Crystallization and optical properties of Rare earth doped-oxyfluoride glass-ceramics for its use in optical fibers

J.J. Velázquez[1], G. Gorni[1], J. Fernández[2], R. Balda[2], A. Durán[1], M.J. Pascual[1]

[1]GlaSS group, Ceramics and Glass Institute (ICV—CSIC), Madrid, Spain

http://glass.icv.csic.es/

[2]LASES group, Applied Physic Department I, Superior school of Engineering, Pais Vasco University, Bilbao, Spain

EAGLES
International Conference on
Rare-Earth Doped Glass Materials and Fibre Lasers
MPNS COST Action MP1401
October 18th – 19th, 2016 | Trento, Italy

Outline

Introduction

Glass and Glass-ceramics (GC) preparation:

$55SiO_2$-$20Al_2O_3$-$15Na_2O$-$10LaF_3$–$xNdF_3$(55Si-10La)

$70SiO_2$-$7Al_2O_3$-$8Na_2O$-$8K_2O$-$7GdF_3$-$xErF_3$–y YbF_3 (70Si-7Gd)

Thermal and Structural Characterization

Optical Properties

Conclusions

Acknowlegdements

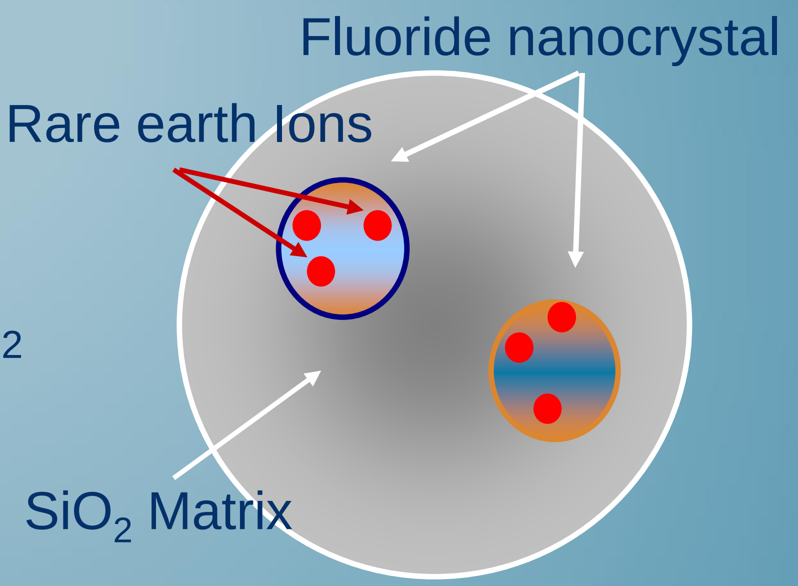
Introduction

EAGLES

Why oxyfluorides glass-ceramics doped with Rare earths ions?

- Enhanced the mechanical properties
- Enhanced the optical properties

(low phonon enviroment (300-400 cm^{-1}))[1,2]



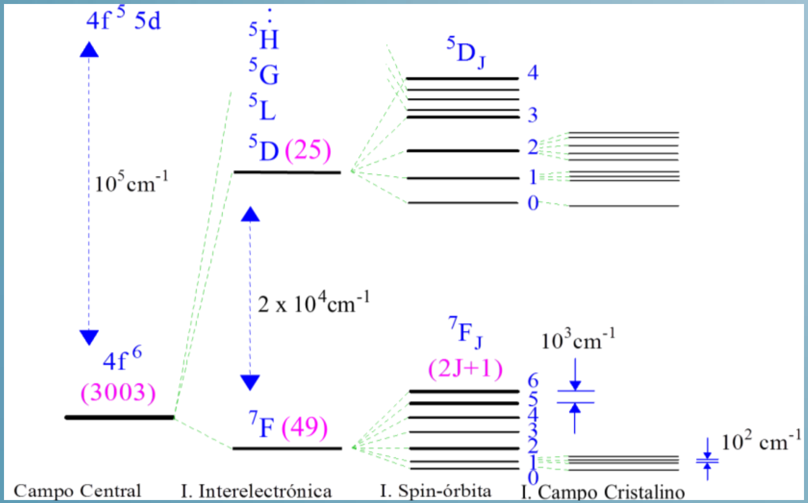
These nanoglass-ceramics combine the optical properties of Rare earths ions in fluoride system with the advantages of elaboration and use of oxides[3,4]

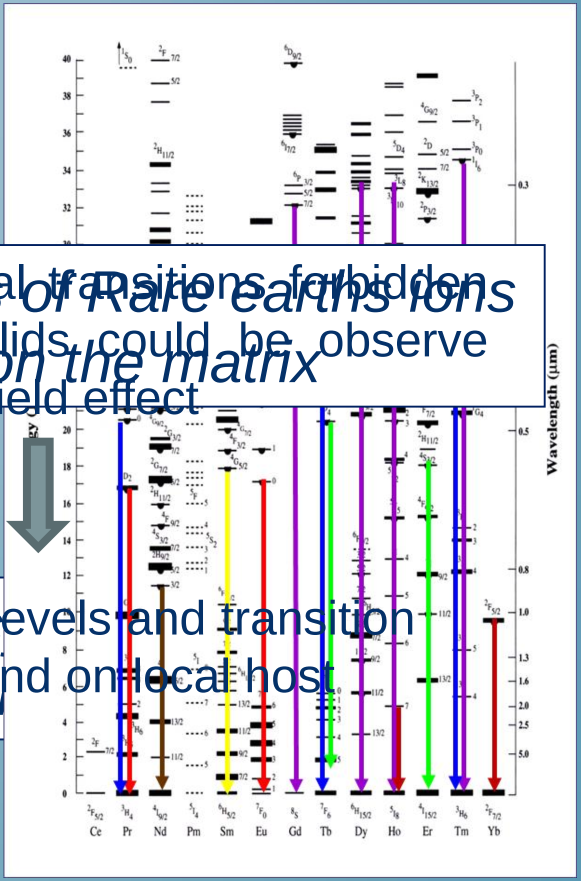
[1]Wang, Ohwaki., App.Phys.Lett, 63, 3268 (1993)
[2,]Fedorov, P.P. Luginina, A., Popov, A.I. J Fluorine Chem. 172, 22-50, (2015)
[3]de Pablos Martín A. et alt : J. Am. Ceram. Soc. 94, [8], 2420-2428 (2011)
[4]de Pablos-Martín A., Durán A., Pascual M. J.: Int. Mater. Rev. 57 [3], 165-186 (2012)

Introduction

Why oxyfluorides glass-ceramics doped with Rare earths ions?

- ✓ 4f electrons of Rare earths ions are partially shielded from the external interactions due to the existence of external electrons (5s, 5d)





- ✓ Intraconfiguracional transitions forbidden in free ion, in solids could be observe due to crystalline field effect

Optical properties of Rare earths ions depends on the matrix

- ✓ Splitting of Stark levels and transition probabilities depend on local host

More efficienc

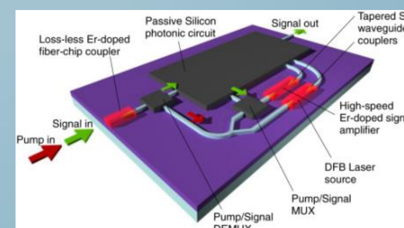
nanocr

Introduction

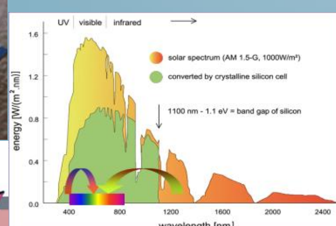
Aplications

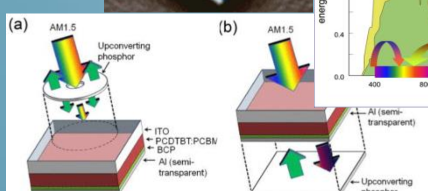
- Fluorescent markers

- Active media on lasers emitters



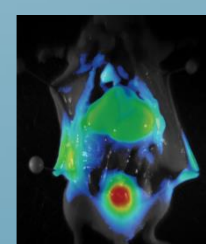
- Integrate photonic devices

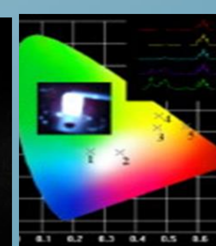


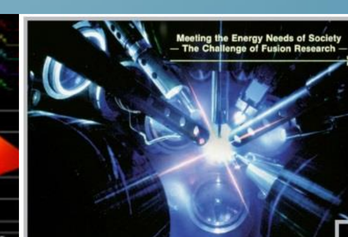


- Enhanced the efficiency of solar cells through photon-conversion processes

- Among others ….





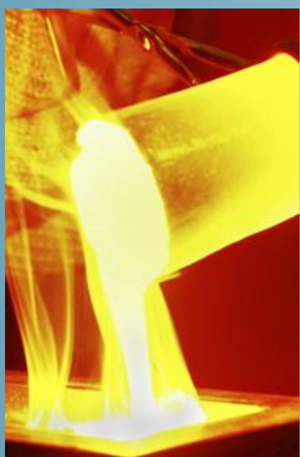


Glass and Glass-ceramics preparation

EAGLES

$70SiO_2$-$7Al_2O_3$-$8Na_2O$-$8K_2O$-$7GdF_3$-$xErF_3$–$yYbF_3$ (% mol)

(70Si-7Gd)



1600ºC during 1h ⟺ 1650ºC during 0.5h

515 °C during 0.5h

Re^{3+} and Re^{3+}-Yb^{3+} doped 70Si-7Gd glasses with the following Re^{3+} concentrations (in mol%) were prepared:

- undoped
- 0.5 Er^{3+}
- 0.5 Er^{3+} – 2Yb^{3+}

1 Glass

2 Glass-ceramics:

550°C-80h

580 ºC-120h

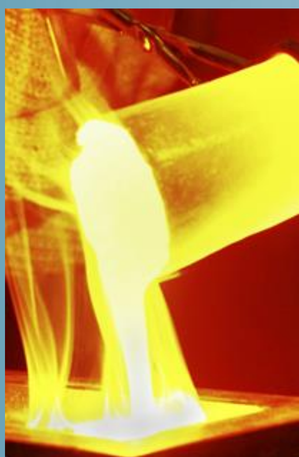
J. J. Velazquez *"Crystallization and optical properties of rare earth doped-oxyfluoride glass-ceramics for its use in optical fibers"*

Glass and Glass-ceramics preparation

EAGLES

$55SiO_2$-$20Al_2O_3$-$15Na_2O$-$10LaF_3$-$xNdF_3$(% mol)

(55Si-10La)



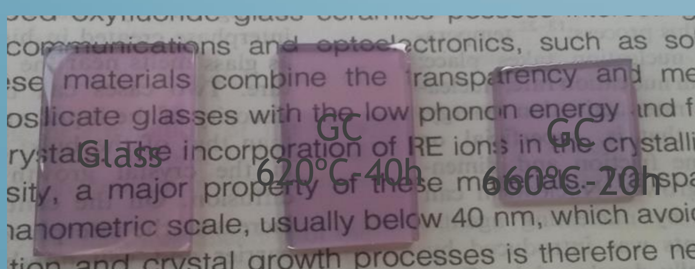
1650ºC during 1.5h ⟷ 550 °C during 0.5h

Re^{3+} doped 55Si-10La glasses with the following Re^{3+} concentrations (in mol%) were prepared:

- undoped
- 0.1, 0.2, 0.5,1,2 Nd^{3+}

1 Glass

2 Glass-ceramics:620ºC 1÷80h
660ºC 20h



J. J. Velazquez "Crystallization and optical properties of rare earth doped-oxyfluoride glass-ceramics for its use in optical fibers"

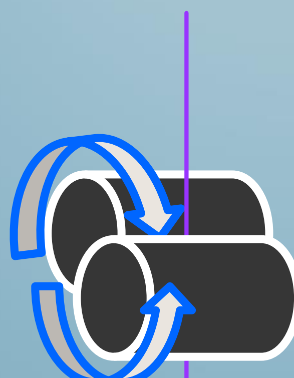
Glass and Glass-ceramics preparation: Fibers

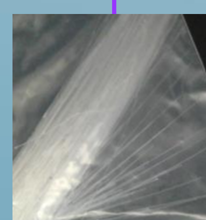
EAGLES

Fibers 55Si-10La

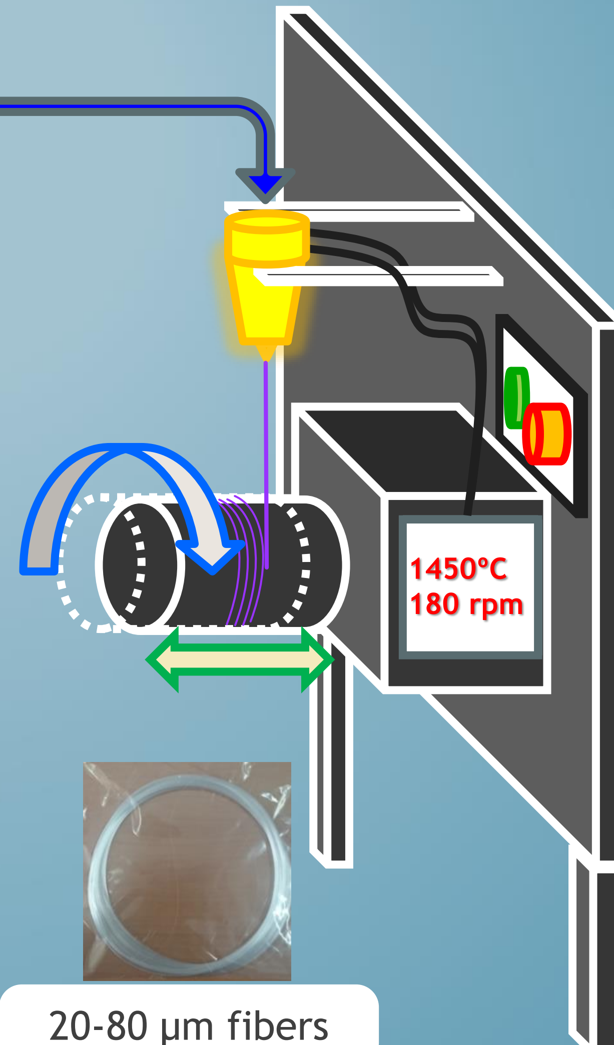
1480°C

log η ~ 2.8 ; GCs 640ºC 40h





150-500 µm fibers



20-80 µm fibers

J. J. Velazquez *"Crystallization and optical properties of rare earth doped-oxyfluoride glass-ceramics for its use in optical fibers"*

Universidad del País Vasco · Euskal Herriko Unibertsitatea

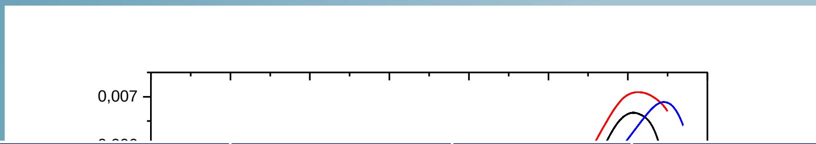
CSIC

Thermal Characterisation: Dilatometry and DTA

EAGLES

GlaSS
Glasses, Glass-ceramics and Sol-gel materials for a Sustainable Society

70Si 7Gd

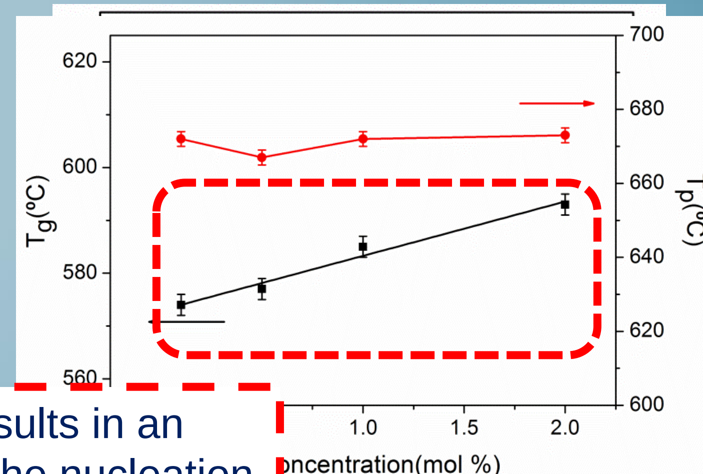


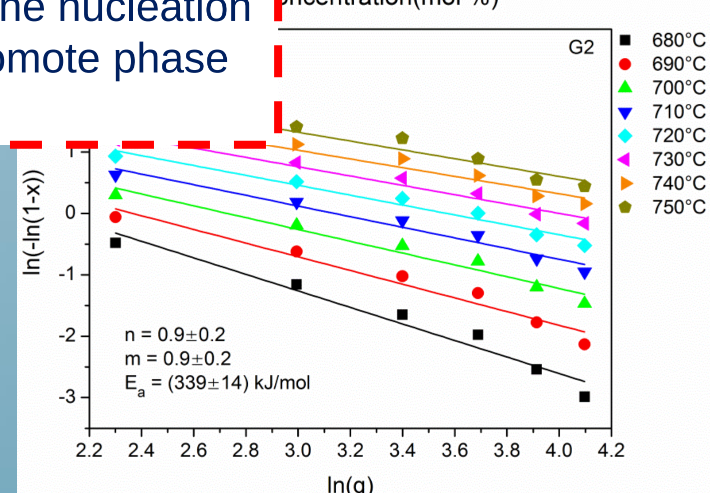
	Undoped	0.5 Er^{3+}	0.5 Er^{3+}-2Yb^{3+}
T_g (ºC) ±3	510	530	546
T_s(ºC) ±6	590		
$\alpha \cdot 10^{-6}$ (K^{-1}) ± 0.5	10.2		

Dopant incorporation results in an increment of the $T_{g,}$ due to the nucleation action of Re^{3+} ions that promote phase separation

Crystallisation mechanism controlled by diffusion that starts from a constant number of nuclei and the crystals growth is in 2D - nanoplates

55Si 10La





J. J. Velazquez *"Crystallization and optical properties of rare earth doped-oxyfluoride glass-ceramics for its use in optical fibers"*

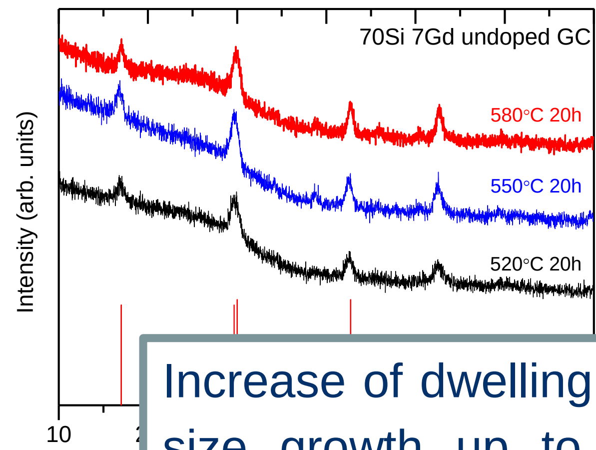
Universidad del País Vasco Euskal Herriko Unibertsitatea

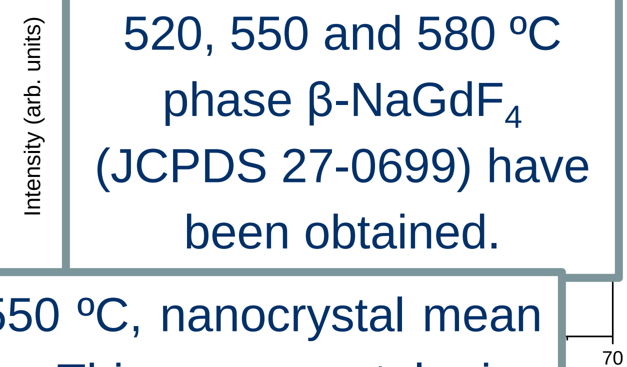
CSIC

Structural characterization: XRD

EAGLES

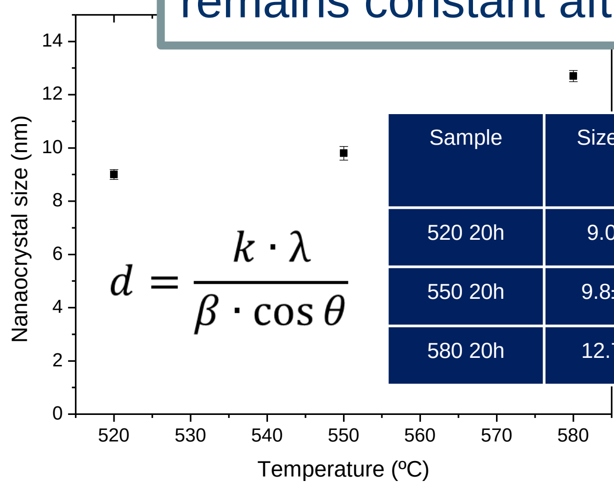
70Si-7Gd





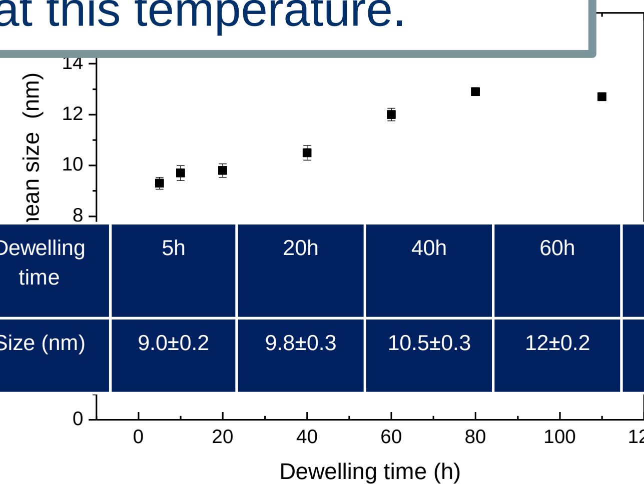
After heat treatment at 520, 550 and 580 ºC phase β-$NaGdF_4$ (JCPDS 27-0699) have been obtained.

Increase of dwelling time at 550 ºC, nanocrystal mean size growth up to 13.0 nm. This nanocrystal size remains constant after 80 h at this temperature.



$$d = \frac{k \cdot \lambda}{\beta \cdot \cos\theta}$$

Sample	Size (nm)
520 20h	9.0±0.2
550 20h	9.8±0.25
580 20h	12.7±0.2



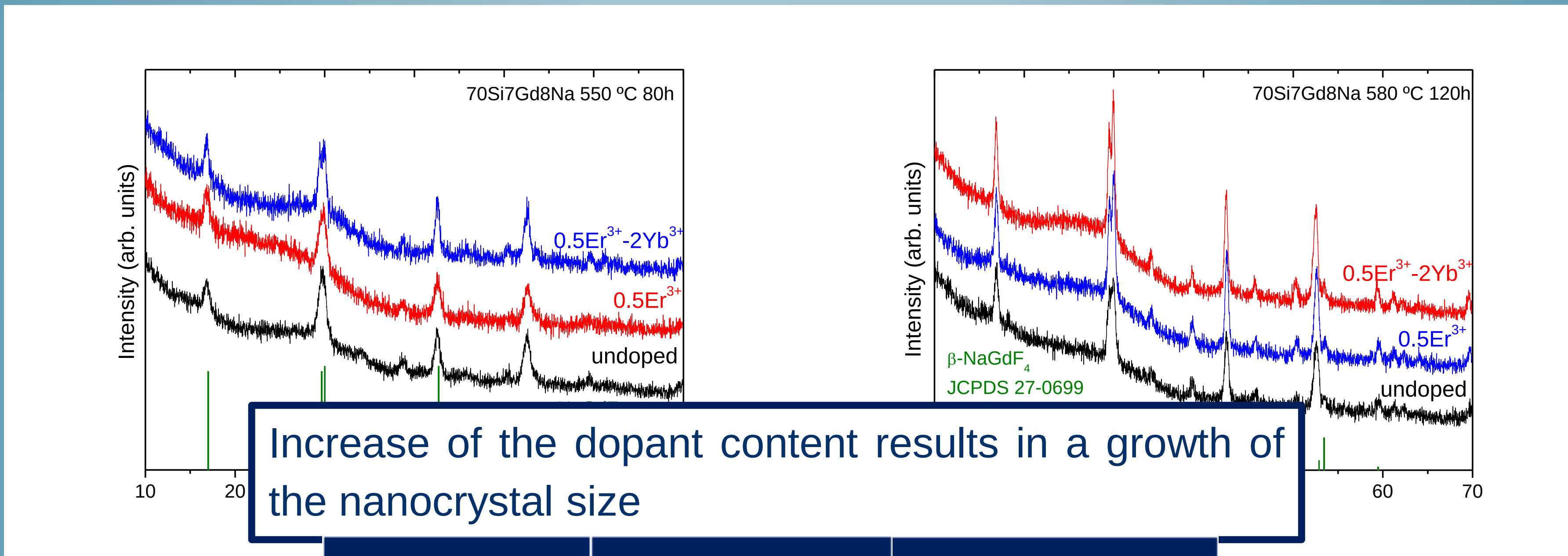
Dewelling time	5h	20h	40h	60h	80h	110h
Size (nm)	9.0±0.2	9.8±0.3	10.5±0.3	12±0.2	12.9±0.1	12.7±0.1

J. J. Velazquez *"Crystallization and optical properties of rare earth doped-oxyfluoride glass-ceramics for its use in optical fibers"*

Structural characterization: XRD

EAGLES

70Si-7Gd



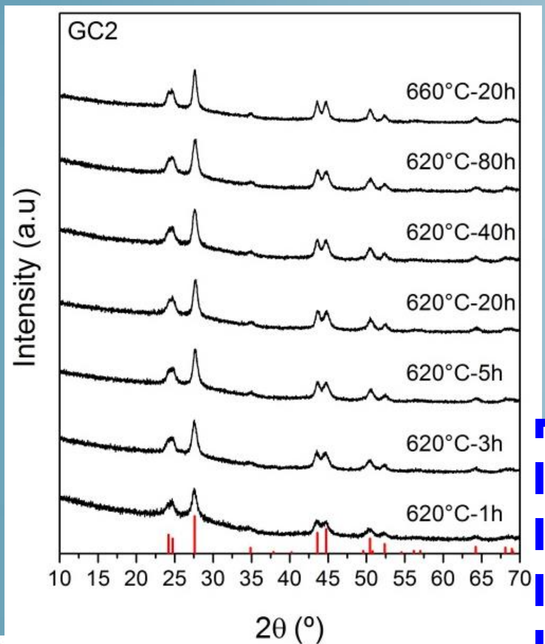
Increase of the dopant content results in a growth of the nanocrystal size

Sample	Size (nm)	Size (nm)
undoped	12.9	17.5
$0.5Er^{3+}$	13.2	20.1
$0.5Er^{3+}$-$2Yb^{3+}$	16.8	23.1

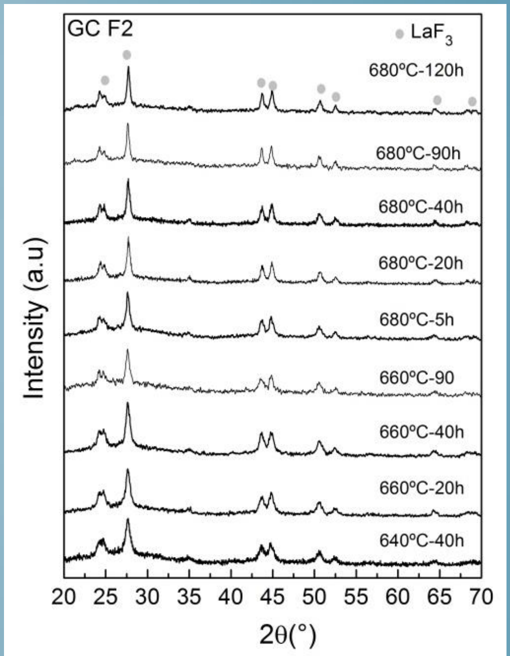
Structural characterization: XRD

EAGLES

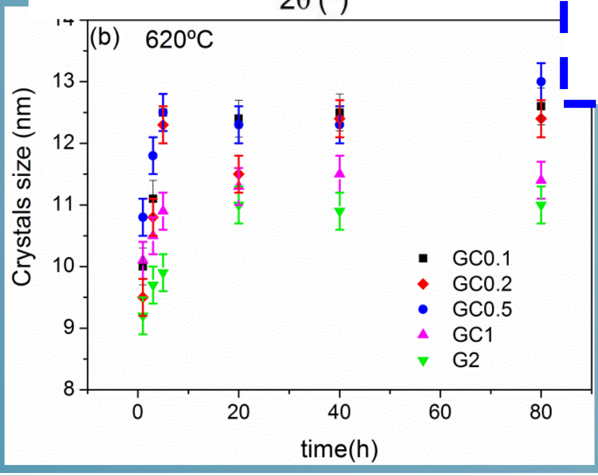
55Si-10La: Bulk and fibers



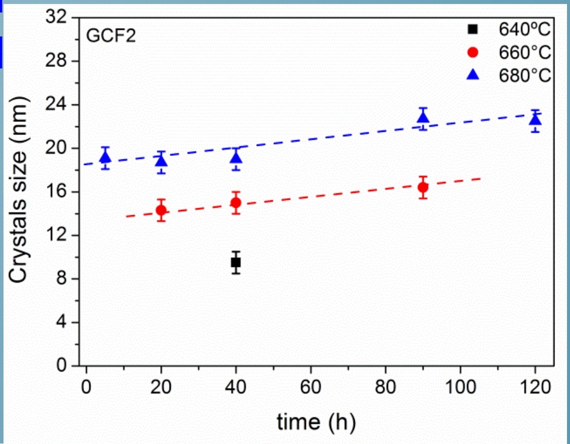
Only LaF_3 crystals precipitate in the glass matrix. The same behaviour is observed for all concentrations



Fibres treated at 620ºC are still amorphous unless treated for t >120h. A higher cooling rate in fibres causes crystallization delay



As Nd^{3+} content increases T_g increases as well and crystals size is smaller



J. J. Velazquez *"Crystallization and optical properties of rare earth doped-oxyfluoride glass-ceramics for its use in optical fibers"*

Universidad del País Vasco Euskal Herriko Unibertsitatea

CSIC

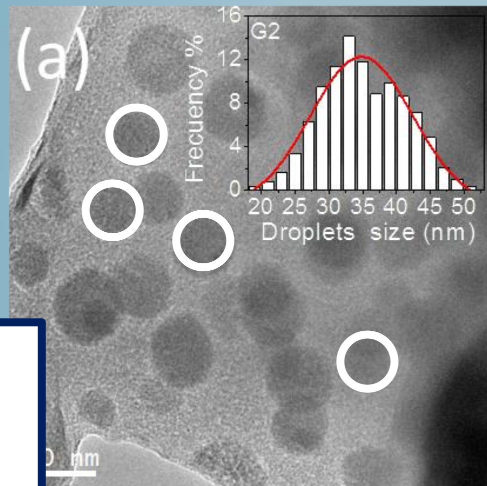
Structural characterization: HRTEM

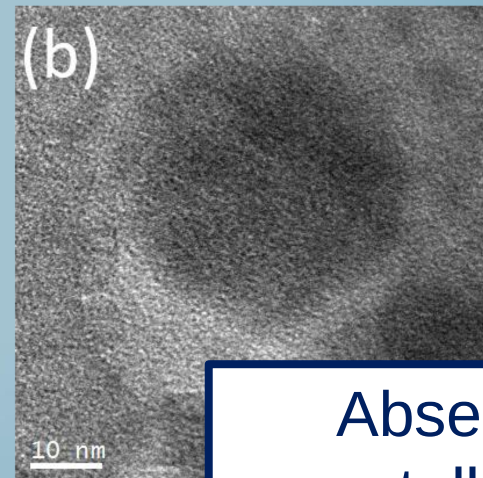
EAGLES

GlaSS
Glasses, Glass-ceramics and Sol-gel materials for a Sustainable Society

Bulk Glass

55Si 10La

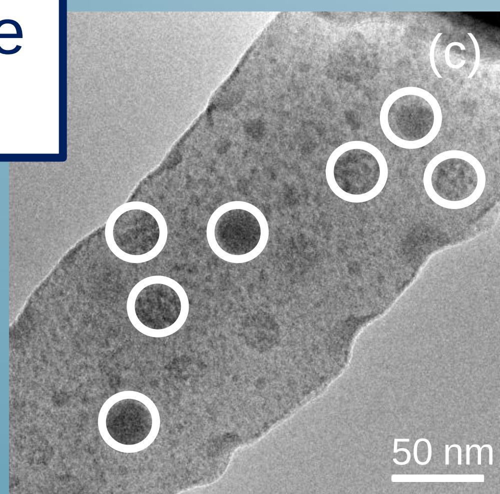


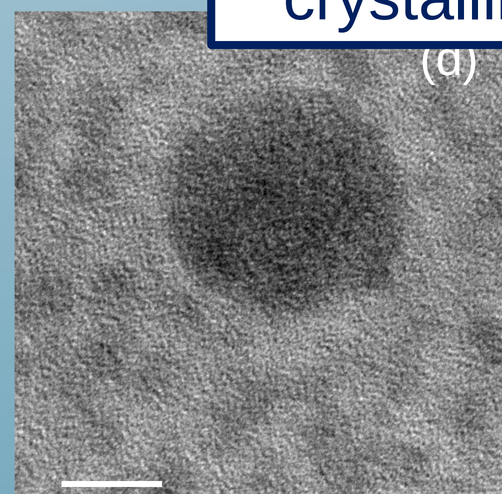


Phase separation droplets in the glass

Absence of any crystalline structure

70Si 7Gd





J. J. Velazquez *"Crystallization and optical properties of rare earth doped-oxyfluoride glass-ceramics for its use in optical fibers"*

Universidad del País Vasco Euskal Herriko Unibertsitatea CSIC

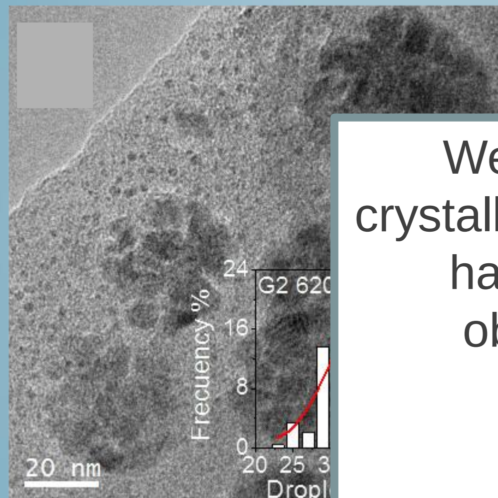
Structural characterization: HRTEM

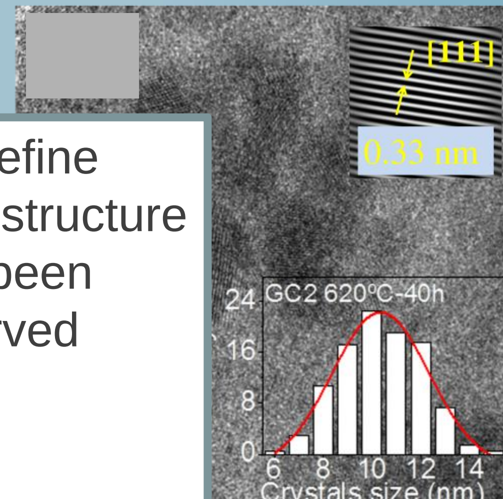
EAGLES

GlaSS
Glasses, Glass-ceramics and Sol-gel materials for a Sustainable Society

Bulk GC

55Si 10La 2Nd^{3+}
GC 620º-40h



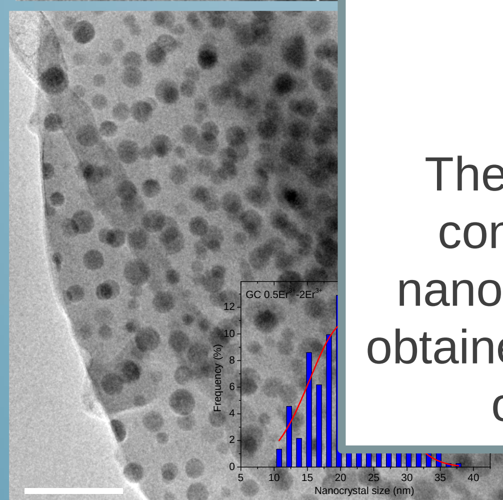


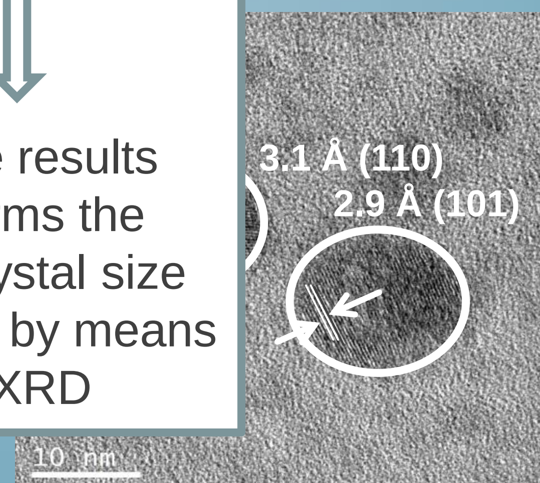
Well define crystalline structure have been observed

⇓

These results confirms the nanocrystal size obtained by means of XRD

70Si 7Gd GC
0.5Er^{3+}-2Yb^{3+}
580°C-120h





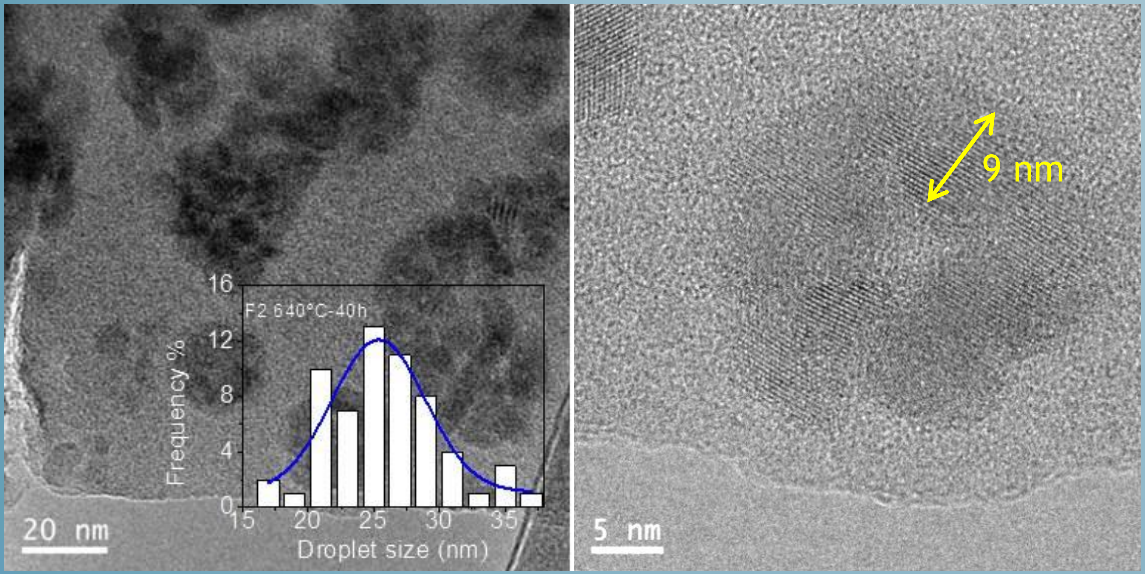
J. J. Velazquez *"Crystallization and optical properties of rare earth doped-oxyfluoride glass-ceramics for its use in optical fibers"*

Universidad del País Vasco Euskal Herriko Unibertsitatea
CSIC

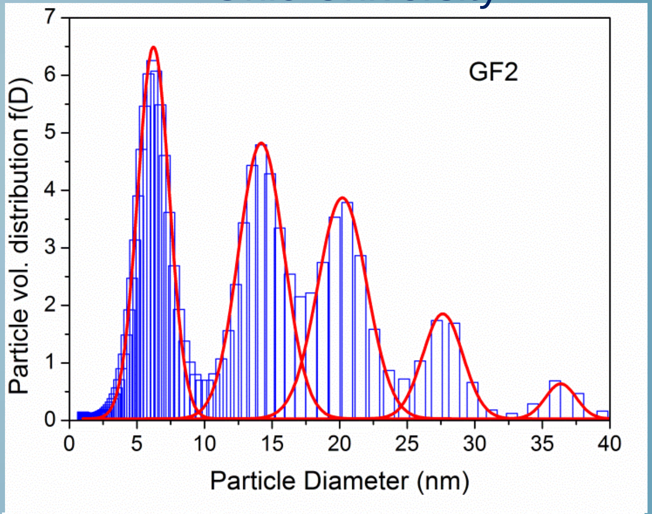
Structural characterization: HRTEM & SAXS

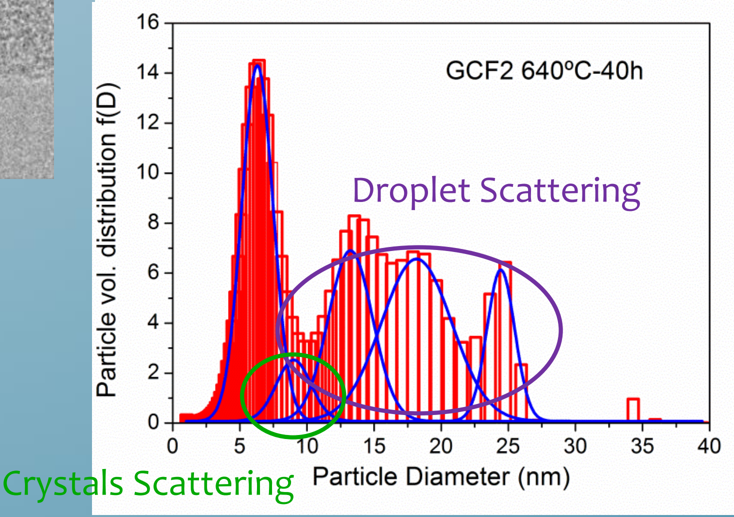
SAXS: Coll. Prof. Gang
Ohio University

Fibers GC



Smaller droplets are formed ~ 10% smaller compared to the bulk material but a narrower distribution is obtained





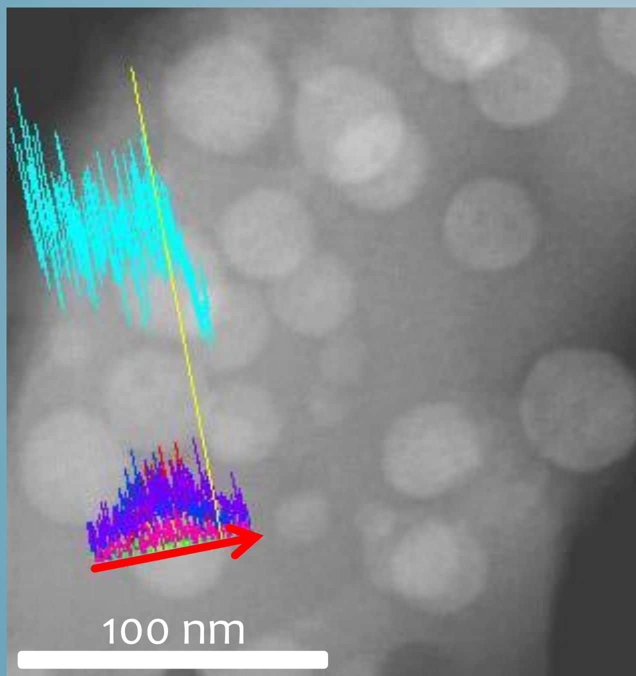
J. J. Velazquez "Crystallization and optical properties of rare earth doped-oxyfluoride glass-ceramics for its use in optical fibers"

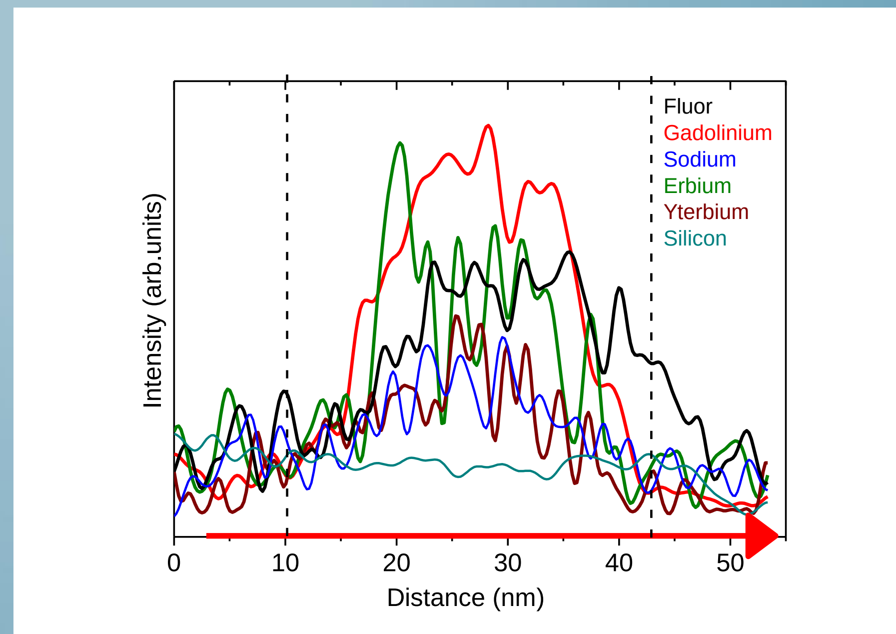
Structural characterization: STEM-EDX

EAGLES

Where are RE^{3+} ions?

70Si 7Gd GC





Gd, Na, F, Er and Yb are concentrate in nanocrystals

J. J. Velazquez "Crystallization and optical properties of rare earth doped-oxyfluoride glass-ceramics for its use in optical fibers"

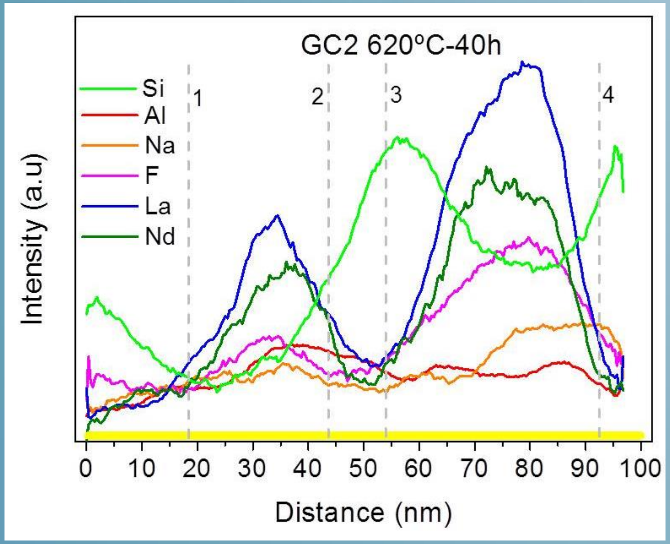
Structural characterization: STEM-EDX

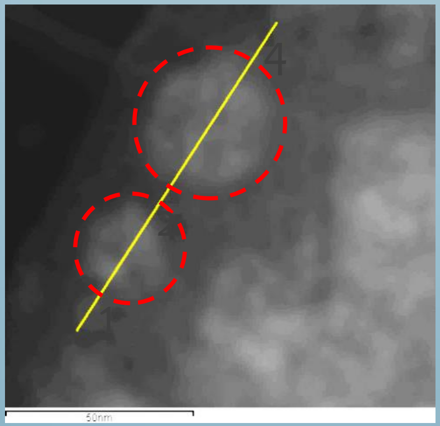
EAGLES

Where are RE^{3+} ions?

55Si 10La

Bulk

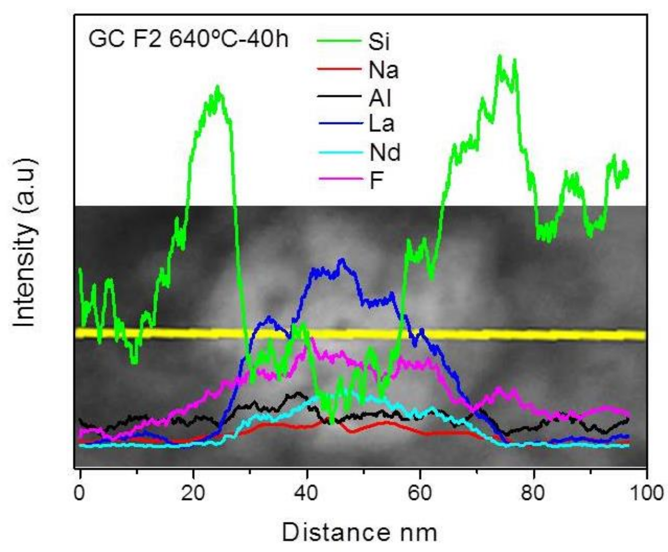




EDX in STEM mode along 100 nm (two nearby droplets were analysed)

A viscous barrier enriched in Si and Al surrounds the droplet.
The droplet is clearly enriched in La, Nd and F.

Fibres



From TEM and EDX the same structure and crystallization behavior as for bulk samples is observed.

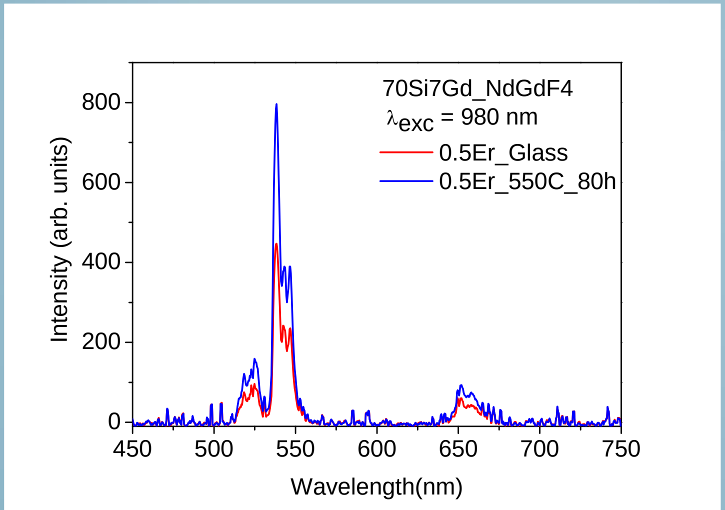
J. J. Velazquez *"Crystallization and optical properties of rare earth doped-oxyfluoride glass-ceramics for its use in optical fibers"*

Optical Characterization: PL

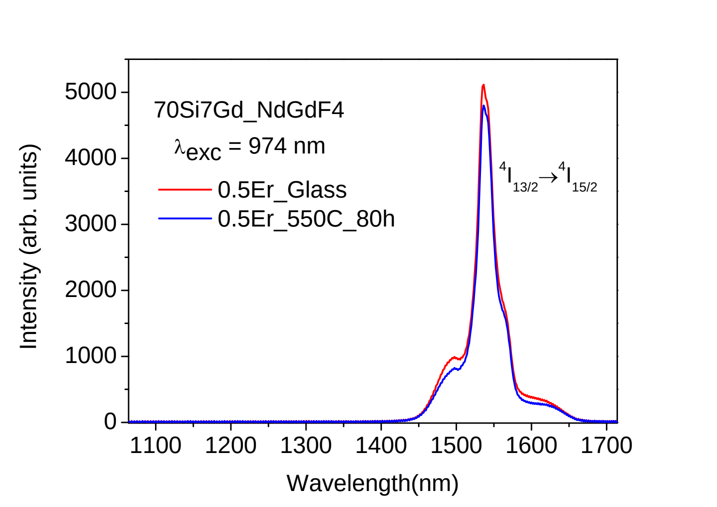
EAGLES

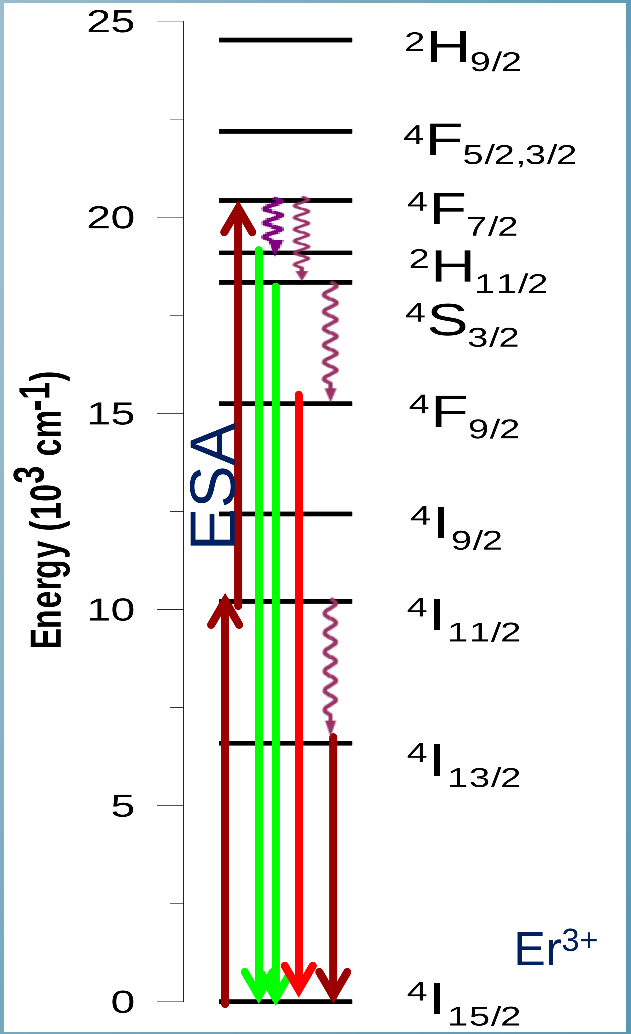
70Si 7Gd: 0.5Er^{3+}

Up-conversion (UC)



Emission spectra



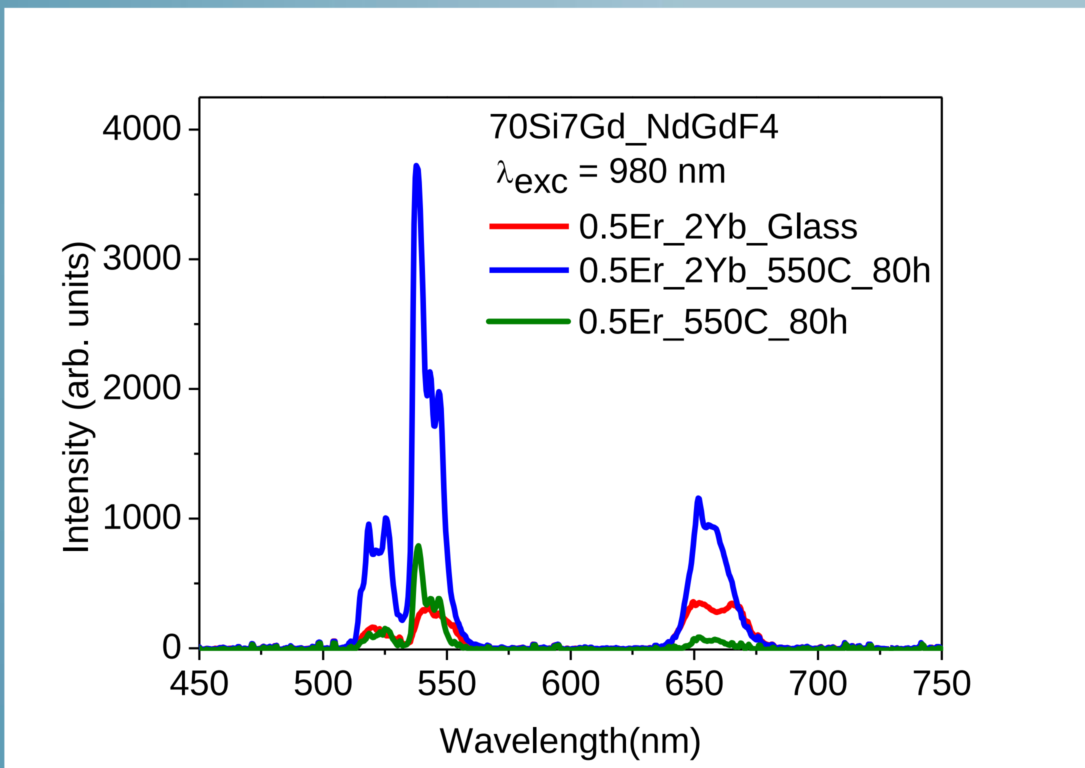


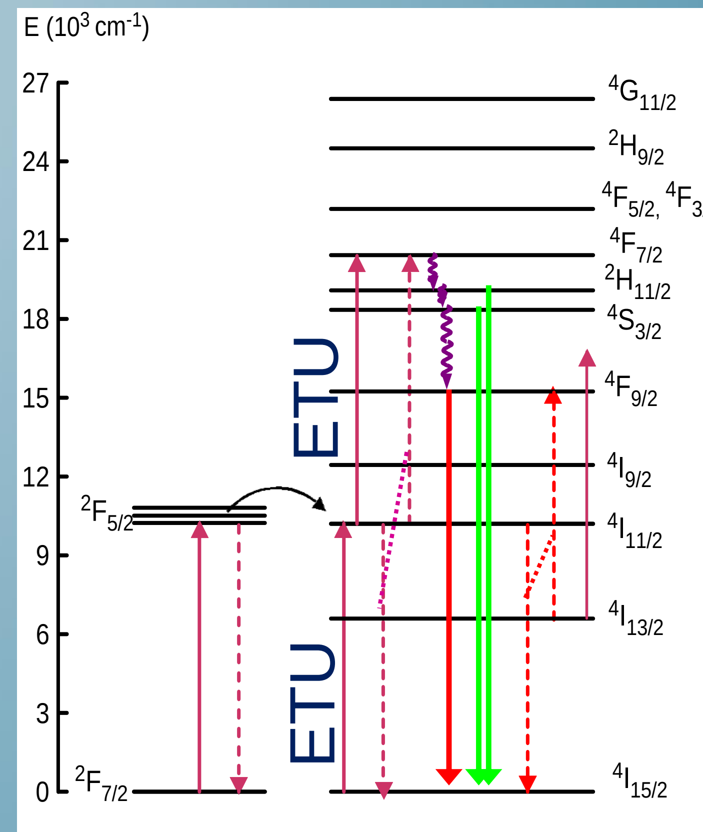
J. J. Velazquez "*Crystallization and optical properties of rare earth doped-oxyfluoride glass-ceramics for its use in optical fibers*"

Optical Characterization: PL

EAGLES

70Si 7Gd: 0.5Er^{3+}-2Yb^{3+}



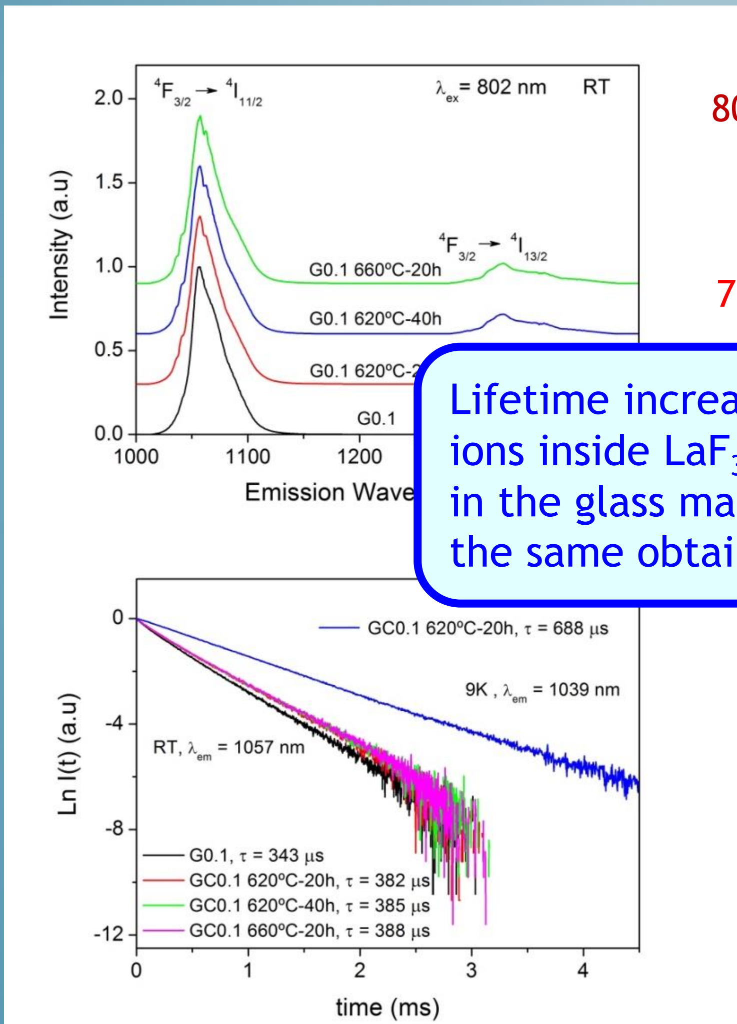


J. J. Velazquez "Crystallization and optical properties of rare earth doped-oxyfluoride glass-ceramics for its use in optical fibers"

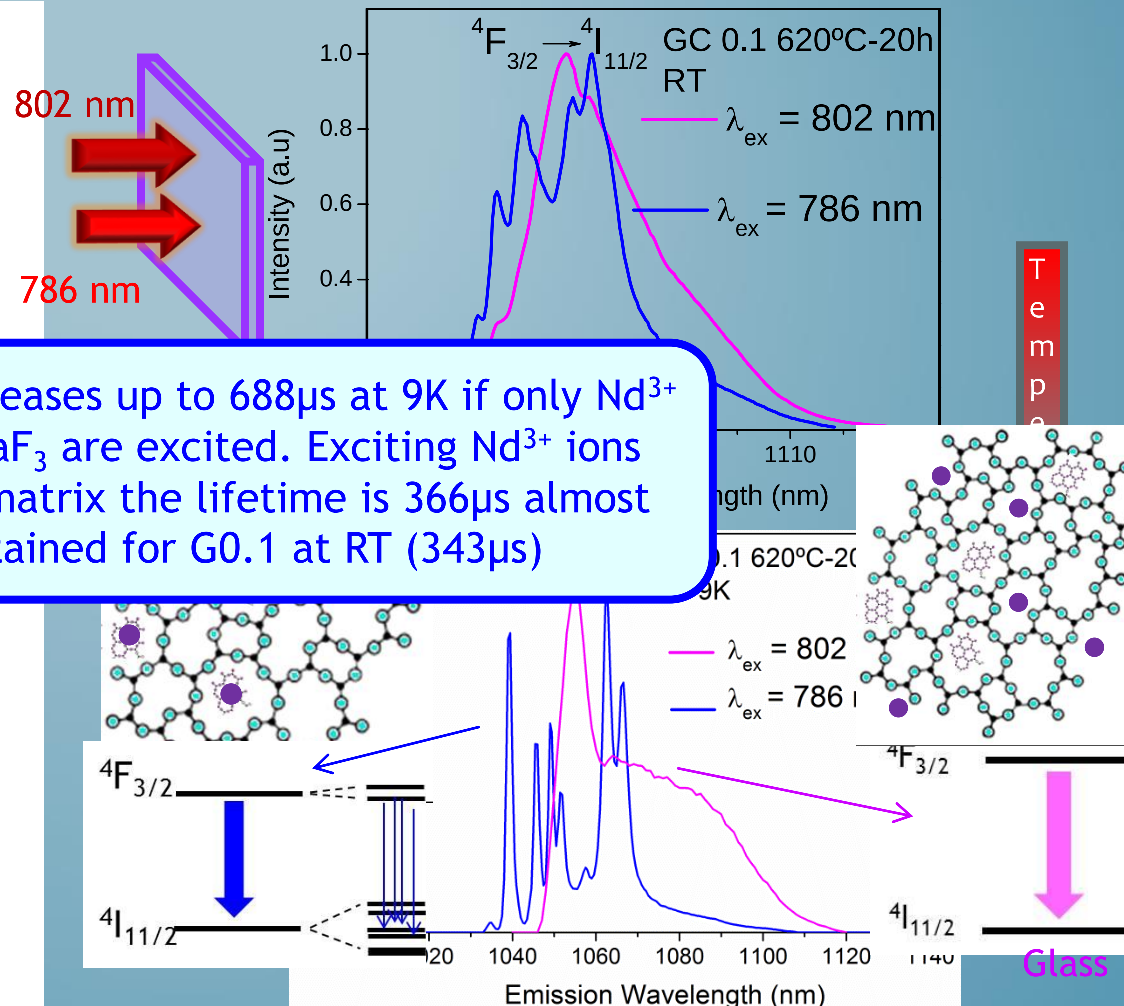
Optical Characterization
PL and lifetime

EAGLES

55Si 10La Bulk



Site Selective Excitation



Lifetime increases up to 688µs at 9K if only Nd^{3+} ions inside LaF_3 are excited. Exciting Nd^{3+} ions in the glass matrix the lifetime is 366µs almost the same obtained for G0.1 at RT (343µs)

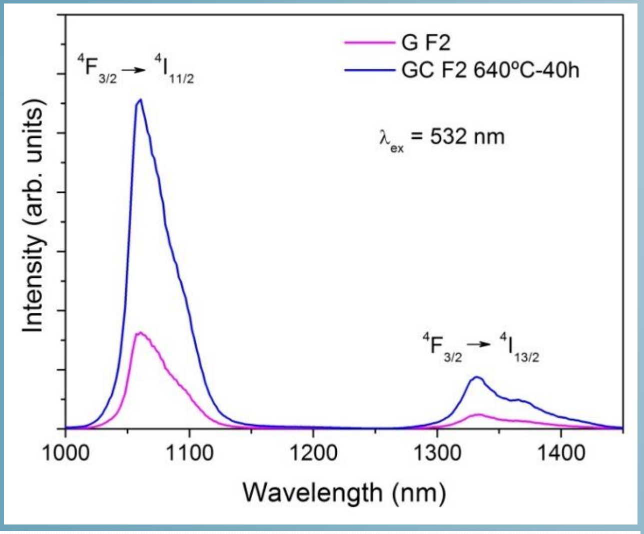
J. J. Velazquez *"Crystallization and optical properties of rare earth doped-oxyfluoride glass-ceramics for its use in optical fibers"*

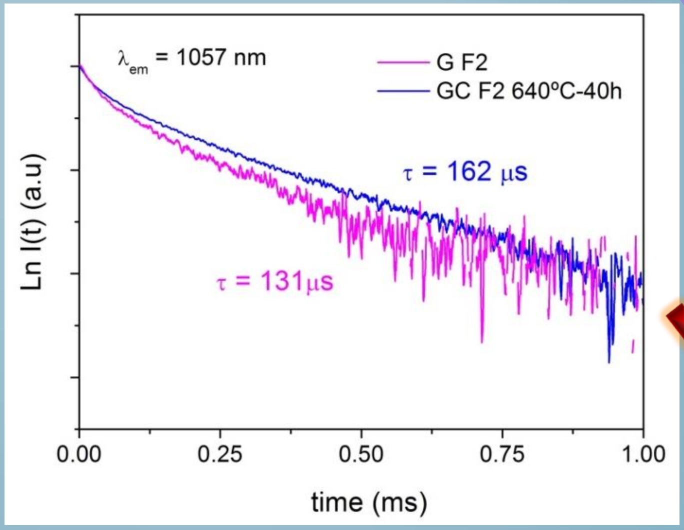
Universidad del País Vasco / Euskal Herriko Unibertsitatea — CSIC

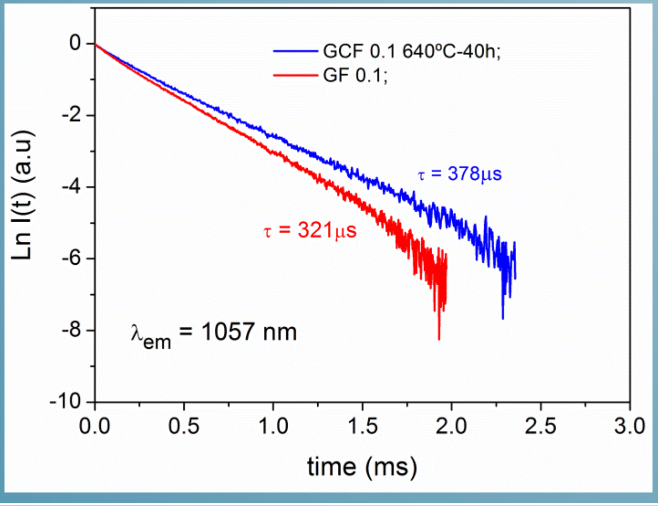
Optical Characterization
PL and lifetime

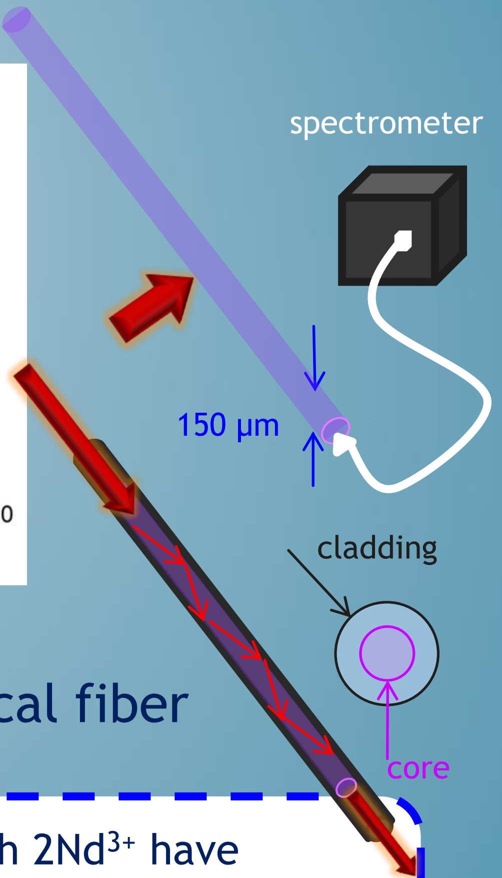
EAGLES

55Si 10La fibers









Next step: GC optical fiber

Glass and GC Fibers doped with $2Nd^{3+}$ have lifetimes of 131 µs and 162 µs, respectively, very similar to the bulk Glass (140 µs) and GC (180 µs). The same behaviour occurs for $0.1Nd^{3+}$

J. J. Velazquez *"Crystallization and optical properties of rare earth doped-oxyfluoride glass-ceramics for its use in optical fibers"*

Universidad del País Vasco Euskal Herriko Unibertsitatea CSIC

GlaSS
Glasses, Glass-ceramics and Sol-gel materials for a Sustainable Society

EAGLES

Conclusions

- ***β-NaGdF$_4$ or LaF$_3$ oxyfluoride glass-ceramics have been successfully obtain by melting quenching method.***
- ***After an adequate heat treatments, Hexagonal β-NaGdF$_4$ or LaF$_3$ nanocrystals with a mean size ranging from 8-30 nm have been obtained.***
- ***According to the HRTEM results, crystallization mechanism occurs through regions of (Na,Gd)- or La- and Si phase separation in the glass, from which the fluoride crystals grow during heat treatment.***
- ***By means of STEM-EDX we confirmed that the RE ions are effectively incorporated into the monocrystalline phases.***
- ***Preliminary optical studies confirms that RE ions are partitioned into the nanocrystalline phase. Moreover, energy transfer processes between Er^{3+}-Yb^{3+} ions or selective excitation of Nd^{3+} ions have been observed in NaGdF$_4$ and LaF$_3$ GC, respectively.***
- ***Structural and optical properties of bulk and fibers in LaF$_3$ are very similar and preliminary studies of fibers can be made on bulk materials. For that, the best content was 0.1 Nd^{3+} ions.***

EAGLES

Prof. Gang Chen and coll.

MAT2013-48246-C2-1-P
MAT2013-48246-C2-2-P
FPDI-2013-16895

EAGLES
International Conference on
Rare-Earth Doped Glass Materials and Fibre Lasers
MPNS COST Action MP1401
October 18th – 19th, 2016 | Trento, Italy

Thank you for you attention !