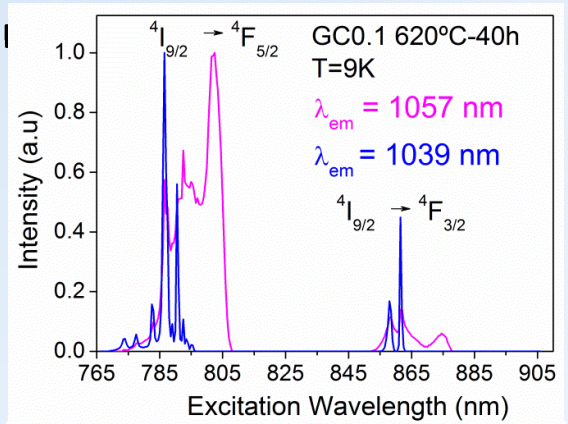
Effect of the cooling rate

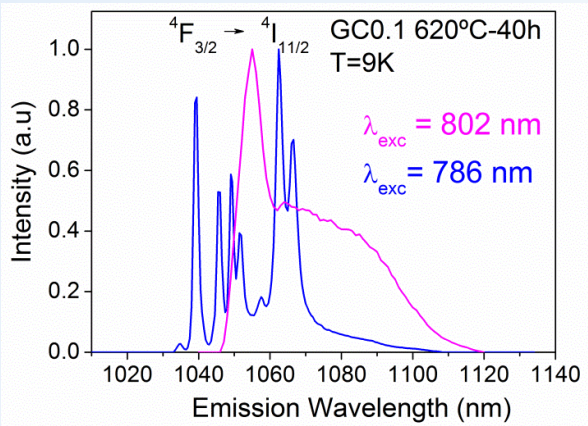


Phase separation occurs during cooling. Thinner fibers cool down fasters and as result a delay in the crystallization process is observed.

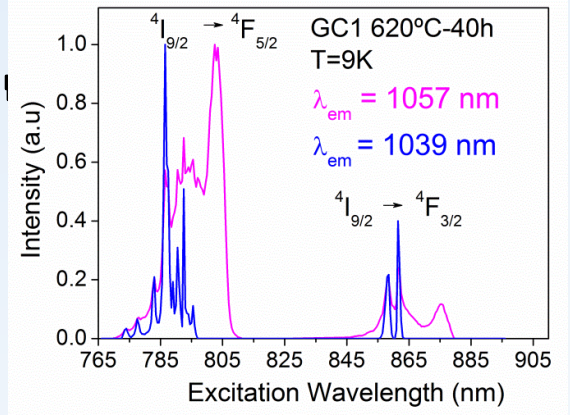
Selective PL and lifetime

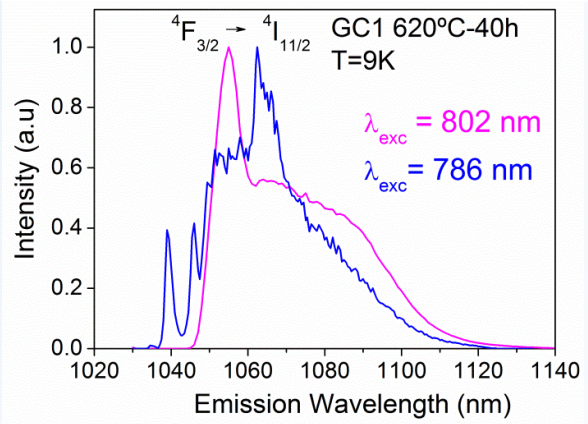
What happens with the other compositions ?





0.1Nd



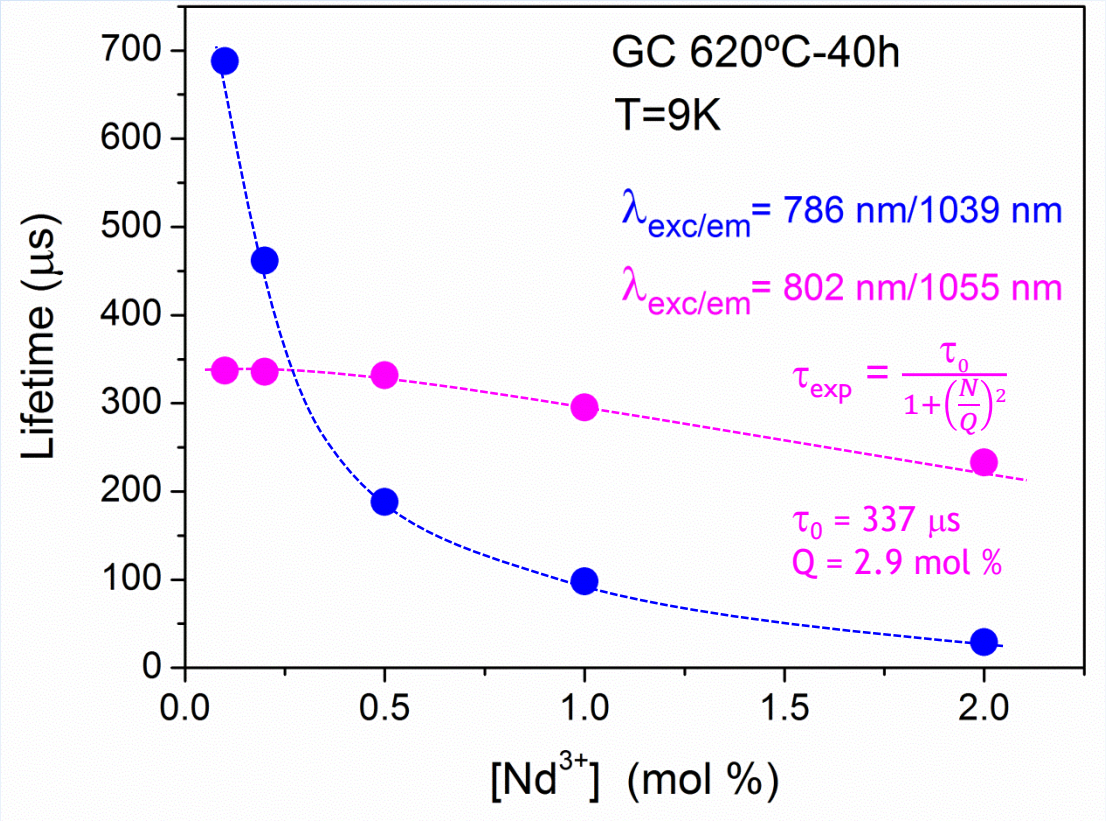


1Nd

Lost of intensity and broader peaks appear for Nd^{3+} emission in LaF_3 NCs increasing the concentration beyond 0.1 mol%

G. Gorni et al. J. Eur. Ceram. Soc. 37 (2017) 1695-1706

Selective PL and lifetime



Stronger quenching of the Nd^{3+} lifetimes in the LaF_3 NCs than in glasses. High diffusion of Nd^{3+} ions from the glass matrix to the LaF_3 NCs

The effective concentration into the NCs is completely different. It can be 10 times (or more) the nominal concentration.

[Nd^{3+}] mol%	[Nd^{3+}] mol % in NCs
0.1	1.2
1	8.6

Calcuted by previous XANES results