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#### Winter College on Fibre Optics, Fibre Lasers and Sensors

12 - 23 February 2007

#### **Spectroscopy of Rare Earth Doped Glasses**

(part I)

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## Spectroscopy of Rare Earth Doped Glasses



The Abdus Salam International Centre for Theoretical Physics



International Atomic Energy Agency

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## **Spectroscopy of Rare Earth Doped Glasses**

## Lessons Plan

Part I - Basics

- I.1 Rare Earth Elements
- I.2 Glass Matrices
- I.3 Rare Earth Doped Glasses (REDG)
- I.4 Theoretical Aspects
- I.5 Spectroscopic Techniques for Optical Assessment

#### Literature



## **Spectroscopy of Rare Earth Doped Glasses**

## Lessons Plan

Part II – Upconversion spectroscopy and Applications of REDG

II.1 Up-conversion Spectroscopy II.2 REDG Ceramics

Applications of REDG II.3 REDG for Lasers II.4 REDG for Fiber Lasers and Amplifiers II.5 REDG Planar and Channel Waveguides II.6 REDG Microbarcodes Literature



## **Spectroscopy of Rare Earth Doped Glasses**

## Lessons Plan

Part III – More Applications and Other Recent Advances in RED Materials

III.1 REDG containing nanoparticles
III.2 REDG for Sensors
III.3 Rare Earth Doped Photonic Materials (An overview from Optical Materials special issue vol 28, 575-893 (2006))

#### Literature



## Spectroscopy of Rare Earth Doped Lecture I

#### Part I - Basics

- I.1 Rare Earth Elements
- I.2 Glass Matrices
- I.3 Rare Earth Doped Glasses (REDG)
- I.4 Theoretical Aspects
- I.5 Spectroscopic Techniques for Optical Assessment

Literature





#### A little bit of history ... the NOT SO RARE RARE EARTH ELEMENTS

....found all over (earth, moon, some stars.....);

....more abundant than Hg and I;

....first one was found in 1794 (Yttrium);

....last one was found in 1945 (Promethium);

....applications: from jewellery to nuclear industry, naturally including PHOTONICS APPLICATIONS.



#### **Rare Earth Elements On The Net**

<u>General Information</u> <u>History</u> <u>Properties</u> <u>Uses</u> <u>Links</u>

http://osoon.ut.ee/~hahha/re/index.html



➢ IN OPTICS, REE were first exploited in 1906, by Becquerel, who identified line narrowing at low temperatures (~85K);

Subsequent years flourished with theoretical work, driven by the development of quantum mechanics, culminating with the work by Dieke and Crosswhite (<u>Appl. Opt. 2, 602(1963))</u>, which is the basis for spectroscopy of REE.





➢At the end of the 1960's, energy transfer and anti-Stokes emission became one of the important ways to study REE in crystals and glasses;

Frequency up-conversion is the experimental method to study emission from frequencies higher than the excitation frequency.



ELEMENTS

REE can be found as divalent, trivalent or tetravalent.

For optics, the <u>trivalent lanthanides</u> are the revelant ions, whose electronics distribution is as follows:

 $[Xe] 4f^{N} 5s^{2} 5p^{6};$ 

L La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

•La and Lu – closed outer shell (N= 0 and 14)

•All the others – outer shell 4f partially filled

(Those REE are the focus of our attention!)

I.1 RARE EARTH ELEMENTS

4f electrons are screened by the other outer-shell configurations ( $5s^2$ ,  $5p^6$ ), because the wavefunction radius is smaller for 4f than for 5s and 5p.



The word **lanthanide** has a Greek origin (" $\lambda \alpha \nu \theta \alpha \nu \epsilon \iota \nu$ ") which means "to lie hidden".



Important consequences and implications:

- 1. Electronic states of 4f weakly affected by the host;
- Energy spectrum is practically independent of host (which means they are determined by 4f);
- In crystals, absorption and emission spectra very narrow (~0.1nm); much broader in glasses;
- 4. The hamiltonian, which will be used to calculate the energy levels, can be written as the sum of the free ion + a perturbative term arising from the host:



The free ion hamiltonian can be given by:

 $H_0 > H_c > H_{so}$  $H_{l} = -\frac{\hbar^{2}}{2m} \sum_{i=1}^{N_{T}} \vec{\nabla}_{i}^{2} - \sum_{i=1}^{N_{T}} \frac{Z^{*} \cdot e^{2}}{r_{i}} + \sum_{i < j}^{N} \frac{e^{2}}{r_{ij}} + \sum_{i=1}^{N} \xi(r_{i}) \vec{S}_{i} \cdot \vec{L}_{i},$ (1.2)Spin-orbit interaction **Kinetic energy Coulombian repulsion** Effective Coulombian potential

 $\xi$ (r) is the spin-orbit coupling parameter N<sub>t</sub> total number of eletrons ; N = 1 to 13

RARF FARTH

ELEMENTS



Last two terms are responsible to rise the degeneracy

Spin-orbit interaction:

Arises from atom magnetic field + spin magnetic dipole



Generates a total angular momentum  $\mathbf{J} = \mathbf{L} + \mathbf{S}$ 

increases with atomic number

On the other hand, the Coulombian interaction decreases as Z increases (since the atomic radius increases, thus increasing the distance between electrons).



I.1 RARE EARTH

**ELEMENTS** 

http://olla.ichf.edu.pl/lect/SS2005/Buenzli\_lecture1.pdf



## Energy levels follows spectroscopic notation:

The characteristic of a quantum state is specified by the notation,

<sup>2S+1</sup>Letter<sub>J</sub>

- S = Spin angular momentum
- J = Total angular momentum

Prescription for the "Letter" symbol

L	0	1	2	3	4	5	6	etc.
Letter	S	Ρ	D	F	G	Н	I	etc.



## E.g.: Ground State of Neodymium

Spectroscopic Notation =  $^{4}$  I  $_{9/2}$ 

Degeneracy = 2J+1 = 10

There are 10 different wave functions describing this state.



### The optically interesting REE

Element	Symbol	Atomic no.	Atomic wt.	Electronic state	Fundamental State	Ionic radius (Å)
Cerium	Ce	58	140,12	$[Xe]4f^15s^25p^6$	${}^{2}F_{5/2}$	1.11
Praseodymium	Pr	59	140,98	$[Xe]4f^25s^25p^6$	$^{3}H_{4}$	1.09
Neodymium	Nd	60	144,24	$[Xe]4f^35s^25p^6$	<sup>4</sup> I <sub>9/2</sub>	1.08
Promethium	Pm	61	145	$[Xe]4f^45s^25p^6$	${}^{5}I_{4}$	1.06
Samarium	Sm	62	150,4	$[Xe]4f^55s^25p^6$	<sup>6</sup> H <sub>5/2</sub>	1.04
Europium	Eu	63	151,96	$[Xe]4f^65s^25p^6$	$^{7}F_{0}$	1.03
Gadolinium	Gd	64	157,25	$[Xe]4f^75s^25p^6$	<sup>8</sup> S <sub>7/2</sub>	1.02
Terbium	Tb	65	158,93	$[Xe]4f^85s^25p^6$	${}^{7}F_{6}$	1.00
Dysprosium	Dy	66	162,5	$[Xe]4f^{9}5s^{2}5p^{6}$	<sup>6</sup> H <sub>15/2</sub>	0.99
Holmium	Но	67	164,93	$[Xe]4f^{10}5s^25p^6$	<sup>5</sup> I <sub>8</sub>	0.97
Erbium	Er	68	167,26	$[Xe]4f^{11}5s^{2}5p^{6}$	${}^{4}I_{15/2}$	0.96
Thulium	Tm	69	168,93	$[Xe]4f^{12}5s^{2}5p^{6}$	${}^{3}H_{6}$	0.95
Ytterbium	Yb	70	173,04	$[Xe]4f^{13}5s^{2}5p^{6}$	${}^{2}F_{7/2}$	0.94











# Glasses

- Amorphous solids
- No crystal structure
- No long-range order
- Resemble "frozen liquids"





# • Re

# Forming a Glass

## Requirements

- Material must have high viscosity at melting point
- Material must have difficulty nucleating crystal
- Procedure
  - Melt material to eliminate crystal structure
  - Cool material quickly through melting temperature
  - Form supercooled liquid
  - Cool until solid











#### **Glass structure**

Bond type	Examples			
Covalent	Oxides (Silicates etc.), chalchegonides, organic high polymers			
Ionic	Halides, Nitrates etc.			
Hydrated ionic	Aqueous salt solutions			
Molecular	Organic liquids			
Metallic	Splat-cooled alloys			

#### KJM3100 V2006



#### Some classes of glasses

OXIDES	METTALIC	$ZnCl_2$
$SiO_2$	Fe - Ni	$BeF_2$
$\text{GeO}_2$	P - B	$ZrF_4$
BeO <sub>3</sub>	Cu - Zn	AlF <sub>3</sub>
$P2O_5$		InF <sub>3</sub>
		GaF <sub>3</sub>

CHALCOGENIDES  $Ga_2S_3 - La_2S_3$   $As_2S_3, As_2Se_3$ Ge - Se

ORGANICS polymers **HALIDES** 



SiO<sub>2</sub>

 $B_2O_3$ 

GeO<sub>2</sub>

 $P_2O_5$ 



15

VA

Ν

Nitrogen

14.0057 16<sup>1</sup>25<sup>1</sup>2p<sup>2</sup>

Р

tosphorus

30.97376

No]31<sup>2</sup>3

0.485

As

Acsenic

74,92160

[Ar]3d<sup>10</sup>4a<sup>2</sup>4p<sup>2</sup>

9,7886

51 'S

Sb

Antimony

121,760

[Kr]4d<sup>10</sup>5s<sup>2</sup>5p

8.6084

83 'S

Bi

Bismuth

208.98038

Haltp

7.2855

°Ρ.

33

"S"...

<sup>3</sup>P.

16

VIA

0

Oxygen 15.9994

10<sup>2</sup>20<sup>2</sup>20<sup>1</sup>

13.6181

s

Sulfur

32.065

[Na]30<sup>2</sup>3p<sup>4</sup>

10.3500

Se

Selenium

78.96

[Ar]]3d<sup>10</sup>4a<sup>2</sup>4p

9.7524

Те

Tellurium

127.60

Kr]4d<sup>10</sup>5s<sup>2</sup>5p

9.0096

Po

Polonium

(209)

[Hg]6p<sup>4</sup> 8.414

<sup>3</sup>P

84

<sup>3</sup>P

<sup>3</sup>P

16 <sup>3</sup>P

34

52





# Quartz

- Quartz is silicon dioxide (silica)
  - Is an excellent network former
    - Slow cooling forms regular network
    - Fast cooling forms irregular network
- High viscosity at melting point
- However, nucleates crystals easily
- Melting point of Quartz is very high





I.2 GLASS MATRICES  $\bullet$ 







In silicate glasses:

B<sup>3+</sup>, Ge<sup>4+</sup>, Al<sup>3+</sup>, Be<sup>2+</sup>, P<sup>5+</sup>: Network formers Triangular or tetragonal coordination

K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>: Network modifiers Large cations, reduces crystallization tendencies



Name	Typical composition	Important property	Principal uses	
Soda glass	15 % Na2O: 85 % SiO2	Cheap	Window glazing	
Soda-lime glass	72 % SiO <sub>2</sub> : 14 % Na <sub>2</sub> O: 14 % CaO	Cheap	Window glazing	
Borosilicate (Pyrex <sup>®</sup> )	80 % SiO <sub>2</sub> : 13 % B <sub>2</sub> O <sub>3</sub> : 7 % Na <sub>2</sub> O	Low coefficient of expansion	Cooking ware, laboratory ware	
Crown glass	9% Na <sub>2</sub> O: 11% K <sub>2</sub> O: 5% CaO: 75% SiO <sub>2</sub>	Low refractive index	Optical components	
Flint glass	45 % PbO: 55 % SiO2	High refractive index	Optical components, 'crystal' glass	
Lead glass	Up to 80 % PbO: SiO2	Absorbs radiation	Radiation shielding	
Silica	100 % SiO2	Very low coefficient of thermal expansion	Optical components, laboratory ware, optical fibre	

#### KJM3100 V2006


## Soda-Lime-Silica Glass

- Adding sodium oxide (soda) lowers melting point
- Adding calcium oxide (lime) makes it insoluble
- Sodium and calcium ions terminate the network and soften the glass
- Soda-lime-silica glass is common glass





## **Borosilicate Glass**

- Soda-lime-silica glass expands much when heated
  - Breaks easily during heating or cooling
- Boron-oxide-silica glass expands less
  - Tolerates heating or cooling reasonably well
- Pyrex and Kimax are borosilicate glasses

### Methods of preparation

I.2 GLASS **MATRICES**  Vapour or Plasma



- •Aerosol

•Cooling •Dissolution •Sol-gel

Liquid

## Solid

- •Decomposition
- •Amorphization by irradiation
- •Amorphization by grinding
- Amorphization by wave

## Typical glass preparation



I.2 GLASS MATRICES



### **GLASS PREPARATION**









Several Important glass hosts Silicates Phosphates Borates Germanates Tellurites

Fluorozirconate

Chalcogenides

**Fluoroindates** 

Sulfides

Antimony

Tungstates

Preparation methods

Transmission window

Phonon Energy

**Phonons** are a <u>quantum mechanical</u> version of a special type of <u>vibrational</u> motion, known as <u>normal</u> <u>modes</u> in <u>classical mechanics</u>, in which each part of a lattice oscillates with the same <u>frequency</u>.

### A phonon is the quanta of energy of such vibrations.

http://dept.kent.edu/projects/ksuviz/leeviz/phonon/phonon.html

Glass	Phonon energy $(cm^{-1})$
Borate	$\sim 1400$
Phosphate	1100 - 1200
Silicate	$\sim 1100$
Germanate	$\sim 900$
Tellurite	$\sim 700$
Fluorozirconate	$\sim 500$
Sulfide (Ga, La)	$\sim 450$

TABLE I. – Maximum phonon energy of various glass matrices.

I.2 GLASS MATRICES



## **REE** incorporation methods

-Can start from doped mixture (with REE) Ex. Fluoroindate glass with Nd<sup>3+</sup> and/or Pr<sup>3+</sup>

(mol. %) 38 InF<sub>3</sub> + 20 SrF<sub>2</sub> + 20 ZnF<sub>2</sub> + (16-x-y) BaF<sub>2</sub> + 2 NaF + 4GaF<sub>3</sub> + x PrF<sub>3</sub> + y NdF<sub>3</sub> ( x = 0.2 ; y = 0.2, 0.1 ).

-Can incorporate element (like in fibers fabrication)



### Rare Earth Doped Glasses (REDG)

Let us remind that, once incorporated in the host, the REDG hamiltonian is given by:

 $H = H_l + H_h ; \qquad (1.1)$ Free ion host

The aperiodic glass structure introduces variations in the  $H_h$  term, leading to an inhomogeneous broadening in the linewidth





## Inhomogeneous broadening





## **Theoretical Aspects**

# Objective: calculate the radiative and nonradiative REE transitions

J.H.Van Vleck J. Phys. Chem. 41 (1937) 67. Studied Absorption and Emission, atributted to 4f and mechanisms: electric dipole, electric quadrupole magnetic dipole

Broer, Gorter, Hoogschagen; Physica 11 (1945) 231 Showed that electric quadrupole and magnetic dipole could not Explain the intense emission of the REE, and forced electric Dipole model would suffice.

B.R. Judd; Phys. Rev. 127 (1962) 750. G.S. Ofelt; J. Chem. Phys. 37 (1962) 511. Independently, introduced definitive formalism based on forced electric dipole



Fluorescence:

# Possible physical process following absorption of a photon by a molecule

Internal Conversion: radiationless transition to lower state when vibrational energy levels "match"

**External Conversion**: radiationless transition to lower state by collisional deactivation

**Intersystem Crossing**: transition with spin change (e.g. S to T)

emission not involving spin change (e.g.  $S \rightarrow S, T \rightarrow T$ ), efficient, short-lived <10<sup>-5</sup> s

**Phosphorescence**: emission involving spin change  $(T \rightarrow S)$ , improbable, long-lived >10<sup>-5</sup> s



# Possible physical process following absorption of a photon by a molecule





#### Luminescence





#### Radiative Transitions - Efficiency

A photon can be emitted when an electron drops from an upper to a lower energy level.

 $P_R = 1/t_R$  - radiative transition probability  $P_{NR} = 1/t_{NR}$  - non-radiative transition probability

The quantum efficiency of luminescense is then

 $\eta = P_{R} / (P_{R} + P_{NR})$  $= (1/t_{R}) / (1/t_{R} + 1/t_{NR})$ 

For high efficiency devices, reduce the probability of non-radiative processes





#### A taste of Judd-Offelt Theory

The oscillator strength of a spectral line due to a electric dipole fundamental to excited state transition is given by:

$$f_{dip.el.} = \chi \cdot \left(\frac{8\pi^2 \cdot m \cdot v}{h}\right) \cdot \left| \langle A | D_q^{(1)} | B \rangle \right|^2$$
(2.1)

$$\chi \text{-} \text{Lorentz field correction}$$
  
m - mass of electron  
h - Planck constant  
v- transition frequency  
q - related to input polarization  
D - atomic displacement operator  
( $\theta_j, \phi_j$ ) =  $\left(\frac{4\pi}{2k+1}\right)^{\frac{1}{2}} \cdot Y_{k,q}(\theta_j, \phi_j)$ ; (2.3)

 $D_{a}^{(k)} = \sum r_{a}^{k} \cdot C_{a}^{(k)} (\theta_{a}, \phi_{a}).$ 

(2 2)



Quim. Nova, Vol. 26, No. 6, 889-895, 2003

#### INTENSITIES OF 4f-4f TRANSITIONS IN GLASS MATERIALS

#### Oscar L. Malta\*

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#### Luís D. Carlos

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#### The Hamiltonian for the free ion

The Hamiltonian,  $H_{\rm FI}$ , for the rare earth free ion is composed by one part due to the central field,  $H_0$ , and by several other interactions, which are generally treated as perturbations. Among these interactions the interelectronic repulsion,  $H_c$ , and the spin-orbit interaction,  $H_{\rm so}$ , are the most relevant.

$$H_{\rm FI} = H_0 + H_c + H_{\rm so} \tag{1}$$

The magnitudes of these interactions follow the order  $\rm H_{_0} > \rm H_{_c} > H$  .



#### The eigenfunctions in the intermediate coupling

Taking into account the fact that the interelectronic repulsion is not diagonal in the quantum number  $\alpha$  and that the spin-orbit interaction is not diagonal in the quantum numbers  $\alpha$ , S and L, these latter are no longer good quantum numbers. As a consequence, after diagonalization of H<sub>FI</sub>, the eigenstates will be given by a linear combination of the states  $|(4f^N)\alpha SLJM_I\rangle$ , that is,

$$(4f^{N})\psi JM_{J} \rangle = \sum_{\alpha S L} C(\alpha SL) |(4f^{N})\alpha SLJM_{J} \rangle$$
(3)

in which the  $C(\alpha SL)$  coefficients of the linear combination satisfies the condition

$$\sum_{\alpha S L} \left| C(\alpha S L) \right|^2 = 1 \tag{4}$$



#### THE LIGAND FIELD

#### The usual form of the ligand field Hamiltonian

Although weak, the interaction between 4f electrons and the chemical environment is responsible for the most interesting spectroscopic features of rare earth ions. The non-spherical even parity part of this interaction, responsible for the Stark splitting of 4f levels, is commonly written as:

$$H_{LF} = \sum_{k,q,i} B_{q}^{k} C_{q}^{(k)}(i)$$
(5)

where the  $B_q^{k^*s}$  (k = 2, 4 and 6) are the so-called ligand field parameters of even rank and  $C^{(k)}$  is a Racah tensor operator of rank  $k^{19-22}$ . The values of k are restricted by parity and triangularity rules for f orbitals<sup>19,20</sup>. The allowed values of q depend on the symmetry of the ligand field around the rare earth ion, and in this expression the index i runs over the 4f electrons.



The total Hamiltonian to be diagonalized is now

$$H = H_{FI} + H_{LF}$$
(6)

The ligand field interaction is also of fundamental importance for the case of 4f–4f transition intensities. These transitions are in principle electric dipole forbidden by Laporte's rule. However, provided that the site occupied by the rare earth ion does not present a center of inversion, Laporte's rule is relaxed due to odd parity terms in the ligand field Hamiltonian. The more general form of  $H_{LF}$  is actually

$$H_{LF} = H_{LF}(even) + H_{LF}(odd)$$
(7)

$$H_{LF}(odd) = \sum_{t,p,i} \gamma_p^t r_i^t C_p^{(t)}(i)$$
(8)

where  $r_i$  is the radial coordinate of the i-th electron,  $\gamma_p^t$ 's (t = 1, 3, 5 and 7) are the so-called odd rank ligand field parameters, and C<sup>(t)</sup> is a Racah tensor operator of rank t. The values of t are restricted by parity and triangularity rules involving f, d and g orbitals<sup>7,8</sup>. Now the index i runs, in principle, over all electrons of the rare earth ion. As

**I.4 THEORETICAL ASPECTS** 



#### The ligand field and symmetry

One of the consequences of the action of  $H_{LF}$  (even) is that J is no longer a good quantum number. This produces the so-called J-mixing effect (a rather small effect due to the weak interaction between the 4f orbitals and the chemical environment), and as a result of the diagonalization of the total Hamiltonian H in equation (6) the final eigenstates have the general form:

$$\left| (4f^{N})\Gamma \right\rangle = \sum_{\alpha,S,L,J,M_{J}} A(\alpha,S,L,J,M_{J};\Gamma) \left| (4f^{N})\alpha SLJM_{J} \right\rangle$$
(9)

with the condition

1

$$\sum_{\alpha,S,L,J,M_J} \left| A(\alpha, S, L, J, M_J; \Gamma) \right|^2 = 1$$
(10)

Each eigenstate given by equation (9) is now labeled by an irreducible representation,  $\Gamma$ , of the symmetry point group.



In Figure 1 a schematic representation of the intra-atomic and ligand field interactions previously discussed is presented.



*Figure 1.* Schematic representation and order of magnitude of the effects of the intra-atomic and ligand field interactions acting on a  $4f^N$  configuration



#### The Judd-Ofelt theory

The electric dipole strength,  $S_{ed}$  (in units of  $e^2$ ), of a transition between two states  $\phi$  and  $\phi'$  is given by

$$S_{ed} = \left| \left\langle \phi' \right| \sum_{i} \vec{r}_{i} \left| \phi \right\rangle \right|^{2}$$
(13)

In the standard Judd-Ofelt theory the initial step is to consider this mixing by means of perturbation theory up to first order in the wavefunctions. If we take the perturbation on the eigenstates given by equation (9), then we may write:

$$\left|\phi\right\rangle = \left|(4f^{N})\Gamma\right\rangle + \sum_{B\beta} \frac{\left\langle B\beta \right| H_{LF}(odd) \left|(4f^{N})\Gamma\right\rangle}{E(\Gamma) - E(B\beta)} \left|B\beta\right\rangle$$
(14)

where B designates an excited configuration of opposite parity and  $\beta$  its states. The state  $|\phi'\rangle$  has a similar expression. The matrix element in equation (13), abbreviated as  $\vec{\mu}_{ed}$ , is consequently given by:

$$\mu_{ed} = \sum_{B\beta} \left[ \frac{\left\langle (4f^{N})\Gamma' \Big| \sum_{i} \vec{r}_{i} \Big| B\beta \right\rangle \langle B\beta \Big| H_{LF}(odd) \Big| (4f^{N})\Gamma \rangle}{E(\Gamma) - E(B\beta)} + \frac{\left\langle (4f^{N})\Gamma' \Big| H_{LF}(odd) \Big| B\beta \right\rangle \langle B\beta \Big| \sum_{i} \vec{r}_{i} \Big| (4f^{N})\Gamma \rangle}{E(\Gamma') - E(B\beta)} \right]$$

$$(15)$$

An interesting estimation of the 4f–4f oscillator strengths can be made from equation (15). For an electric dipole allowed transition the oscillator strength can be as high as 1. For rare earth ions the ligand field interaction is typically of the order of 100 cm<sup>-1</sup> and the interconfigurational energy differences for the lowest excited configuration of opposite parity (4f<sup>N-1</sup> 5d) is typically of the order of 10<sup>5</sup> cm<sup>-1</sup>. This gives a factor of 10<sup>-3</sup> in equation (15), which squared leads to the typical order of magnitude of 4f–4f oscillator strengths (10<sup>-6</sup>).





## After some more manipulation, one can show that:

$$S_{ed} = \frac{1}{2J+1} \sum_{\lambda=2,4,6} \Omega_{\lambda}^{ed} \left\langle (4f^{N})\psi'J' \right\| U^{(\lambda)} \| (4f^{N})\psi J \right\rangle^{2}$$
(20)

where

$$\Omega_{\lambda}^{ed} = (2\lambda + 1) \sum_{t,p} \frac{\left| B_{\lambda t p}^{ed} \right|^2}{2t + 1}$$
(21)

Judd-Ofelt parameter



About nonradiative transitions:

$$\frac{1}{\tau_T} = A_T(\alpha J) + W_T(\alpha J) = \frac{1}{\tau_R} + \frac{1}{\tau_{NR}}$$

where:

- $A_{\tau}(\alpha J)$  is the total radiative relaxation rate;
- $W_{\tau}(\alpha J)$  is the total nonradiative relaxation rate;
- $\tau_R$  is the excited state radiative lifetime;
- $\tau_{NR}$  is the excited state nonradiative lifetime, given by  $W_T(\alpha J)^{-1}$ .



Regarding  $W_T(\alpha J)$  the following empirical relation has been demonstrated

$$W_{AB}(T) = W_{AB}(0) \cdot \left[\frac{e^{\hbar \cdot \omega} / K_B \cdot T}{e^{\hbar \cdot \omega} / K_B \cdot T} - 1\right]^{\Delta E / \hbar \cdot \omega}$$

Where:

- $W_{AB}(O)$  is the multiphonon emission rate at low temperature;
- $\hbar\omega$  is the maximum phonons energy;
- ∠E is the energy diference between the levels involved in the phonon transition
- • $K_B$  is the Boltzmann constant and *T* is the temperature.







### Spectroscopic Techniques for Optical Assessment

Absorption Luminescence Raman spectroscopy Brillouin spectroscopy Up-conversion spectroscopy







FIG. 1. Absorption spectrum of  $Pr^{3+}$  in fluoroindate glass at room temperature (sample with x=0.2).

The glass samples studied have the following compositions: (mol. %)  $(39-x)InF_3-20$   $ZnF_3-16BaF_2-20SrF_2$ . 2GdF<sub>3</sub>-2NaF-1GaF<sub>3</sub>-xPrF<sub>3</sub> (x=0.05; 0.1; 0.2; 1; 2). In F<sub>3</sub> was obtained by fluoration of In<sub>2</sub>O<sub>3</sub> at 400 °C with NH<sub>4</sub>F and HF in a platinum crucible. Then, all the fluoride components were mixed and heated in a dry box under argon atmosphere at 700 °C for melting and 800 °C for fining. After the fining process the melt was poured and cooled into a preheated brass mold. The obtained samples have a good optical quality and are nonhygroscopic. Previous studies with this material have been reported recently.<sup>4,7,9–11</sup>

L. E. E. de Araújo, A. S. L. Gomes, C. B. de Araújo, Y. Messaddeq, A. Florez, and M. A. Aegerter, <u>Phys. Rev. B **50**</u>, <u>16219</u> (<u>1994</u>).



The absorption coefficient is related to the Imaginary part of the refractive index through

$$\alpha(\lambda) = \frac{4\pi}{\lambda} n_i(\lambda).$$

Other related quantity to the absorption spectra are:

Transmission

$$T(\lambda) = \frac{I(\lambda)}{I_0(\lambda)}.$$

Optical  $OD(\lambda) = -\log(T(\lambda))$  or  $T(\lambda) = 10^{-OD(\lambda)}$ . Density

Extinction  $\varepsilon(\lambda) = \frac{\alpha(\lambda)}{C} = -\frac{\log(T(\lambda))}{C \cdot L}$ , coefficient (C is the concentration in mol /-1),  $\varepsilon$  in mol<sup>-1</sup> l cm<sup>-1</sup>)



The absorption cross section

$$\sigma(\lambda) = \frac{\alpha(\lambda)}{N} \,,$$

where N is the absorption centers density in cm<sup>-3</sup>

The amount of power absorbed by an ion:

 $P(\lambda)=\sigma(\lambda)I(\lambda),$ 







cw or pulsed excitationVarying

•Varying  $\lambda_{exc}$  while looking at one emission leads to excitation spectrum

Typical experimental setup





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I.5 SPECTROSCOPIC TECHNIQUES FOR OPTICAL ASSESSMENT


## Fluorescence decay time (lifetime)



Two kinds of decay times can be considered:

1) Mean duration of the fluorescence  $\tau_{\rm m} = \frac{\int_0^\infty t\phi(t)dt}{\int_0^\infty \phi(t)dt}$ .

2) 1/e decay time  $\tau_e$ 



 $\phi(\tau_e) = \phi(0)/e.$ 

For a purely exponential decay

$$\phi(t) = \phi(0) \exp\left[-\frac{t}{\tau}\right]$$
 and  $\tau = \tau_{\rm m} = \tau_e$ .

Integration of the I(t) equation gives:

$$\int_{-\infty}^{\infty} I(t) = \int_{0}^{\infty} \phi(t) dt \int_{-\infty}^{\infty} K(t) dt.$$



The quantum yield  $\Phi$  of an absorbing system is given by

$$\Phi = N_{\rm em}/N_{\rm abs}.$$

## Where

- N<sub>em</sub> is the number of spontaneous emitted photons per unit time
- N<sub>abs</sub> is the total number of absorbed photons per unit time

(difficult to measure)



We can write:

$$N_{\rm abs} = N_{\rm T} \frac{P_{\rm abs}}{\eta \omega} = N_{\rm T} \sigma_{\rm abs}(\omega) \frac{I}{\eta \omega}.$$

Considering negligible the T dependence of  $\sigma$ :

$$N_{\rm em} = N_{\rm abs} \frac{\tau_{\rm meas}}{\tau_{\rm r}}.$$

Therefore:

$$\Phi = \tau_{\rm meas} / \tau_{\rm r}.$$



In general, the fluorescence decay function is not exponential, due to local inhomogeneities.

For most cases, it can be described by a stretched exponential:

 $\phi(t) = \phi(0)[\exp[\frac{t}{\tau}]^{\beta}], \text{ where } 0 < \beta < 1.$ 



If two different components of the fluorescence Decay function can be observed, then:

 $\phi(t) = A\phi_A(t) + B\phi_B(t)$ 

Where A and B described the relative amount Of the chemical species.

In particular cases when the decay curves exhibit two well separated components, it is possible to determine the amount of the two kinds of ions involved in the process:

$$\phi(t) = A_1 \exp\left[-\frac{t}{\tau_1}\right] + A_2 \exp\left[-\frac{t}{\tau_2}\right].$$
$$N = N_1 + N_2 = A_1 \tau_1 + A_2 \tau_2.$$



The temporal evolution of the blue emission is illustrated in Fig. 3 for the studied samples. As can be seen a similar behavior is observed for all samples, with rise and decay times which are  $Pr^{3+}$  concentration dependent. The solid lines represent the fitting to the expression  $(e^{-t/\tau_d} - e^{-t/\tau_r})$  for each sample where  $\tau_r$  and  $\tau_d$ represent the rise and decay times of the upconverted fluorescence, respectively. The values obtained for  $\tau_r$  and  $\tau_d$  are shown in Table I. Their dependence with the Pr<sup>3+</sup> concentration is due to energy transfer among the excited ions and their neighbors.<sup>23</sup>

(b)

280

350

(d)

100

80



## Raman and Brillouin scattering for optical glasses characterization









## Ge<sub>x</sub>S<sub>1-x</sub> glasses compositions with 11<x<45





Absorption and emission cross-section measurement

**The McCumber Theory** 

Based on general assumptions:

<sup>6</sup> 1 -there is a thermal distribution of population among the individual Stark level components of each Stark manifold.

2. the energy width of each individual Stark level is small compared with kBT, where kB is the Boltzmann constant and T is the absolute temperature.





Fig. 14. – Absorption and emission cross-section spectra of  $\text{Er}^{3+}$  ion at 1.5  $\mu$ m of a silicate glass, which illustrate the McCumber-Miniscalco-Quimby procedure. Adapted from [42].

I.5 SPECTROSCOPIC TECHNIQUES FOR OPTICAL ASSESSMENT The McCumber relation states that the absorption cross-section  $\sigma_{\rm a}(\nu)$  and the emission cross-section  $\sigma_{\rm e}(\nu)$  between these manifolds are related by

$$\sigma_{\rm e}(\nu) = \sigma_{\rm a}(\nu) \exp[(\varepsilon - h\nu)/k_{\rm B}T],$$

 $\mathcal{E}$  is as the net free energy required to excite one Er<sup>3+</sup> ion from the  ${}^{4}I_{15/2}$  to the  ${}^{4}I_{13/2}$  state at temperature *T*:

$$\exp\left[\frac{\varepsilon}{k_{\rm B}T}\right] = \frac{\sum_{j=1}^{8} \exp\left[-\frac{E_{1j}}{k_{\rm B}T}\right]}{\sum_{j=1}^{7} \exp\left[-\frac{E_{2j}}{k_{\rm B}T}\right]} \exp\left[\frac{E_{0}}{k_{\rm B}T}\right] = C \exp\left[\frac{E_{0}}{k_{\rm B}T}\right],$$
$$E_{0} = E_{21} - E_{11}$$





Fig. 15. – Absorption and emission cross-sections of  $\text{Er}^{3+}$  ion at  $1.5\,\mu\text{m}$  in the tellurite glasses of molar composition (a) 75 TeO<sub>2</sub>: 12 ZnO: 10 Na<sub>2</sub>O: 2 PbO: 1 Er<sub>2</sub>O<sub>3</sub> and (b) 75 TeO<sub>2</sub>: 12 ZnO: 10 Na<sub>2</sub>O: 2 GeO<sub>2</sub>: 1 Er<sub>2</sub>O<sub>3</sub> [91].



The effective bandwidth  $\Delta \lambda$ , related to the emission cross-section, is defined by

$$\Delta \lambda = \int \sigma_{\rm e}(\lambda) d\lambda / \sigma_{\rm P}(\lambda),$$

where  $\, \sigma_{\rm P}(\, \lambda )$  is the peak value of the emission cross-section



TABLE II. – Effective bandwidth ( $\Delta\lambda$ ), absorption ( $\sigma_{\rm a}$ ) and emission ( $\sigma_{\rm e}$ ) cross-sections for the  ${}^{4}I_{13/2} \leftrightarrow {}^{4}I_{15/2}$  transition of Er<sup>3+</sup> at the indicated wavelength for some glass hosts.

Host matrix	$\lambda$ (nm)	$\overset{\sigma_{\mathrm{a}}}{(10^{-21}\mathrm{cm}^2)}$	$\overset{\sigma_{\rm e}}{(10^{-21}{\rm cm}^2)}$	$\Delta\lambda$ (nm)	Ref.
Al-P silica	1531	6.6	5.7	43	[87]
Silicate L22	1536	5.8	7.3	20	[87]
Silicate (Baccarat)	1537	4.3	5.1	18	[42]
Fluorophosphate L11	1533	7	7	27-43	[87]
Fluorophosphate L14	1531	5	5	63	[87]
${\rm GeO_2}{\operatorname{-SiO_2}}$	1530	7.9	6.7	25	[69]
$Al_2O_3$ - $SiO_2$	1530	5.1	4.4	55	[69]
${\rm GeO_2} ext{-}{\rm Al_2O_3 ext{-}SiO_2}$	1530	4.7	4.4		[69]
Tellurite	1532	7.9	8.2	66	[91]





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