Action MP1401

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Photoluminescence of Antimony-Germanate Glass Nanocomposites

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CNR DSFTM Scienze fisiche e tecnologie della materia

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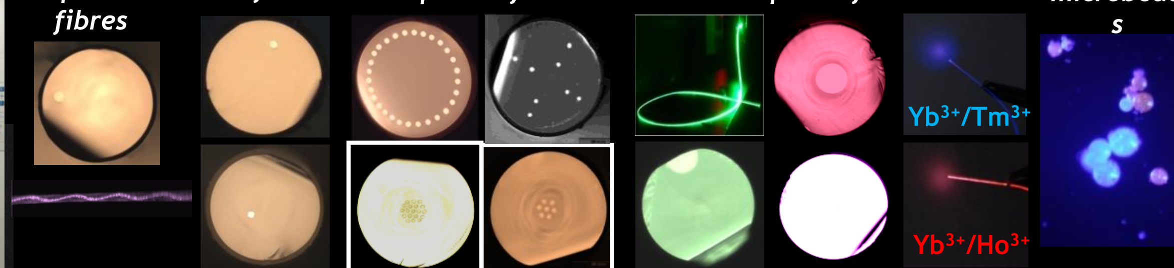
Photonics Bialystok Research Group

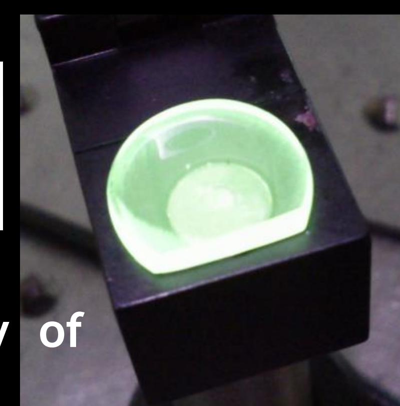
RE - doped optical fibres, photonics materials

Dominik Dorosz, PhD, DSc, Assoc. Prof.

- **Marcin Kochanowicz**, PhD – optical fiber technology
- **Jacek Żmojda**, PhD – active optical glasses
- **Piotr Miluski**, PhD – active glasses and polymers in sensors
- PhD students

Helical core optical fibres | *1,8-21 µm ASE fibres* | *Multicore supermode optical fibers* | *Upconversion optical fibre* | *Polymer microbead s*





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Bialystok University of Technology

Outline

Antimony-gemanate glass, glass-ceramics and glass nanocomposites

The ways of excitation energy transfer in glassy **nanocomposites**

Experiment – focus on optical and basic material properties of glass nanocomposite:

- effect of **Ag doping**
- effect of **thermal treatment**
- effect of **glass modification**

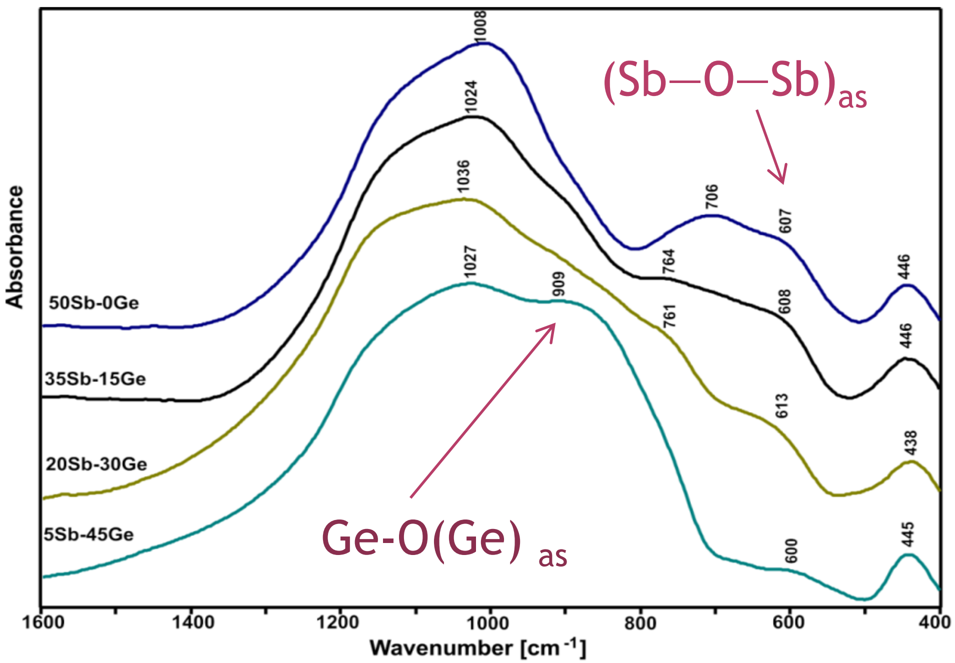
Conclusions and perspectives

SGS glass: $(50\text{-}x)Sb_2O_3$ - $xGeO_2$ - $50SiO_2$

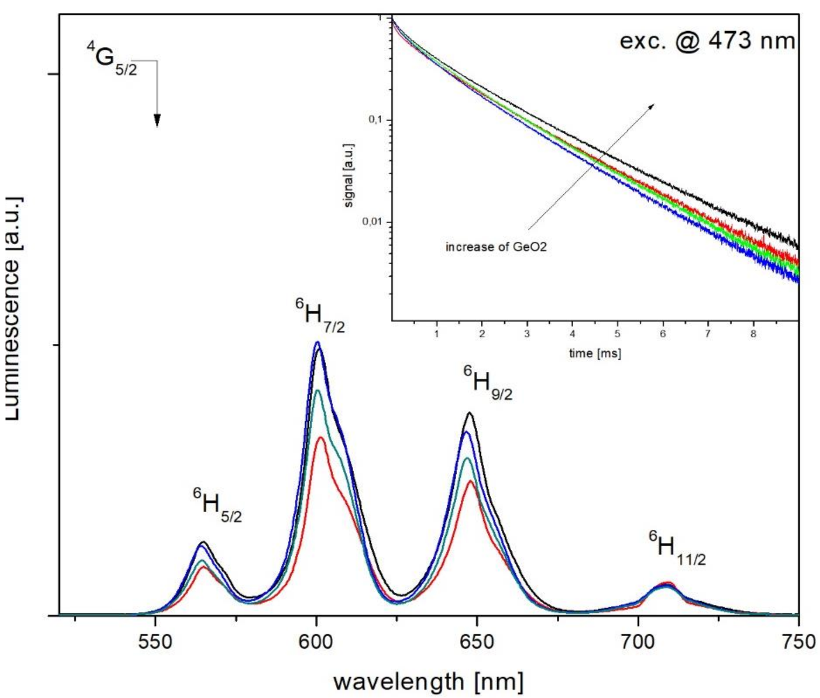
PARAMETER	VALUE
Refractive index n (@632.8 nm)	1.62 – 1.73
Mass density ρ [g/cm3]	3.35 – 3.66
Transmission window [µm]	0.35 – 3.5
Transformation temperature [°C]	432 - 552
Thermal stability factor ΔT[°C]	**168 - 235**
Maximum phonon energy [cm-1]	1007

Advantages:
- high thermal stability
- high solubility of RE ions
- efficient energy transfer

Disadvantages:
- posibility of phase separation



J. Zmojda, et al. Journal of Molecular Structure 1126, (2016) 207-212

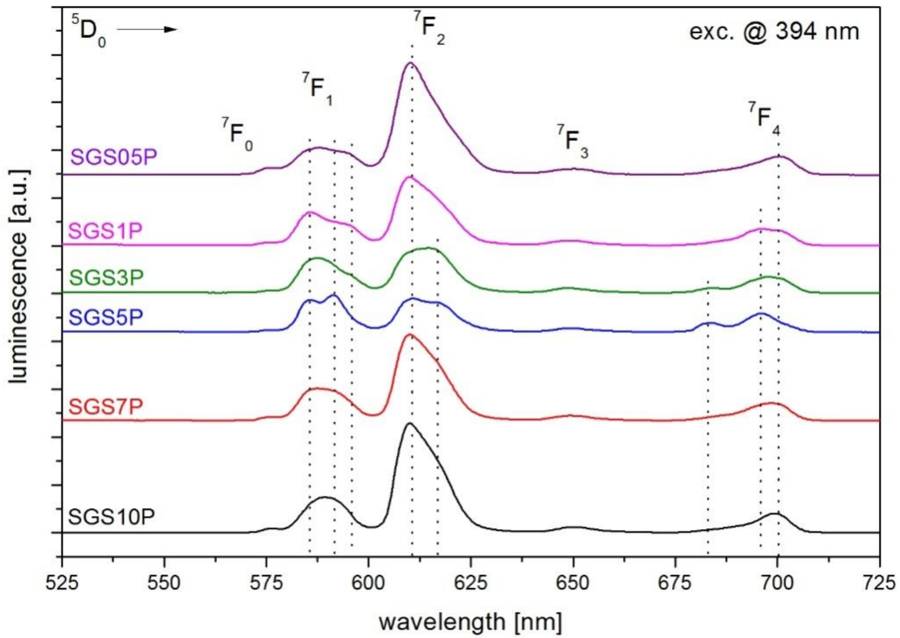


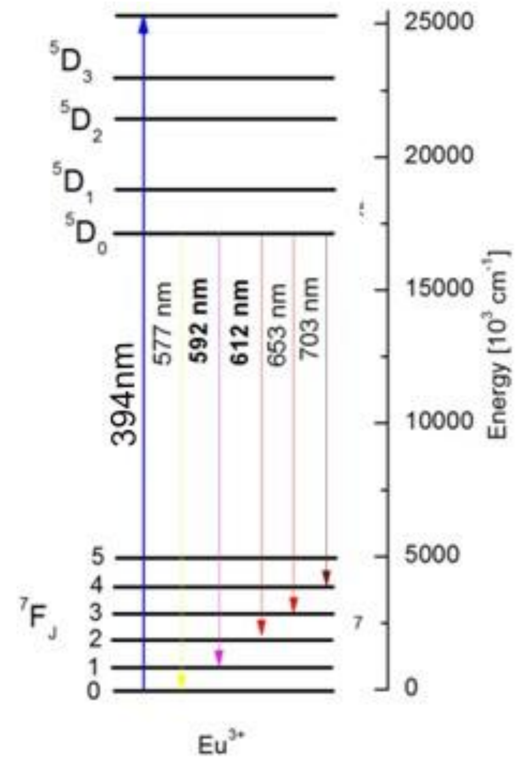
ANTIMONY-GEMANATE GLASS-CERAMICS

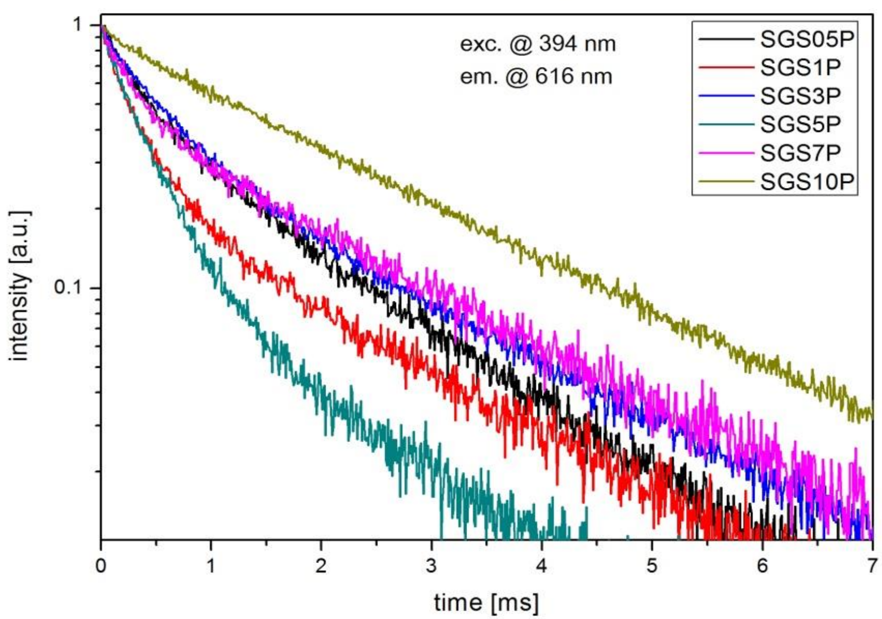
$50[Sb_2O_3 - GeO_2] - (50-x)SiO_2 - xP_2O_5 - 0.5Eu_2O_3$

- where x = 0.5, 1, 3, 5, 7, 10

SGSxP: Sb_2O_3 - GeO_2 - (50-x)SiO_2 - xP_2O_5- Eu_2O_3

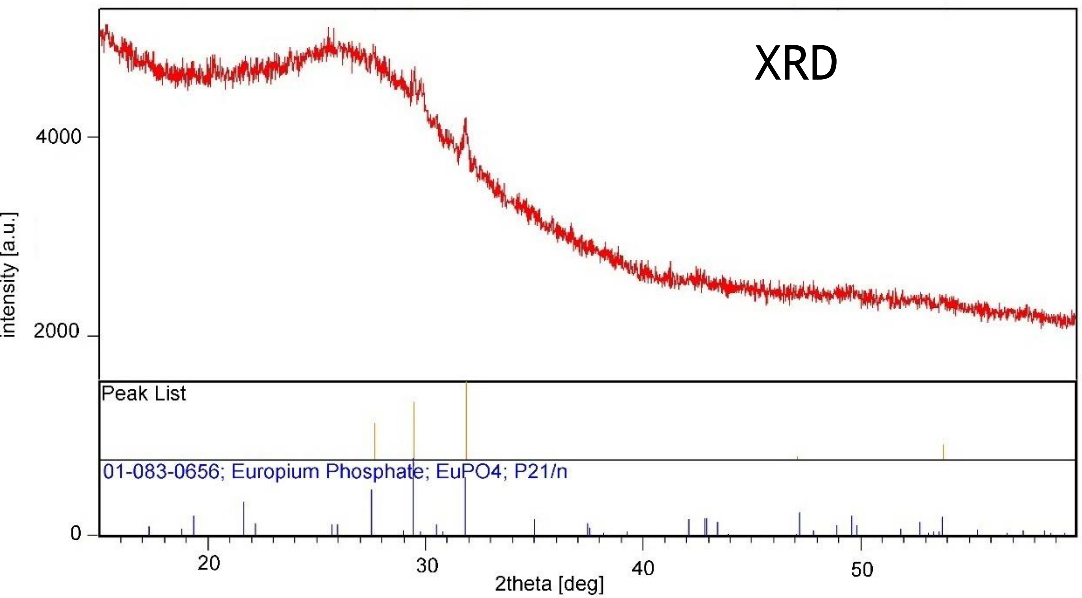


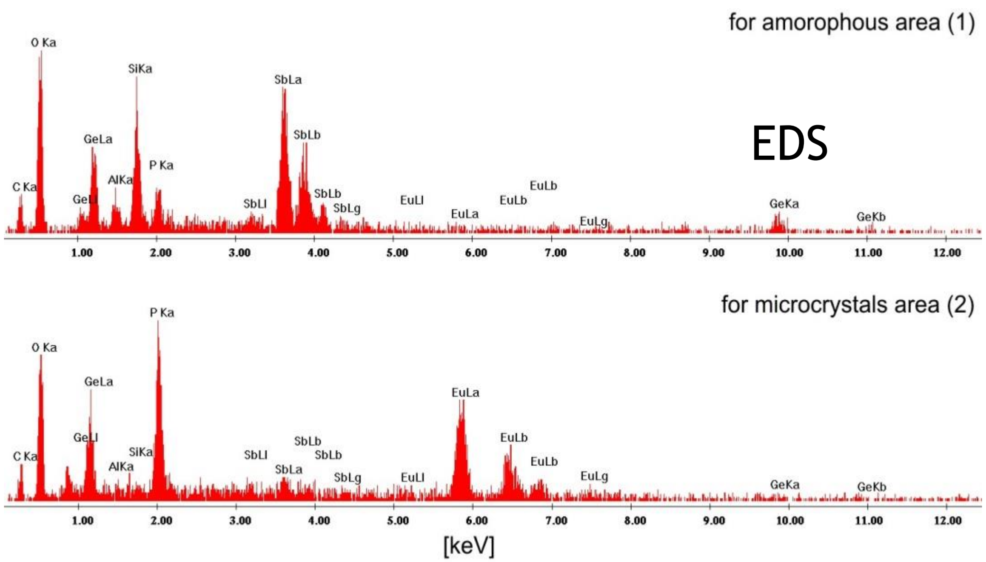




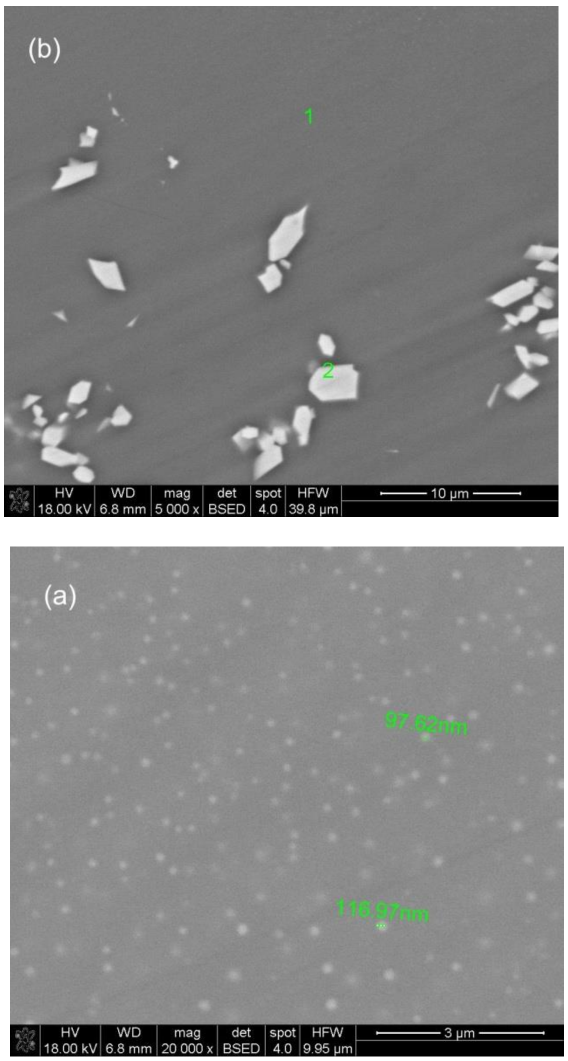
Glass	P_2O_5 [mol. %]	$R={}^7F_2/{}^7F_1$	LT [ms]
SGS05P	0.5	4.24	1.29
SGS1P	1	2.02	1.29
SGS3P	3	1.27	1.86
SGS5P	5	0.92	0.83
SGS7P	7	2.66	1.72
SGS10P	10	3.03	1.99

Structural properties of SGSxP





SEM

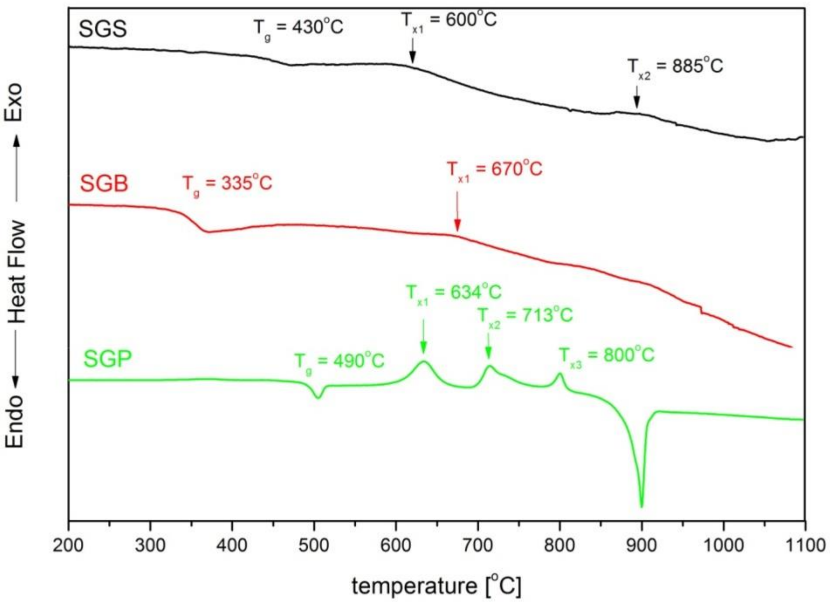


J.Żmojda, et.al, *Materials* **2017**, *10*, 1059

Effect of modification of glass by high-phonon modifiers - SiO_2, B_2O_3 and P_2O_5

SGX glasses:

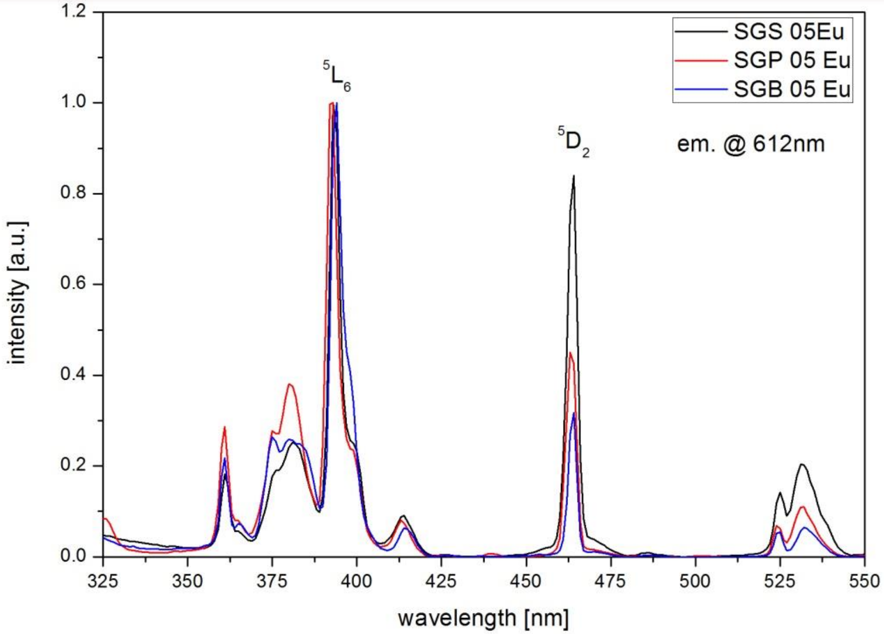
- **SGS** $50[Sb_2O_3 - GeO_2] - 50SiO_2$
- **SGB** $50[Sb_2O_3 - GeO_2] - 50B_2O_3$
- **SGP** $50[Sb_2O_3 - GeO_2] - 50P_2O_5$

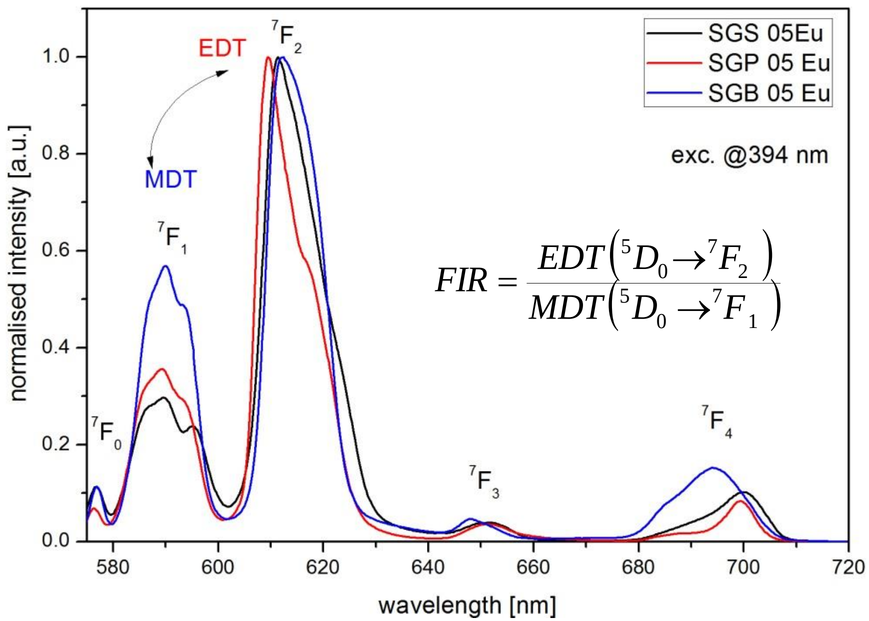


DSC curves of SGX glasses

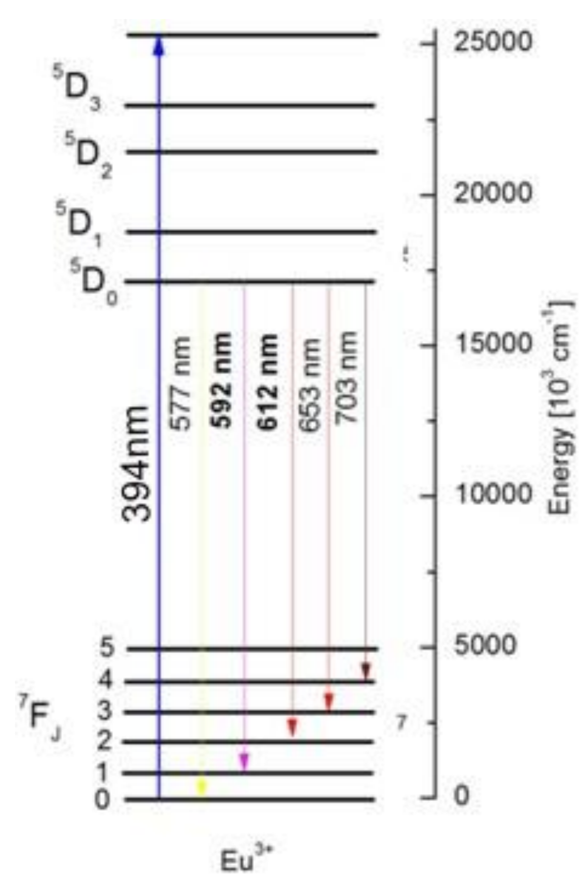
Parameter	SGS	SGB	SGP
T_g [°C]	430	335	490
T_{x1} [°C]	600	670	634
ΔT [°C]	230	335	144

SGX glasses doped with Eu_2O_3





$$FIR = \frac{EDT\left({}^5D_0 \rightarrow {}^7F_2\right)}{MDT\left({}^5D_0 \rightarrow {}^7F_1\right)}$$



SGX	Asymmetry ratio
SGS	4.8
SGB	2.2
SGP	3.6

Surface Plasmon Resonace

There are four main ways to obtain enhancement or quenching of luminescence signal in glassy nanocomposites:

- Energy ransfer from surface of metal NPs to RE ions (plasmonic effect) – strongly depends on material (n), size and shape of nanoparticles and theirs content
- Direct energy transfer between metal NPs and RE ions – depends on size of NPs
- Re-absorption proces by NPs observed in energy transfer between RE ions and metal NPs
- Migration of excitation energy between RE ions

Green – enhancement

Red - quenching

Experimental

Glasses SGS_AgRE: Sb_2O_3 - GeO_2 –SiO_2 - Al_2O_3 - Na_2O

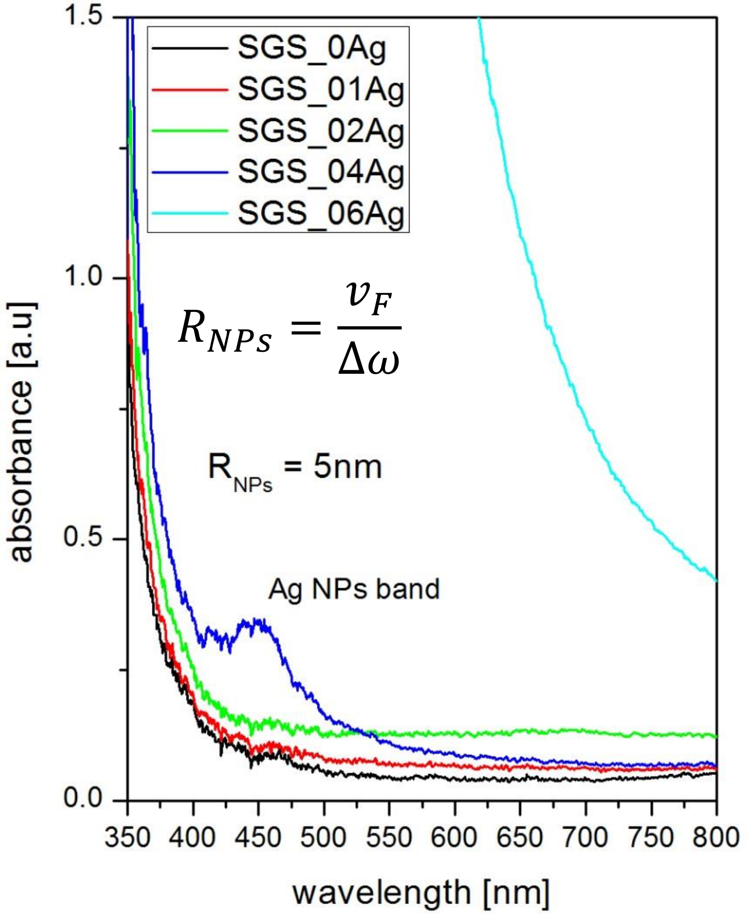
co-doped with x*Ag^+/Eu^{3+}*

Step 1:
all samples doped with $0.2Eu_2O_3$ and $xAgNO_3$

Melting at 1450C by 30min

Annealing at 400C by 2h and slowly cooling by 12h

Optical characterization



Absorbance spectra of SGSxAg glasses modified by different content of $AgNO_3$

Step 1:

Redox potential

$$Sb^{3+} + 2Ag^{+} \rightarrow Sb^{5+} + 2Ag^{0} E^{o} = 0.95 \text{ V}$$

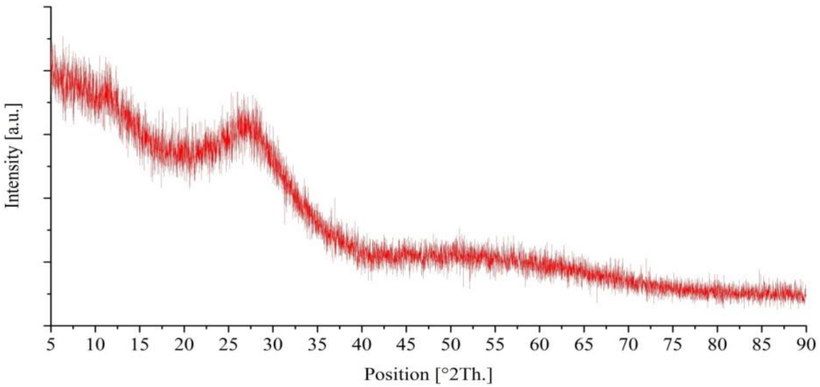
where

$$Sb^{5+} + 2e^{-} \rightarrow Sb^{3+} \quad E^{o} = 0.649 \text{ V}$$

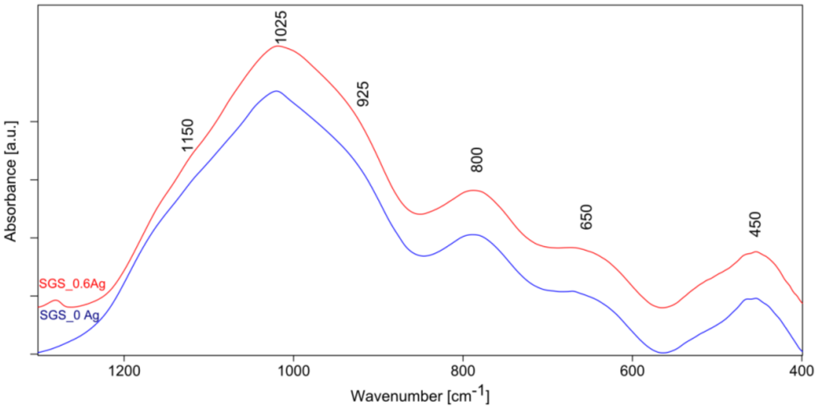
$$Ag^{+} + 1e^{-} \rightarrow Ag^{0} \quad E^{o} = 0.7996 \text{ V}.$$

T. Som, B. Karmakar, Plasmonics 5 (2010) 149;

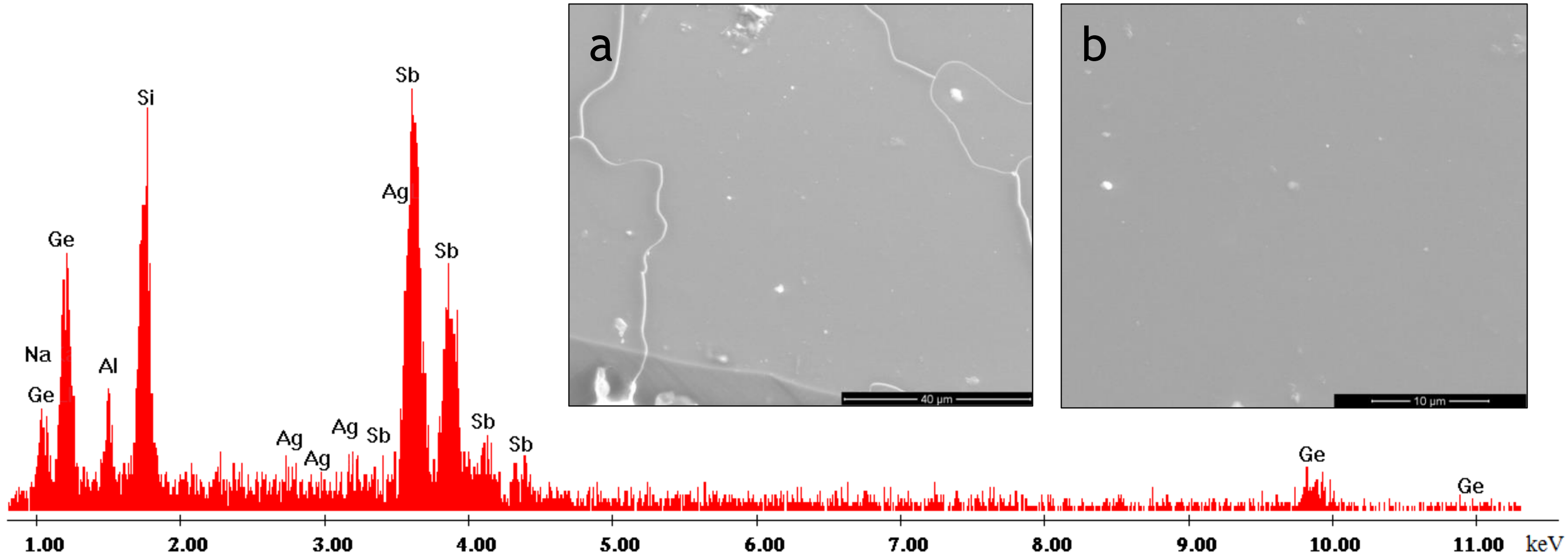
Structural and material properties



XRD diffractograph of SGS_06Ag glass sample.

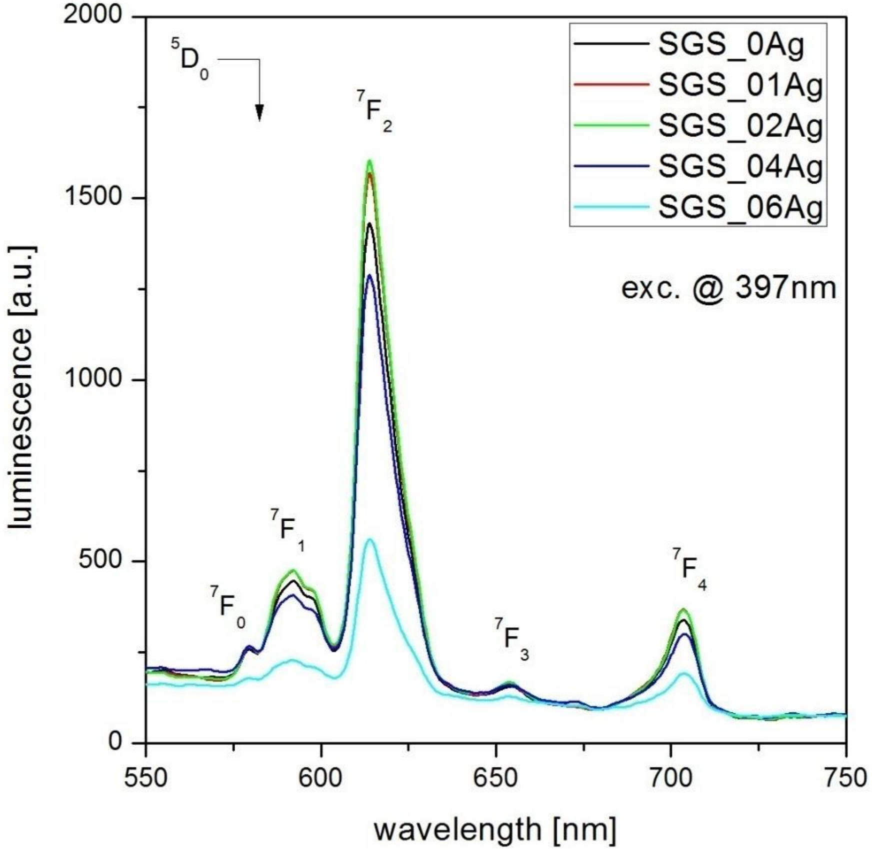


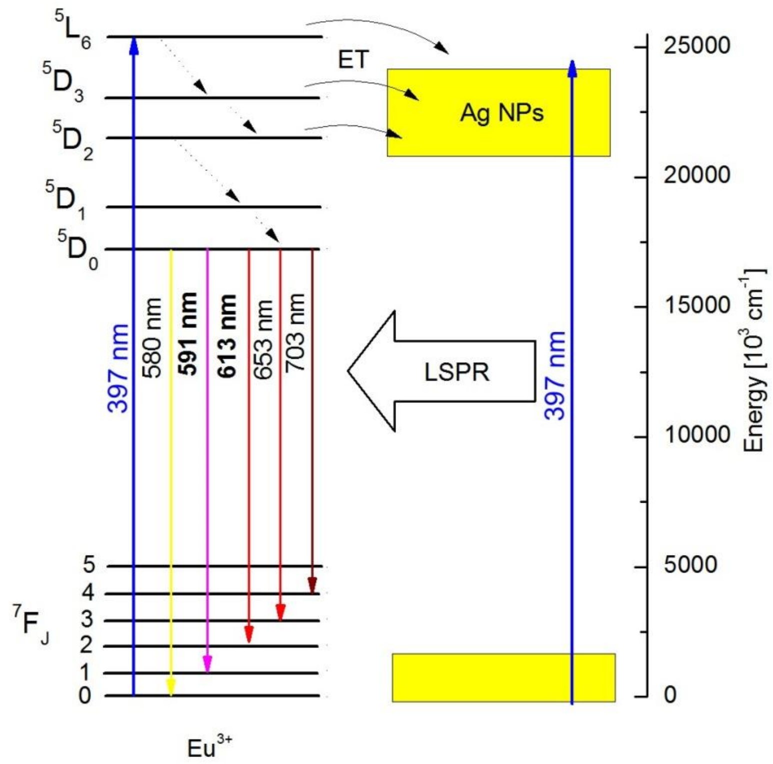
MIR spectra of SGS_0Ag and SGS_06Ag glass sample.



EDS analysis of SGS_06Ag glass sample. (inset) SEM pictures of SGS_06Ag glass sample (a – picture with magnification of 2 000x,b –picture with magnification of 5 000x).

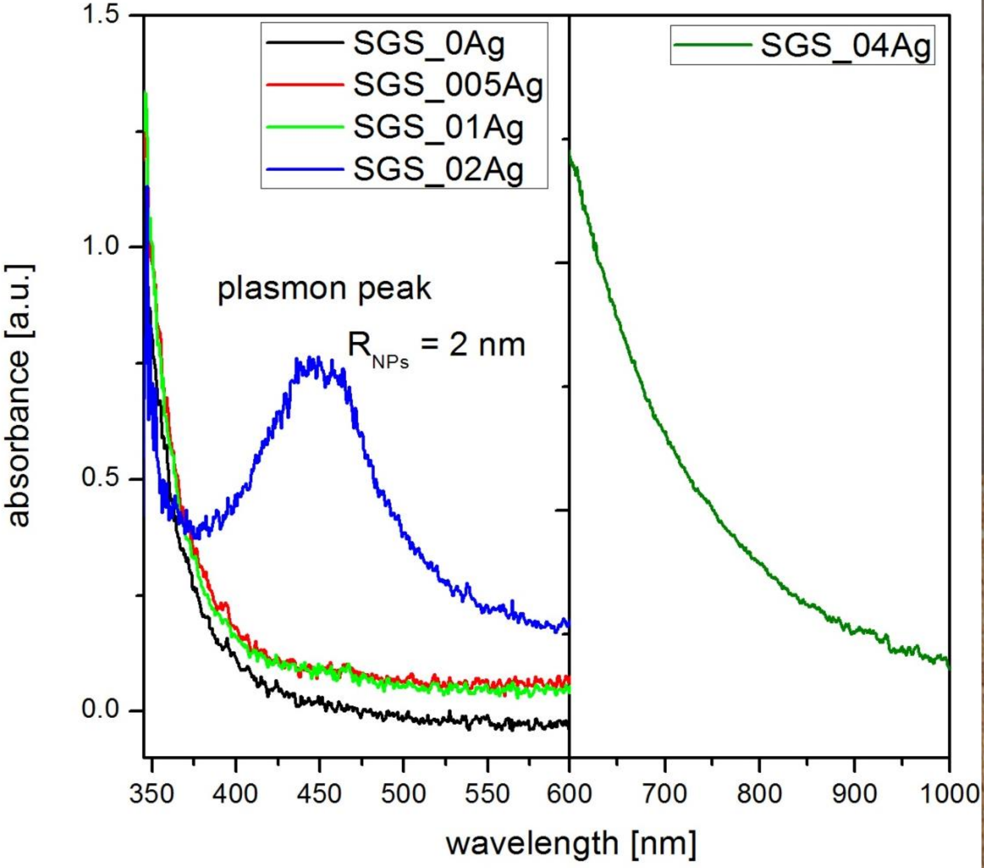
Luminescence vs Ag content





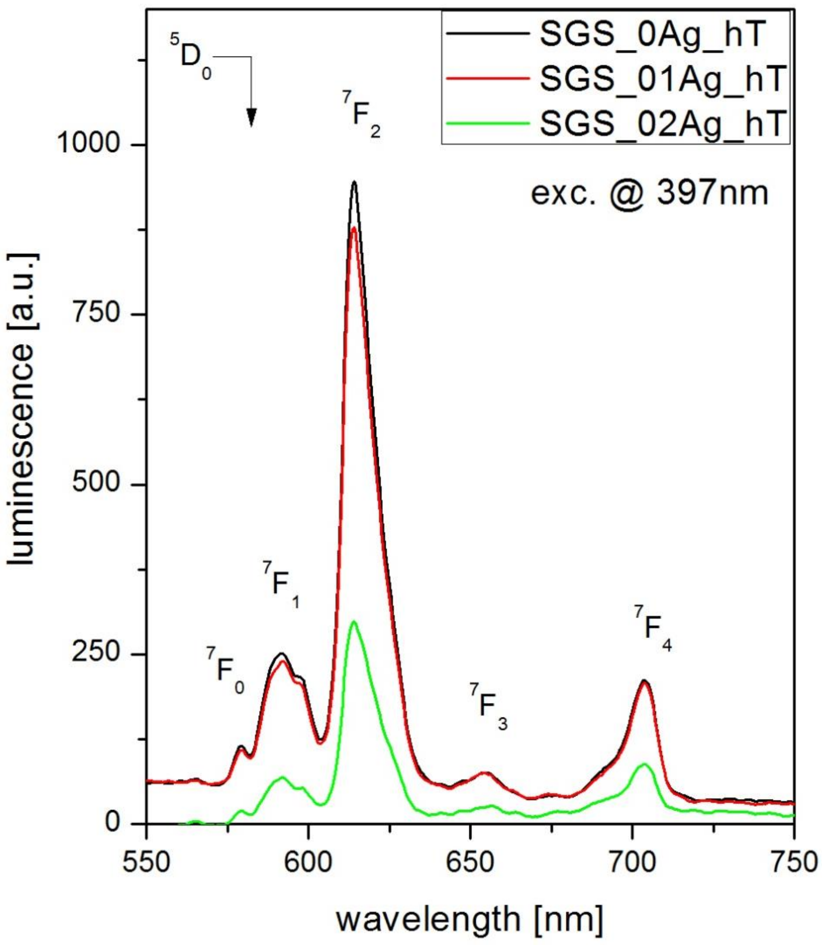
Luminescence spectra of ***SGS*** *glasses with different content of AgNO3 excited under* ***397 nm.***
(right) Simplified energy diagram with possible transition mechanisms.

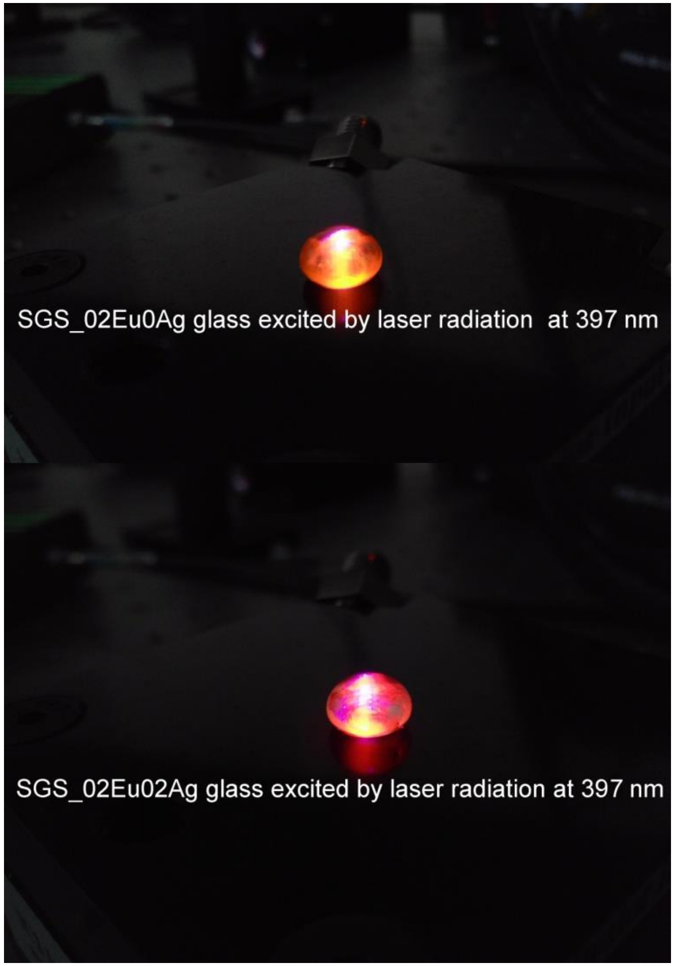
Effect of heat-treatment



Absorbance spectra of SGSxAg glasses after heat-tereatment process @ 440C by 2 hours

Luminescence after HT





*Luminescence spectra of **SGS** glasses with different content of AgNO3 excited under **397 nm** after heat-treatment process at **440C by 2 hours***

Experimental

Glasses SGS_xAgRE: Sb_2O_3 - GeO_2 - SiO_2 - Al_2O_3 - Na_2O

co-doped with xAg^{+}/Eu^{3+}

Step 1:
all samples doped with $0.2Eu_2O_3$ and $xAgNO_3$

Melting at 1450C by 30min

Annealing at 400C by 2h and slowly cooling by 12h

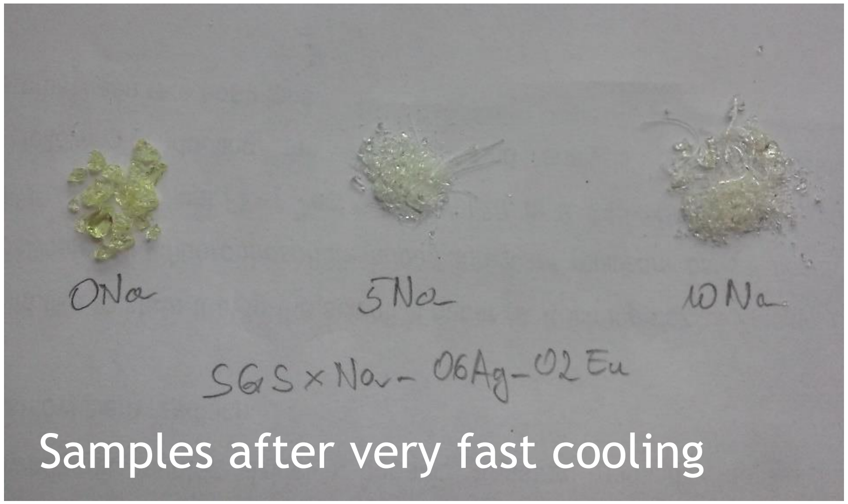
Step 2:
only **SGSxNa_06Ag02Eu**

Melting at 1450C by 30min

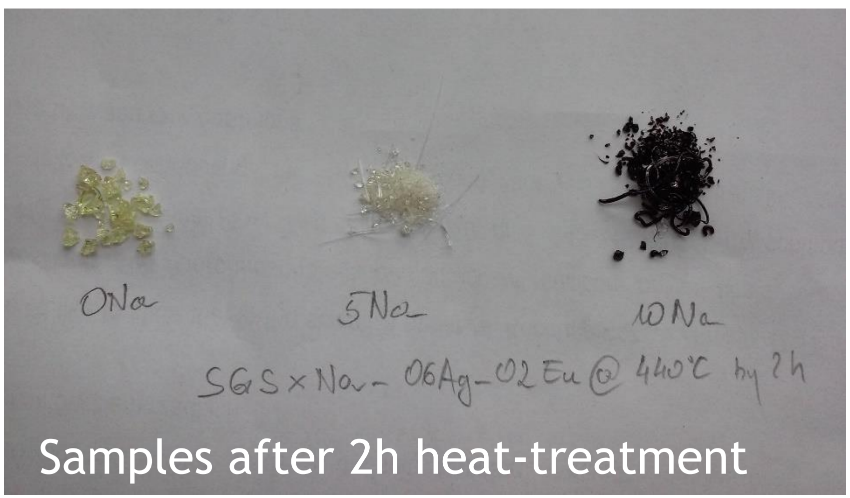
Very fast water cooling without annealing

Minimalisation of thermochemical reduction process by glass modification – perspectives for nanocomposite optical fiber

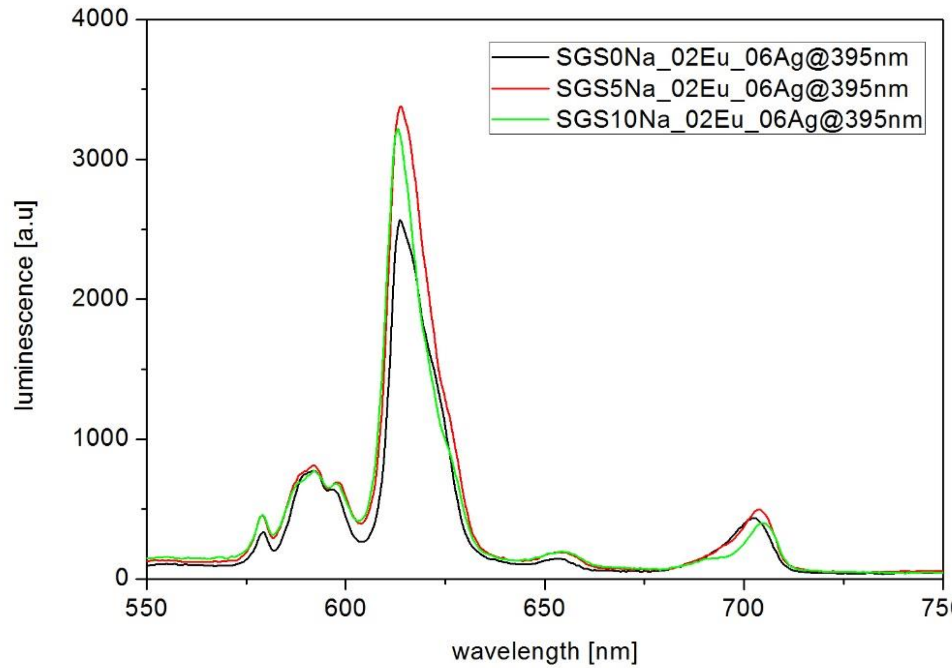
Step2: Water cooling without anealing



Samples after very fast cooling



Samples after 2h heat-treatment



Experimental

Glasses SGB_AgRE: Sb_2O_3 - GeO_2 – (1-x)B_2O_3 - Al_2O_3 - xNa_2O

co-doped with 0.6*Ag^+/0.2Eu^{3+}*

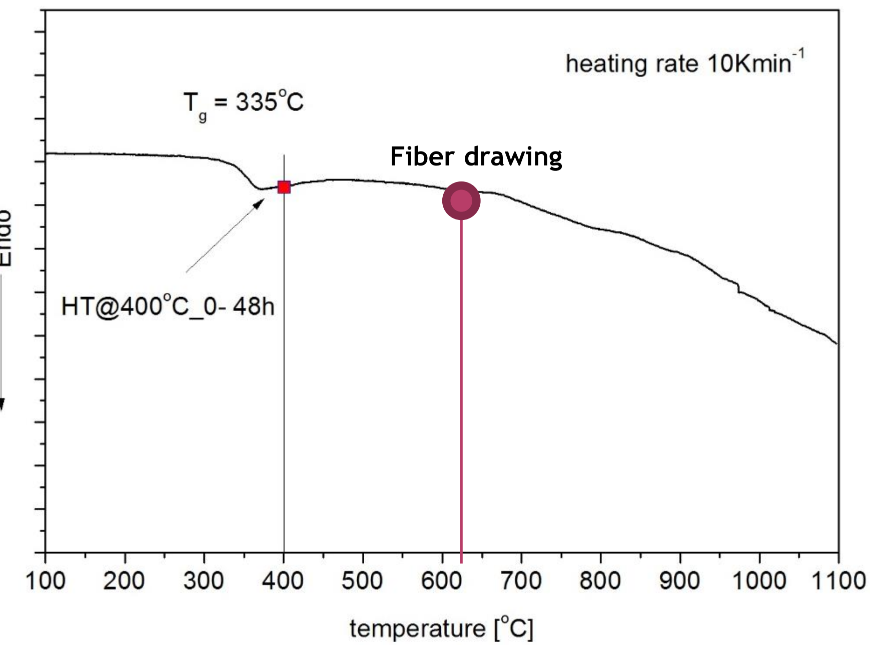
Melting
1150°C

Annealing
300°C

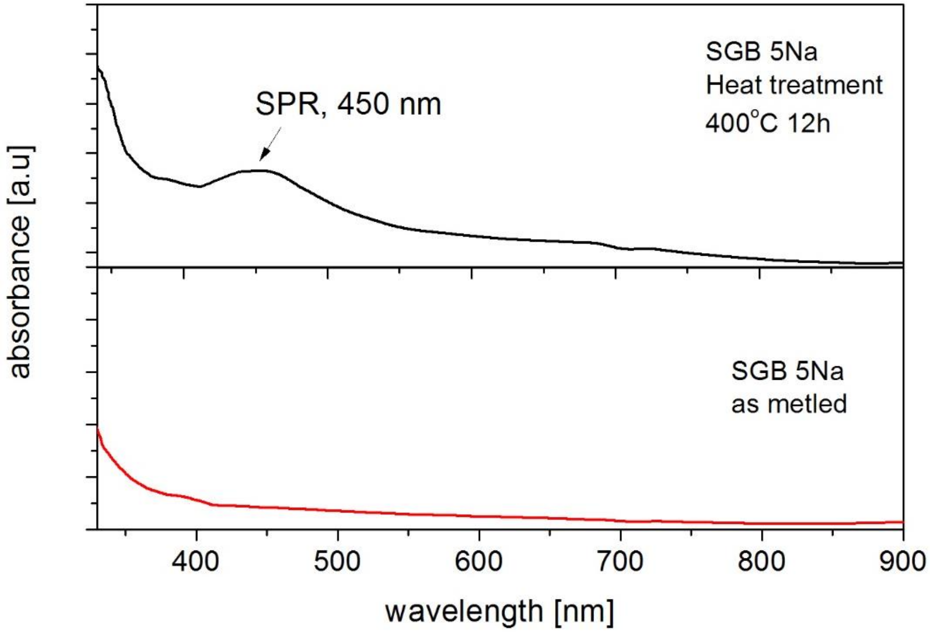
Heat treatment
400°C
12-48h

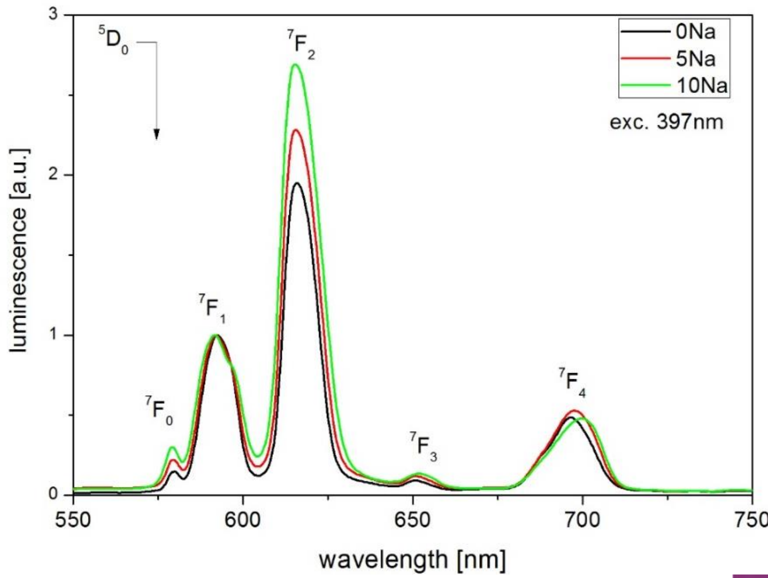
Fiber Drawing
630°C

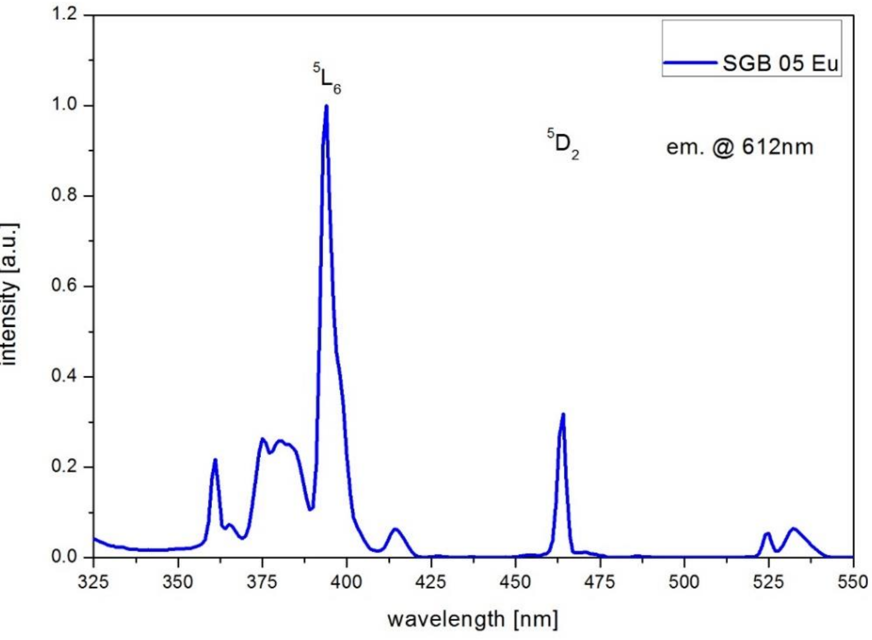
Heat treatment
400°C
12-48h

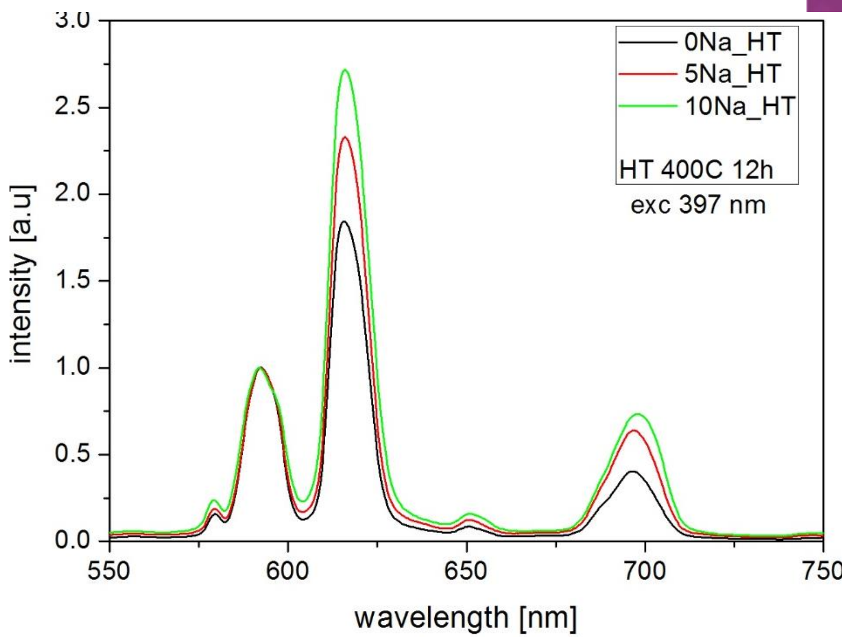


Spectroscopic characterization of SGB_06Ag02Eu Glasses

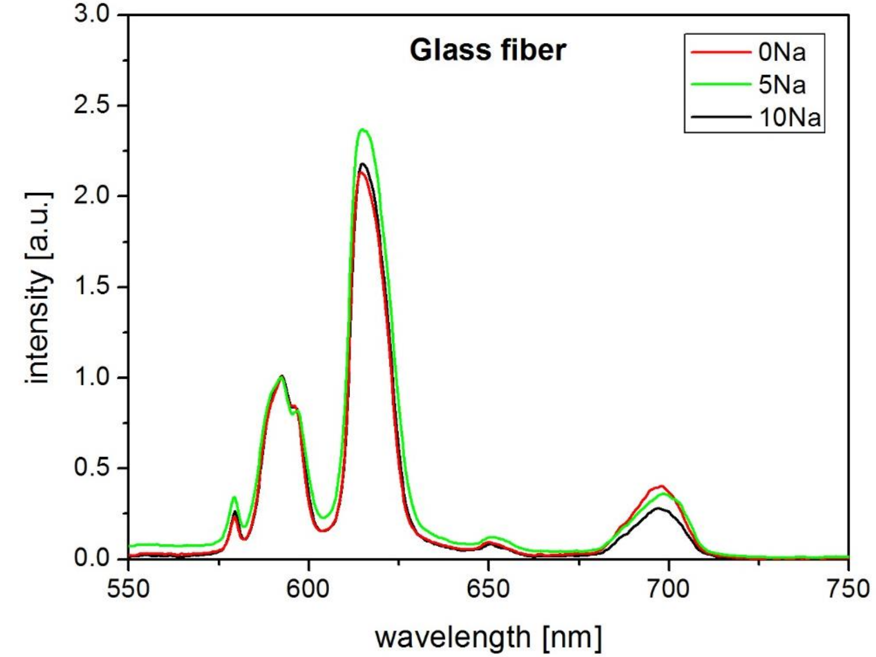


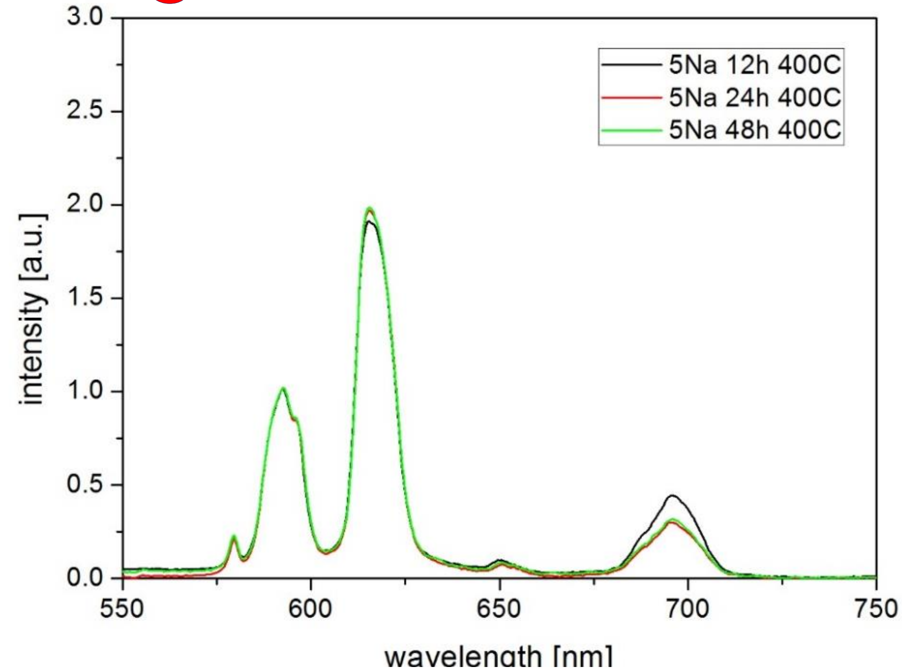


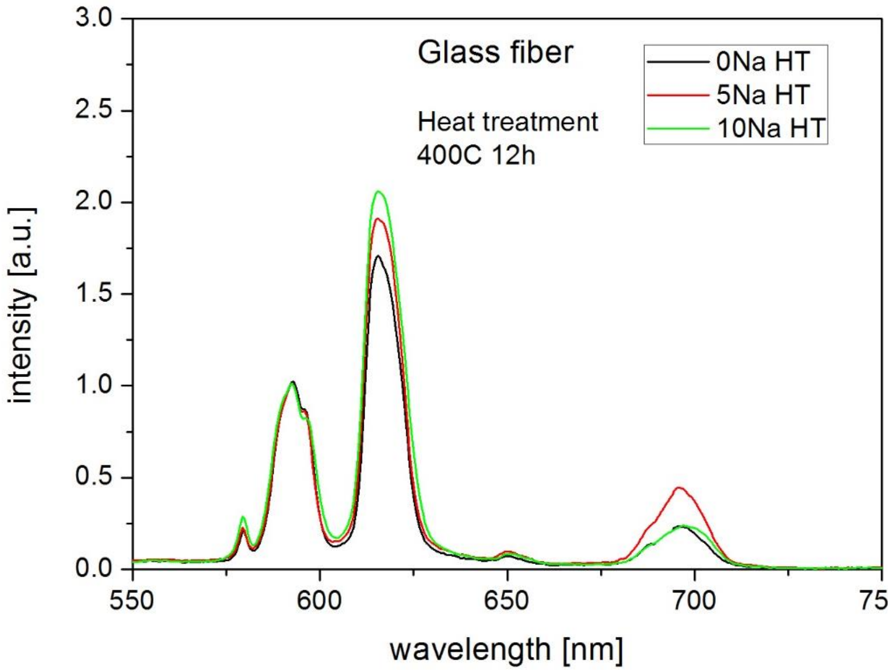


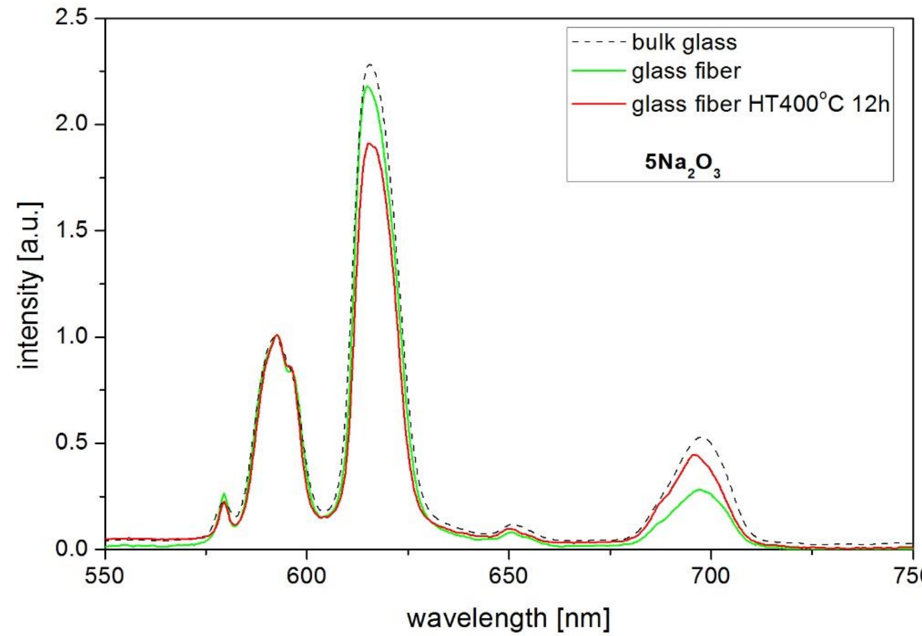


Photoluminescence of SGB06Ag02Eu Glass Fiber









Conclusions and perspectives

- Thermally stable glass **Sb_2O_3 + GeO_2 +SiO_2 + Al_2O_3 + Na_2O (SGS)**
- Partial crystallisation effect in SGS glasses modified by P2O5 (up to 10mol%) directly in melt-quenching proces (petrurgic method)
- Effect of Ag reduction during standard melt-quenching process (one-step method)
- Enhancement of luminescence signal at 613 nm ($^5D_0 \rightarrow {}^7F_2$) for laser excitation at 395 nm in glasses doped with 0.2AgNO3
- Modification of chemical composition of SGS glass to minimize termochemical reuction of Ag ions (content of Na)
- Antimony – germanate – borate (SGB) glasses enables to fabricate optical fibers with SPR luminescence enhancement (Eu/Ag- nanoparticles)
- Construction and luminescence study of **optical fibers co-doped with Ag/ Au nanoparticles and RE ions**

Acknowledgments

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