Rare-earth doped chalcogenide glasses for mid-IR sensor applications

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Introduction

- Gas sensors in the infrared range based on "molecular fingerprint" absorption spectra of gas

- Application fields : environment, security, health, chemistry

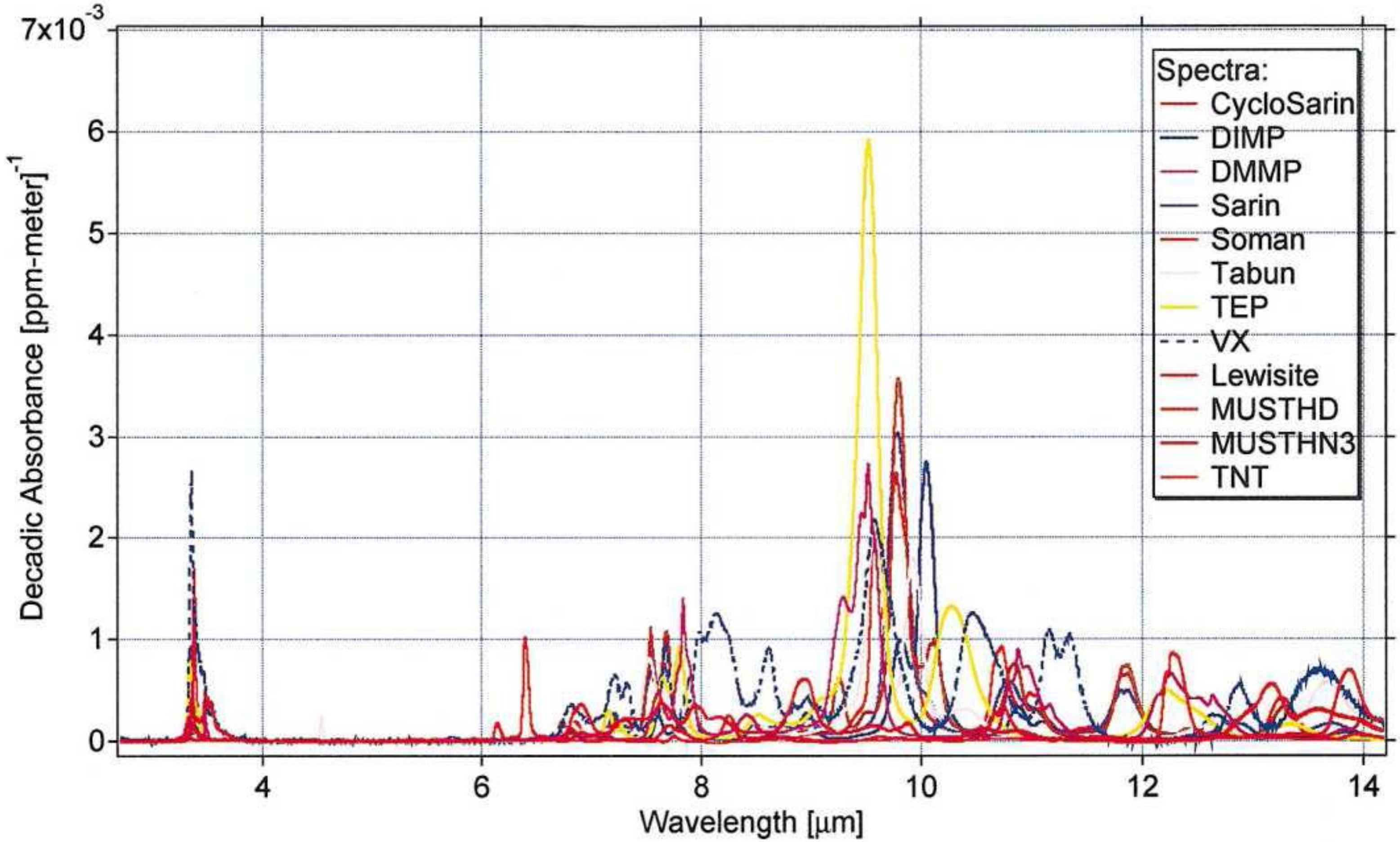
→ Requiring bright infrared sources, IR waveguides, IR detectors

- Chalcogenide glass : wide transparency band (up to 20 µm for telluride based glass)

- Possibility of rare earth incorporation : active IR waveguide

Introduction

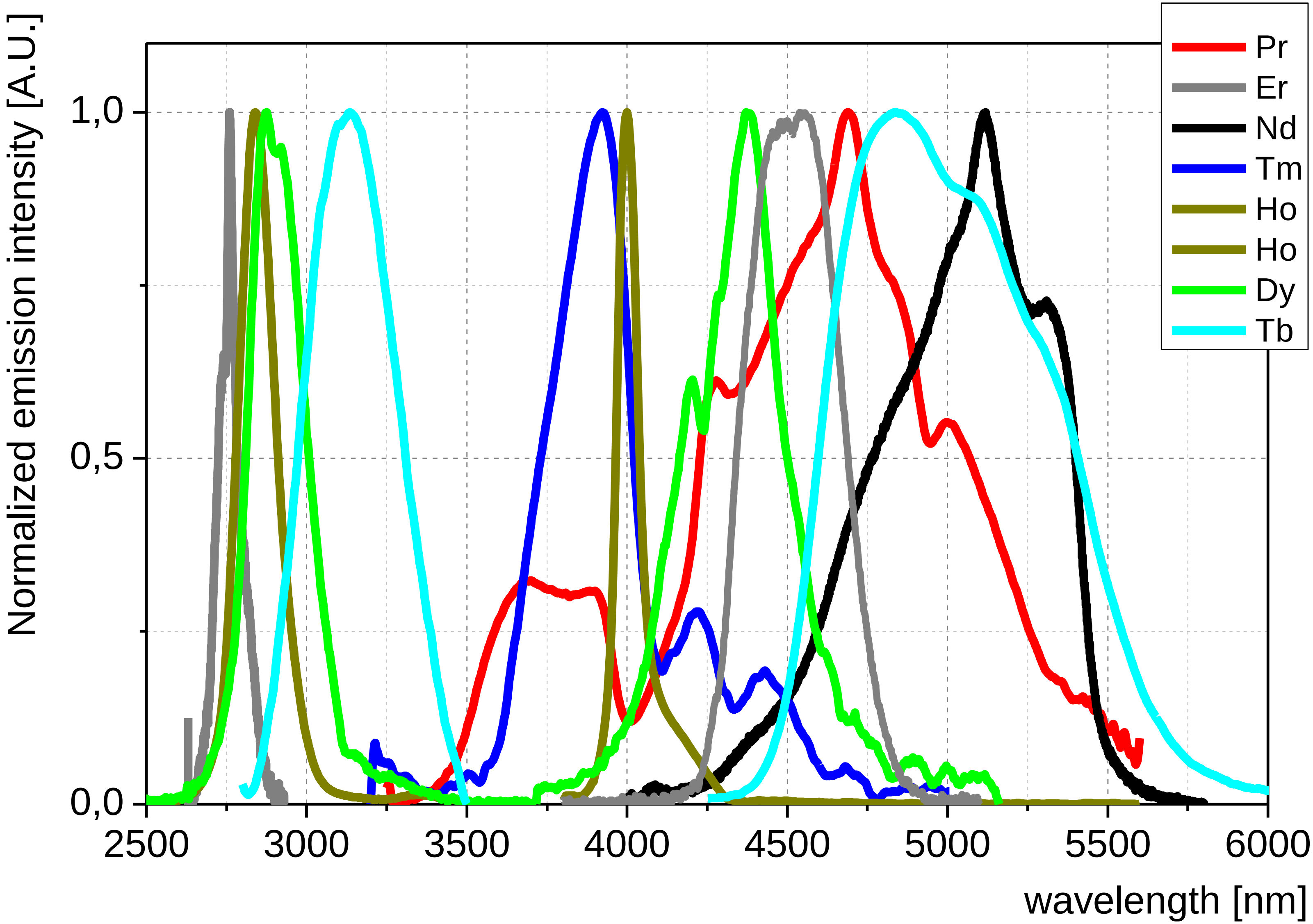
Absorption lines of hazardous gases in the 3-14µm spectral region



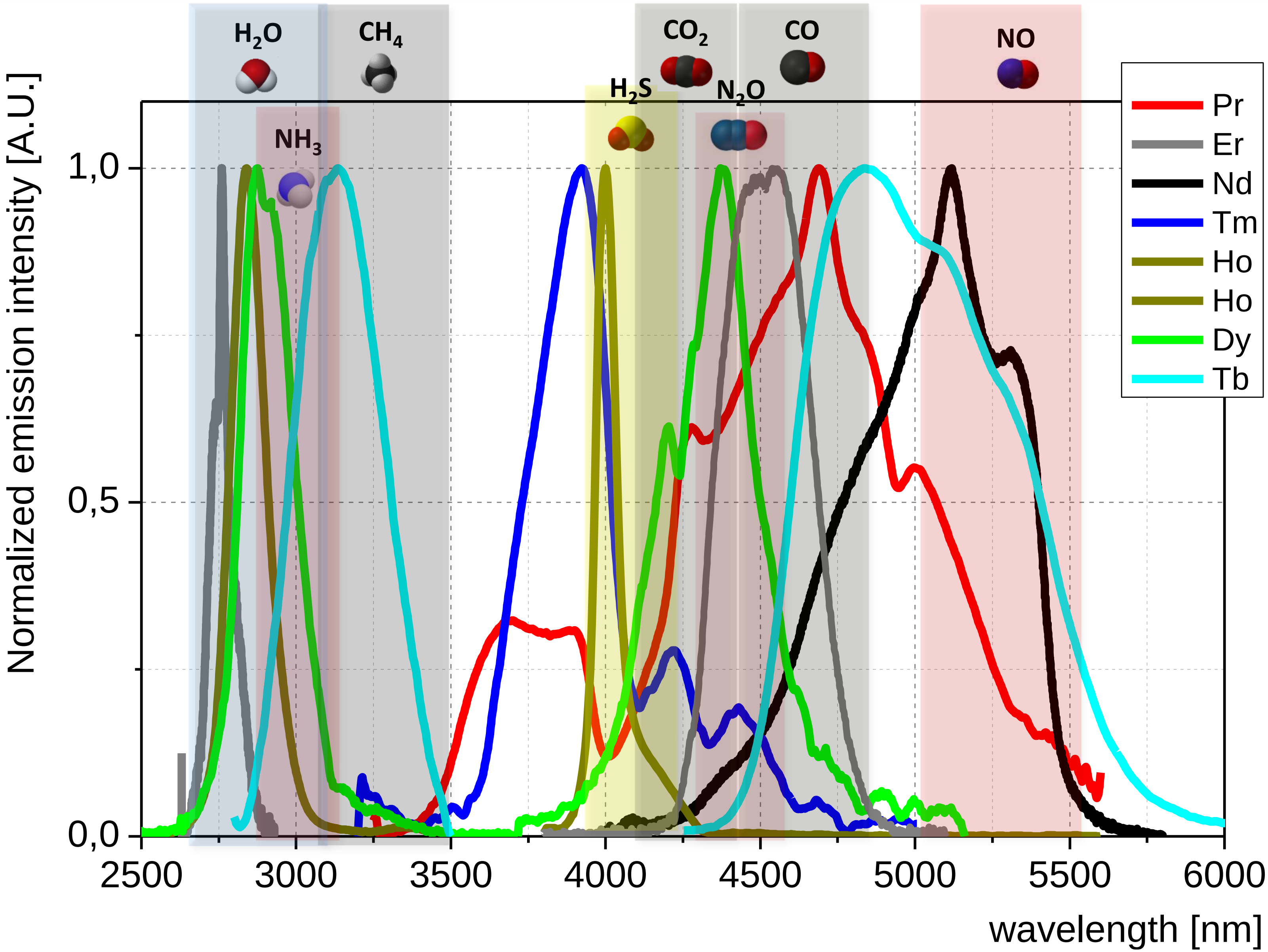
Bande II: CO_2 (4,3µm), CO (4,7µm), CH_4 (3,4µm)

Introduction

Examples of rare-earth emissions in the 2-6 µm spectral window

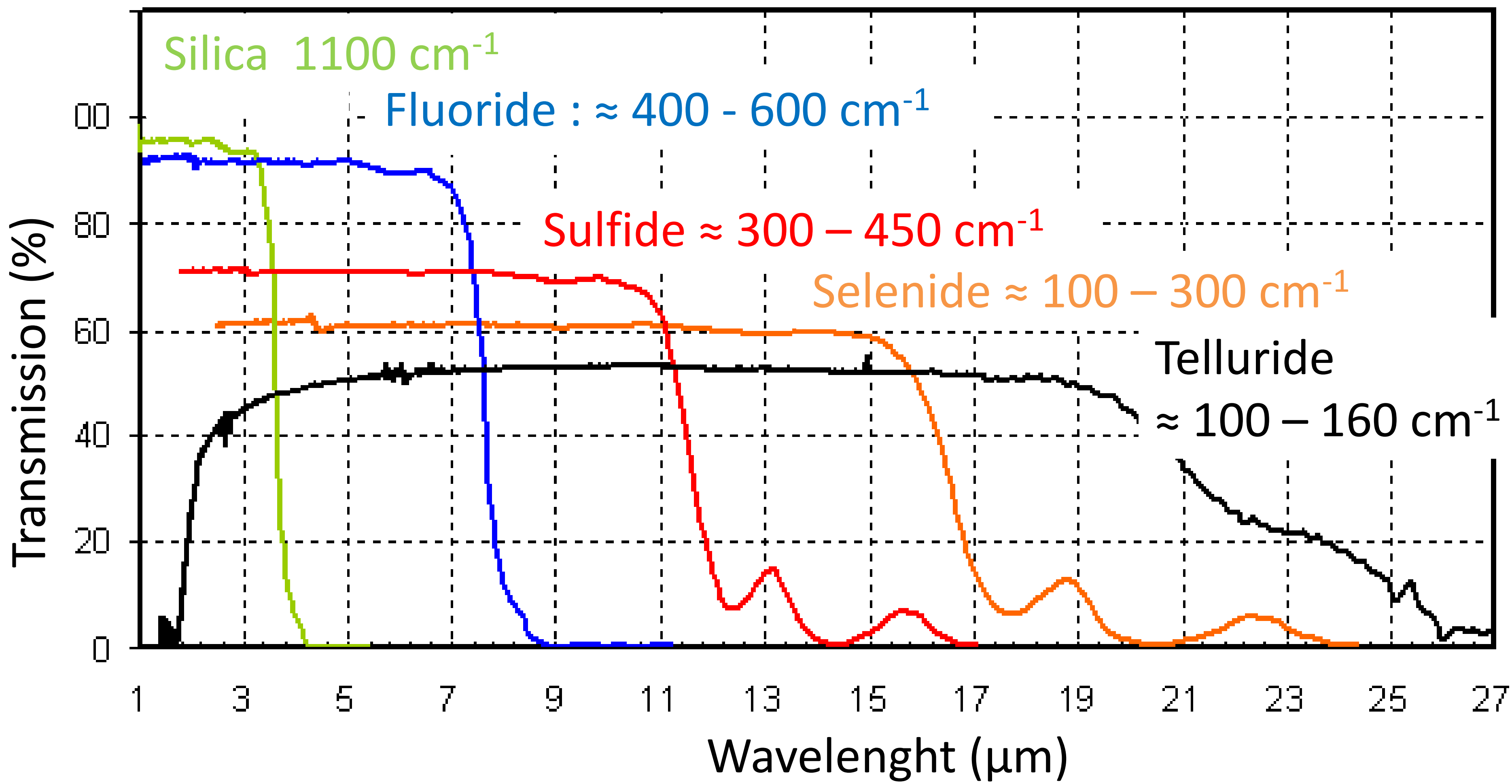


Introduction



Introduction

Transparency optical window and phonon energy of some glass matrix



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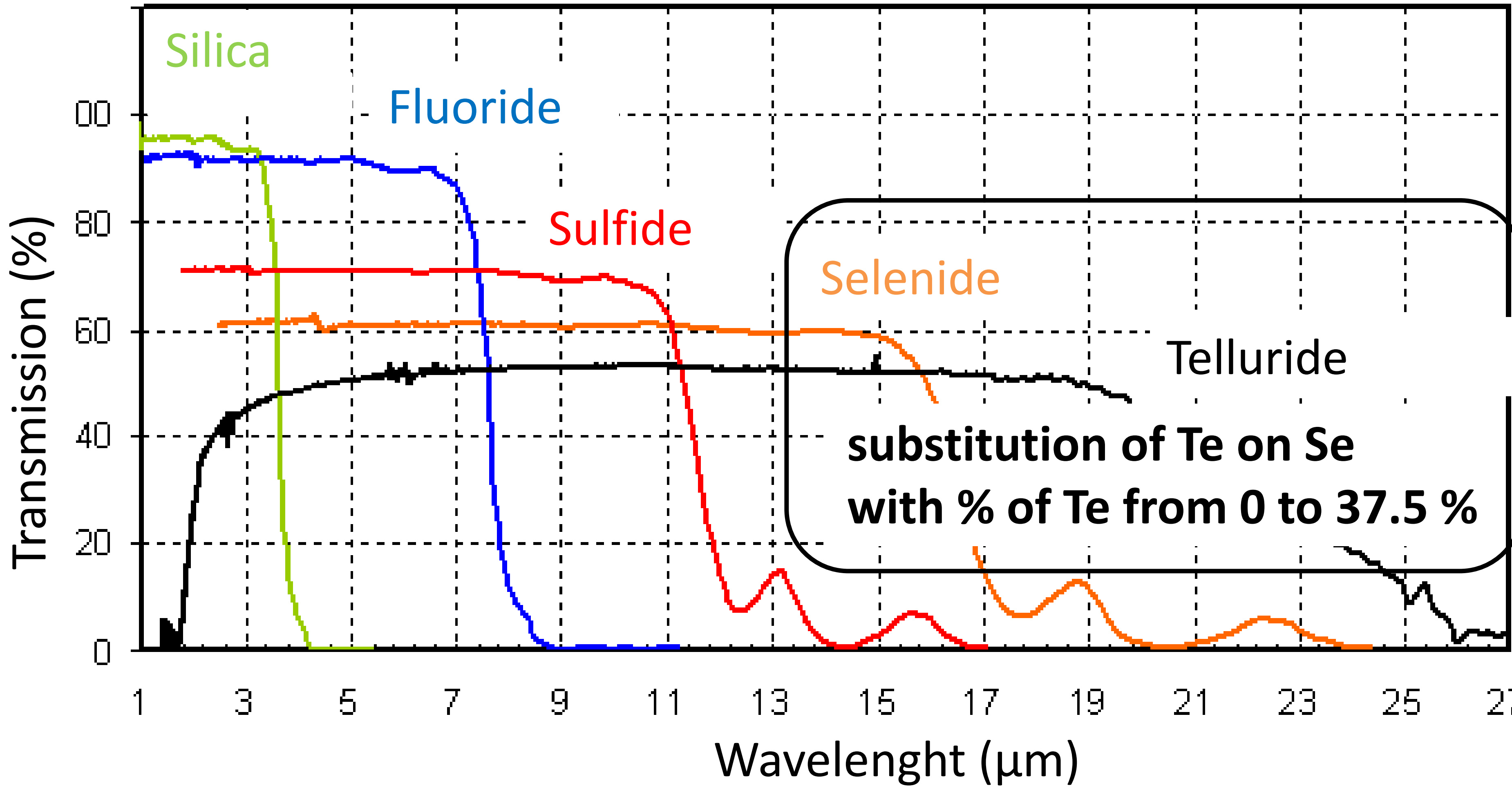
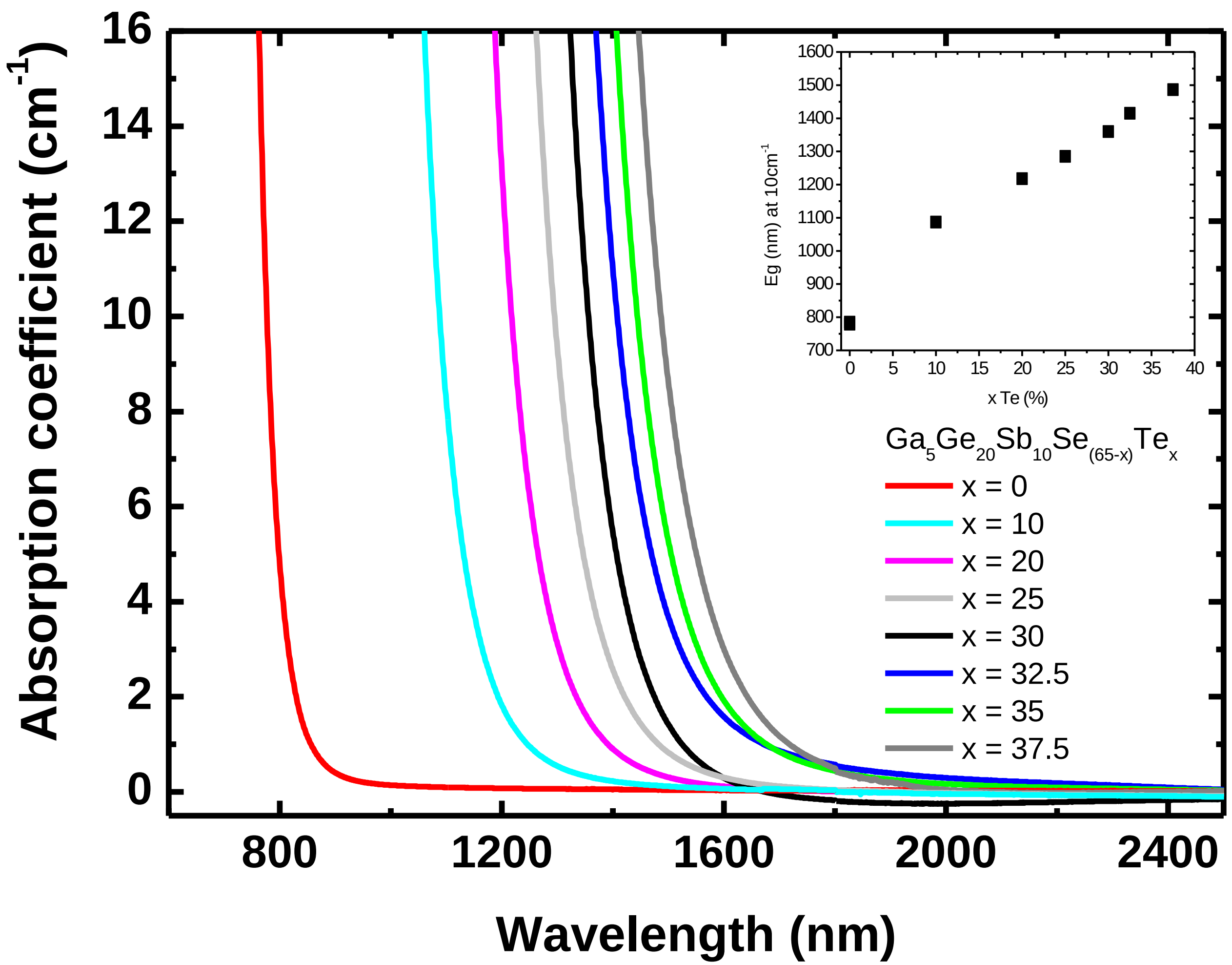
Transparency optical window and phonon energy of some glass matrix



substitution of Te on Se with % of Te from 0 to 37.5 %

Glass system : $Ga_5Ge_{20}Sb_{10}Se_{(65-x)}Te_x$

Absorption coefficient : electronic band gap

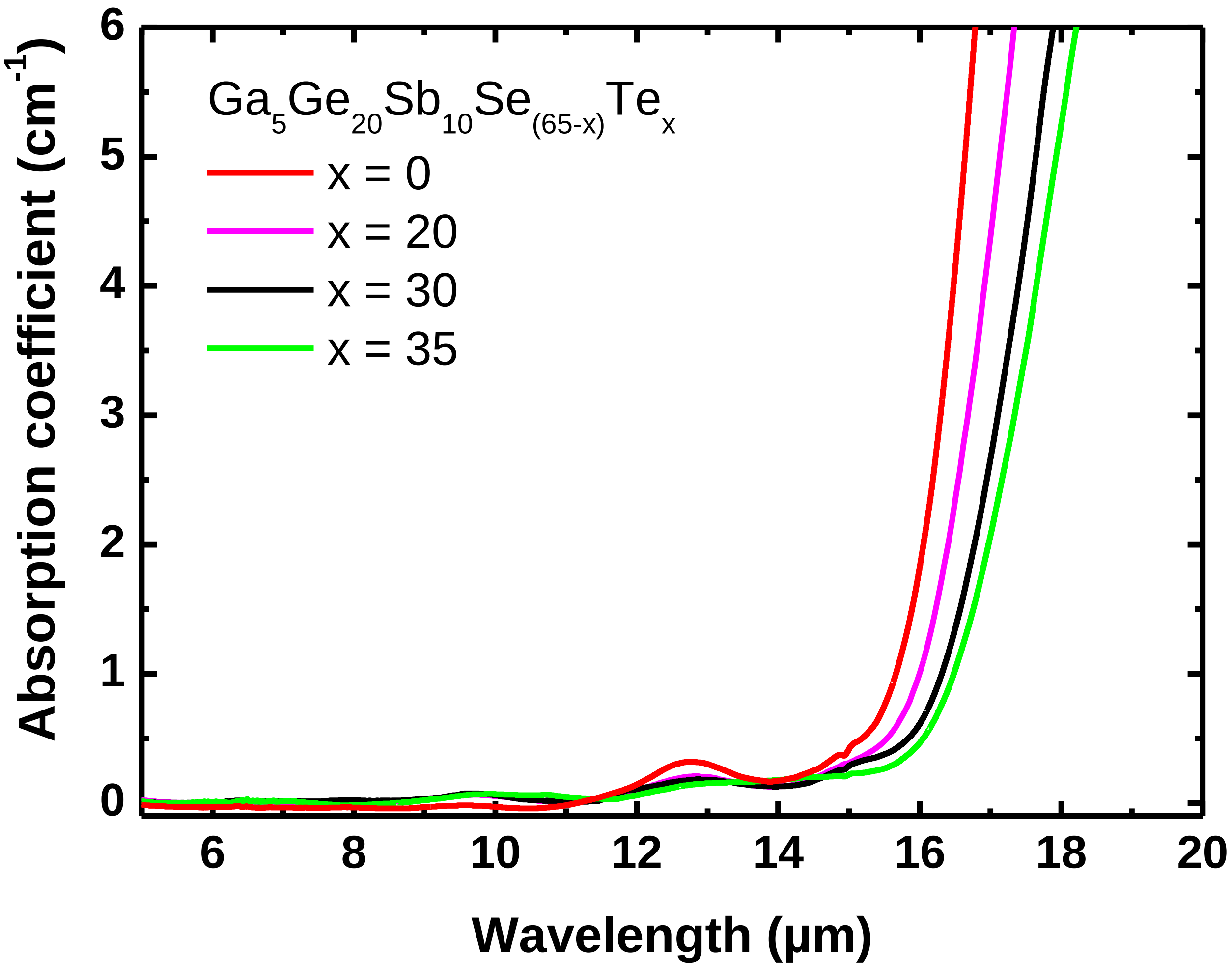


→ Red shifted

→ E_g increased linearly with the Te adding

Glass system : $Ga_5Ge_{20}Sb_{10}Se_{(65-x)}Te_x$

Absorption coefficient : IR cut off



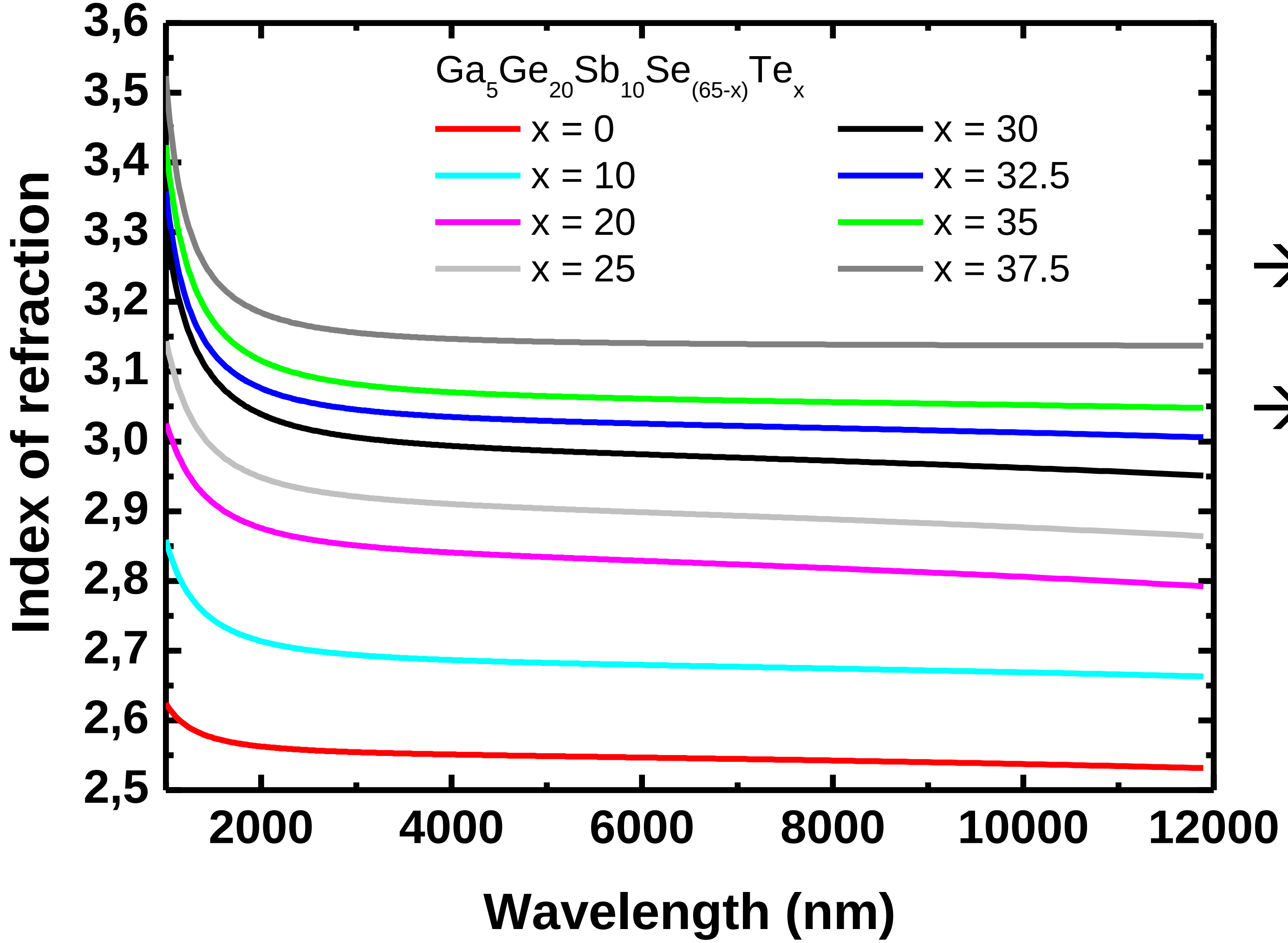
→ $\frac{Te}{Se+Te} \approx 57\ \%$ substitution on chalcogen

→ Red shifted ≈ 1.4 µm (at 6 cm^{-1})

→ Transparence to 16 µm

Glass system : $Ga_5Ge_{20}Sb_{10}Se_{(65-x)}Te_x$

VASE ellipsometry spectroscopy : refractive index

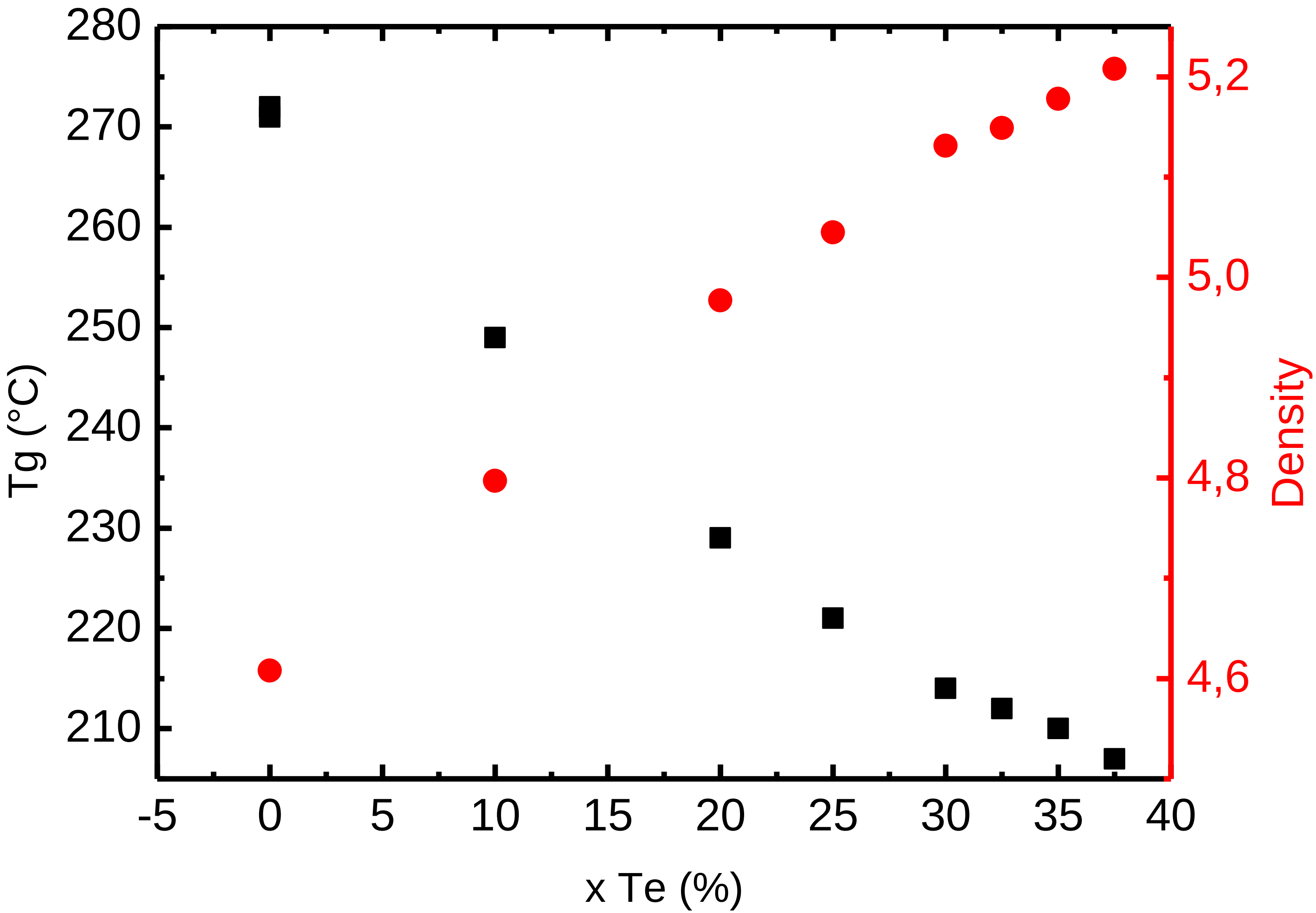


→ Low dispersion

→ n increasing with %Te

Glass system : $Ga_5Ge_{20}Sb_{10}Se_{(65-x)}Te_x$

Density and thermal properties



Glass system : $Ga_5Ge_{20}Sb_{10}Se_{(65-x)}Te_x$

Sample	ΔT (°C) (± 2 °C)
x = 0	> 150
x = 10	> 150
x = 20	> 150
x = 25	134
x = 30	120
x = 32.5	100
x = 35	84
x = 37.5	73 vitroceramic

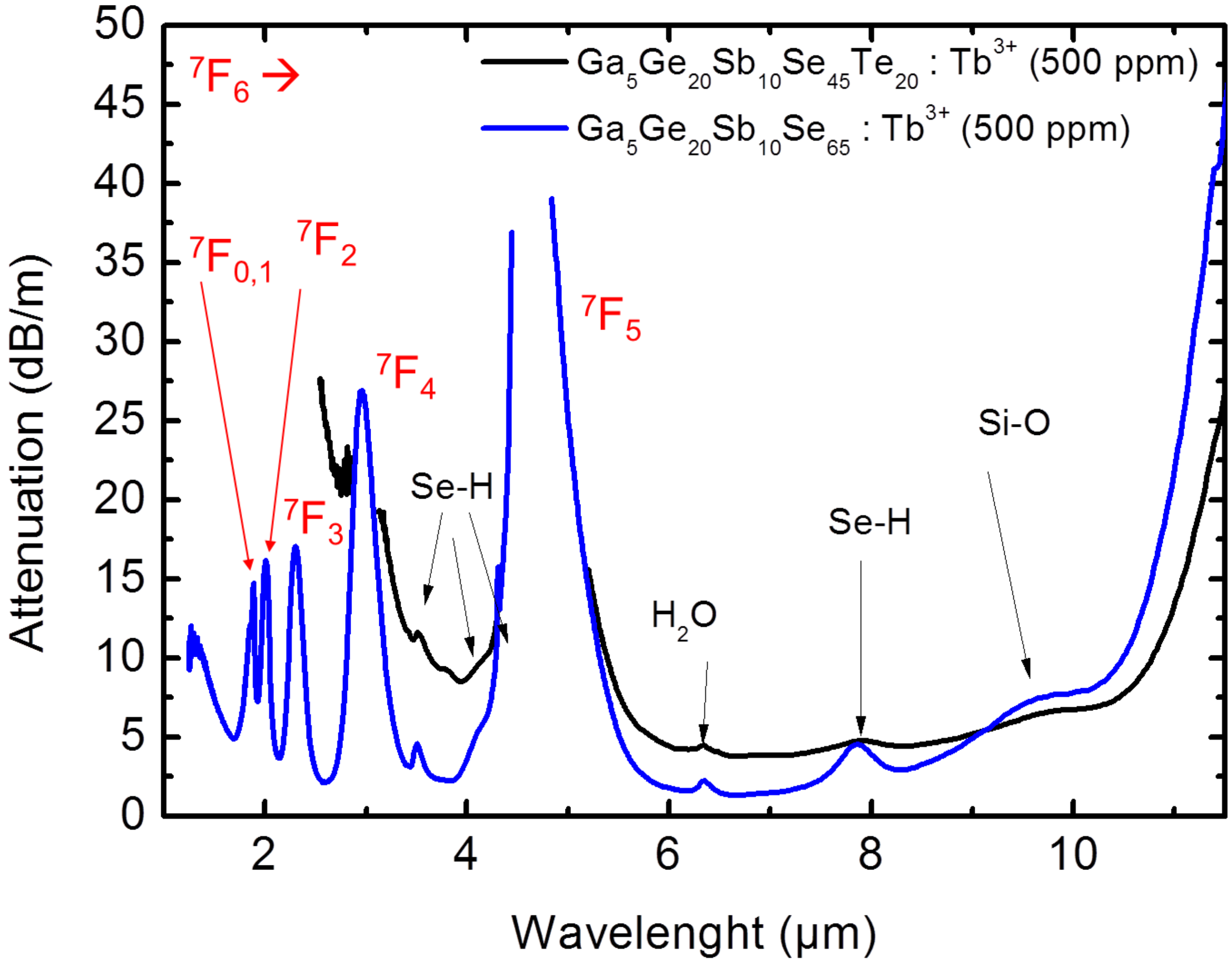
Tb^{3+} doping

Phonon energy :

$Ga_5Ge_{20}Sb_{10}Se_{65}$ ≈ 200 cm^{-1}

$Ga_5Ge_{20}Sb_{10}Se_{45}Te_{20}$ ≈ 160 cm^{-1}

Tb^{3+} doped glass : bulk and fiber



Attenuation :

4 dB/m (telluride)

1.3 dB/m (selenide)

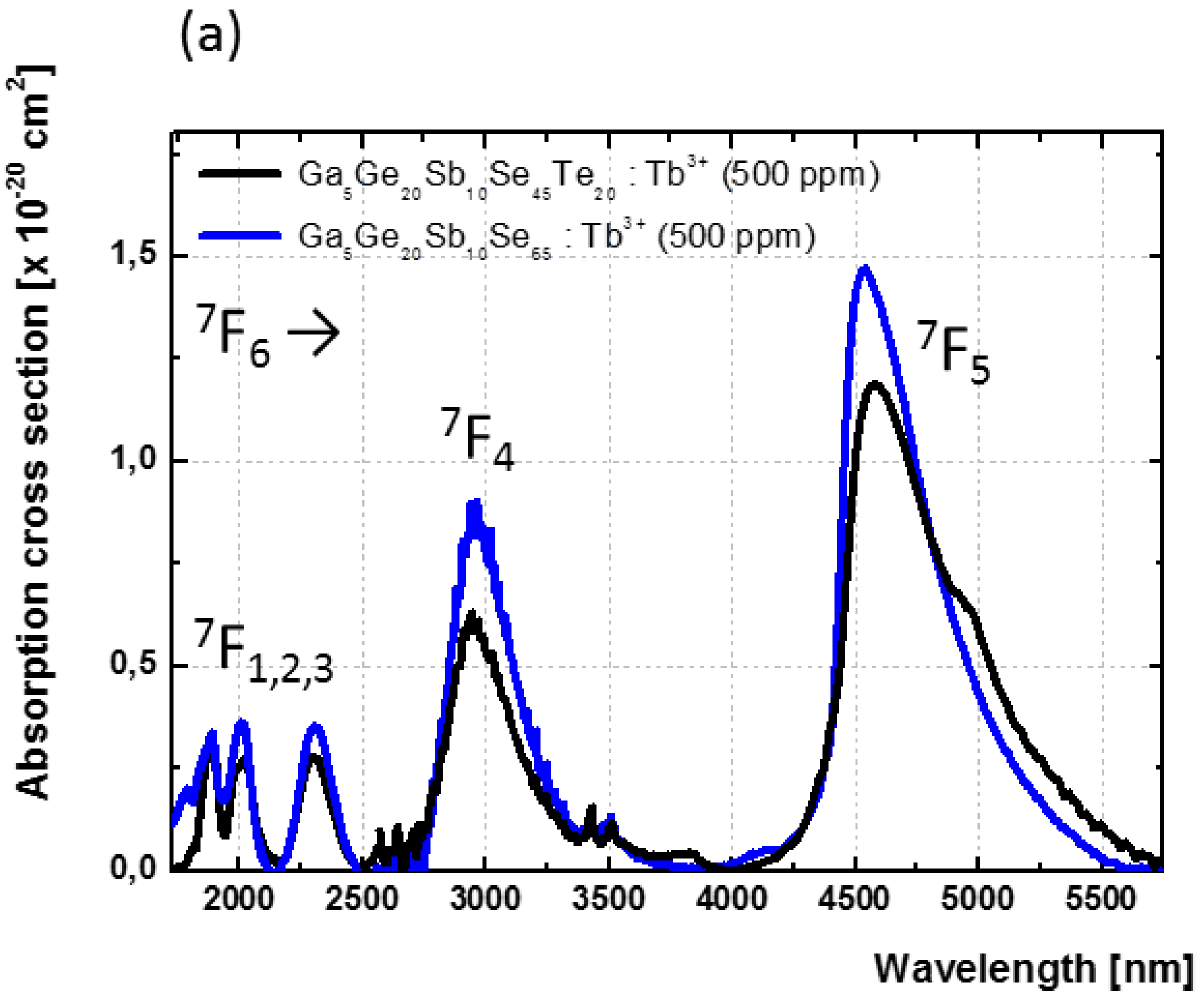
[SeH] :

≈20 ppm (telluride)

≈ 33 ppm (selenide)

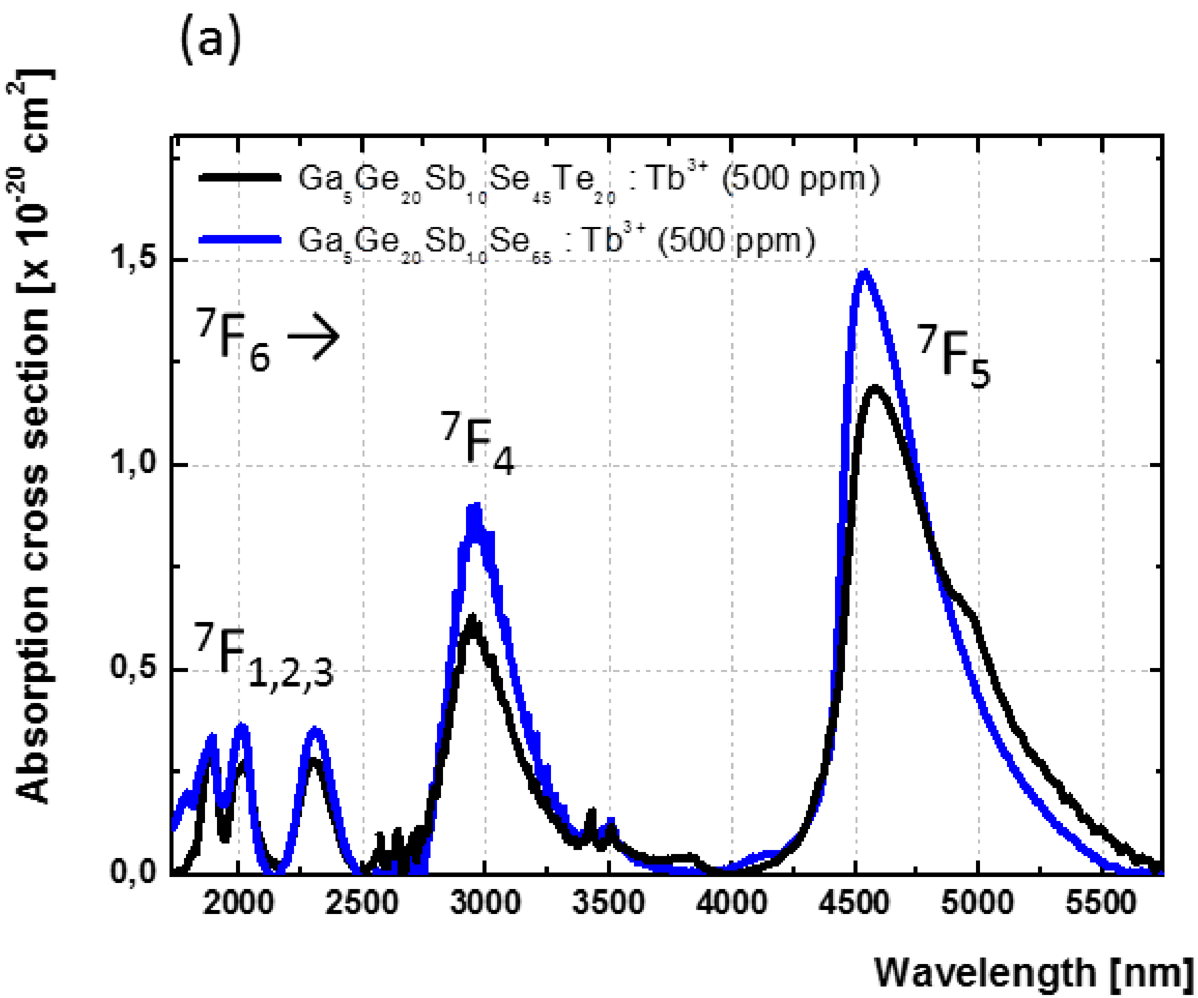
Tb^{3+} doped glass : bulk and fiber

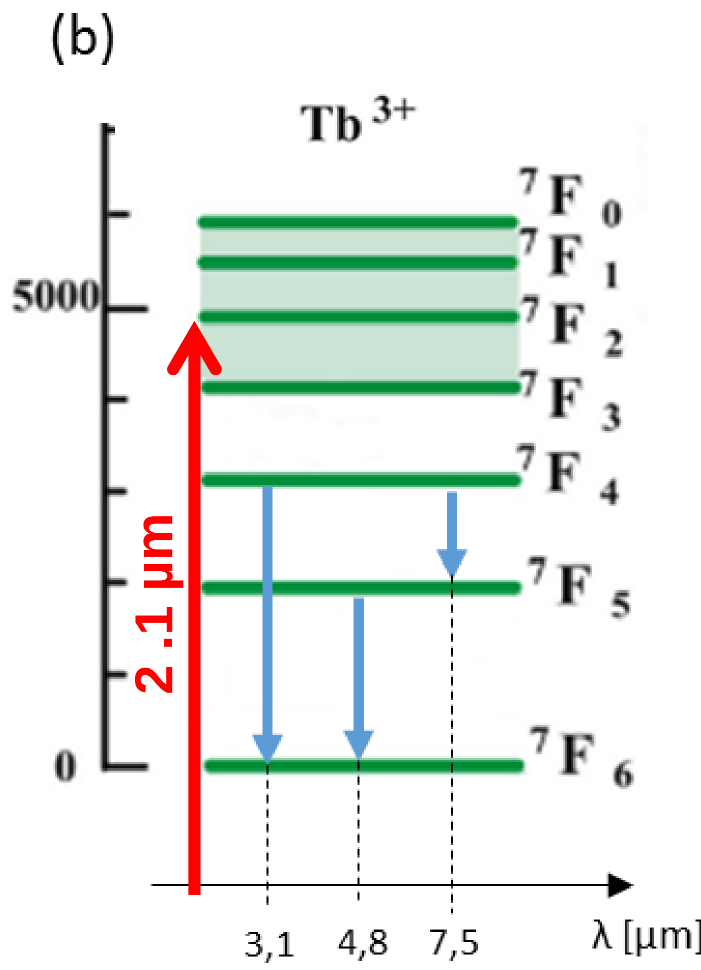
Absorption cross section



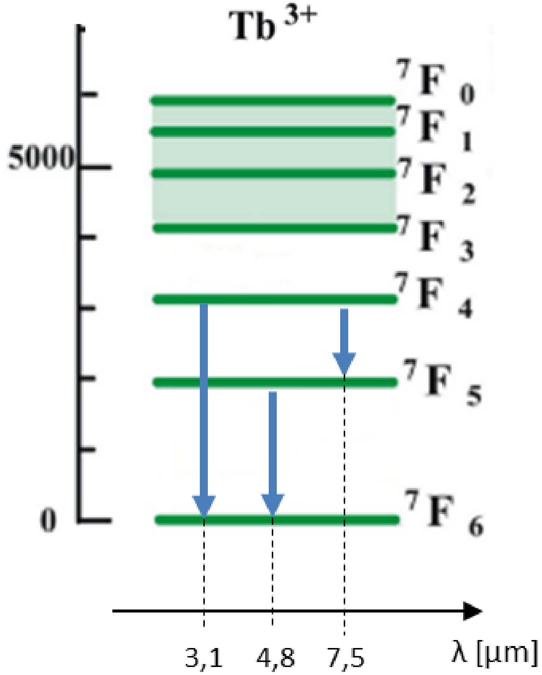
Tb^{3+} doped glass : bulk and fiber

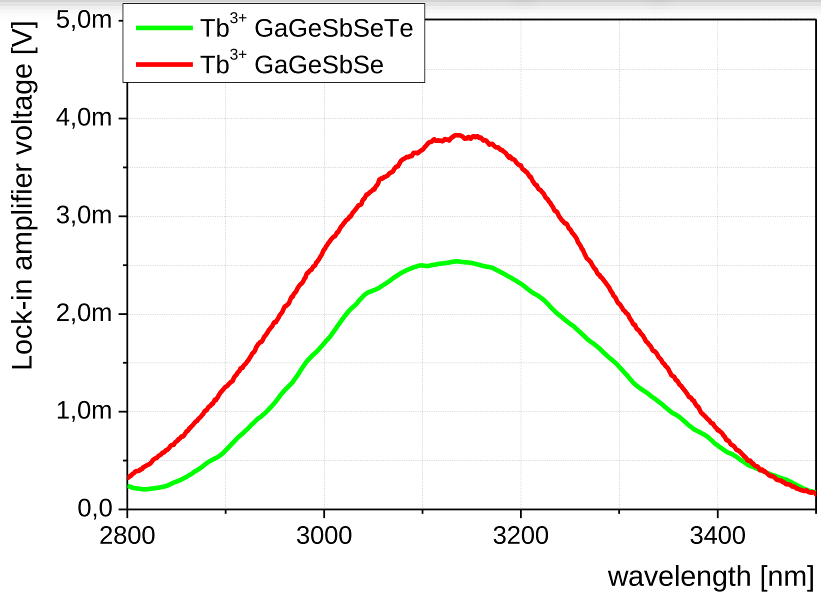
Absorption cross section



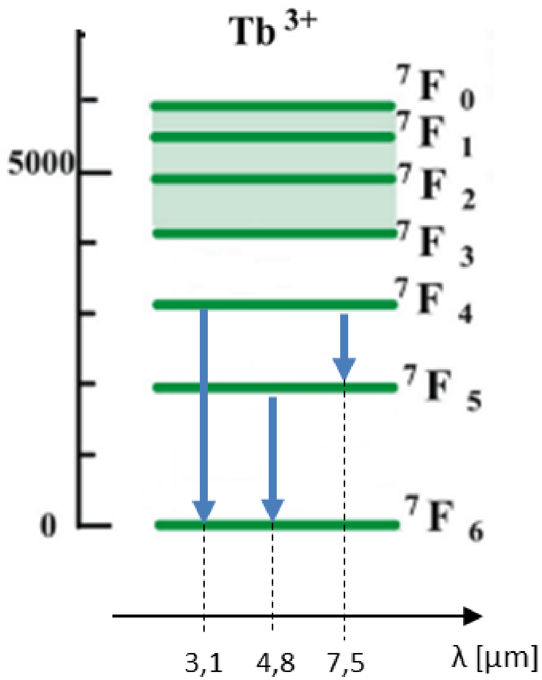


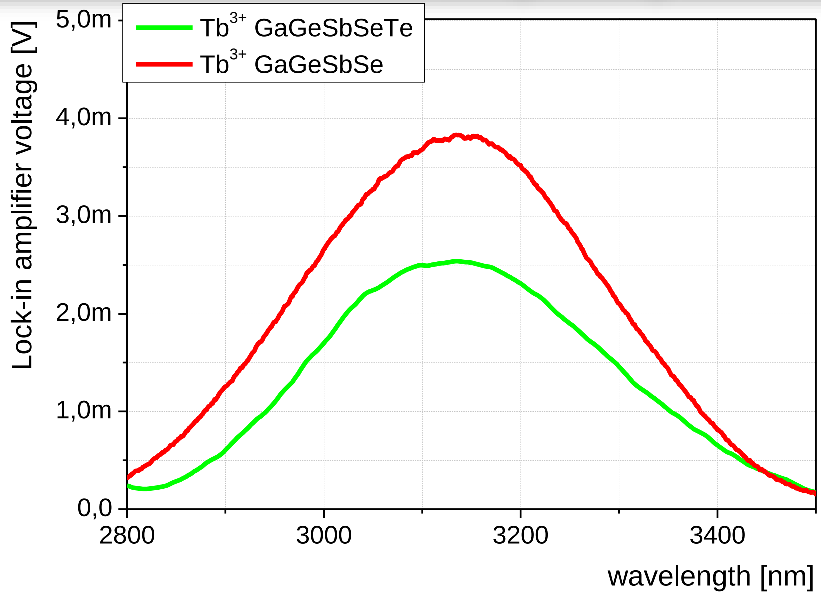
Tb^{3+} doped glass : luminescence properties





Tb^{3+} doped glass : luminescence properties

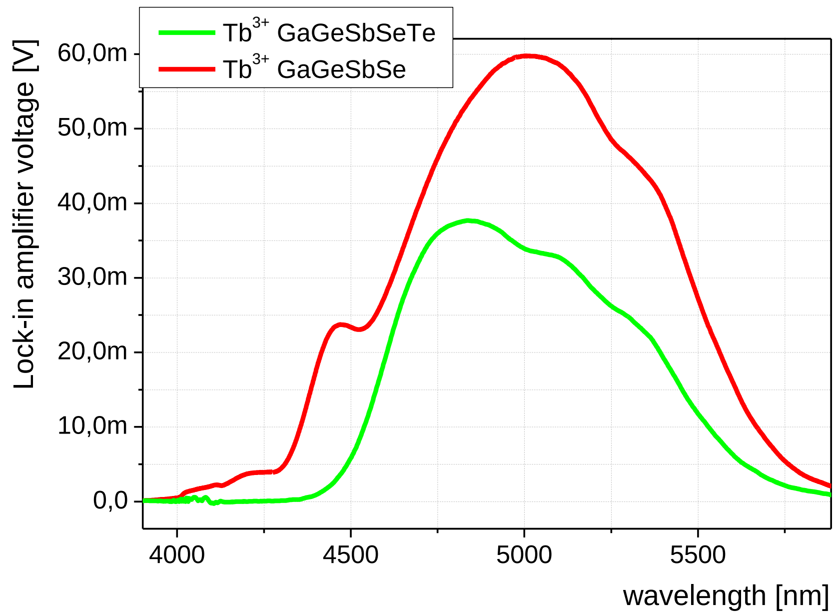




τ at 4.8 µm :

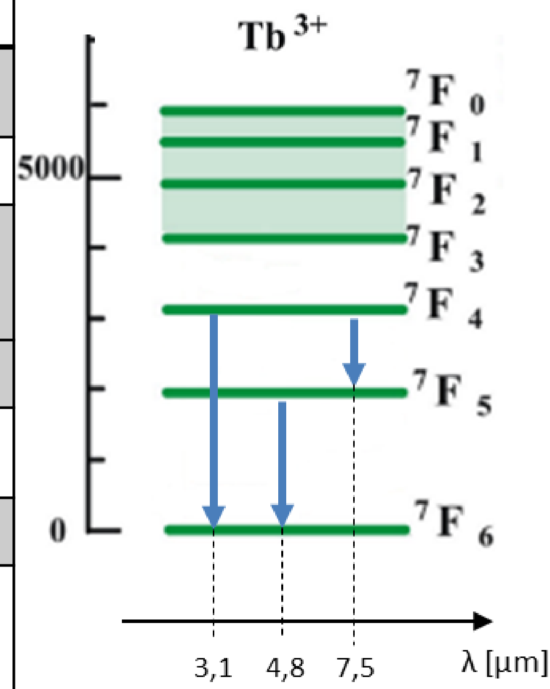
Tb^{3+}:$Ga_5Ge_{20}Sb_{10}Se_{45}$ ≈ 8.9 ms

Tb^{3+}: $Ga_5Ge_{20}Sb_{10}Se_{45}Te_{20}$ ≈ 7.8 ms



Tb^{3+} doped glass : luminescence properties

Tb³⁺ GaGeSbSe					
Transition	λ (µm)	β	τ_{rad} [ms]	τ_{exp} [ms]	η
$^7F_5 \rightarrow {}^7F_6$.	4.8	1	**20.0**	**8.9**	**0.44**
$^7F_4 \rightarrow {}^7F_5$	7.9	0.07	7.2	-	-
$^7F_4 \rightarrow {}^7F_6$	3.1	0.93			
Tb³⁺ GaGeSbSeTe					
Transition	λ (µm)	β	τ_{rad} [ms]	τ_{exp} [ms]	η
$^7F_5 \rightarrow {}^7F_6$.	4.8	1	**24.0**	**7.8**	**0.32**
$^7F_4 \rightarrow {}^7F_5$	7.9	0.06	8.7	-	-
$^7F_4 \rightarrow {}^7F_6$	3.1	0.94			



- Quantum efficiency η ($\eta = \tau_{exp} / \tau_{rad}$)
- Tb^{3+} luminescence quenching is stronger in GaGeSbSeTe than in GaGeSbSe→ pure selenide more suitable for having a strong mid-IR emission

Conclusion

- High purity syntheses of $Ga_5Ge_{20}Sb_{10}Se_{65-x}Te_x$ (x = 0 to 37.5)

- Substitution of Se by Te :
  - Electronic band gap, IR cut off, T_g density and refractive index : linear evolution

- Tb^{3+} ions are efficiently introduced in $Ga_5Ge_{20}Sb_{10}Se_{65}$ and $Ga_5Ge_{20}Sb_{10}Se_{45}Te_{20}$:
  - MIR emission in the range 4.3 – 6.0 µm ($^7F_5 \rightarrow {}^7F_6$)
  - quantum efficiency higher for selenide matrix
  - emission from the level $^7F_4$ is measure in the range 2.8 – 3.4 µm → first step towards 7.5 µm emission.

- Tb^{3+} mid-IR emission : attractive potential for gas sensor !

Thank you for your attention

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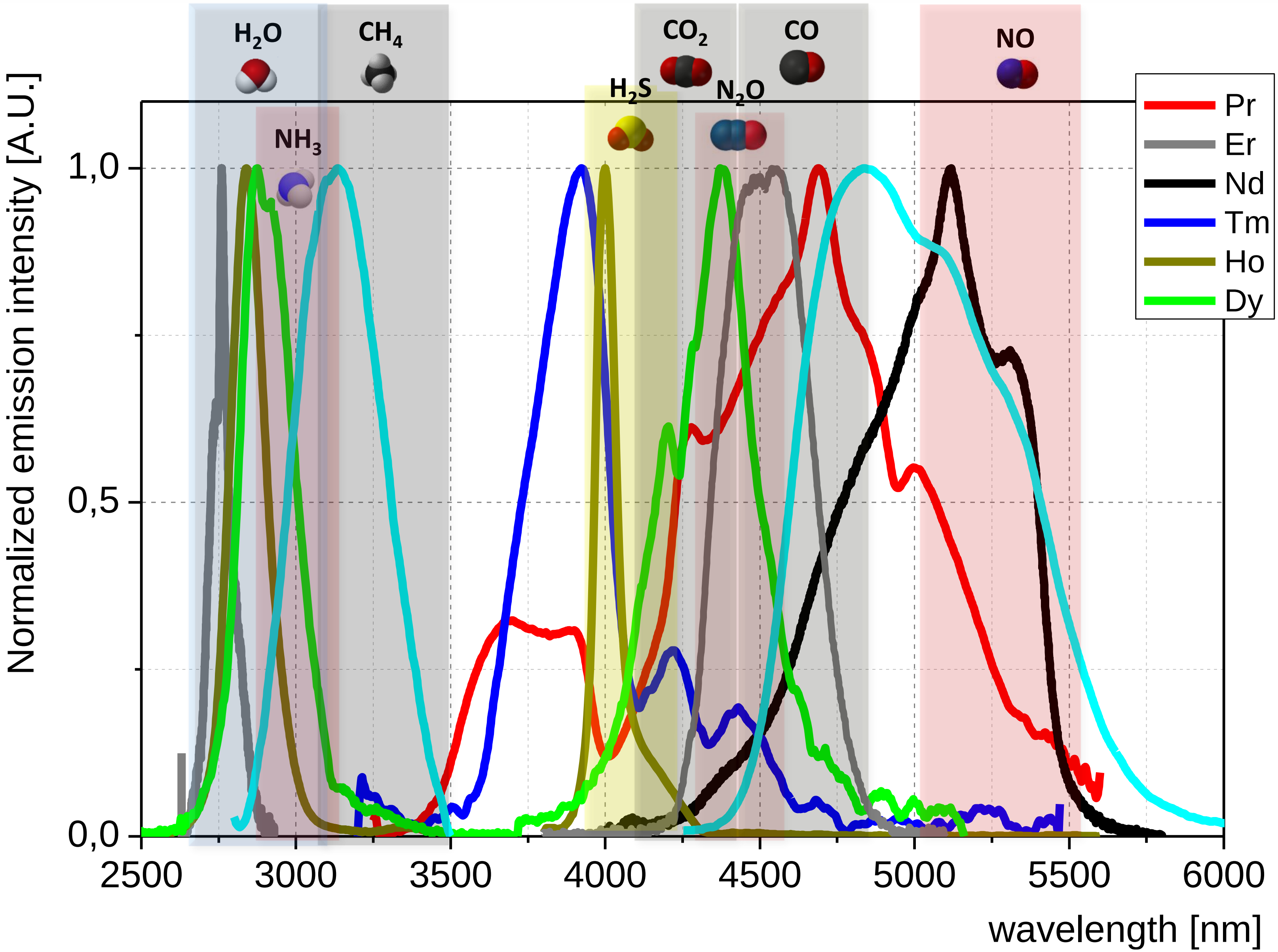

Glass system : $Ga_5Ge_{20}Sb_{10}Se_{(65-x)}Te_x$

Sample	Theoretical composition	EDS experimental composition (± 0.5%)	[Se-H] (ppm) (± 1 %)	ΔT (°C) (± 2 °C)
x = 0	$Ga_5Ge_{20}Sb_{10}Se_{65}$	$Ga_{4.98}Ge_{19.87}Sb_{9.86}Se_{65.29}$	33	> 150
x = 10	$Ga_5Ge_{20}Sb_{10}Se_{45}Te_{10}$	$Ga_{4.98}Ge_{19.86}Sb_{10.08}Se_{55.47}Te_{9.61}$	23	> 150
x = 20	$Ga_5Ge_{20}Sb_{10}Se_{45}Te_{20}$	$Ga_{5.05}Ge_{20.05}Sb_{10.30}Se_{45.41}Te_{19.20}$	20	> 150
x = 25	$Ga_5Ge_{20}Sb_{10}Se_{40}Te_{25}$	$Ga_{5.09}Ge_{20.01}Sb_{10.48}Se_{40.47}Te_{23.95}$	33	134
x = 30	$Ga_5Ge_{20}Sb_{10}Se_{40}Te_{30}$	$Ga_{5.63}Ge_{18.94}Sb_{10.91}Se_{34.87}Te_{29.66}$	16	120
x = 32.5	$Ga_5Ge_{20}Sb_{10}Se_{40}Te_{32.5}$	$Ga_{5.23}Ge_{20.17}Sb_{10.75}Se_{32.48}Te_{31.38}$	13	100
x = 35	$Ga_5Ge_{20}Sb_{10}Se_{40}Te_{35}$	$Ga_{5.00}Ge_{20.19}Sb_{10.70}Se_{30.05}Te_{34.06}$	8	84
x = 37.5	$Ga_5Ge_{20}Sb_{10}Se_{27.5}Te_{37.5}$	$Ga_{5.69}Ge_{19}Sb_{10.08}Se_{28.25}Te_{36.98}$	4	73 vitroceramic
x = 0 : Tb^{3+}	$Ga_5Ge_{20}Sb_{10}Se_{65}$	$Ga_{5.33}Ge_{20.28}Sb_{9.15}Se_{65.24}$	-	> 150
x = 20 :Tb^{3+}	$Ga_5Ge_{20}Sb_{10}Se_{45}Te_{20}$	$Ga_{5.44}Ge_{19.52}Sb_{10.48}Se_{45.48}Te_{19.07}$	-	> 150

% Te increasing :

→ band gap red shifted

→ Tg decreasing and increasing of the density

→ ΔT decreasing