TAMPERE UNIVERSITY OF TECHNOLOGY

United Nations Educational, Scientific and Cultural Organization

International Year of Light 2015

Novel Glasses and Glass-Ceramics for Photonics

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Optoelectronics Research Centre
Tampere University of Technology

Optoelectronics Research Centre (ORC)

- Established in 2000
- The largest optoelectronics research centre in Finland
- One of the largest university based research lab in Europe for Molecular Beam Epitaxy (MBE) technology
- 55 people, 6 M€ funding (>60% external funding)
- >25 ongoing research projects funded by EU (FP7 & H2020), ESA, Academy of Finland, Tekes, and industry
- >23 M€ in equipment investment

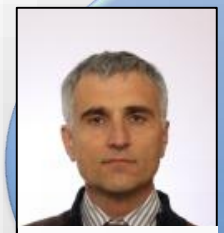
- **In January 2017, Photonics Laboratory**

- 7 research groups

PHOTONICS Laboratory

Mircea Guina

Optoelectronics



Serge Mordon

Surface Science

Mika Valden

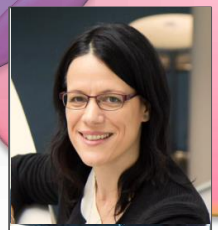
Nano-photonics

Tapio Niemi

Applied Optics

Juha Toivonen

Photonic Glasses



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Nonlinear Optics

Martti Kauranen

Gaetano Assanto

Ultrafast Optics

Goery Genty

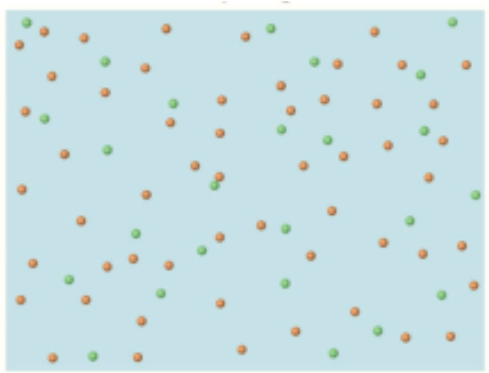
Control of the site of the Rare-Earth in glass

Different approaches to control the site of the rare-earth

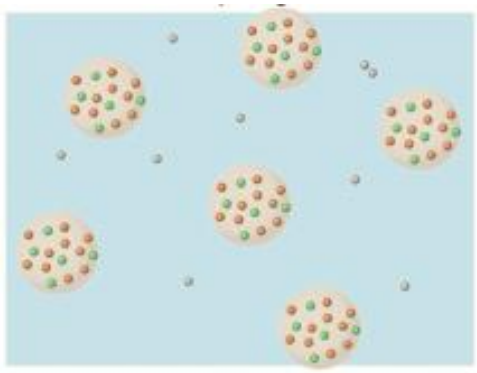
1) GC obtained by heat treating the glass leading to in-situ particles growth in glass
2) Particles-containing glass obtained by doping directly the glass with the nanoparticles.

Schematic diagram of RE distribution in various glasses*

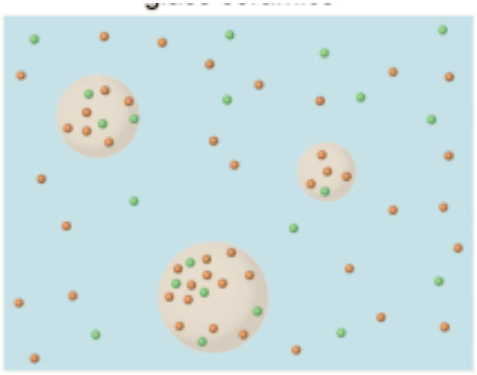
Glass



Particles-containing glass



Glass-ceramic (GC)



J. Zhao et al, Adv. Optical Mater. 2016, doi: 10.1002/adom.201600296

Nanoparticles-containing glasses

Involving the nanoparticles approach to manufacture doped optical fibers has been pointed out to improve doping efficiency.

Based on *, it should be possible to control, using nanoparticles, rare-earth optical response independently of the core glass matrix composition which is of paramount importance for determining the optical properties.

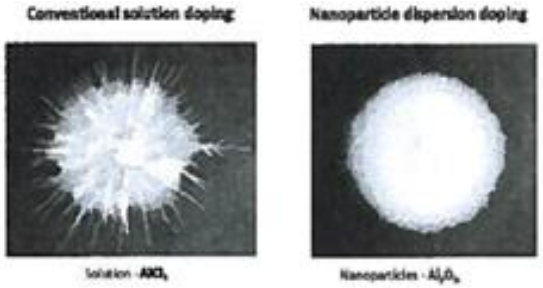
Some commercial erbium doped fibers with high SiO_2 content (>90mol%) are already processed using this doping technology by Draka: the doping of the commercial glass occurred when the solution of the nanoparticles in stable suspension impregnates a layer of silica glass produced by MCVD.

A. Le Sauze et al, Technical digest of OAA 03, Otara, Japan, WC 5, (2003) 254-256

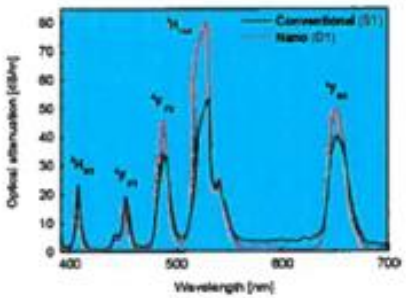
Nanoparticles-containing glasses

Based on *, the nanoparticles doping in SiO_2 glass fiber leads to

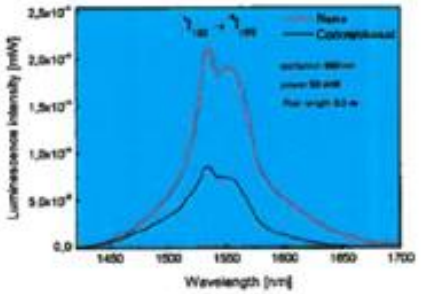
- Better homogeneity



- Lower Background losses
- Enhancement of absorption and luminescence properties of the Er^{3+} ions



Absorption of optical fibers



Luminescence

Due to the transformation of Alumina into Mullite with the assumption that the Er^{3+} ions are distributed in the Mullite structure

* *J. Mrazek, I. Kasik, poster presented at ICG 2013 on Dispersion of Al_2O_3 NP in silica matrix*

Nanoparticles-containing glasses

Er^{3+}-Al_2O_3 nanoparticles containing phosphate/silicate glasses were prepared. However, **no enhancement of the Er^{3+} spectroscopic properties** was observed*.

From the spectroscopic properties of the nanoparticles-containing glasses, we found no evidence that the Er^{3+}-Al_2O_3 nanoparticles remain in the glass after melting. We suspect diffusion of the nanoparticles into the glass matrix

⇒ NOT possible to control the site of the Er^{3+} using nanoparticles doping process in glasses

Can we actually control the site of the rare-earth using microparticles???

* *L. Petit et al, Bulletin of Materials Science, 38 (5) (2015) 1-4*

Glass-ceramics

Based on *, glass ceramics (GCs) also control the chemical environment of the Er^{3+}.

Additionally, GCs combine the mechanical and optical properties of the glass with some advantages of Er^{3+}-doped single crystals (higher absorption/emission cross-section and longer lifetimes of luminescence)

* *G. Dantelle et al,* Optical Materials, 28 (2006) 638–642.

Outline

Our latest development of novel active glasses and glass-ceramics

- Microparticles - containing glasses
  -effect of the melting parameters and of the glass composition on persistent luminescence properties

- Er doped glass-ceramics
  -effect of the glass crystallization on the luminescence properties of erbium

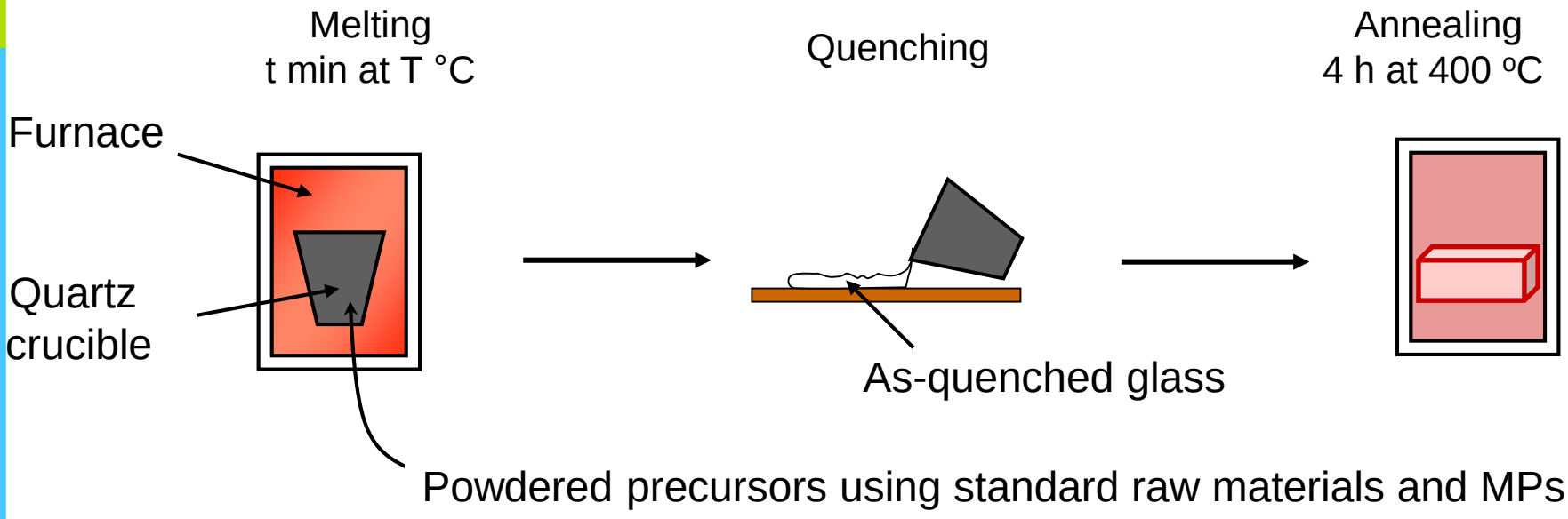
- Conclusion

Glass preparation

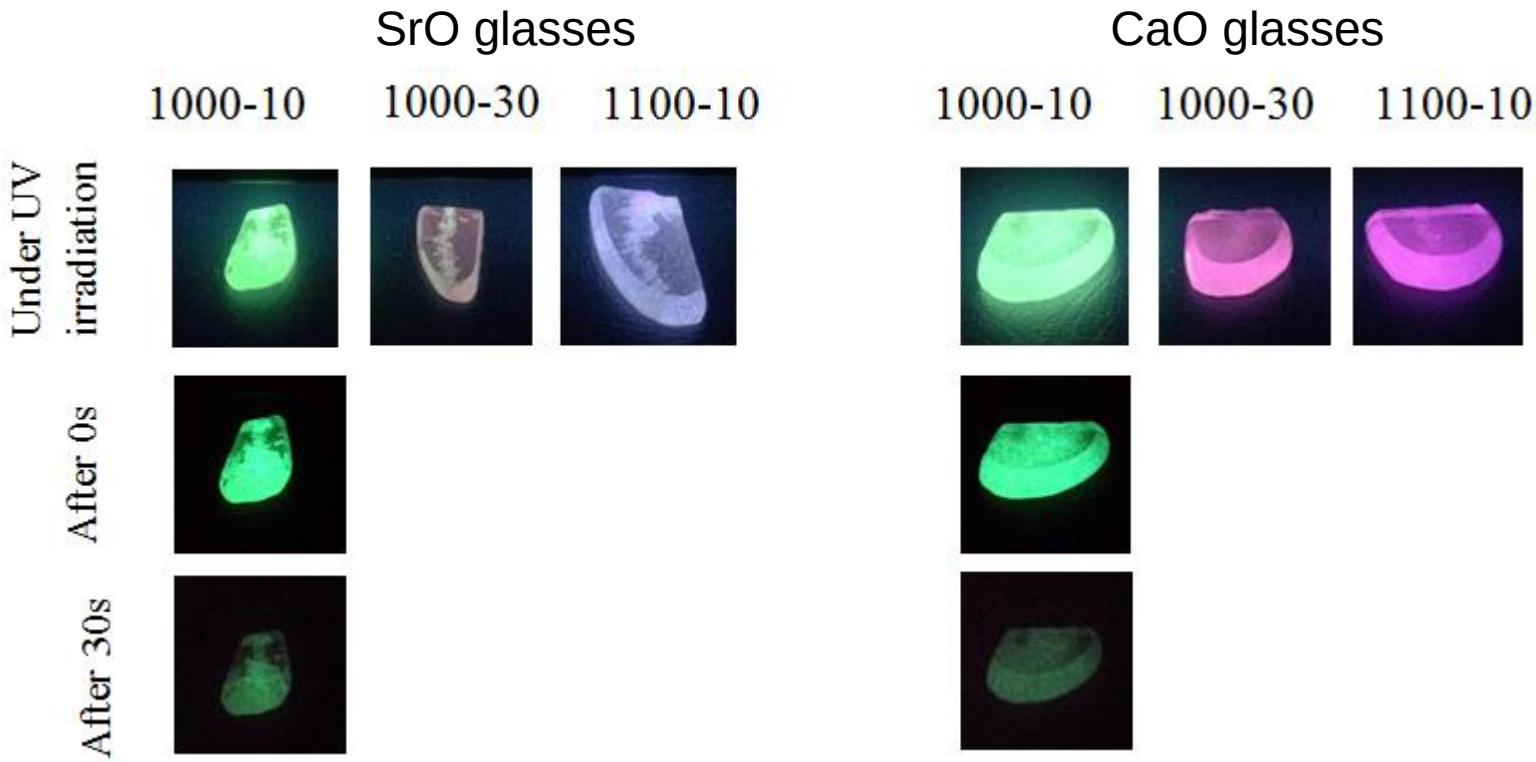
Composition of the glasses: $50P_2O_5$-$10Na_2O$-40CaO/SrO (CaO and SrO glasses)

Composition of the microparticles (MPs): $SrAl_2O_4:Eu^{2+},Dy^{3+}$ microparticles from Jinan G.L. New Materials, China, BG-01 (3 weight%)

Glasses prepared using standard melting method in air



Pictures of the glasses



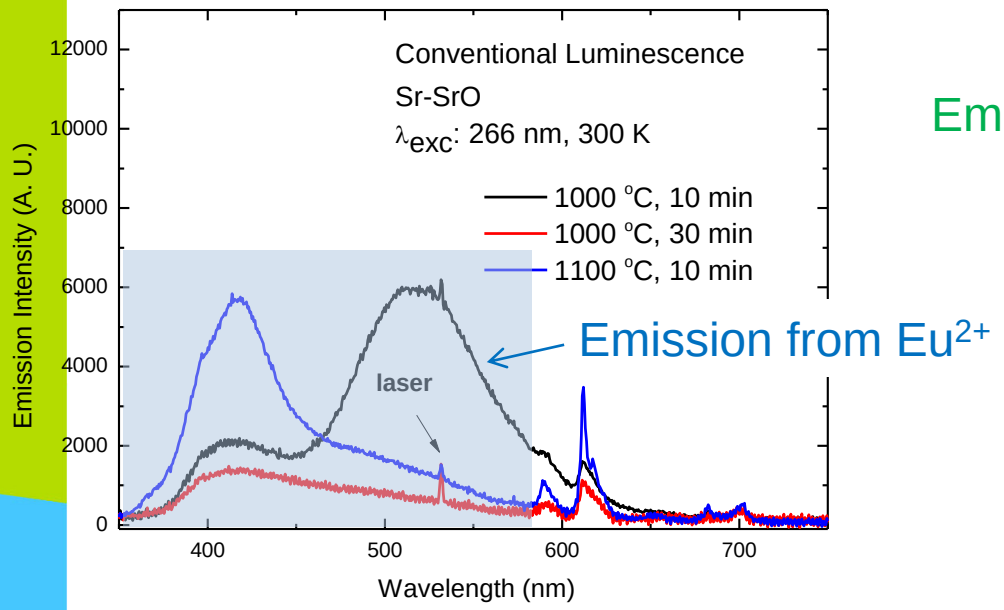
Only the glasses melted at 1000°C for 10 min exhibit a green persistent emission after stopping the UV irradiation

⇒ Possible to prepare a phosphate-based glass which still contains $SrAl_2O_4:Eu^{2+},Dy^{3+}$ microparticles

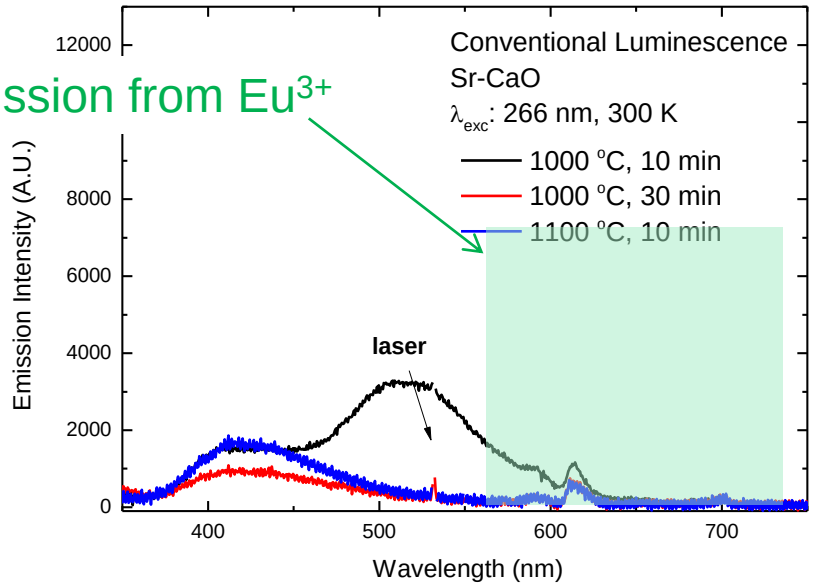
Note: not uniform distribution of microparticles in the glass matrices

Conventional luminescence spectra

SrO glasses



CaO glasses



Some Eu^{2+} ions are oxidized to Eu^{3+} ions during the preparation of the glasses. Larger amount of Eu^{3+} ions suspected in the SrO glasses

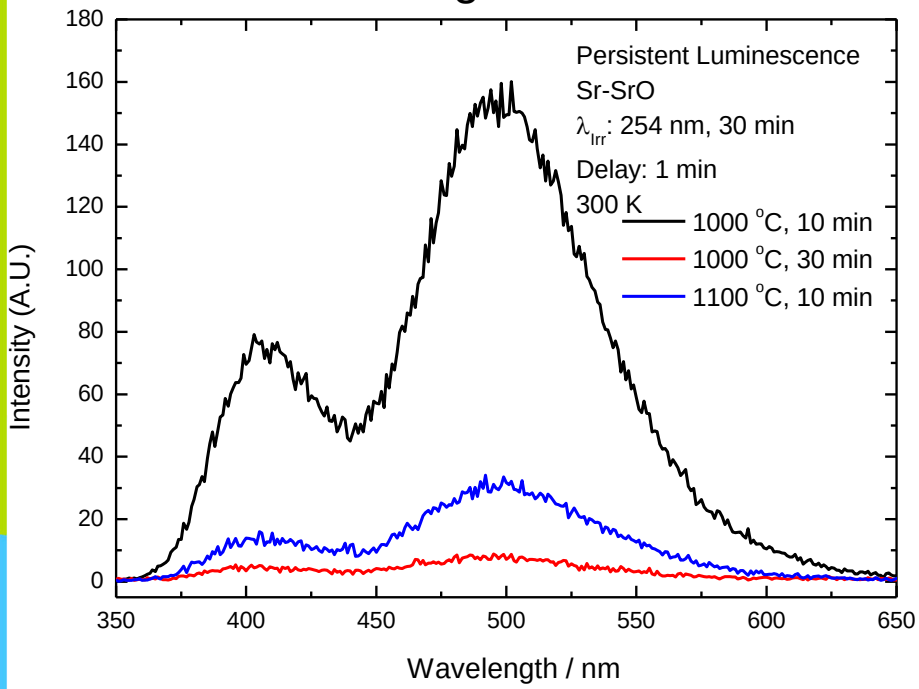
About the 2 bands in the 350 – 575nm range (Eu^{2+} located in two different cation sites)

- Their ratio depends on the melting condition: decrease of the band at 525nm when the temperature and duration of the melting increase

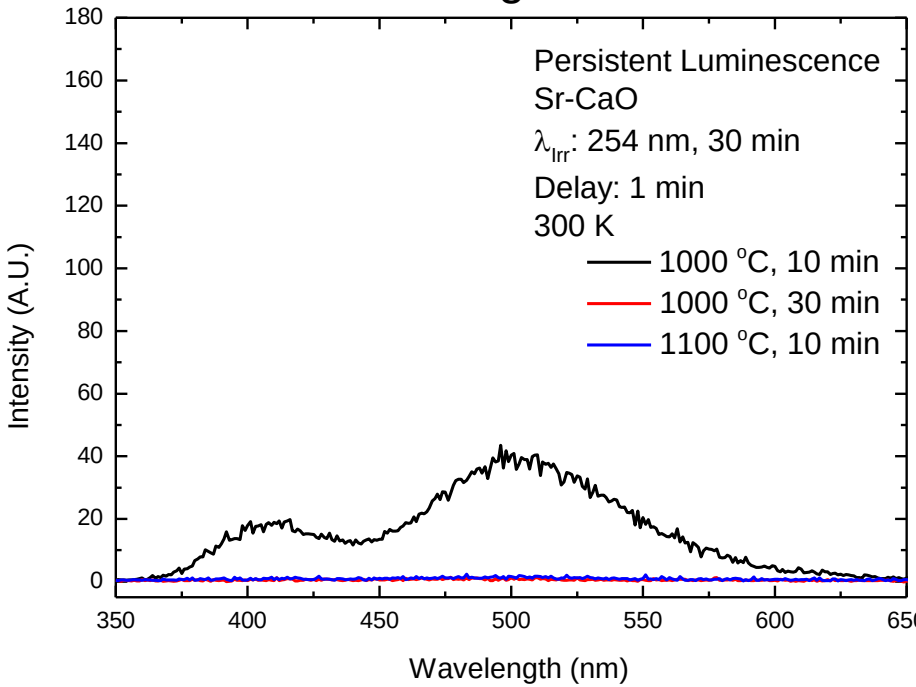
$\Rightarrow$ Eu^{2+} sites change depending on the glass processing. Similar Eu^{2+} sites expected in both glass systems.

Persistent luminescence spectra

SrO glasses



CaO glasses



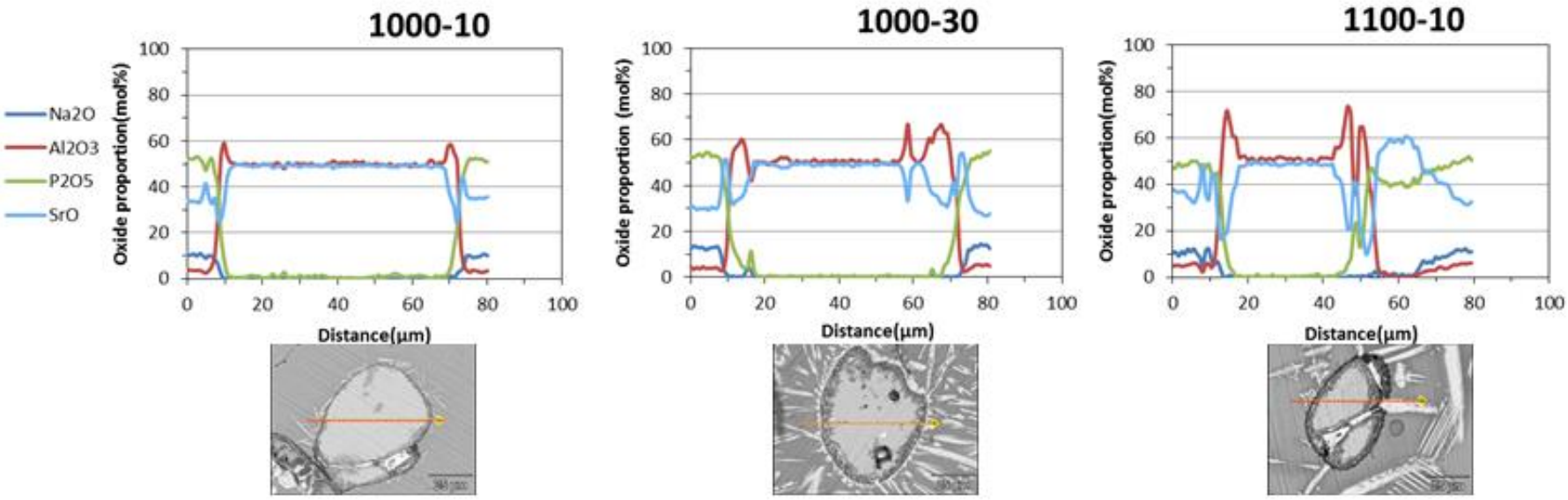
Two broad bands which can be attributed to the $4f^6 5d^1 \rightarrow 4f^7$ transition of Eu^{2+} located in two sites in the monoclinic $SrAl_2O_4$ structure

The bands intensity significantly higher in the SrO glasses than in the CaO glasses

In the SrO glasses, an increase in the duration and the temperature of the melting reduces the intensity whereas almost no persistent luminescence could be detected in the CaO glasses when melted at 1000°C for 30 min or at 1100°C for 10 min

Radial SEM/EDS MP composition analysis

SrO glasses

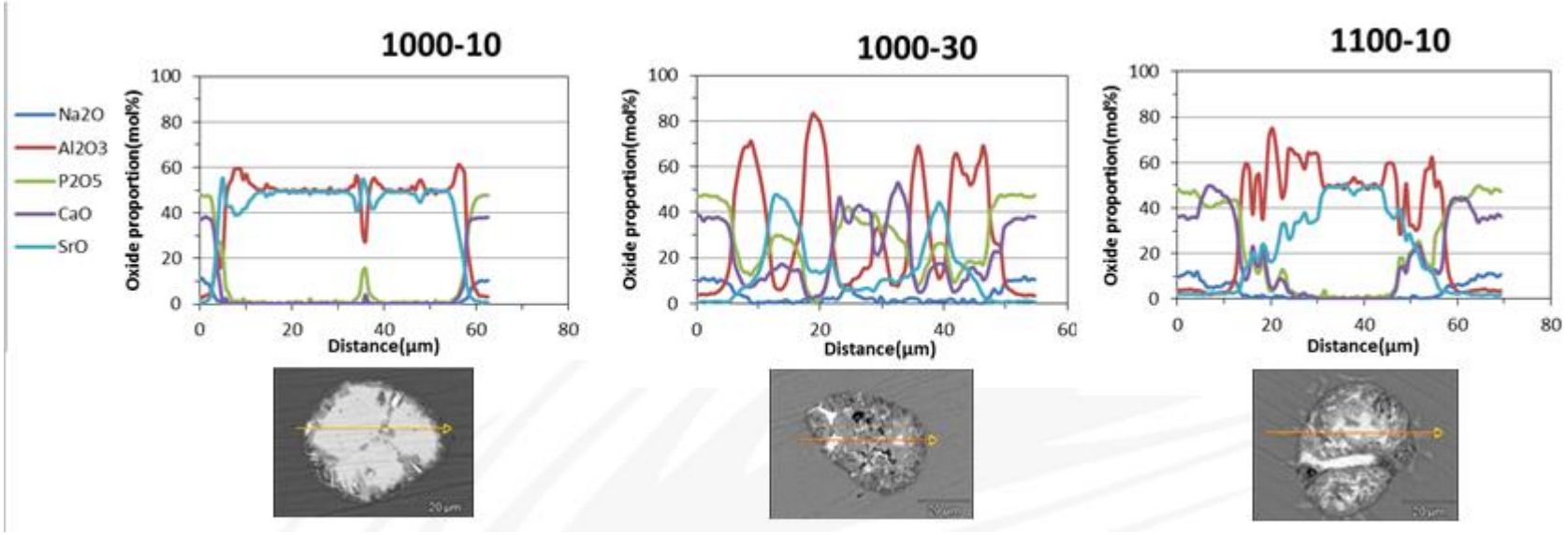


The composition of the glass matrix in accordance with the theoretical one with a trace of Al_2O_3.

The MPs exhibit an outlayer rich in Al and are also surrounded by crystals which appear to be Sr-rich.
The MPs in the SrO glass maintain their composition integrity in the center
$\Rightarrow$ MPs are stable in the SrO glass

Radial SEM/EDS MP composition analysis

CaO glasses



As seen in the SrO glasses: the composition of the glass matrix in accordance with the theoretical one with a trace of Al_2O_3 from the MP.

The MPs are also surrounded by Al-rich layer and by crystals which appear to be Ca-rich confirming that the crystals are formed using elements from the glass matrix and not from the MPs.

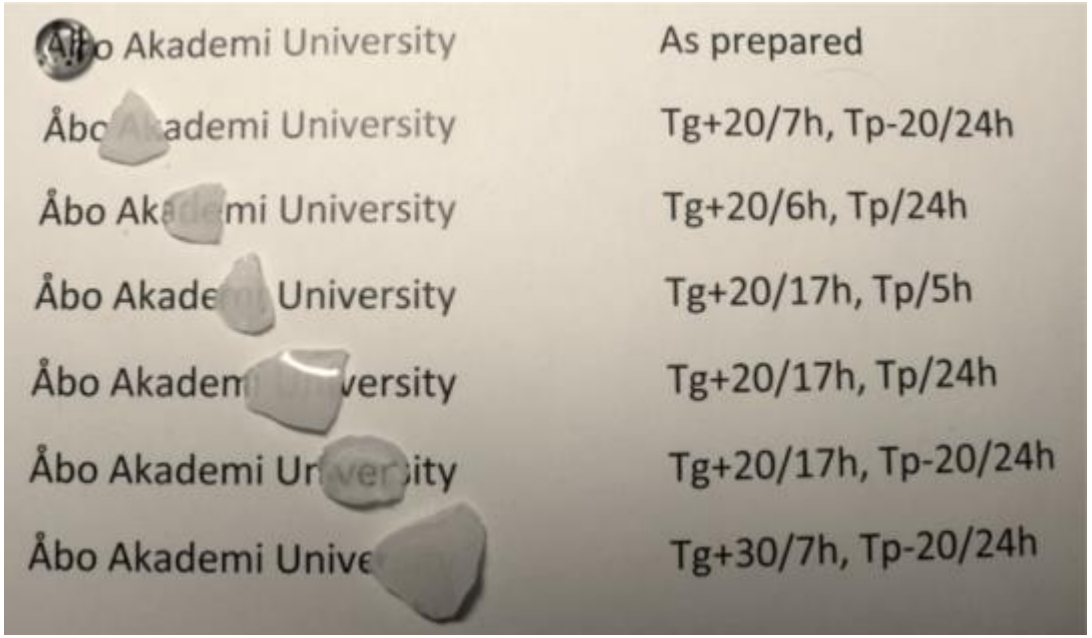
Compared to the SrO glasses: a lower number of crystals can be observed around the MP & the MP degrade when melted for 30min at 1000°C or for 10min at 1100°C.

Glass-ceramics processing*

- **Glass system of investigation:** silicate glass

$50SiO_2 – 1.5Al_2O_3 – 0.5P_2O_5 – 26.7B_2O_3 – 20.7Na_2O – 0.12Er_2O_3 – 0.48La_2O_3$ (mol%)

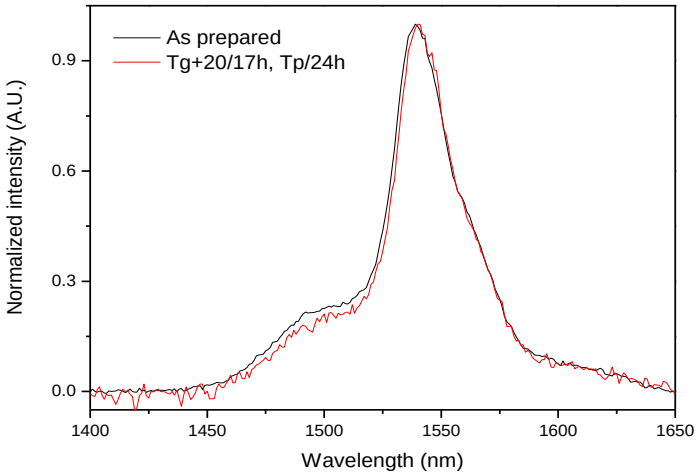
Depending on the heat treatment conditions, the transparent glass became translucent/opaque.



L. Petit et al, Materials Chemistry and Physics, 147 (2014) 1099-1109

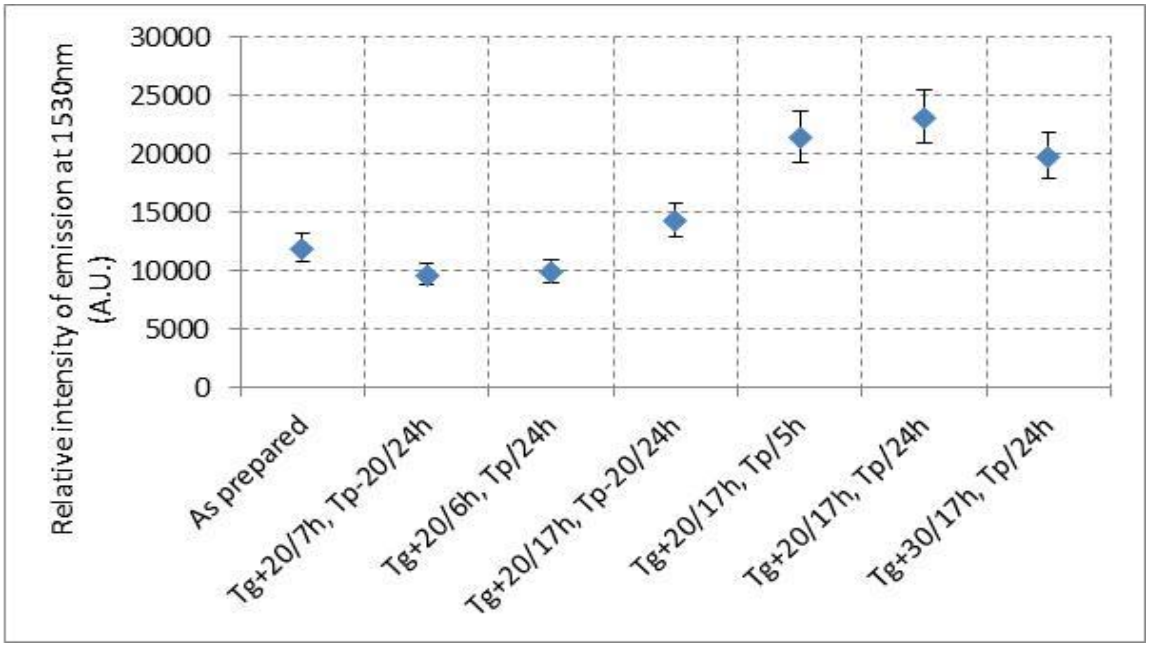
Emission properties

Normalized emission band at 1530nm
(λ_{exc} = 365 nm)



Site of the Er^{3+} ions not strongly modified by the heat treatment.

Relative emission intensity at 1530 nm of the GCs
(λ_{exc} = 365 nm)



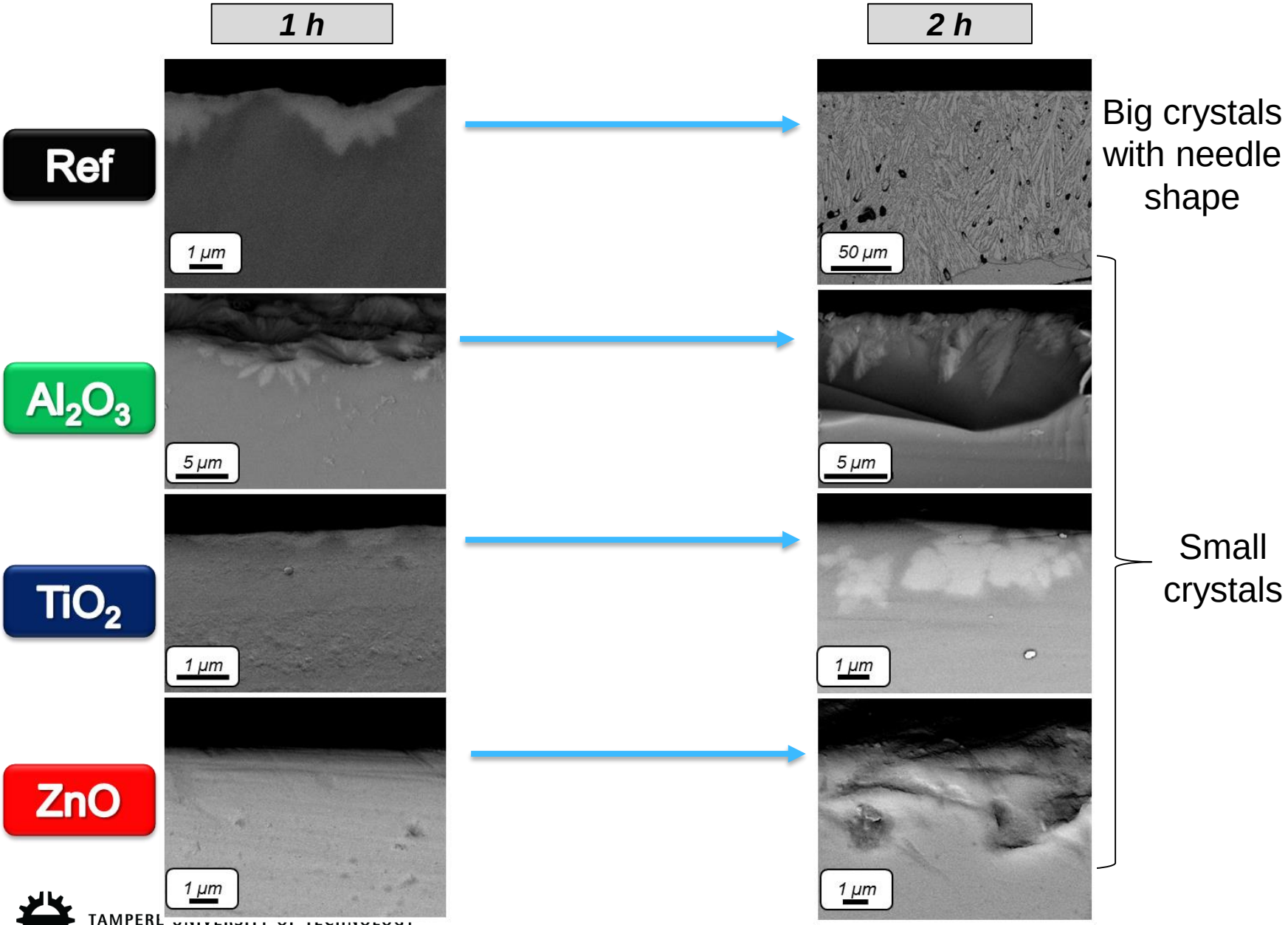
A slight increase in the emission at 1530nm observed when the temperature and duration increased.

Phosphate based GCs

Glass system: **$(50P_2O_5 - 40SrO - 10NaO)_{1-x} - 0.25Er_2O_3 – xAl_2O_3/TiO_2/ZnO$ (mol%)**

Heat treatment after annealing
Tg+20°C for 17 h, Tp-40°C for 2 h

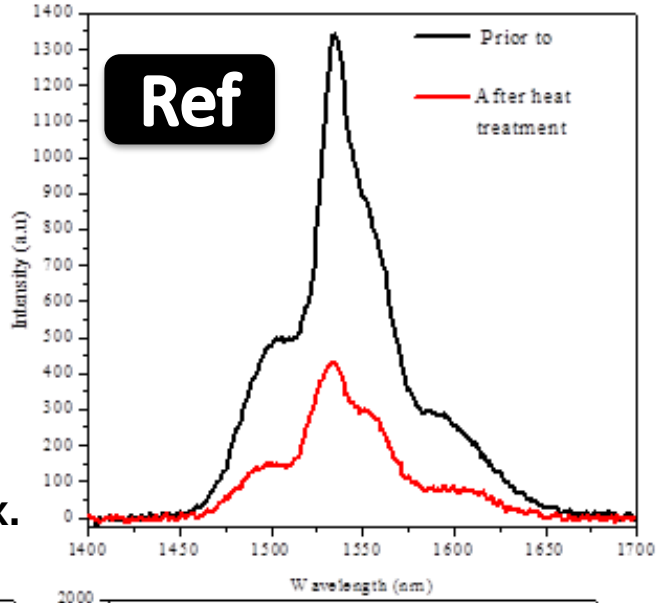
SURFACE CRYSTALLIZATION

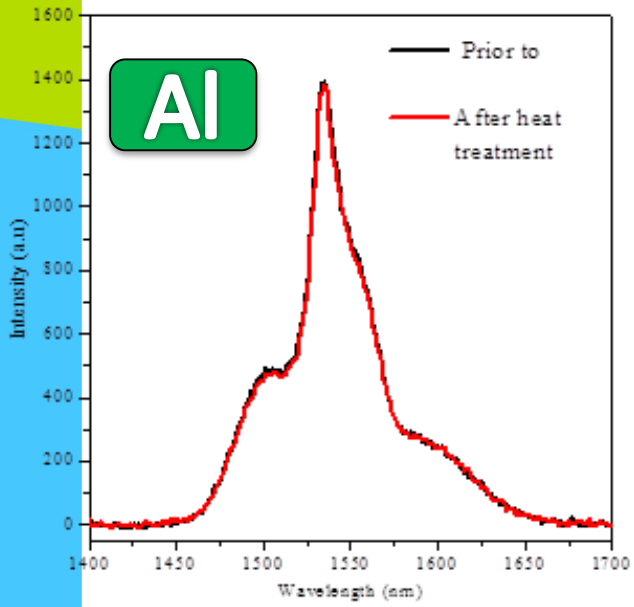


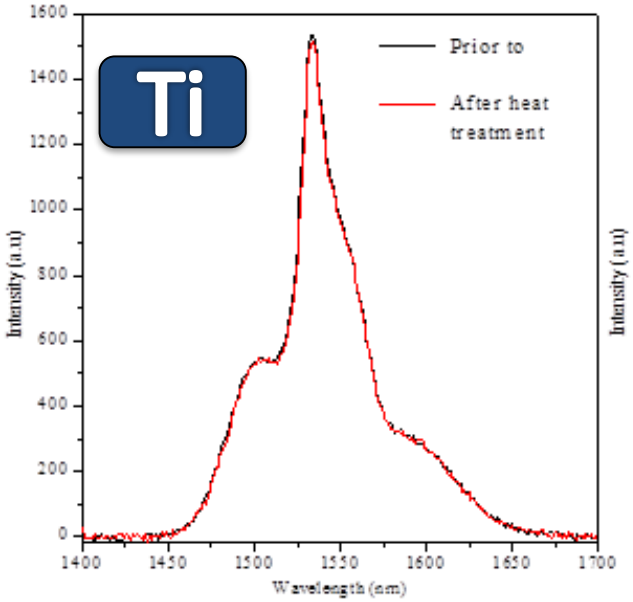
PRELIMINARY RESULTS

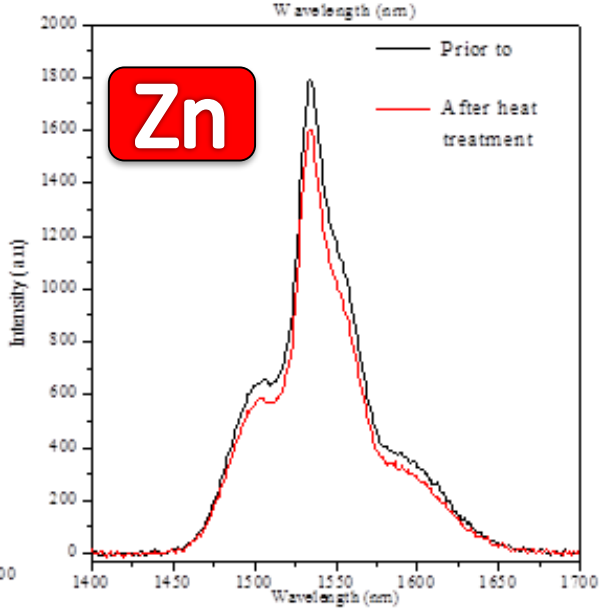
**Excitation at 976 nm & measured at the surface*

- **No sharp peaks observed.**
- **Crystals seems to be Er^{3+} ions free.**
- **Er^{3+} ions are suspected to remain in the glass matrix.**









Conclusion

- Actually possible to process particles containing glasses which possess the spectroscopic properties of the particles when using microparticles:
- The stability of the microparticles depends on the glass composition
  - The presence of large Sr-based crystals around the MPs in the $50P_2O_5$-$40SrO$-$10Na_2O$ system seems to limit the diffusion of Al and Eu^{2+} ions from the MPs into the glass leading to more intense and longer persistent luminescence than the glasses within the $50P_2O_5$-$40CaO$-$10Na_2O$ system due to the less degradation of the microparticles.

Based on *, other important parameters to consider are the doping temperature and also the dwell time to balance the survival and dispersion of the particles in the glass melt.

*J. Zhao et al, Adv. Optical Mater. 2016, doi: 10.1002/adom.201600296

Conclusion

- Novel silicate GCs with slight enhancement of the emission properties of the glasses due to changes in the glass structure.
- The addition of Al, Zn and Ti in phosphate glass increases the glass stability against crystallization, the Zn glass being the least crystallized.
- Er ions are suspected to remain in the glass.

Acknowledgement

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- Åbo Akademi University (Prof. L. Hupa)

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- **France:** University of Bordeaux (Dr. Cardinal and Dr. Glorieux)
- **Italy:** Politecnico di Torino (Prof. Milanese),
- **USA:** MIT (Prof. Hu) and Clemson University (Prof. Ballato)

Opportunities in TUT

Post Doc Call 2016

Tampere University of Technology (TUT) is seeking to hire promising post doc researchers who are in the beginning of their careers. The aim is to support highly qualified postdoctoral researchers who are outstanding in their field and to strengthen the scientific profile of TUT.

The call, opening 15 Dec 2015, is open to postdoctoral researchers who
- hold an applicable doctoral degree
(the dissertation must be submitted and proof must be available by 1 March 2016)
- have completed their doctoral degree no longer than 4 years* prior to the deadline
(degree certificate issued 15.1.2012–15.1.2016)
- have not lived in Finland for longer than 12 months during the last 36 months before the deadline

*For applicants with children, 1 year per child will be added to the permitted duration.

The research work will be conducted in one of the existing research groups at TUT. The candidates are requested to contact the research group they wish to join. To find out more about TUT's research groups please visit the departments' web pages:
http://www.tut.fi/en/about-tut/departments/index.htm

The closing date for the applications is 15 Jan 2016. The position is filled from the beginning of March 2016 or as soon as possible. The duration of the contract will be two years.

For further information concerning research work, please contact the research group relevant to your field of interest (http://www.tut.fi/en/about-tut/departments/index.htm). For information on general issues, please contact the Coordinator Laura Himanen (laura.himanen(at)tut.fi, +358 40 198 1834)