Optical properties of rare-earth doped oxyfluoride glasses

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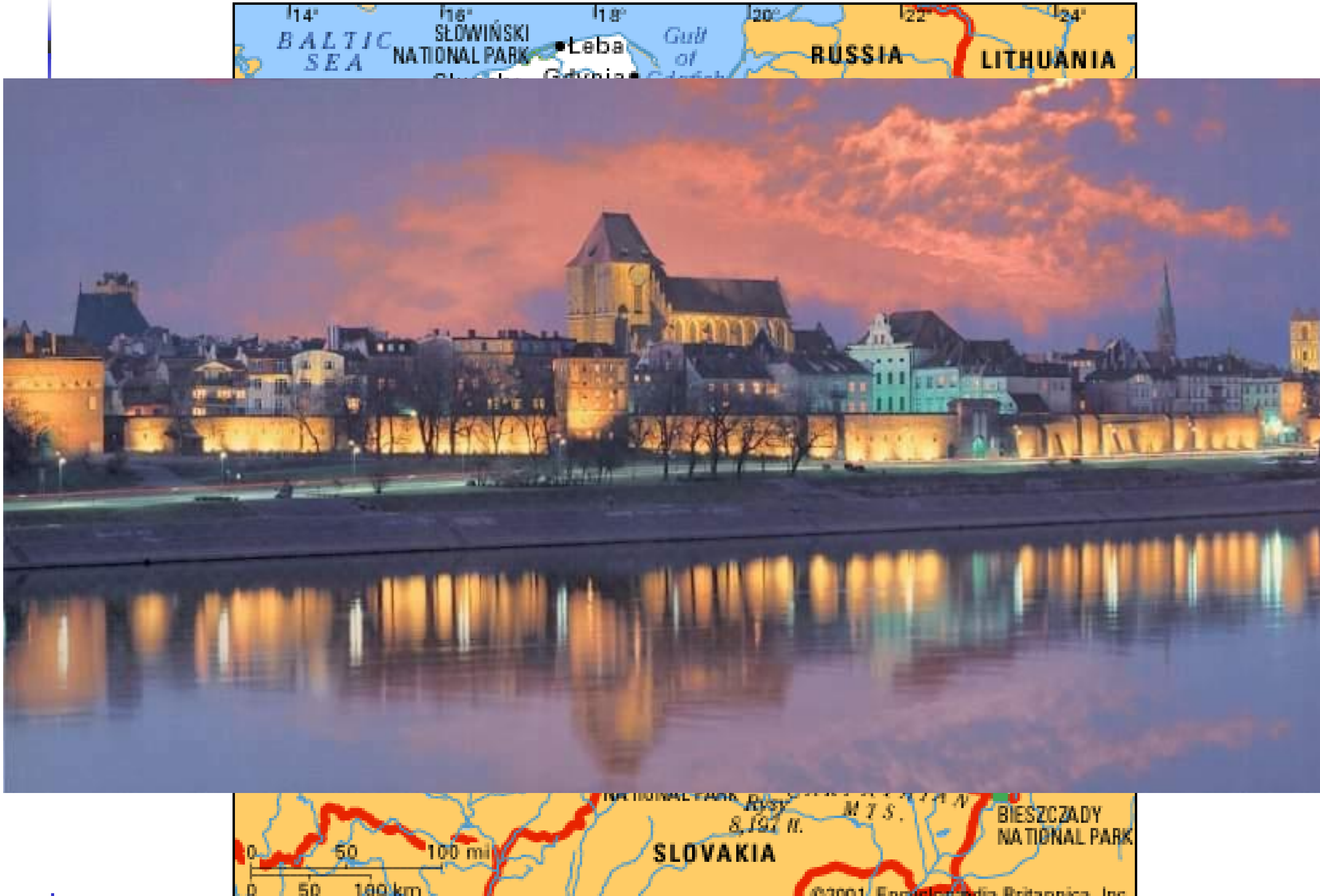
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Outline

- ***Introduction***
- ***Linear optical properties of rare-earth doped oxyfluoride glasses***
  - ***Absorption spectra***
  - ***Refractive index (n) and extinction coefficient (k)***
  - ***Optical energy band gap***
- ***Nonlinear optical properties of rare-earth doped oxyfluoride glasses***
  - ***Third order nonlinear optical susceptibility***
    - ***Nonlinear transmission***
    - ***Degenerate Four Wave Mixing***
- ***Conclusions***

Er^{3+} and Yb^{3+} -doped glasses

- Rare-earth doped optical waveguides are well known for
  - their amplifying and lasing characteristics

but may also be of interest for
  - their intensity-dependent refractive index (n_2).

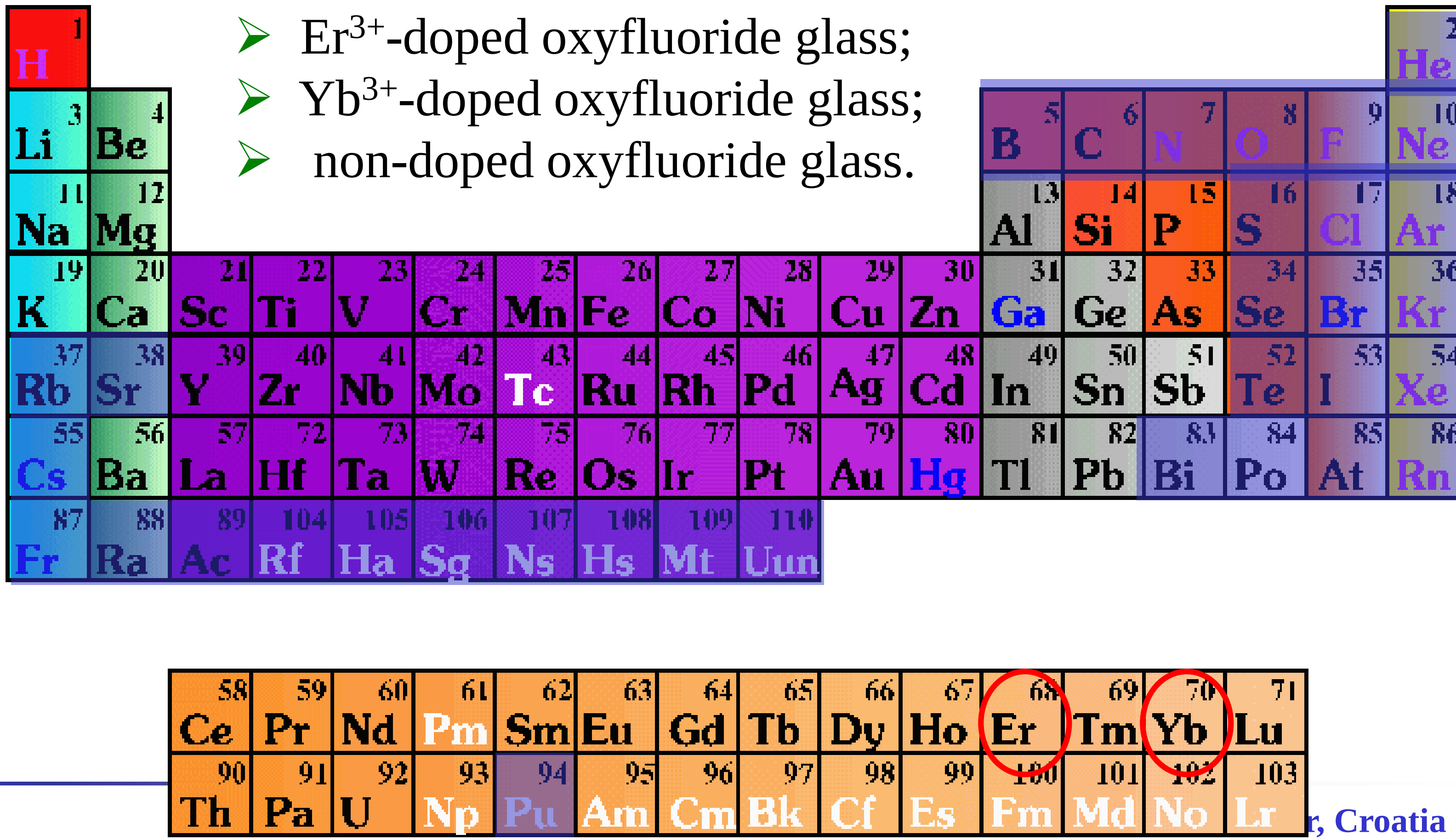
- Precise knowledge of the dispersion of **absorption coefficient**, **linear** and **nonlinear refractive index** of the rare-earth doped oxyfluoride glasses is especially important for:
  - opto-electronic device applications,
  - all-optical switching device,
  - integrated-optics working over a wide wavelength range.

Materials

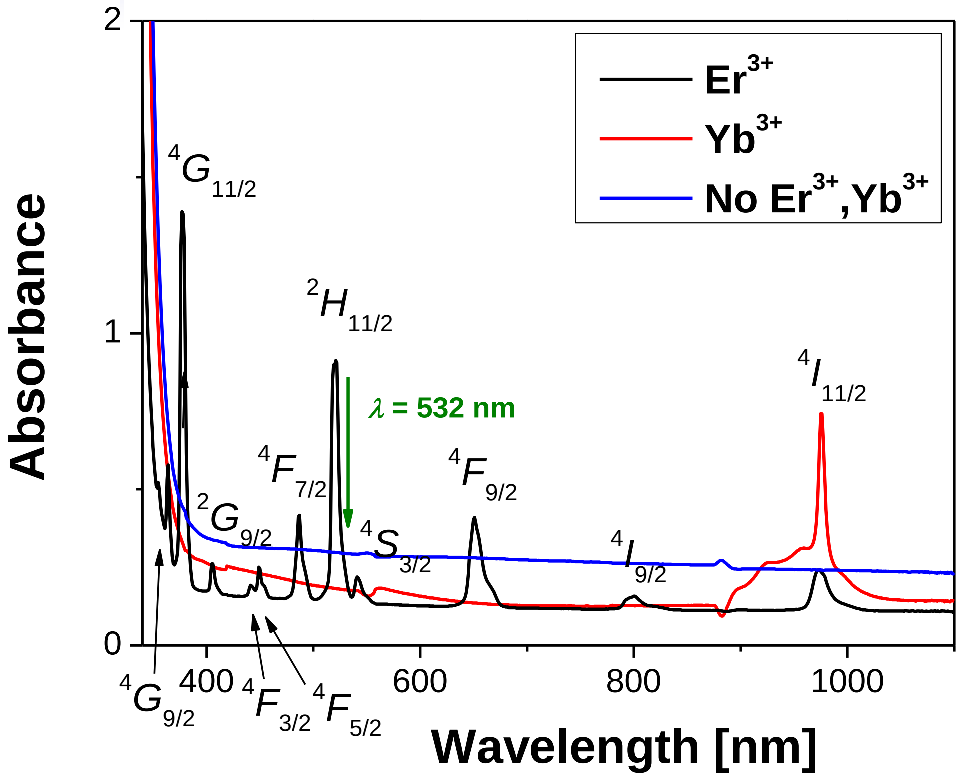
✓ Studied composition:

$32(SiO_2):9(AlO_{1.5}):31.5(CdF_2):18.5(PbF_2):5.5(ZnF_2):3.5(\textbf{RE}\text{-}F_3)$ mol%, where RE: **Er**$^{3+}$ or **Yb**$^{3+}$

- Er^{3+}-doped oxyfluoride glass;
- Yb^{3+}-doped oxyfluoride glass;
- non-doped oxyfluoride glass.

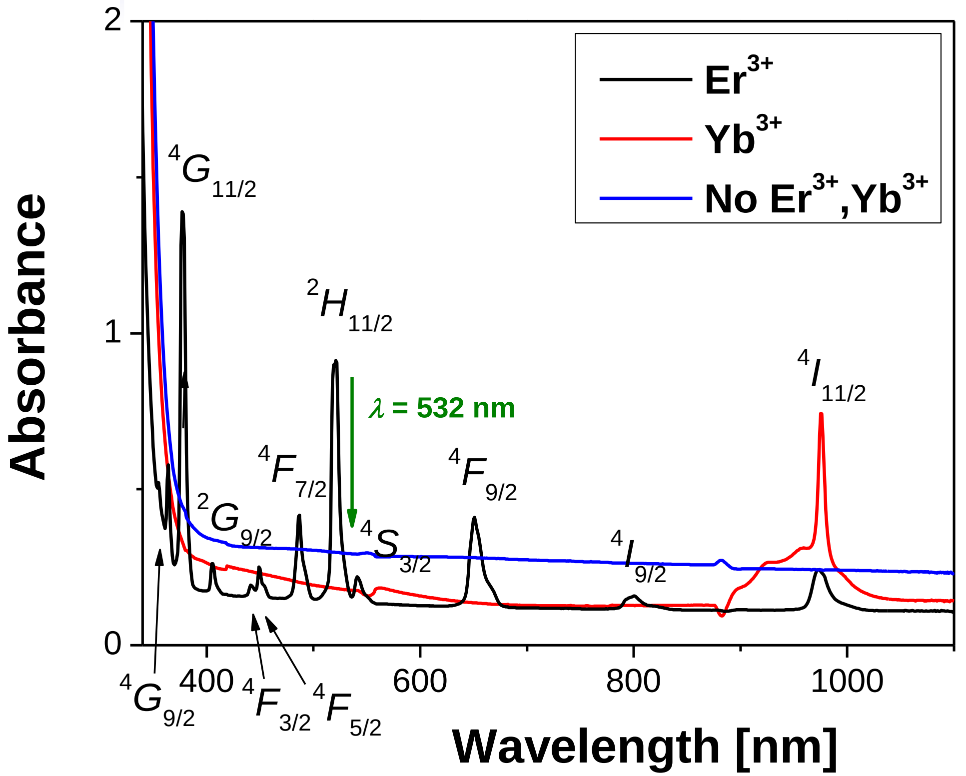


Absorption spectra of Er^{3+} and Yb^{3+}



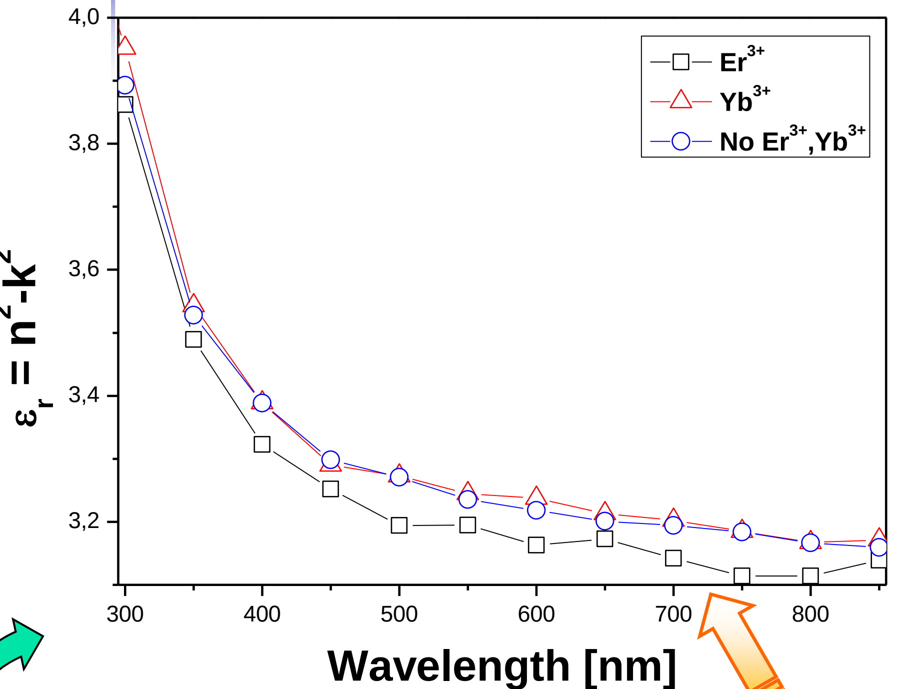
- linear absorption spectra of Er^{3+}-doped glass displayed 11 absorption bands corresponding to Er^{3+} transitions from ground state, $^4I_{15/2}$, to various excited states;
- the absorption bands, $^4I_{15/2} \rightarrow {}^4G_{11/2}$ and $^4I_{15/2} \rightarrow {}^2H_{11/2}$ located at 377 and 521 nm, are most intense and are called hypersensitive transitions (HSTs);
- HSTs are sensitive to small changes of environment around rare-earth ions.

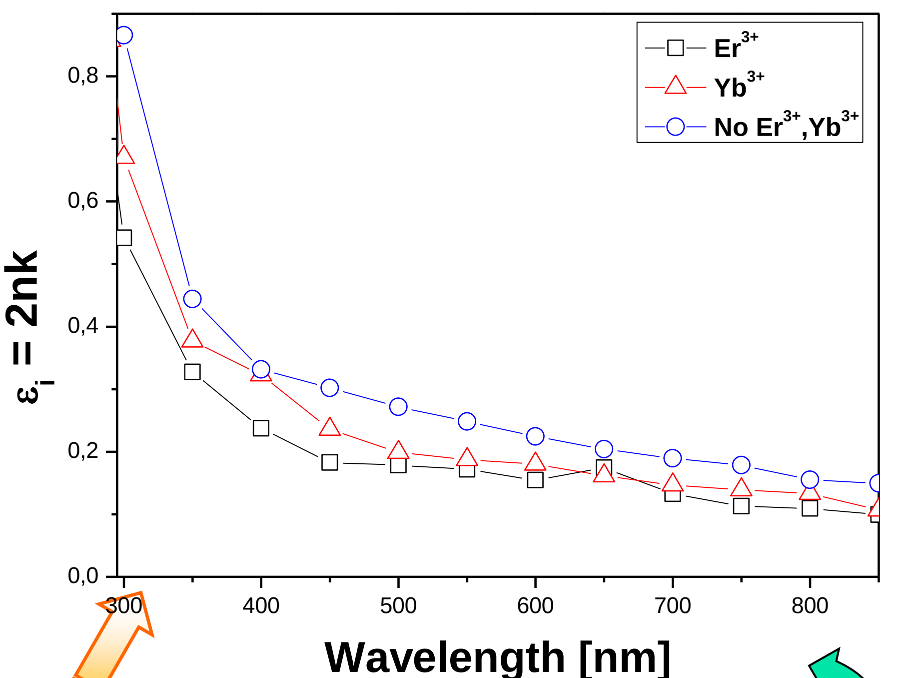
Absorption spectra of Er^{3+} and Yb^{3+}



- ✓ linear absorption spectrum of Er^{3+}-doped glass displayed 11 absorption bands corresponding to Er^{3+} transitions from ground state, $^4I_{15/2}$, to various excited states;
- ✓ in the case of Yb^{3+}-doped glass there are one big band at 975nm and small at 560 nm.

Real (ε_r) and imaginary (ε_i) parts of the dielectric constant



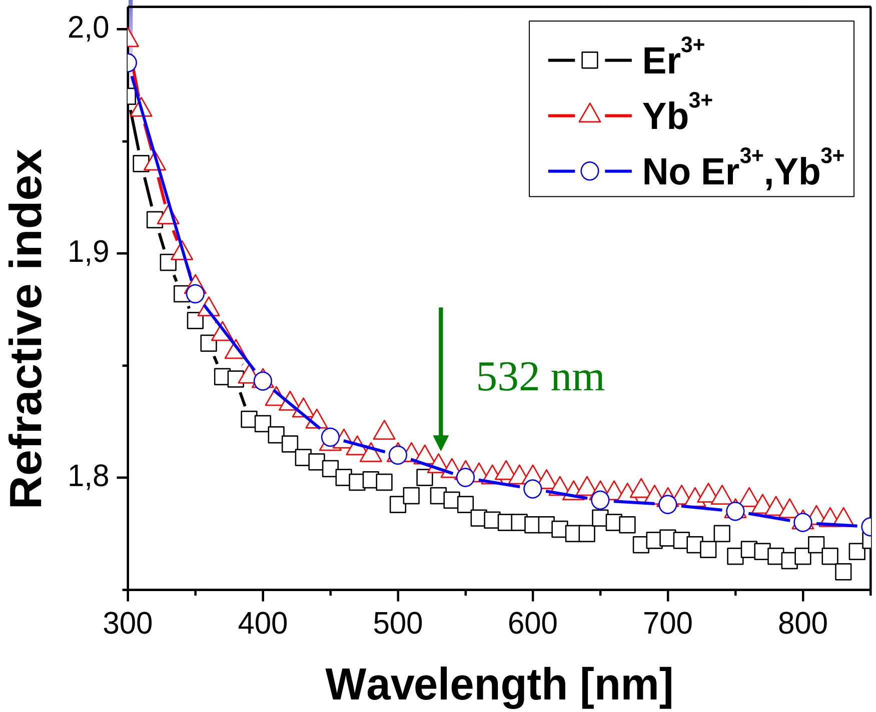


Real part ($\boldsymbol{\varepsilon_r}$) is associated with the term that shows how much it will lower the speed of light in the material

$$\begin{cases} \varepsilon_r = n^2 - k^2 \\ \varepsilon_i = 2nk \end{cases}$$

Imaginary part (ε_i) shows how a material absorbs energy from an electric field

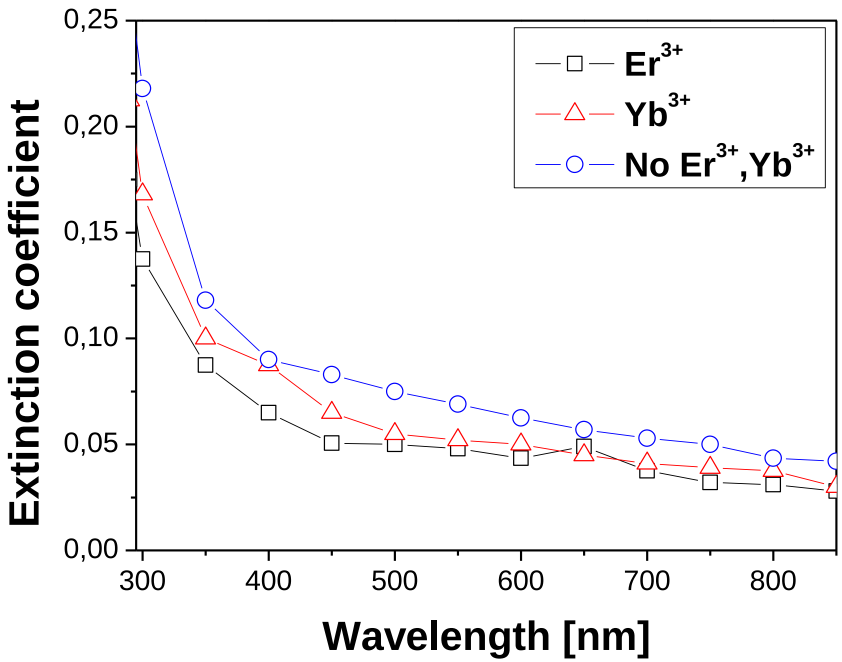
Refractive index of Er^{3+} and Yb^{3+}



Samples	n_{532nm}
Er^{3+}	1.79
Yb^{3+}	1.81
No	1.81

- ✓ far from the absorption bands and beyond the optical band gap, n ↘ with ↗ λ thus displaying normal dispersion;
- ✓ this behaviour can be described using a well-known first order Sellmeier relation.

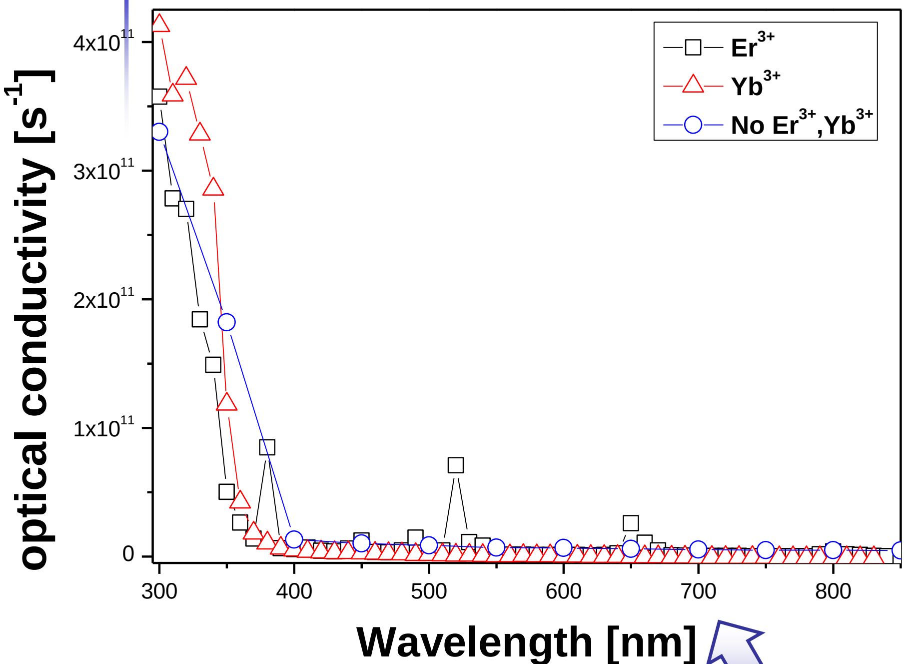
▪ *Extinction coefficient*



✓ *k* is a measure of the fraction of light lost due to reflection, scattering and absorption per unit distance of the participating medium;

✓ *k* ↘ with ↗ λ $\Rightarrow$ the fraction of light lost due to reflection, scattering and absorbance decreases.

Optical conductivity



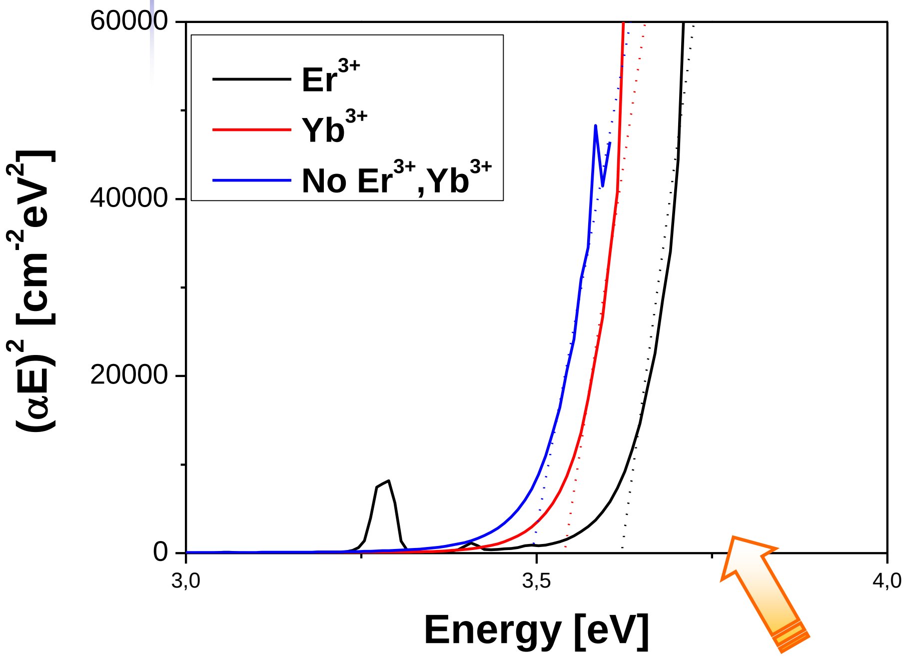
Samples	n	α cm^{-1}	σ s^{-1}
Er^{3+}	1.79	3.12	$1.33 \cdot 10^{10}$
Yb^{3+}	1.81	2.45	$1.06 \cdot 10^{10}$
No	1.81	2.68	$1.16 \cdot 10^{10}$

$$\sigma = \frac{\alpha n c}{4\pi}$$

λ = 532 nm = 2.33 eV

The optical response of the material is most conveniently studied in terms of the optical conductivity.

Optical energy band gap of Er^{3+} and Yb^{3+}



Samples	E_g [eV]
Er^{3+}	3.65
Yb^{3+}	3.55
No	3.50

$$(\alpha h\nu) = B\left(h\nu - E_g^{opt}\right)^n$$

Tauc method

where

B is the band tailing parameter,

n = 1/2 for a direct allowed transition,

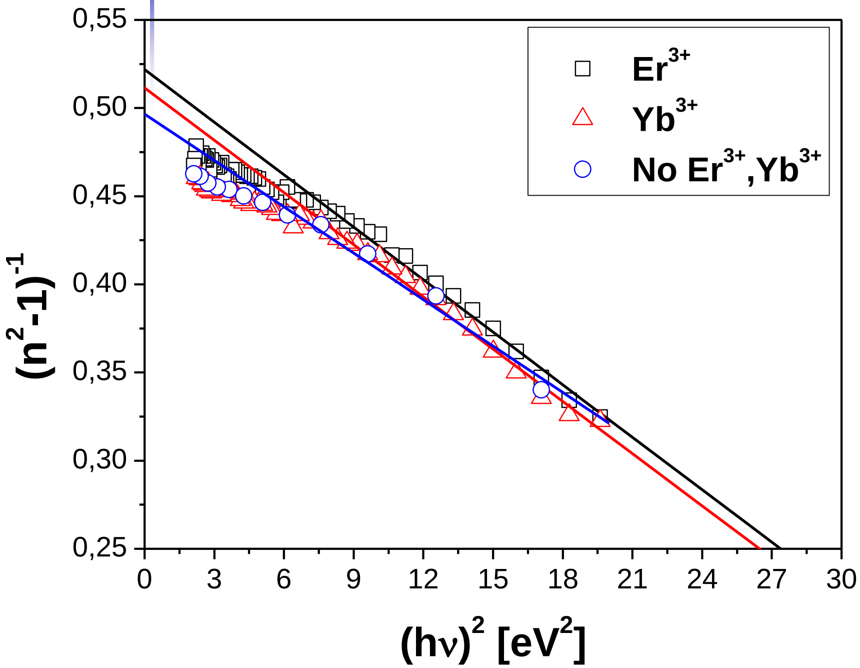
n = 2 for an indirect allowed transition,

n = 3/2 for a direct forbidden transition,

n = 3 for an indirect forbidden transition.

Optical energy band gap

single-effective oscillator model - **Wemple and DiDomenico**



$$n^2 - 1 = \frac{E_d E_0}{E_0^2 - (h\nu)^2}$$

E_0 is the single oscillator energy (the average energy gap),

E_d is the dispersion energy, which is a measure of the average strength of the interband optical transitions.

Samples	E_0 eV	E_d eV	$E_{g\,(W\text{-}D)}$ eV
Er^{3+}	7.25	13.89	3.63
Yb^{3+}	7.19	14.07	3.60
No	7.05	16.49	3.53

The values of E_0 and E_d can be directly determined from the slope $(E_0E_d)^{-1}$ and the intercept on the vertical axis (E_0/E_d).

$$E_g = E_0/2$$

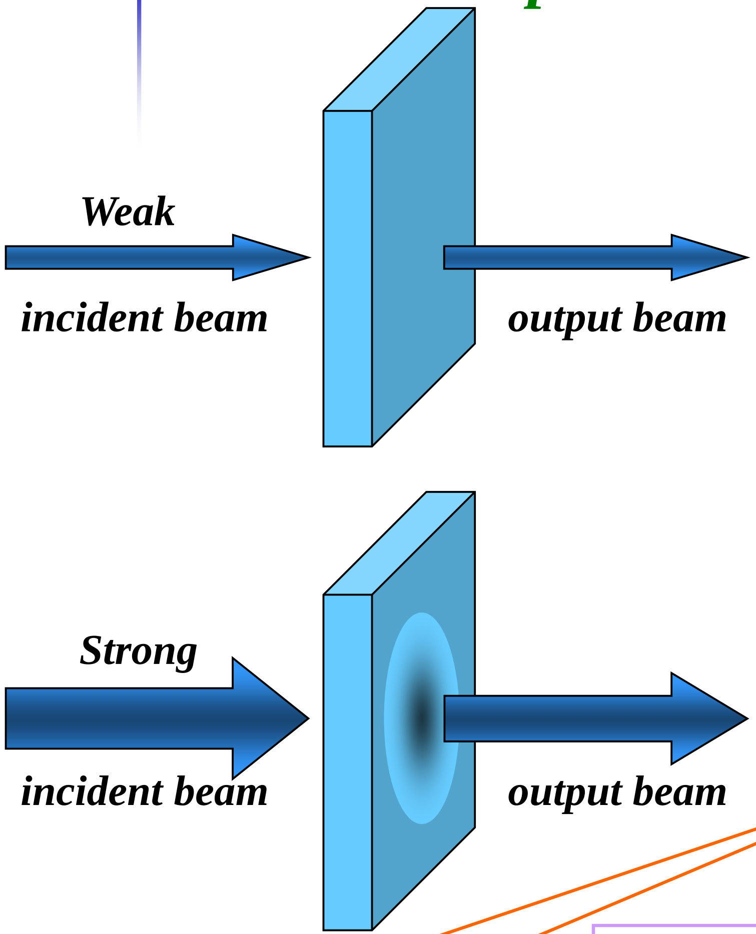
Optical energy band gap

Samples	$E_{g\,(W\text{-}D)}$ [eV]	$E_{g\,(T)}$ [eV]
Er^{3+}	**3.63**	**3.65**
Yb^{3+}	**3.60**	**3.55**
No	**3.53**	**3.50**

Wemple and DiDomenico method

Tauc method

Nonlinear polarization



$$\vec{P} = \chi^{<1>}\vec{E}$$

$$\vec{P} = \vec{P}^{L} + \vec{P}^{NL}$$

$$\vec{P} = \chi^{<1>}\vec{E} + \overbrace{\chi^{<2>}\vec{E}\vec{E} + \chi^{<3>}\vec{E}\vec{E}\vec{E} + \ldots}$$

- linear effects;
- second order nonlinear optical effects;
- third order nonlinear optical effects;

- ***Third order nonlinear optical susceptibility***

$$\chi^{<3>} = \chi_R^{<3>} + i\chi_I^{<3>}$$

related to the two photon absorption;

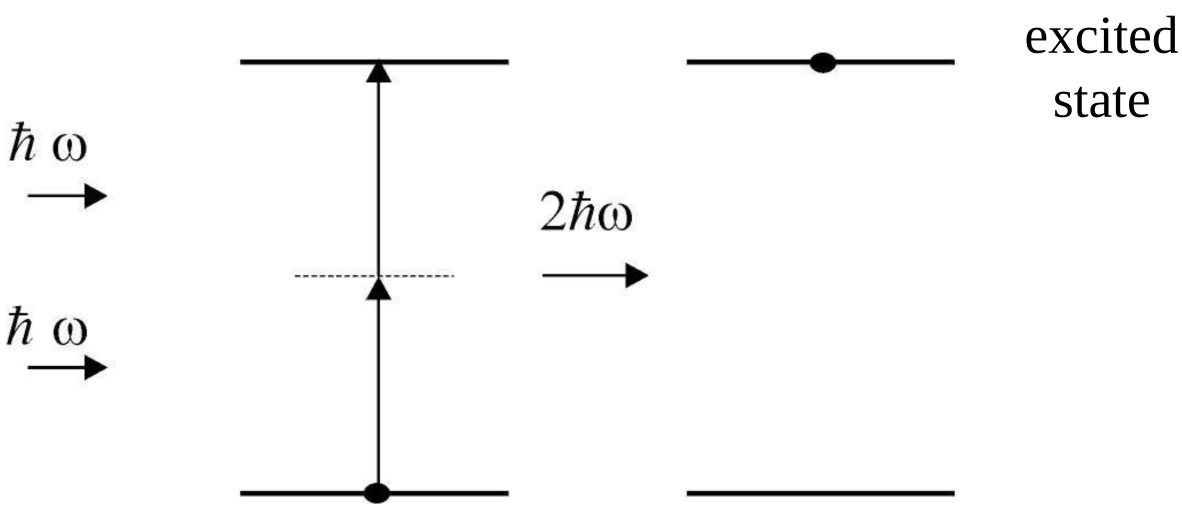
related to
the nonlinear refractive index changes;

$$\chi_I^{<3>} = \frac{n^2 c\,\lambda}{48\pi^3}\beta$$

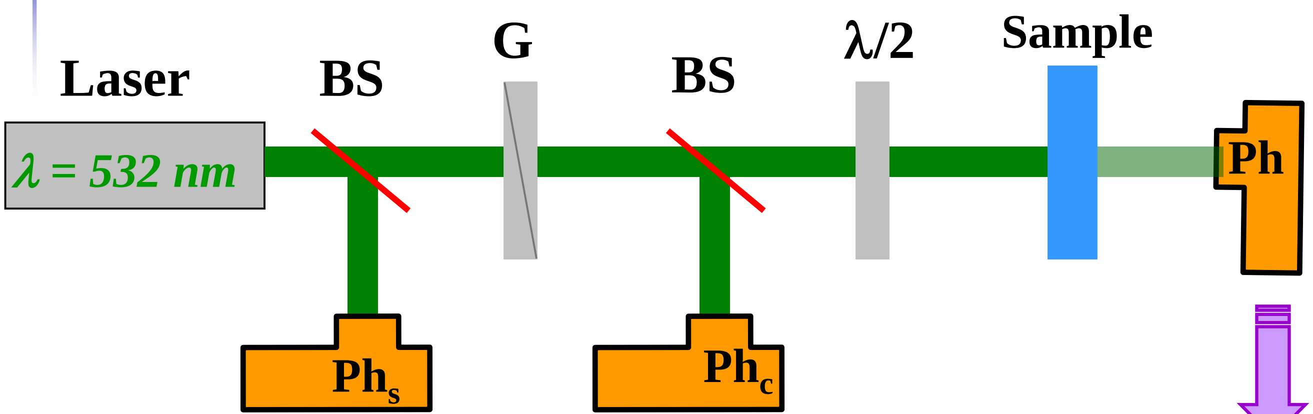
$$\chi_R^{<3>} = \frac{n^2 c}{12\pi^2} n_2$$

Two-photon absorption is the simultaneous absorption of two photons in order to excite the electron from a ground state to an excited state.

$$E_g/2 < h\nu < E_g$$



Two Photon Absorption (nonlinear transmission)

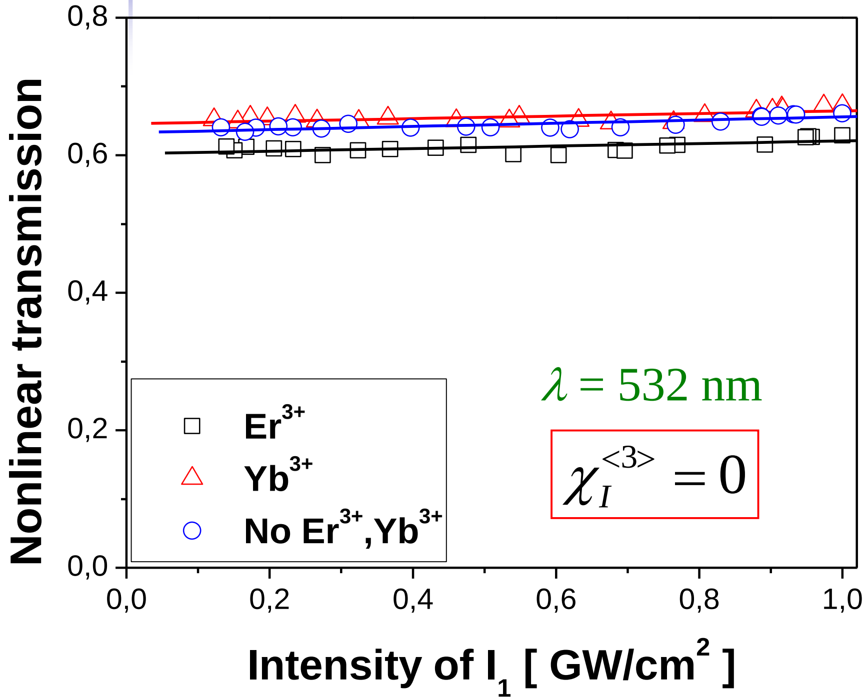


$$\frac{\partial I_1}{\partial z} = -(\alpha + \beta I_1) I_1$$

$$T = \frac{I(L)}{I(0)} = \frac{\alpha(1-R)^2 \exp(-\alpha L)}{\alpha + \beta I(0)(1-R)(1-\exp(-\alpha L))}$$

$$\beta = \frac{48\pi^3}{n^2 c \lambda} \chi_I^{<3>}$$

Nonlinear transmission of Er^{3+} and Yb^{3+}



Samples	α [cm^{-1}]
Er^{3+}	3.12
Yb^{3+}	2.45
No	2.68

$$R = \frac{(n-1)^2}{(n+1)^2}$$

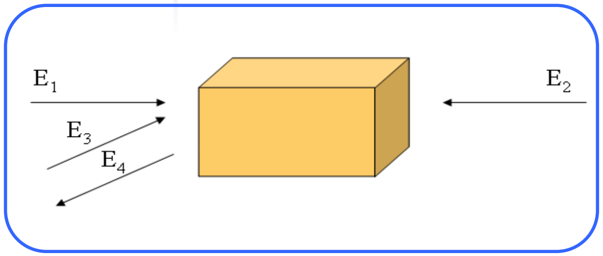
$$T = \frac{I(L)}{I(0)} = (1-R)^2 \exp(-\alpha L)$$

$$T = \frac{I(L)}{I(0)} = \frac{\alpha (1-R)^2 \exp(-\alpha L)}{\alpha + \beta I(0)(1-R)(1-\exp(-\alpha L))}$$

$$\chi_I^{<3>} = \frac{n^2 c \lambda}{48\pi^3} \beta$$

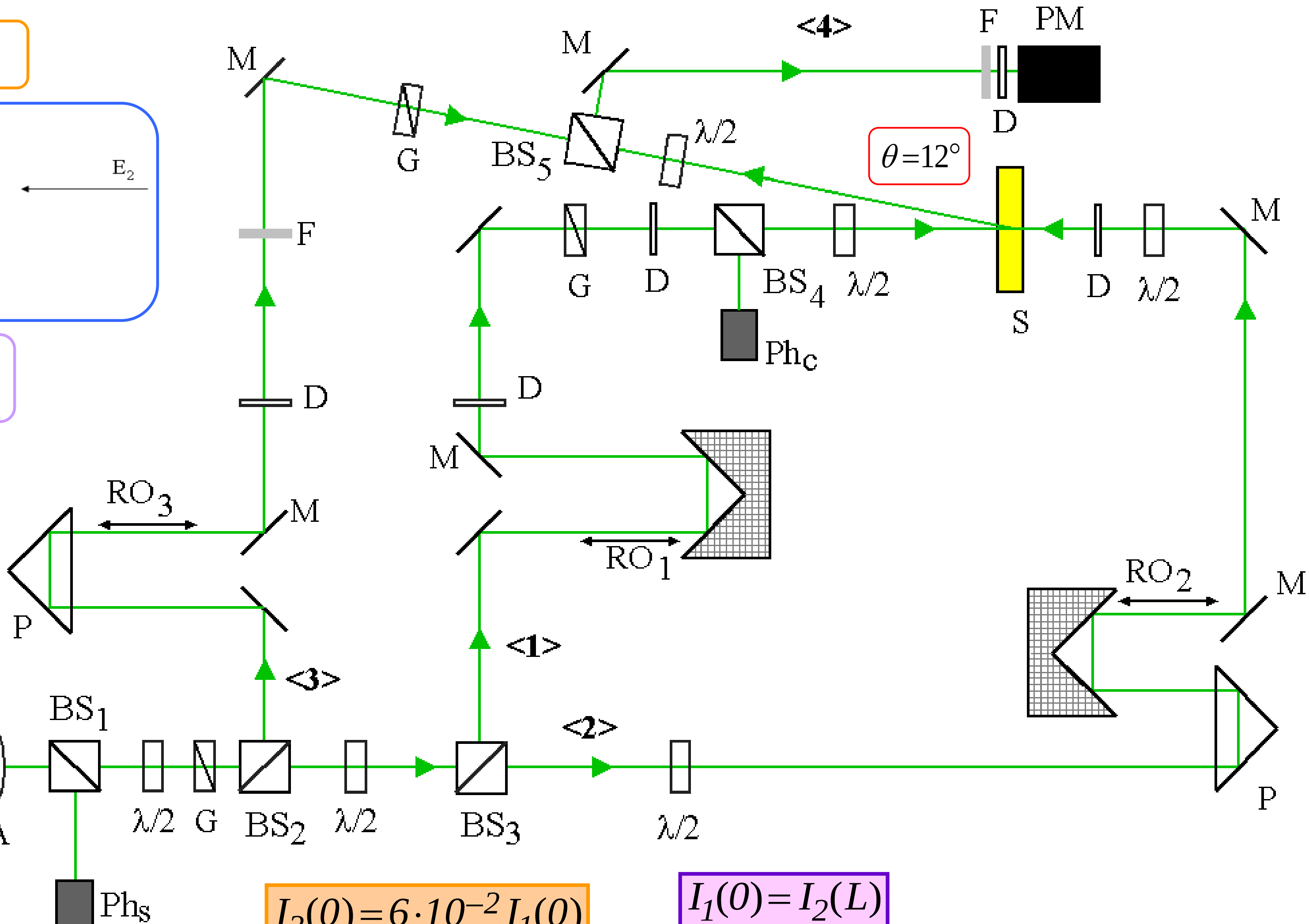
Degenerate Four Wave Mixing method

$$\omega_4 = \omega - \omega + \omega$$



$$\vec{k}_1 = -\vec{k}_2, \quad \vec{k}_4 = -\vec{k}_3$$

30ps
1 - 10 Hz
532 nm

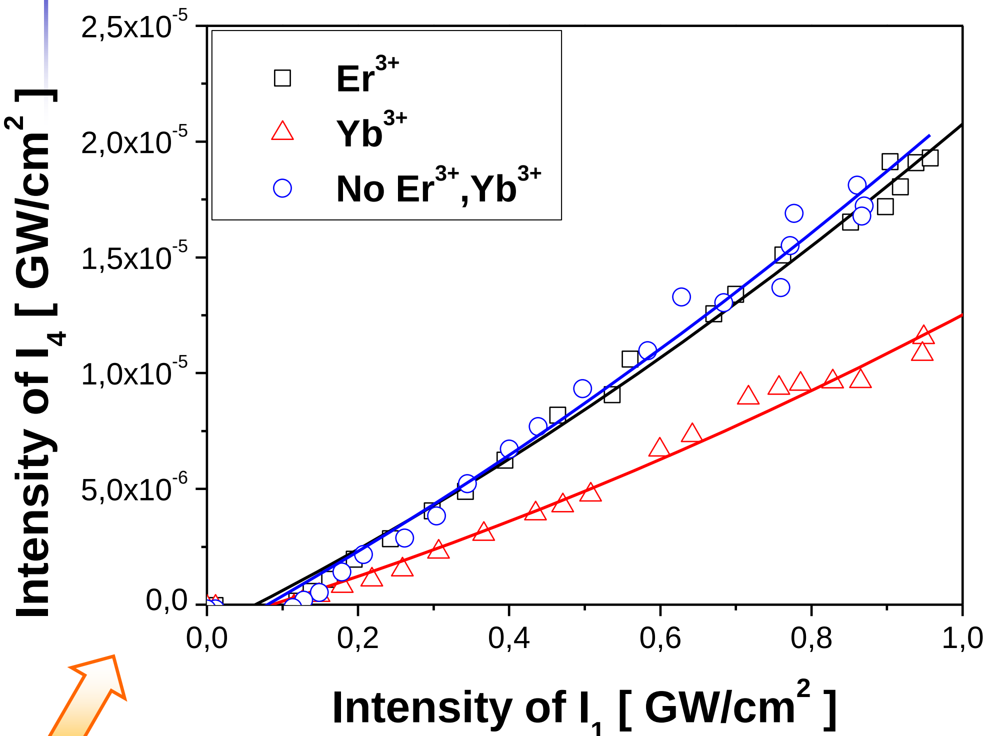


$$I_3(0) = 6\cdot 10^{-2} I_1(0)$$

$$I_1(0) = I_2(L)$$

DFWM_2.swf

Degenerate Four Wave Mixing



Samples	$\chi^{<3>}$ [esu]
Er^{3+}	$2.78\cdot10^{-12}$
Yb^{3+}	$1.97\cdot10^{-12}$
No	$2.67\cdot10^{-12}$

$$R=\frac{I_4(0)}{I_3(0)}=\left(\frac{48\pi^3}{n^2c\lambda}\chi^{<3>}\right)^2\frac{I_1(0)I_2(0)\exp(-\alpha L)}{\left[p\coth(pL)+\frac{\alpha}{2}\right]^2}$$

$$I_3(0)=6\cdot10^{-2}I_1(0)$$

$$p^2=\frac{\alpha^2}{4}-\left(\frac{48\pi^3}{n^2c\lambda}\chi^{<3>}\right)^2I_1(0)I_2(0)$$

Third order nonlinear optical susceptibility $\chi^{<3>}$

λ = 532 nm = 2.33 eV

Samples	L [mm]	n	α [cm^{-1}]	$\chi^{<3>} \cdot 10^{12}$ [esu]	$n_2 \cdot 10^{14}$ [cm^2 W^{-1}]	$F \cdot 10^{13}$ [esu cm]
Er^{3+}	1.089	1.79	3.12	2.78	3.43	8.91
Yb^{3+}	1.083	1.81	2.45	1.97	2.39	8.04
No	1.068	1.81	2.68	2.67	3.23	9.96

$$n_2 = \frac{12\pi^2}{n^2 c}\chi^{<3>}$$

$$F = \frac{\chi^{<3>}}{\alpha}$$

$$\chi_{SI}^{<3>}\left[\frac{m^2}{V^2}\right] = 1.4 \cdot 10^{-8}\,\chi_{CGS}^{<3>}[esu]$$

Conclusions

- Linear and nonlinear optical properties of Er^{3+} and Yb^{3+} doped oxyfluoride glasses were determined;

- It was found that $\chi^{<3>}$, α, σ and n_2 of Er^{3+}-doped oxyfluoride glass are higher than for Yb^{3+}-doped oxyfluoride glass at 532 nm.

- It was found that $E_g(Er^{3+}) > E_g(Yb^{3+}) > E_g(No)$.

- It should be also noted that the values of E_g calculated using the Wemple-DiDomenico method are in good agreement with those determined using the method of Tauc.

Looking for collaboration

Ellipsometer V-VASE (J.A.Woollam Co.) + FTIR device Sendira (Sentech GmbH):

- ✓ three angles of incidence: 65°, 70° and 75°,
- ✓ MIR–vis–UV spectral range: **193 nm** (6.5 eV) – **20 000 nm** (0.06 eV).

Luminescence measurements:

- ✓ UV-vis spectral range: 200 nm – 2000 nm,
- ✓ temperature range: 10 K - 300 K using 325 nm (He-Cd laser - 20 mW).

FTIR measurements: 500 cm^{-1} – 4000 cm^{-1}.

X-Ray Diffraction (XRD).

Atomic Force Microscopy (AFM).

- ***Looking for collaboration***

Thermal properties (such as diffusivities, effectivities and conductivities) using photopyroelectric and infrared radiometry techniques.

Raman Perkin-Elmer Raman-Micro 200 system:

✓ spectral range of 100 - 3200 cm^{-1}.

The Raman scattering was excited using the near-infrared laser operating at 785 nm, collected in the backscattering geometry and detected using a CCD.


THANK YOU