Advanced Glass Science
(4016101)

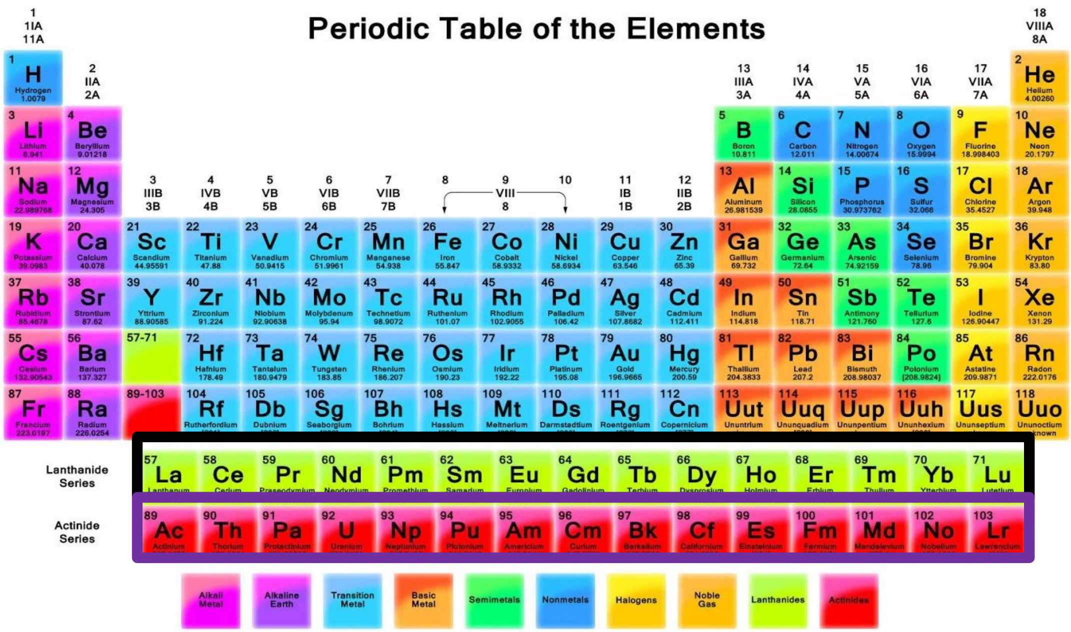
Instructor: Asst.Prof.Dr. Jakrapong Kaewkhao

Course Outline:

Week 7: - Lanthanide element in glass
- *Case studies from international publications*

Book: A.K., Varshneya. ***Fundamentals of inorganic glasses***
A., Paul A, ***Chemistry of glasses***
J.E. Shelby, ***Introduction to glass science and technology***

Lanthanide group



La = [Xe] $4f^0 5d^1 6s^2$

Ce = [Xe] $4f^1 5d^1 6s^2$

Pr = [Xe] $4f^3 6s^2$

Nd = [Xe] $4f^4 6s^2$

Pm = [Xe] $4f^5 6s^2$

Sm = [Xe] $4f^6 6s^2$

Eu = [Xe] $4f^7 6s^2$

Gd = [Xe] $4f^7 5d^1 6s^2$

Tb = [Xe] $4f^9 6s^2$

Dy = [Xe] $4f^{10} 6s^2$

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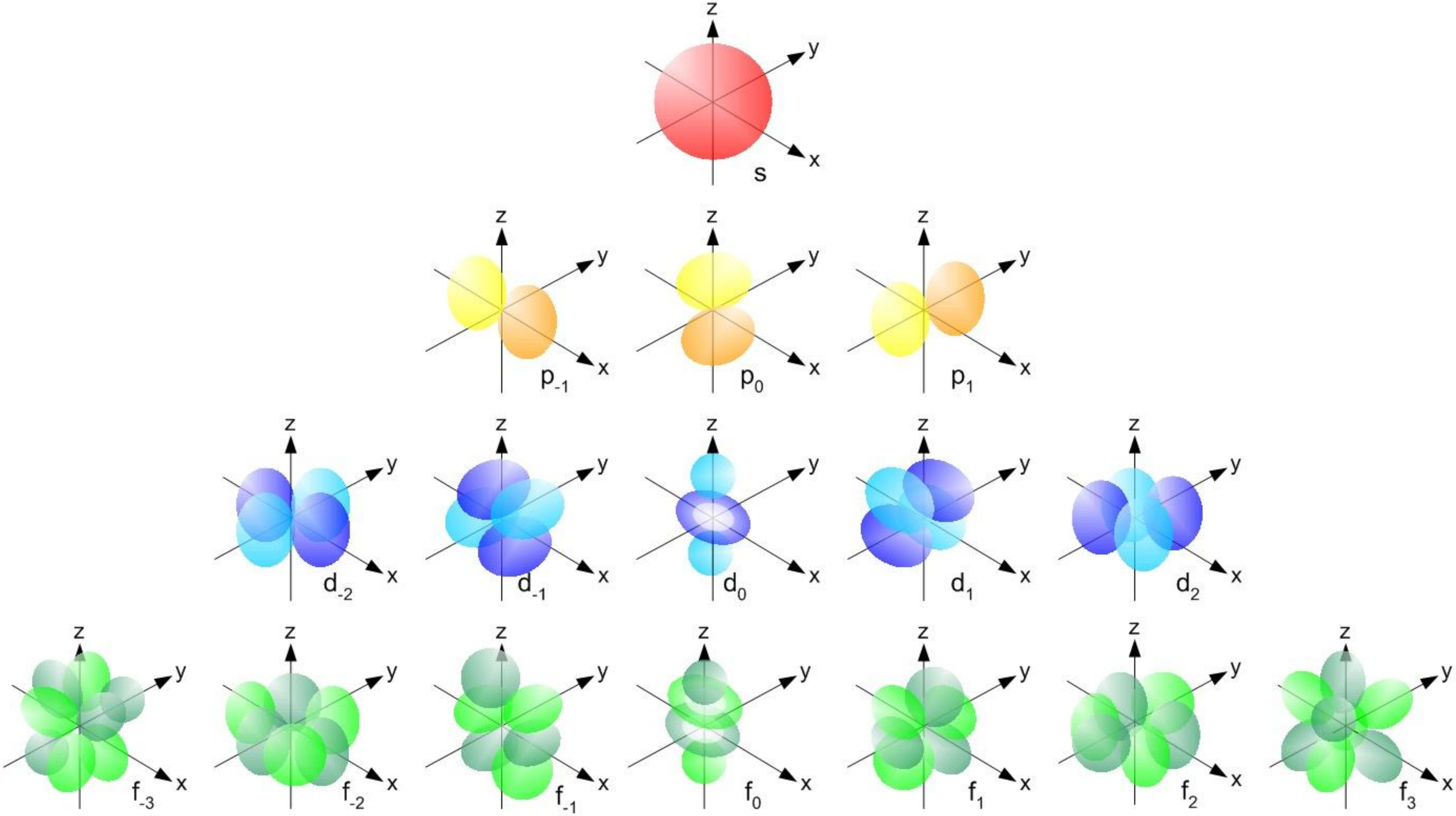
Lu = [Xe] $4f^{14} 5d^1 6s^2$

Low energy: $4f^n 5d^1 6s^2$ → La, Ce, Gd, Lu

High energy: $4f^{n+1} 6s^2$ → Pr, Nd, Pm, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb

Shape of Orbital



http://chemwiki.ucdavis.edu/@api/deki/files/8855/Single_electron_orbitals.jpg

Shape of Orbital

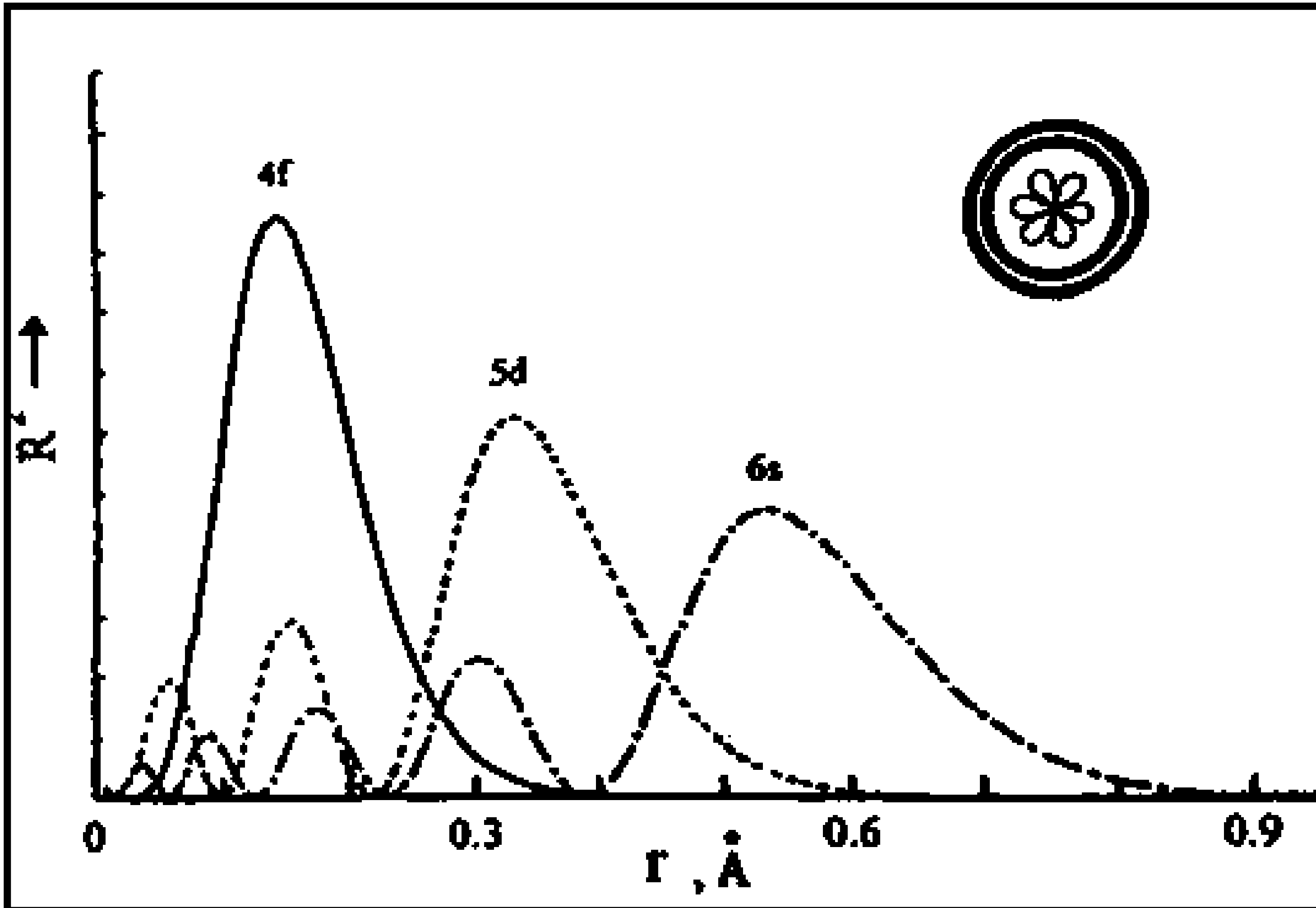


Fig. 1 Comparable shape of orbital 4f, 5d, 6s

Shape of Orbital

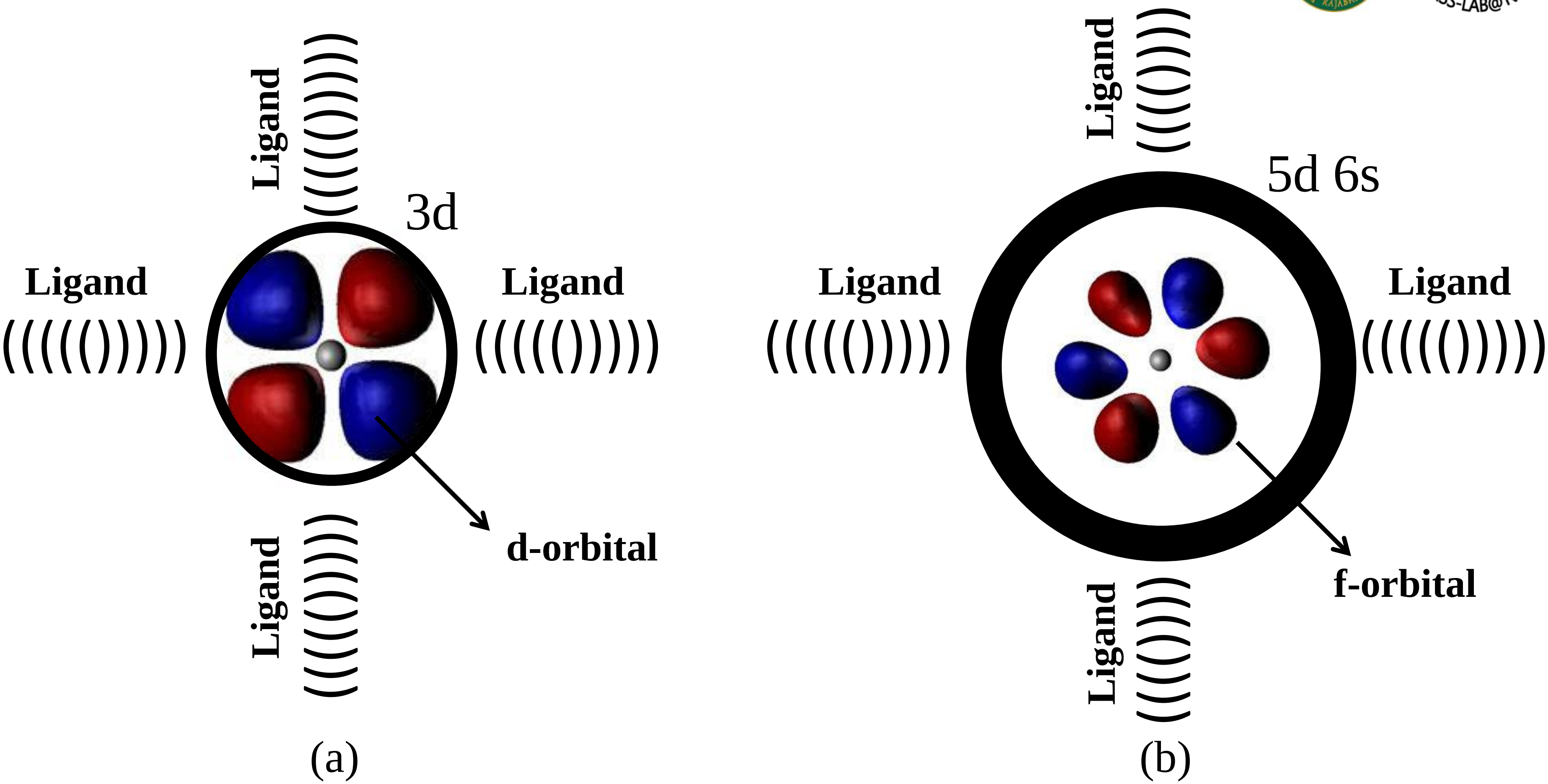


Fig. 2 Comparison environmental influences such as ligand to (a) d orbital (b) f orbital

***Ref >> http://www.d.umn.edu/~pkiprof/ChemWebV2/AOs/**

Shape of Orbital

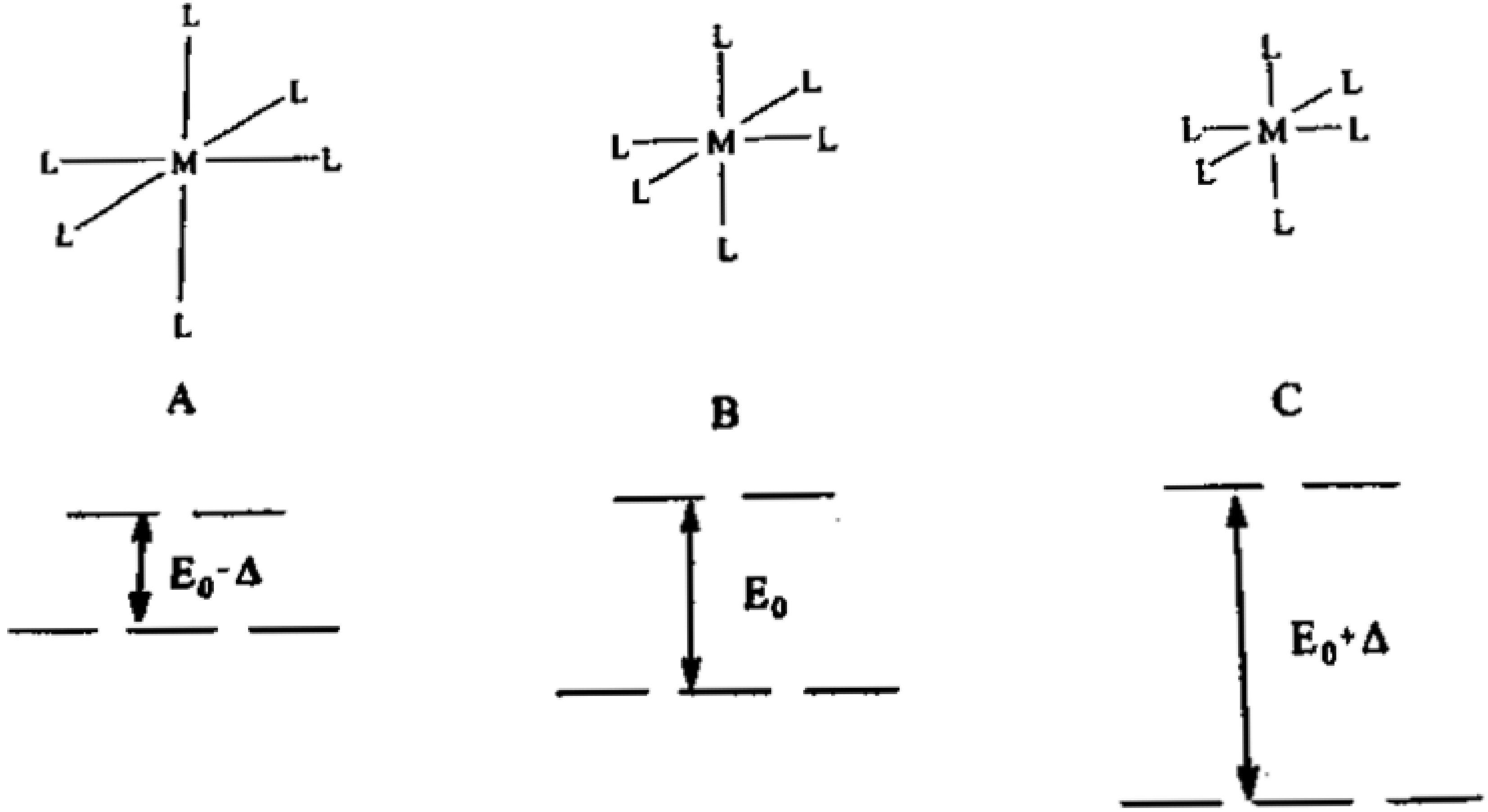


Fig. 3 The change of energy level of d-orbital

Characteristics of Lanthanide

LANTHANIDE

57 138.91	58 140.12	59 140.91	60 144.24	61 (145)	62 150.36	63 151.96	64 157.25	65 158.93	66 162.50	67 164.93	68 167.26	69 168.93	70 173.04	71 174.97
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
LANTHANUM	CERIUM	PRASEODYMIUM	NEODYMIUM	PROMETHIUM	SAMARIUM	EUROPIUM	GADOLINIUM	TERBIUM	DYSPROSIUM	HOLMIUM	ERBIUM	THULIUM	YTTERBIUM	LUTETIUM

$4f^n$ - electrons shielded by $6s^2$ and $5p^6$ electrons and so:

- Similar patterns in any ligand environment (all materials)
- Several excited states, suitable for optical pumping.
- Emit narrow line, monochromatic light and have long decay lifetimes.
- Luminescence in all spectral ranges

Characteristics of Lanthanide

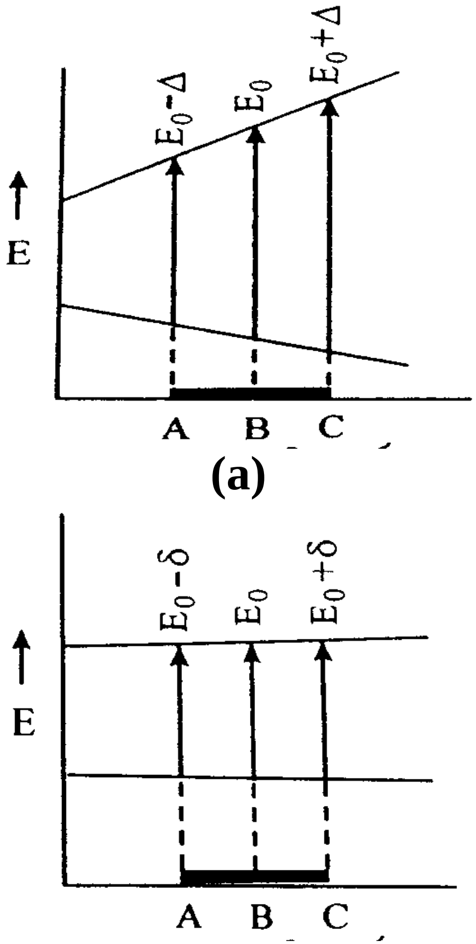


Fig. 4 Comparison the change of energy level (a) d orbital (b) f orbital

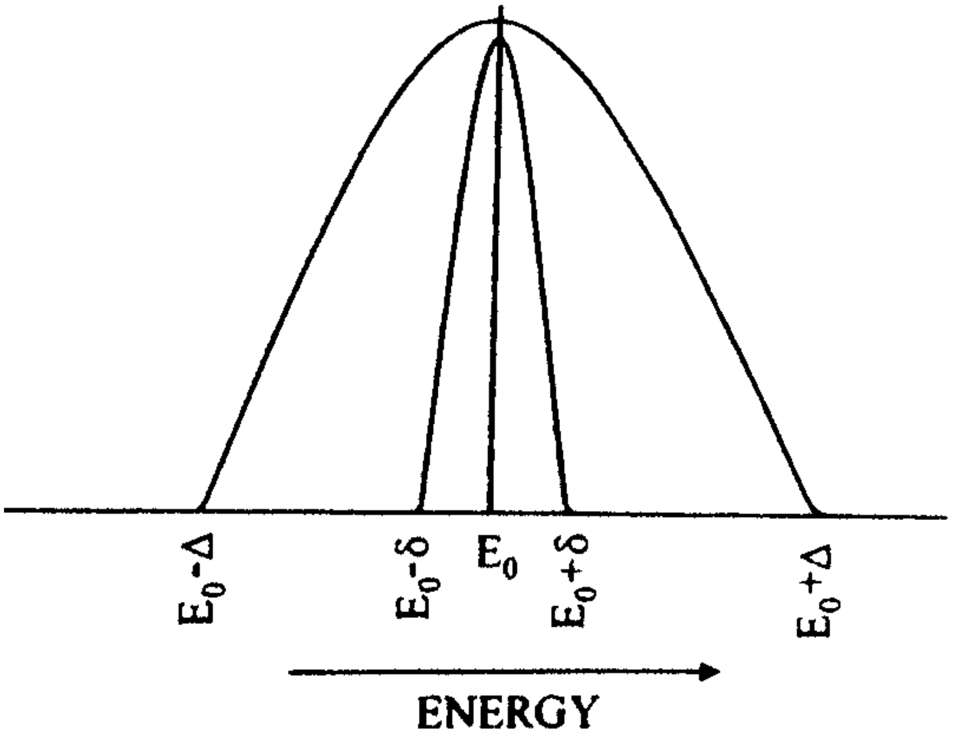


Fig. 5 Peak width-narrow from energy level

Characteristics of Lanthanide

Cr^{3+} : $1s^2\ 2s^2 2p^6\ 3s^2\ 3p^6\ 3d^3$

Nd^{3+} : $1s^2\ 2s^2 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^3\ 6s^2 5p^6$

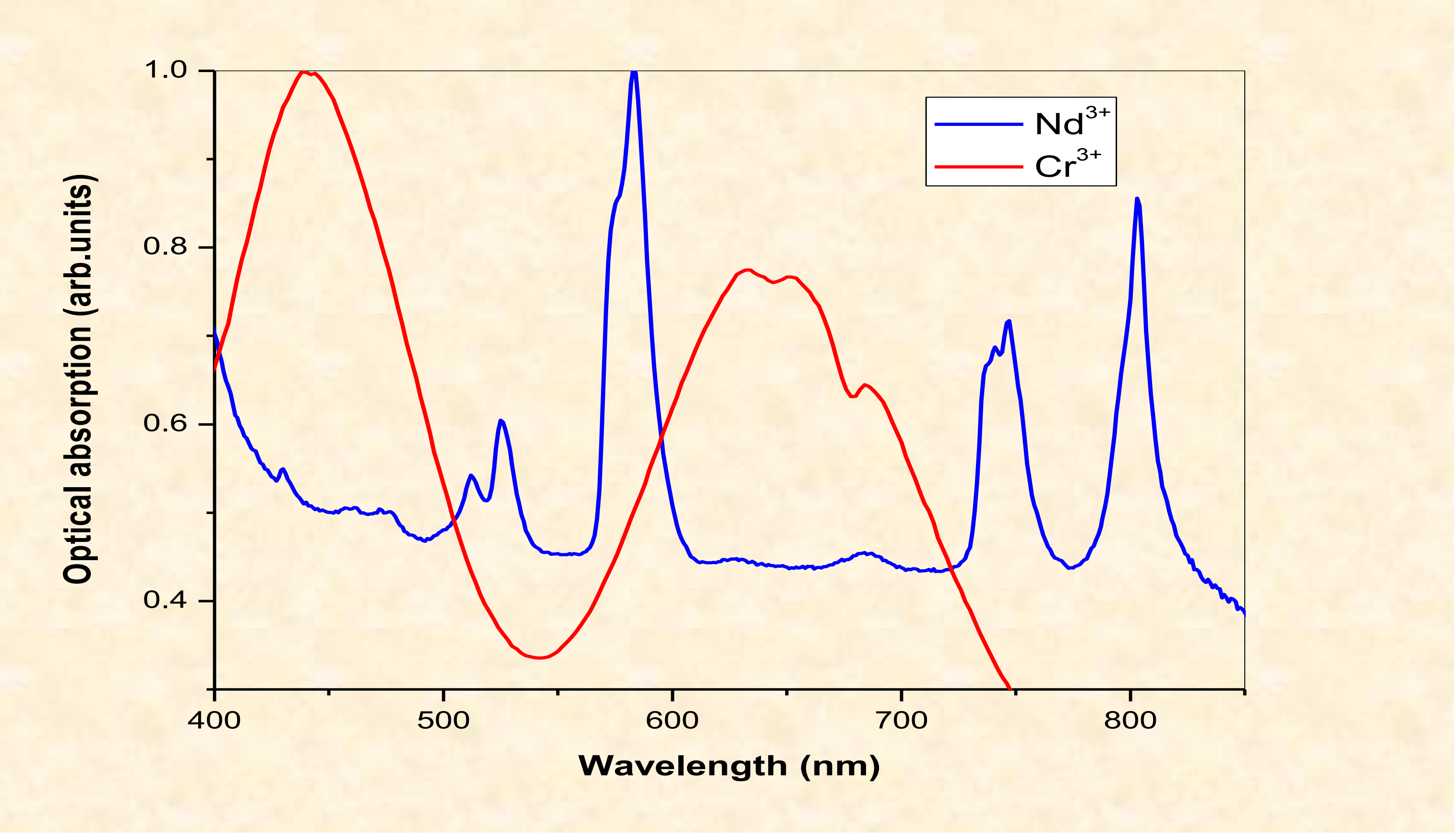
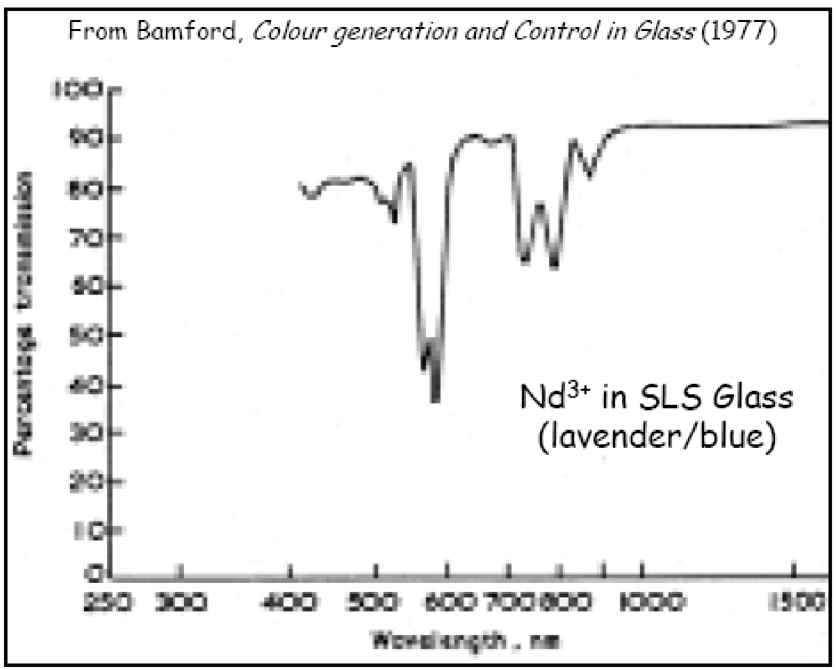


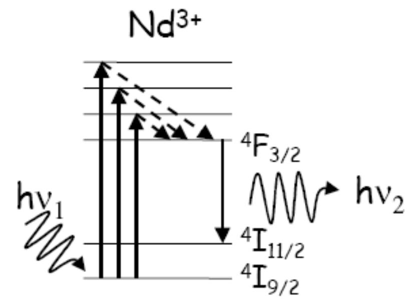
Fig. 6 Comparison Absorption spectrum of Cr^{3+} and Nd^{3+}

Absorption of Lanthanide

- Electronic transitions in 4f orbitals
- Generally sharper absorption bands than those associated with transition metal 3d orbitals
- More effectively shielded from 'chemical variations' by outer 5s/5p electrons
- Much weaker absorption coefficients



More important consequence of RE-ions is fluorescence colors



- UV absorption ($h\nu_1$), excite electrons from the ground state ($^4I_{9/2}$) to excited states
- Non-radiative transfer to longer-lifetime excited state ($^4F_{3/2}$)
- Fluorescence by de-excitation back to the $^4I_{11/2}$ground state- emission of visible light ($h\nu_2$) depends on energy level differences.
  - Emitted in phase, same direction as incident photon

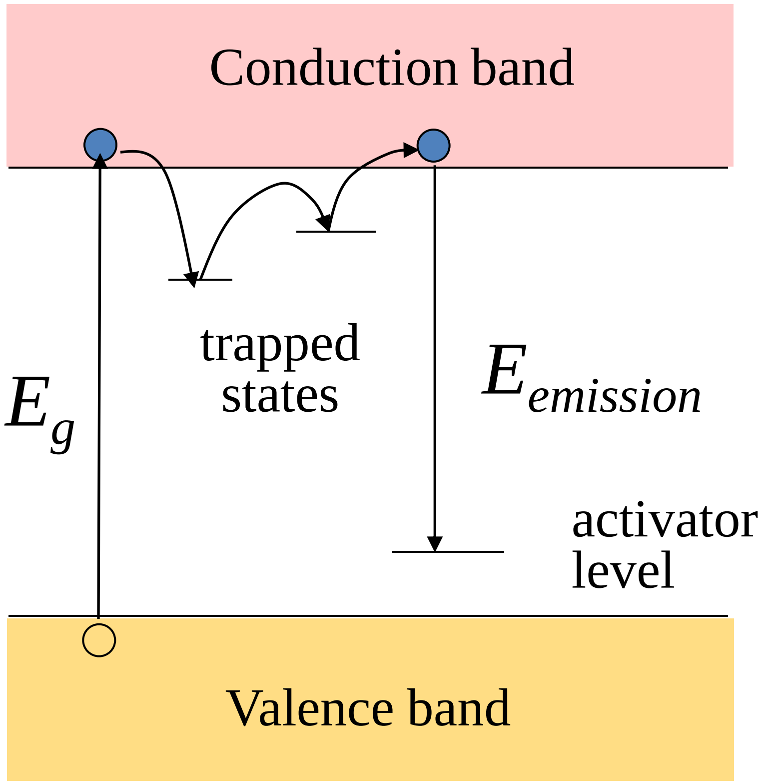
Absorption of Lanthanide

Ions	Color	Wavelength (nm)
La^{3+}	Colorless	-
Ce^{3+}	Colorless	210, 222, 238, 252
Pr^{3+}	Green	444, 469, 482, 588
Nd^{3+}	Reddish	354, 522, 574, 740, 742, 798, 803, 868
Pm^{3+}	Pink; Yellow	548, 568, 702, 736
Sm^{3+}	Yellow	362, 374, 402
Eu^{3+}	Pinkish	376, 394
Gd^{3+}	Colorless	272.9, 273.3, 275.4, 275.6

Ions	Color	Wavelength (nm)
Tb^{3+}	Pinkish	369, 378, 488
Dy^{3+}	Yellow	350, 365, 910
Ho^{3+}	Pink; Yellow	287, 361, 451, 537, 640
Er^{3+}	Reddish	364, 379, 487, 523, 652
Tm^{3+}	Green	360, 682, 780
Yb^{3+}	Colorless	975
Lu^{3+}	Colorless	-
Y^{3+}	Colorless	-

Luminescence of Lanthanide

- Luminescence – emission of light by a material
  - material absorbs light at one frequency & emits at another (lower) frequency.

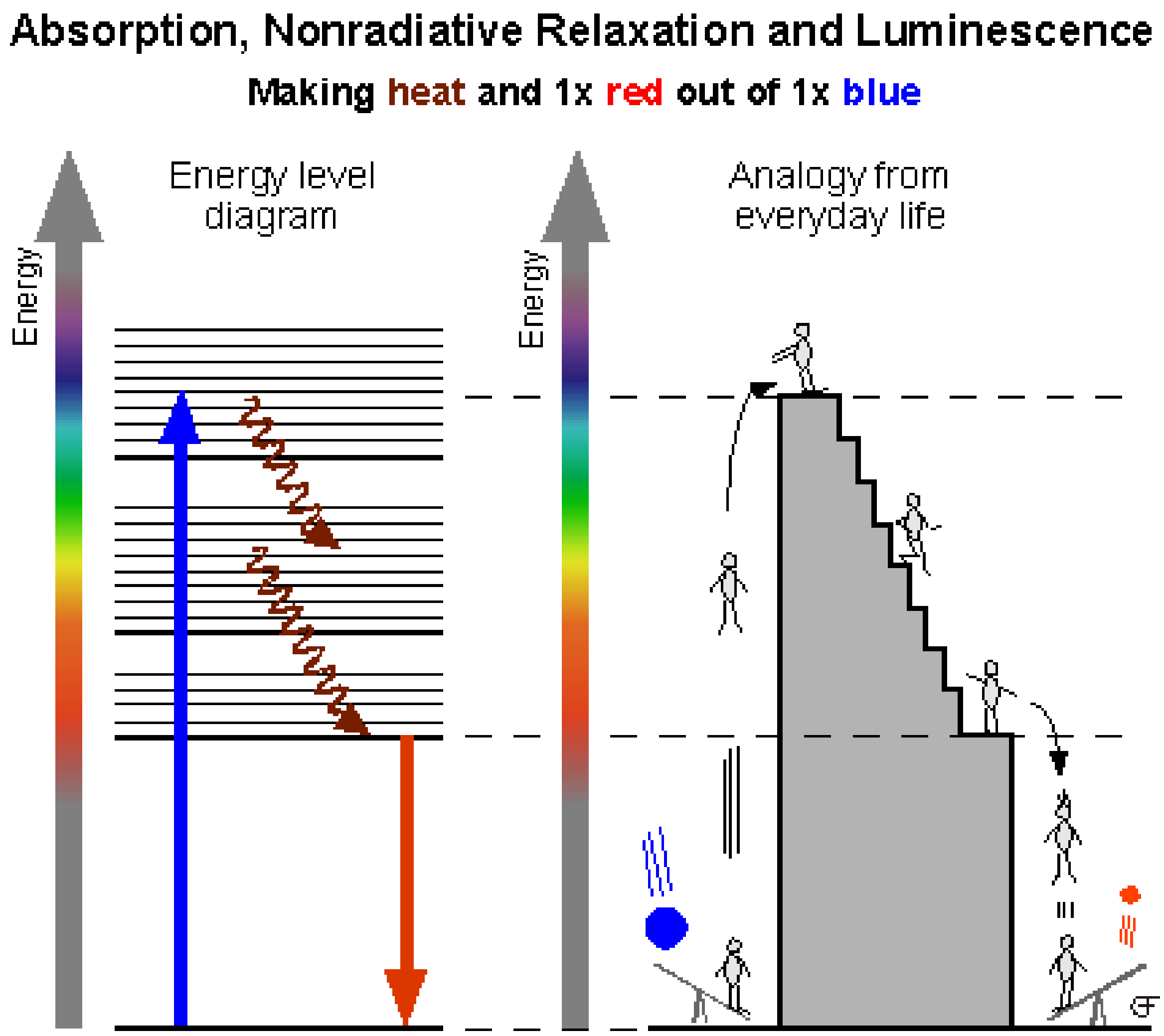


How stable is the trapped state?

- If very stable (long-lived = $>10^{-8}$ s) = phosphorescence
- If less stable ($<10^{-8}$ s) = fluorescence

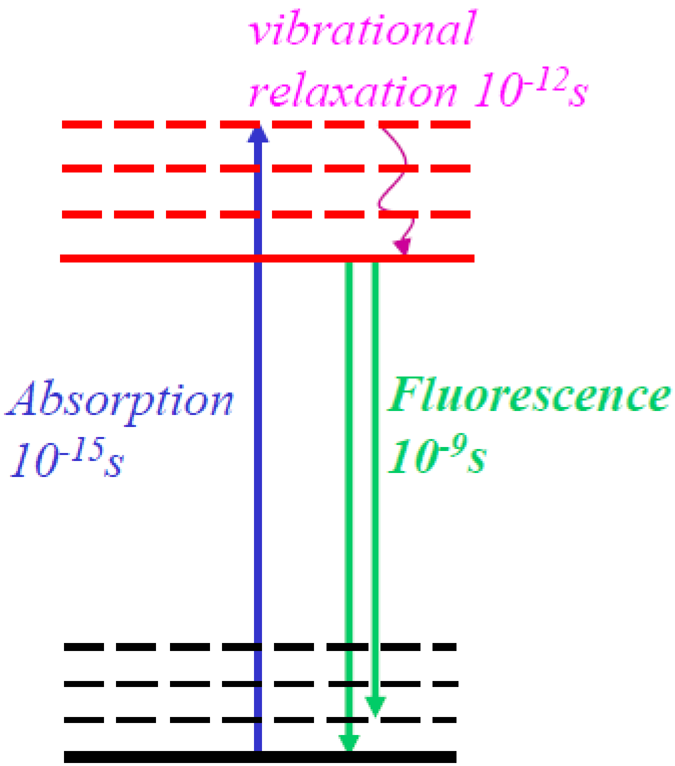
Example: Glow in the dark toys. Charge them up by exposing them to the light. Reemit over time. -- phosphorescence

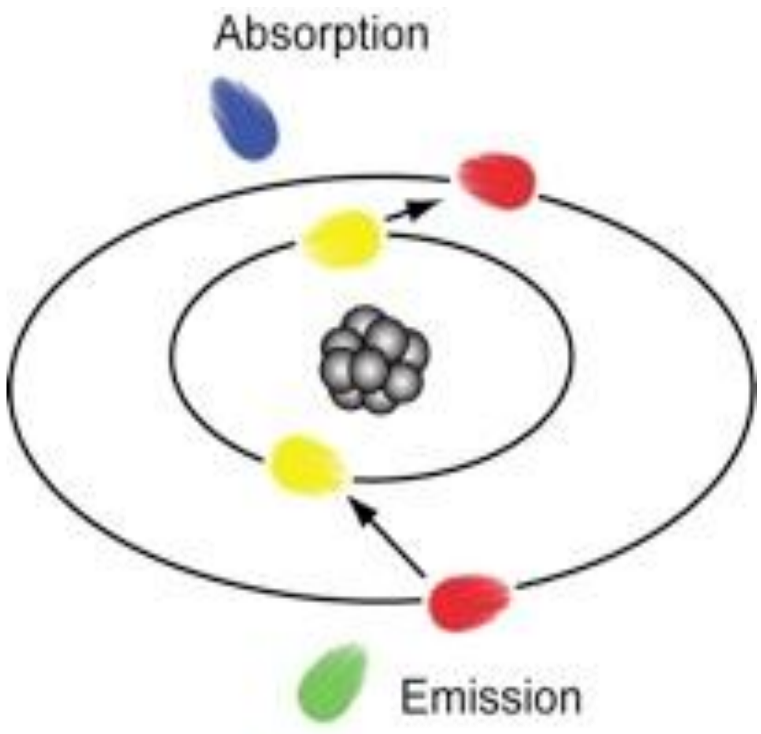
Luminescence of Lanthanide



Luminescence Lifetime

Fluorescence Lifetime:Measure the average time it takes for a molecule after absorption to return to its ground state





Luminescence Lifetime

Luminescence

Excitation of states by external energy & de-excitation converts it to EM radiation (UV, IR) Photo-, radio-, cathode- & electro-luminescence

Fluorescence: 0.1ns < τ < 100μs
Luminescence during excitation

Phosphorescence: 100μs < τ < 1s
Luminescence after excitation

Scintillation
(Crystals, Glass, Ceramic, Polymer)

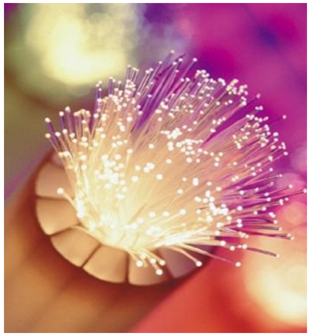
Other Fluorescence (Phosphors)
Crystals, Powders, Glass

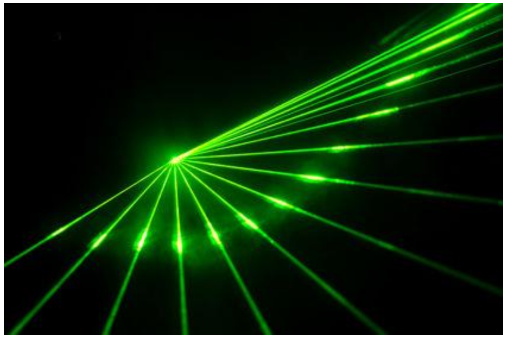
f-d transition:
Eu^{2+}, Ce^{3+}, Pr^{3+}

f-f transition:
Eu^{3+}, Dy^{3+}, Sm^{+}, Pr^{3+}, Tm^{3+}

Development of Lanthanide ion in glass

- Solid state lasers
- Optical fiber amplifiers
- Light converters
- Acousto-optic modifiers
- Phosphors
- Optical storage materials
- Sensors
- Planar waveguides, etc.





Advanced Materials Research Vol. 979 (2014) pp 147-150

doi:10.4028/www.scientific.net/AMR.979.147

The Photoluminescence and Physical Properties of Eu^{3+} Ions in Li_2O-Y_2O_3-B_2O_3 Glass System

E. Kaewnuam[1,a], P. Prongsamrong[1,b], H.J. Kim[2,c], J. Kaewkhao[1,3,d], N. Chanthima[1,3,e*]

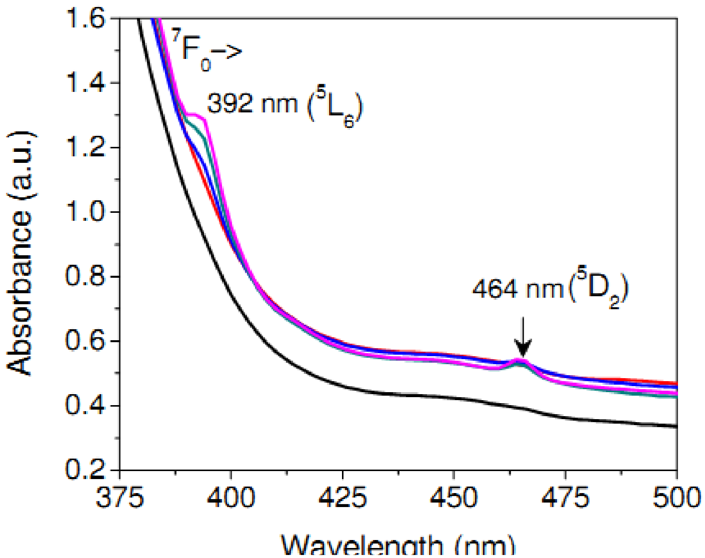


Fig. 7 The optical absorption spectra of LiYBO:Eu^{3+} glass sampleS

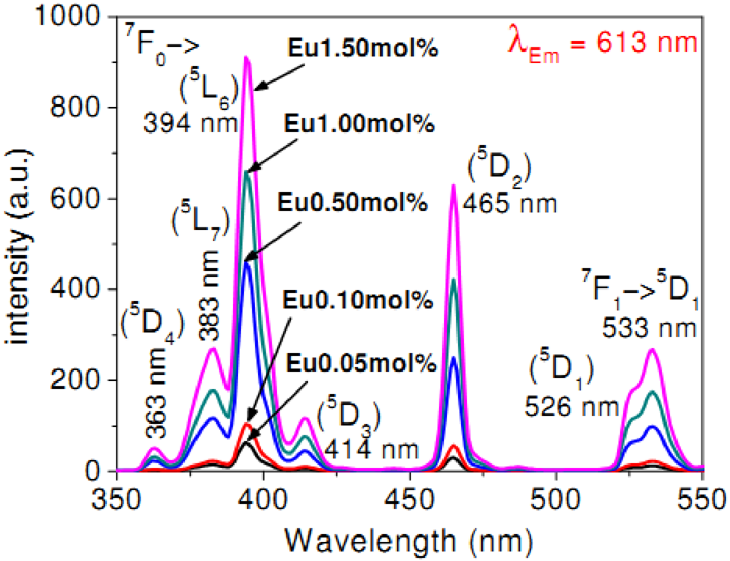


Fig. 8 The excitation spectra of LiYBO:Eu^{3+} glass samples

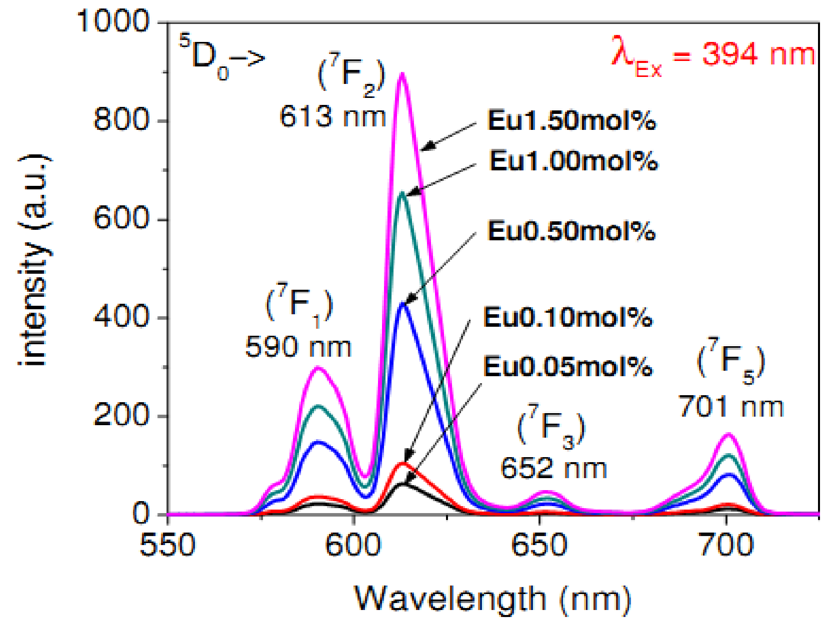


Fig. 9 The emission spectra of LiYBO:Eu^{3+} glass samples

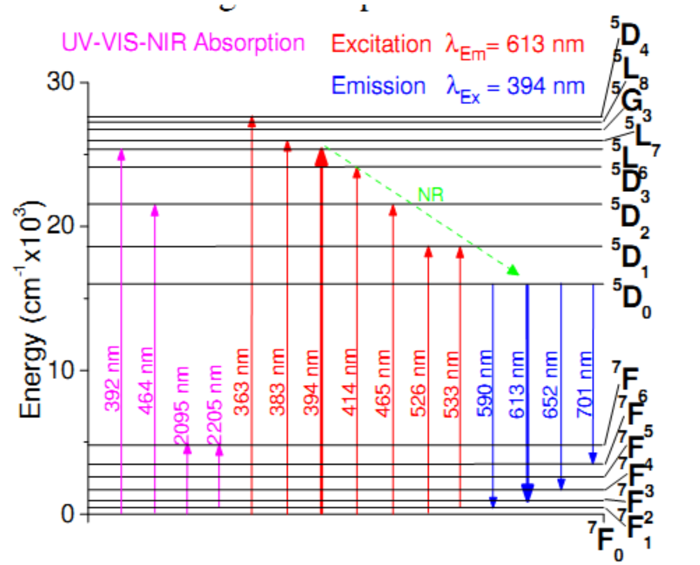


Fig. 10 Energy level of LiYBO:Eu^{3+} glass samples

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doi:10.4028/www.scientific.net/AMR.979.171

The Photoluminescence, Optical Absorption and Physical Properties of Dy^{3+} Ions in Li_2O-La_2O_3-B_2O_3 Glass System

N. Wantana[1,a], H.J. Kim[2,b], O. Chamlek[1,c],
J. Kaewkhao[3,4,d], N. Chanthima[3,4,e*]

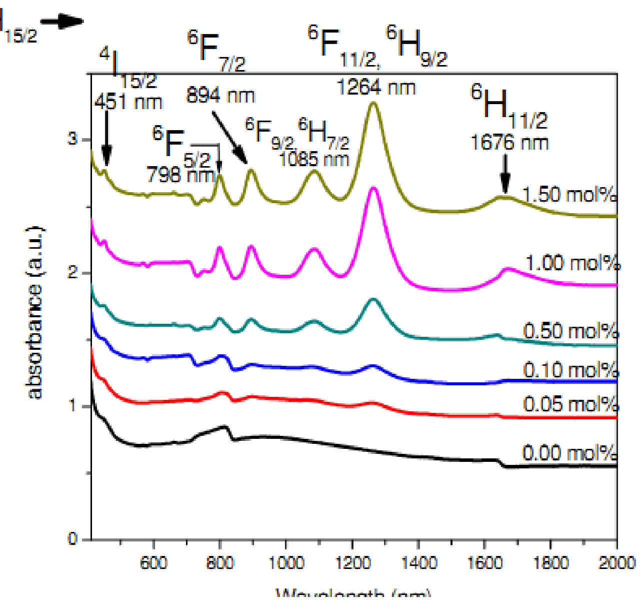

Fig. 11 The optical absorption spectra of LiLaBO:Dy^{3+} glass sampleS

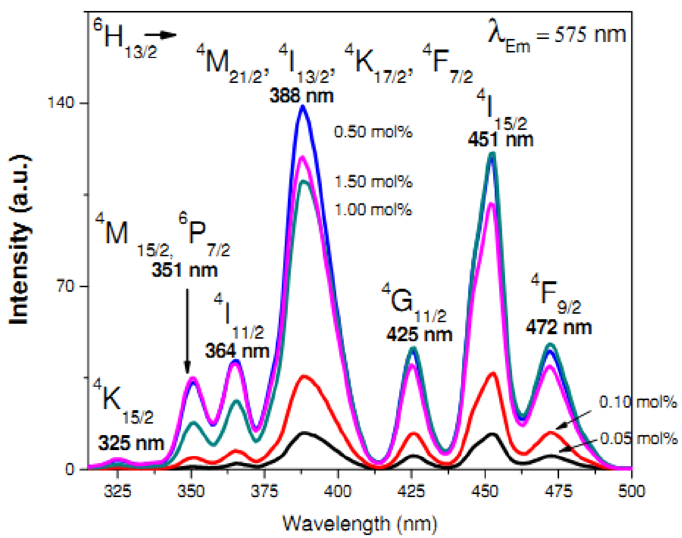

Fig. 12 The excitation spectra of LiLaBO:Dy^{3+} glass samples

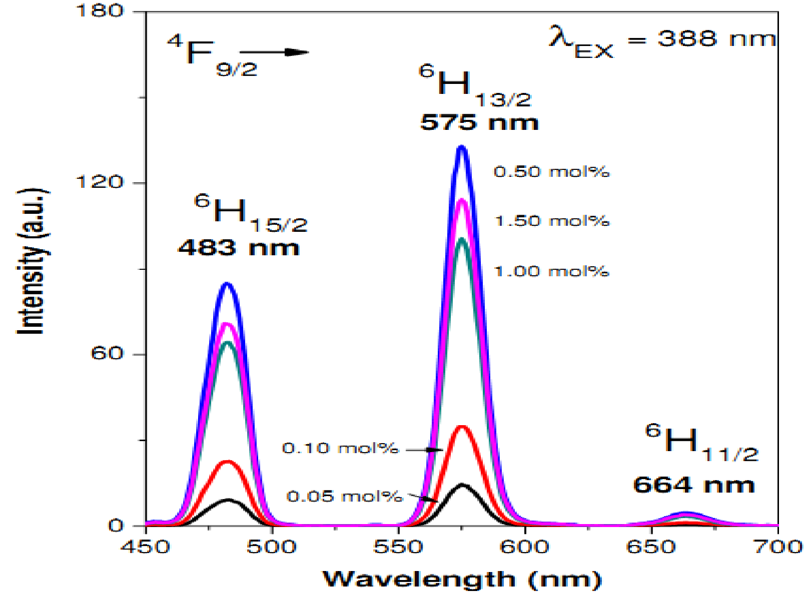

Fig. 13 The emission spectra of LiLaBO:Dy^{3+} glass samples

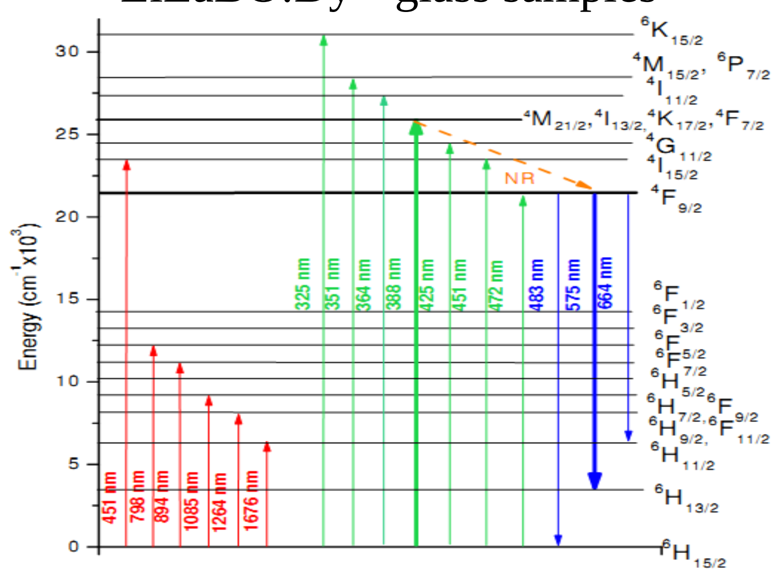

Fig. 14 Energy level of LiLaBO:Dy^{3+} glass samples

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doi:10.4028/www.scientific.net/AMR.979.479

Luminescence and Optical Properties of Li_2O_3:Gd_2O_3:B_2O_3:Sm_2O_3 Glasses System

W. Sa-ardsin[1,a], P. Yasaka[2,b], J. Kaewkhao[1,2,c], K. Boonin[1,2,d*]

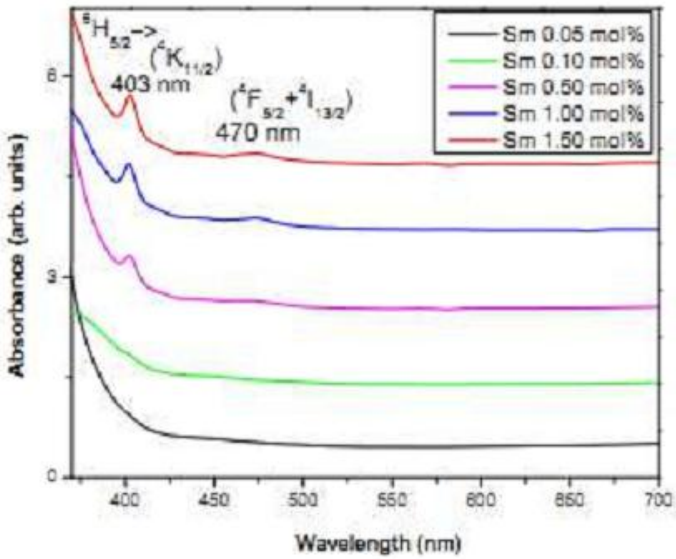

Fig. 15 The optical absorption spectra of LGBOBO:Eu^{3+} glass samples

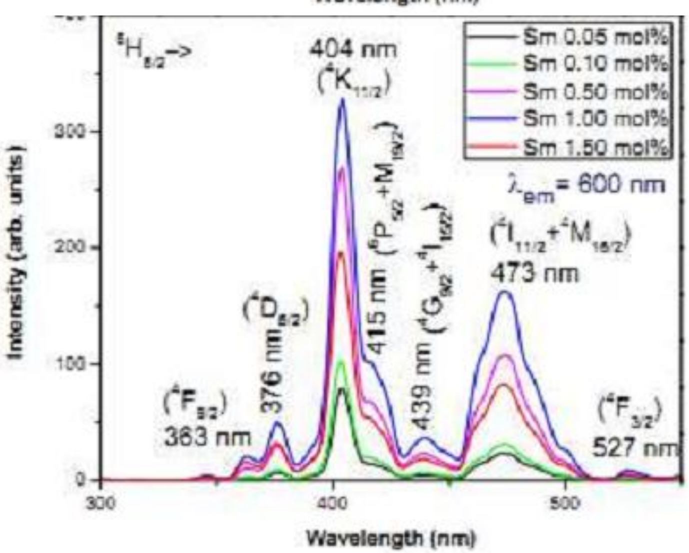

Fig. 16 The excitation of LGBO:Eu^{3+} glass samples

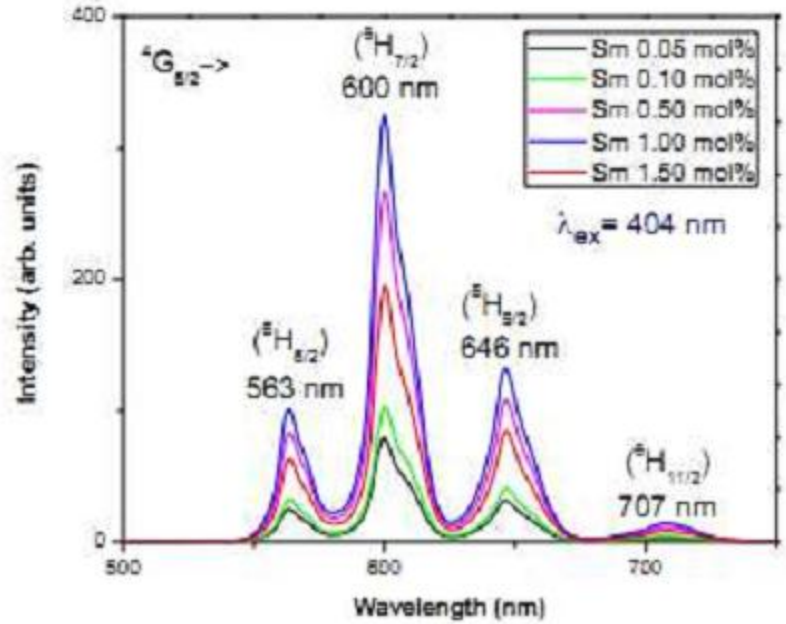

Fig. 17 The emission spectra of LGBO:Sm^{3+} glass samples

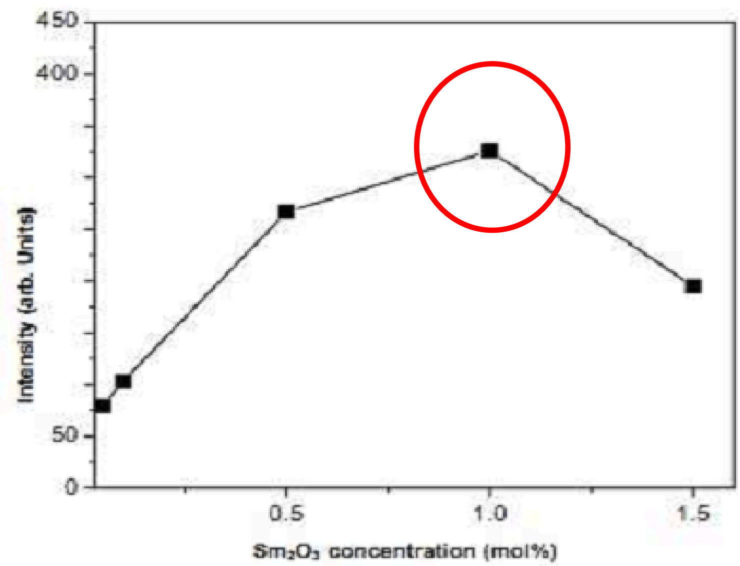

Fig. 18 Concentration quenching of LGBO:Sm^{3+} glass samples

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doi:10.4028/www.scientific.net/AMR.974.86

Investigation of Er^{3+} Doped in Na_2O-Al_2O_3-BaO-CaO-Sb_2O_3-B_2O_3-SiO_2 Glasses: Physical, Optical and Visible Luminescence Properties

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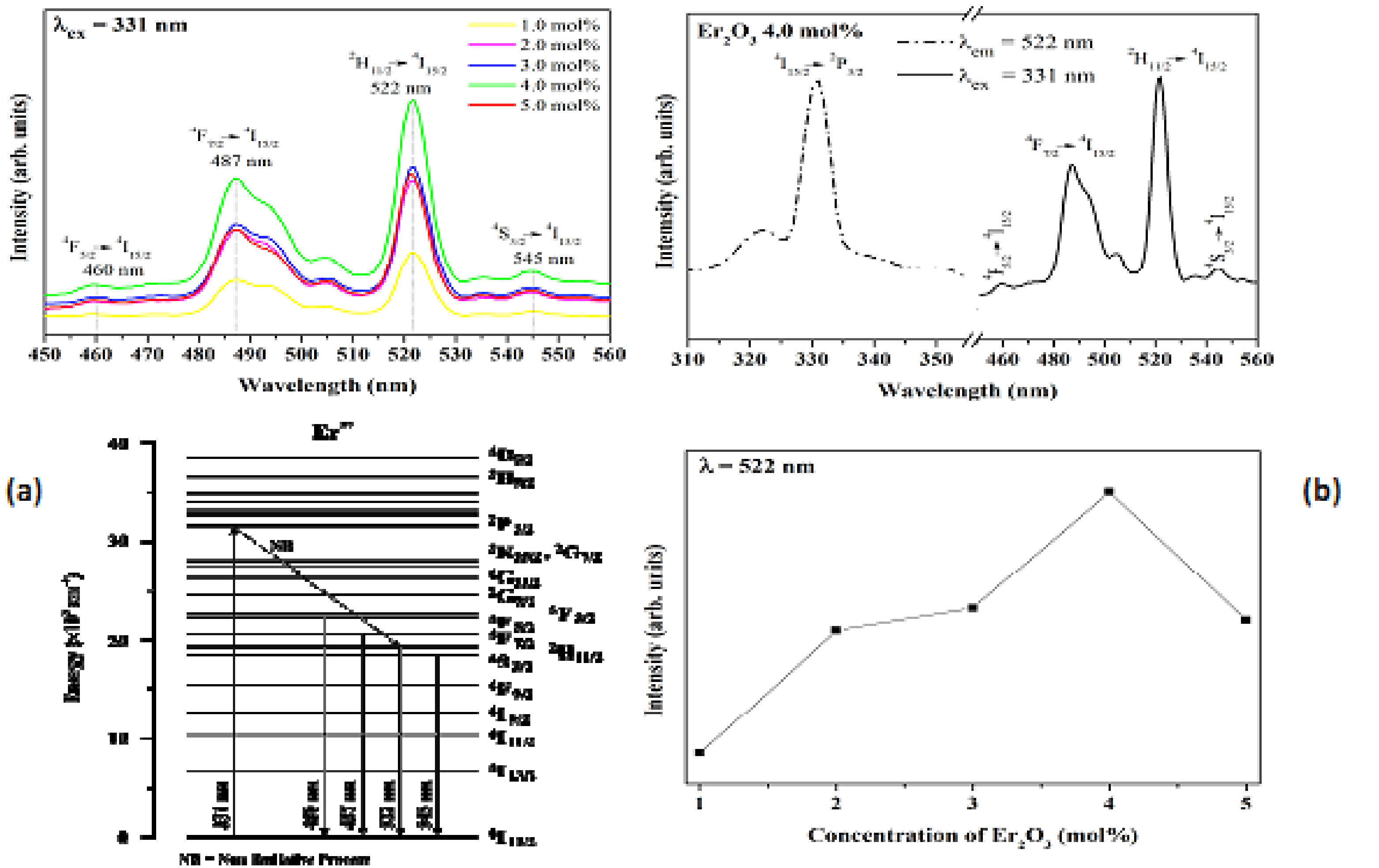
(a) Visible luminescence spectra of Er^{3+} doped in glass samples
(b) Excitation and emission spectra (4 mol% of Er_2O_3)
(c) Schematic of Energy levels and luminescence processes
(d) A plot of emission intensity over Er_2O_3 doping concentration



(a)

(b)

(c)

(d)

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http://dx.doi.org/10.1155/2014/751973

Research Article

Up- and Downconversion Luminescence Properties of Nd^{3+} Ions Doped in Bi_2O_3–BaO–B_2O_3 Glass System

R. Ruamnikhom,[1] P. Limsuwan,[1] M. Horprathum,[2] N. Chanthima,[3] H. J. Kim,[4] S. Ruengsri,[5] and J. Kaewkhao[3]

Nd_2O_3 (mol%)	Glass system
0.00	$40.00Bi_2O_3 : 20.00BaO : 40.00B_2O_3$
0.50	$40.00Bi_2O_3 : 20.00BaO : 39.50B_2O_3 : 0.50Nd_2O_3$
1.00	$40.00Bi_2O_3 : 20.00BaO : 39.00B_2O_3 : 1.00Nd_2O_3$
1.50	$40.00Bi_2O_3 : 20.00BaO : 38.50B_2O_3 : 1.50Nd_2O_3$
2.00	$40.00Bi_2O_3 : 20.00BaO : 38.00B_2O_3 : 2.00Nd_2O_3$
2.50	$40.00Bi_2O_3 : 20.00BaO : 37.50B_2O_3 : 2.50Nd_2O_3$

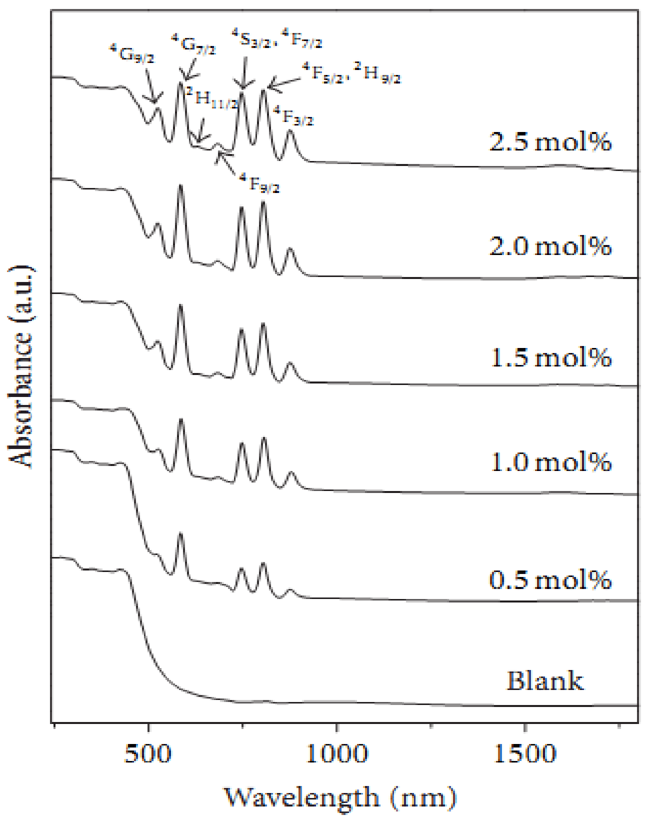


Fig. 19 The optical absorption spectra of Nd^{3+} -doped BiBaBo glass samples

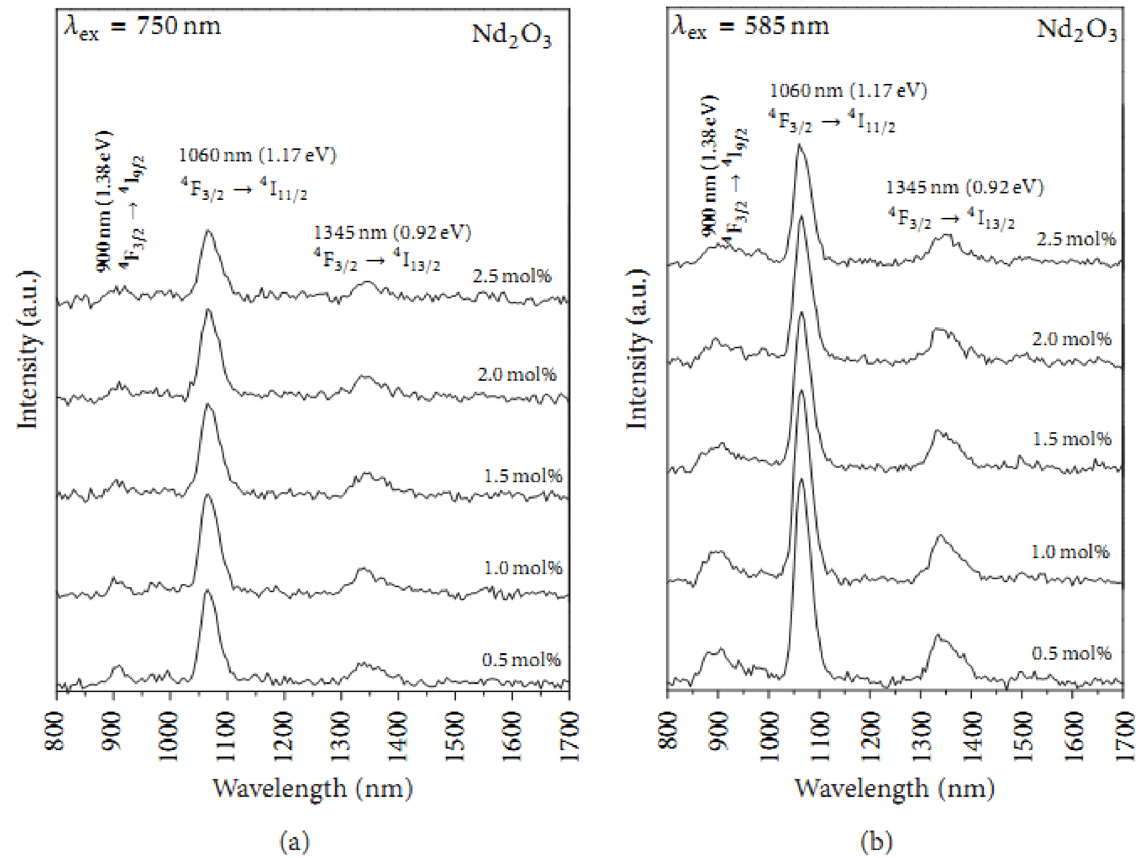


Fig. 20 The NIR emission spectra of Nd^{3+} -doped BiBaBo glass samples when excited by 585 and 750 nm

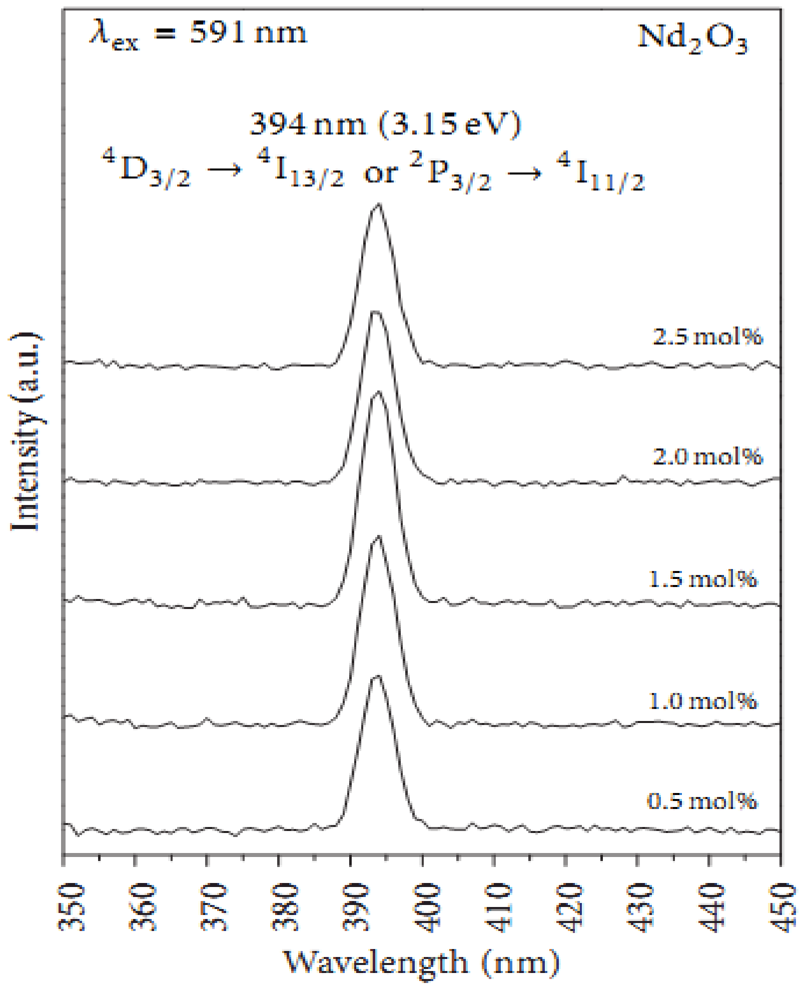


Fig. 21 The upconversion luminescence spectra of Nd^{3+} -doped BiBaBo glass samples when excited by 591 nm

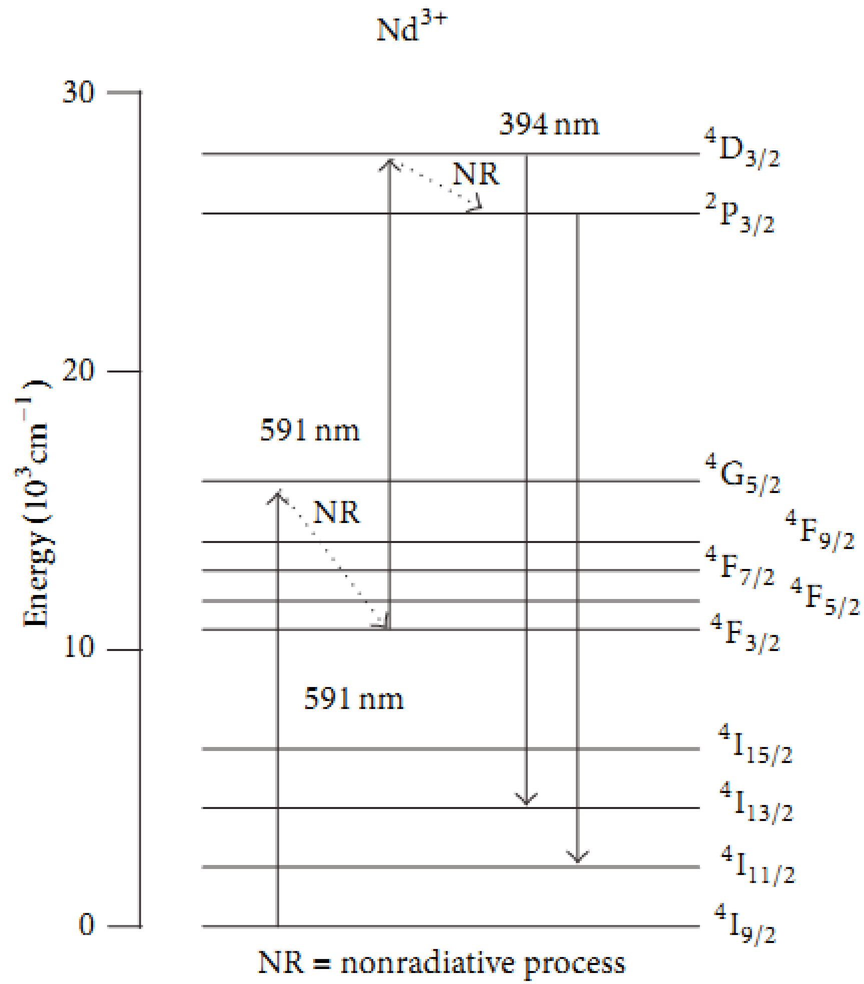


Fig. 22 Energy level of Nd^{3+} -doped BiBaBo glass samples

Appl. Phys. B
DOI 10.1007/s00340-013-5502-6

Applied Physics B
Lasers and Optics

Optical properties of Yb^{3+} ions in fluorophosphate glasses for 1.0 µm solid-state infrared lasers

K. Venkata Krishnaiah · C. K. Jayasankar ·
V. Venkatramu · S. F. León-Luis · V. Lavín ·
S. Chaurasia · L. J. Dhareshwar

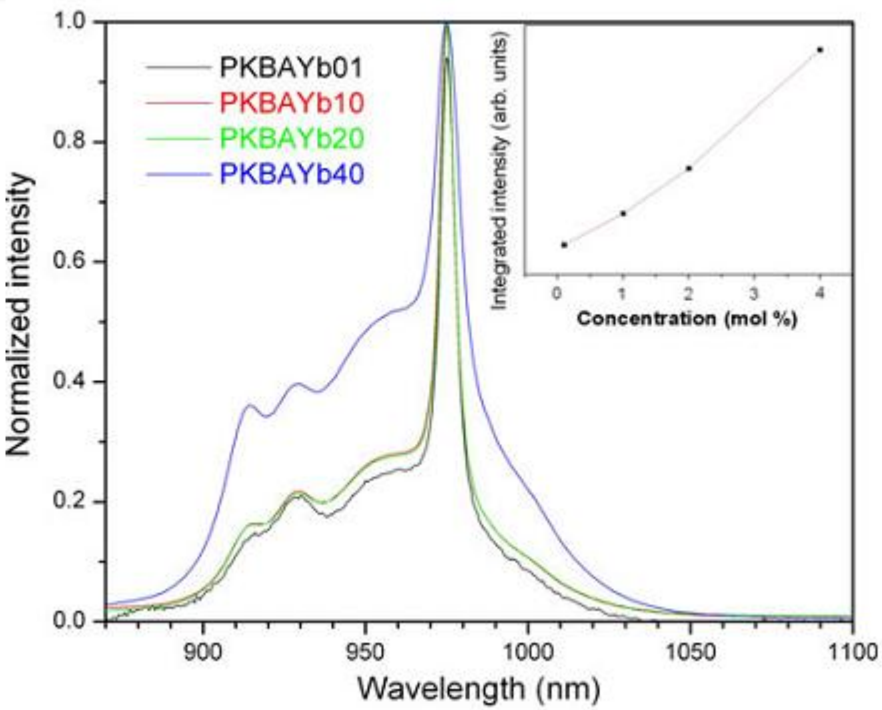


Fig. 23 The optical absorption spectra of Yb^{3+} -doped glass samples

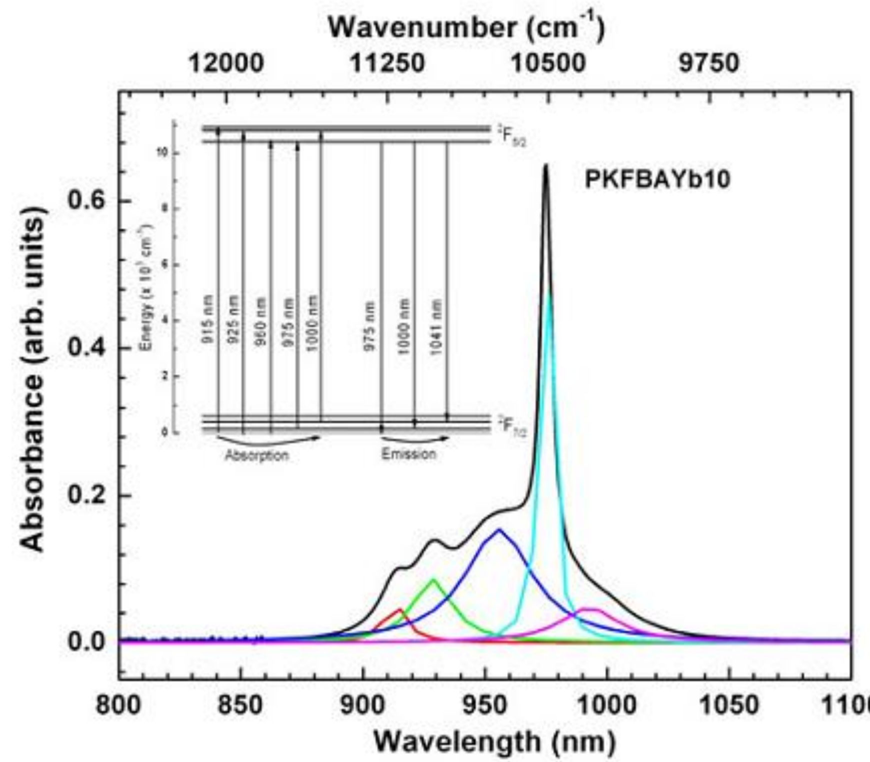


Fig. 24 Deconvolution of the optical absorption spectra of Yb^{3+} -doped glass samples

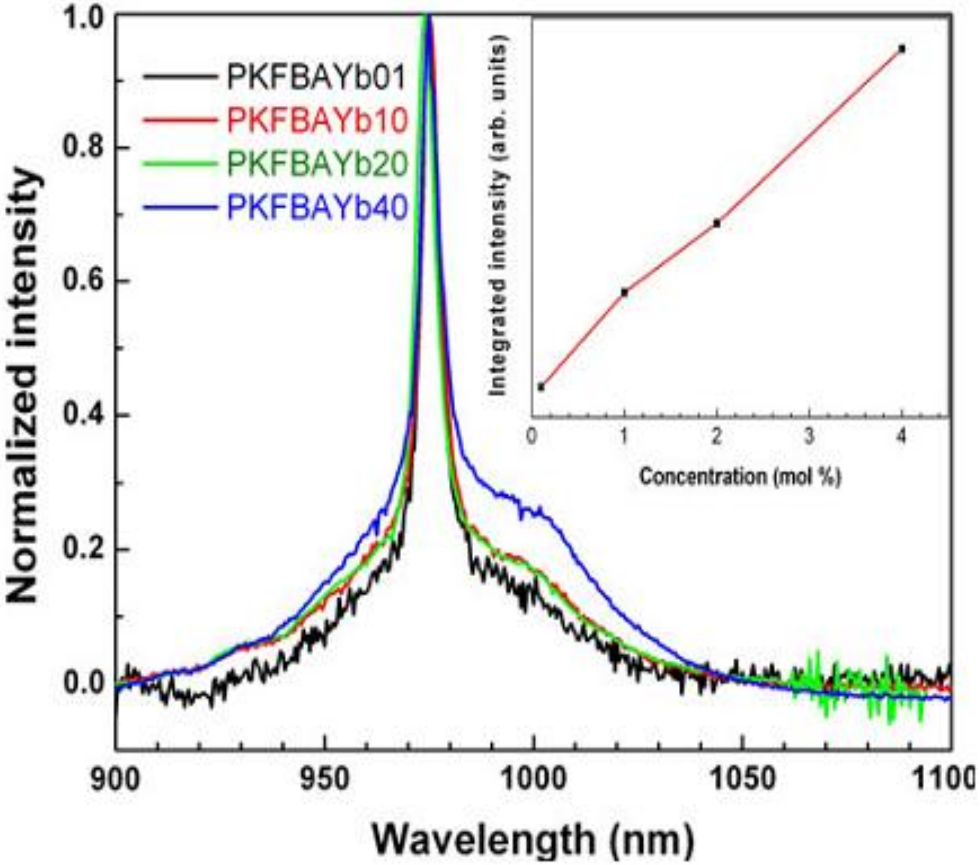


Fig. 25 The emission spectra of Yb^{3+} -doped glass samples

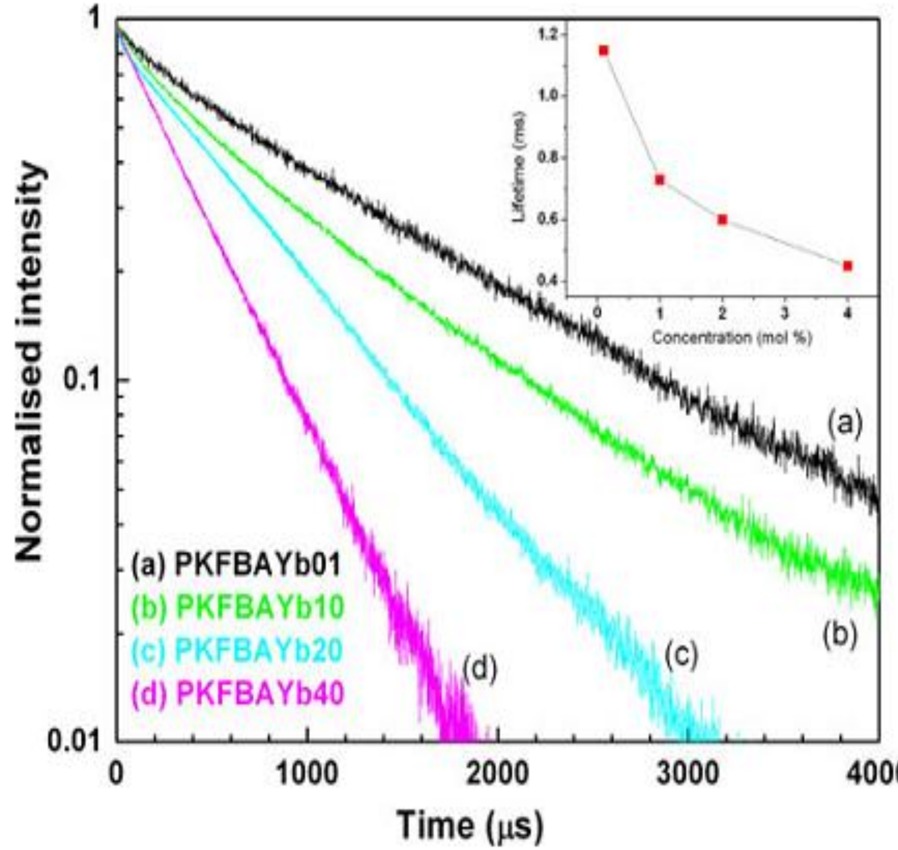
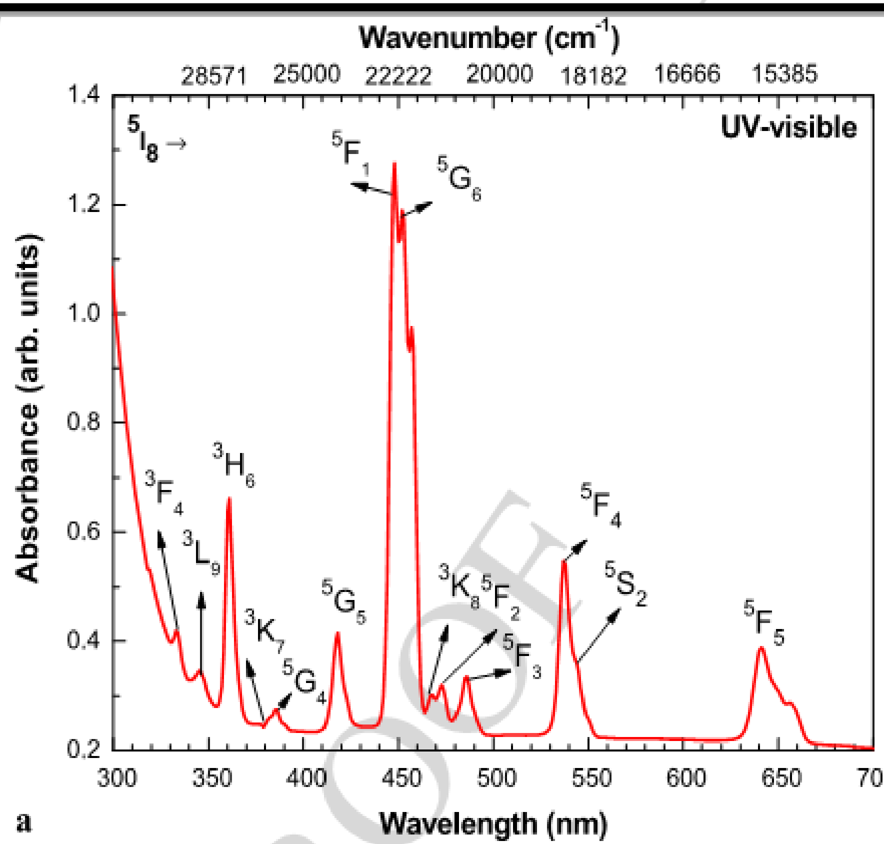


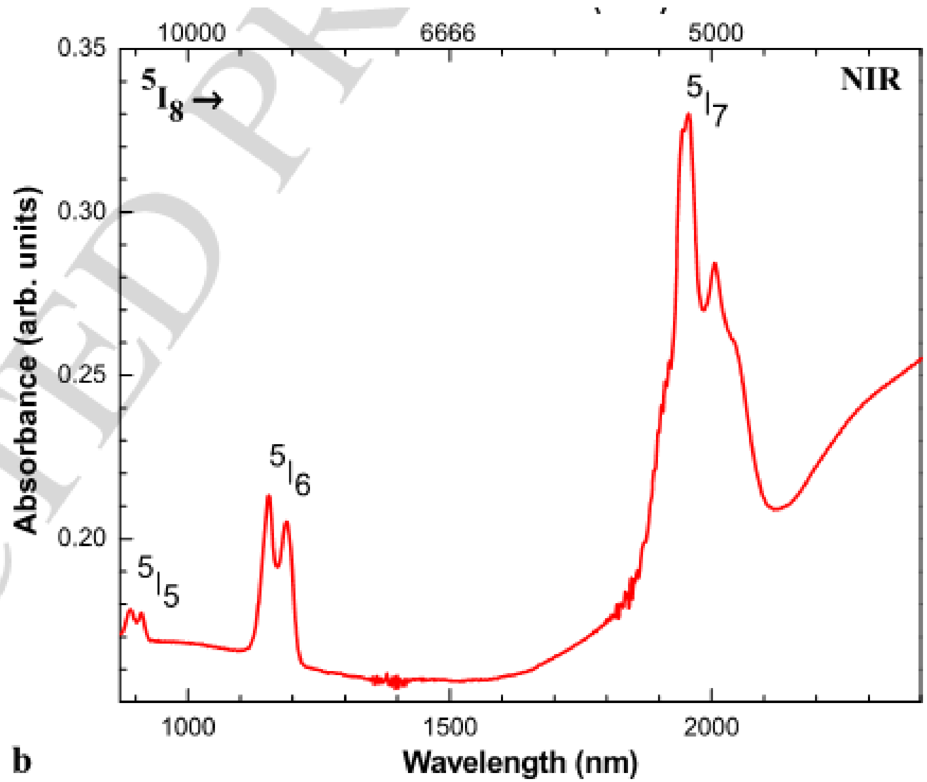
Fig. 26 The decay curveof Yb^{3+} -doped glass samples

Appl Phys A
DOI 10.1007/s00339-013-7852-7
Applied Physics A
Materials Science & Processing

Spectroscopic properties of Ho^{3+}-doped K–Sr–Al phosphate glasses

K. Linganna · M. Rathaiah · V. Venkatramu ·
C.K. Jayasankar





Visible NIR

Fig. 27 The optical absorption spectra of Ho^{3+} -doped glass samples

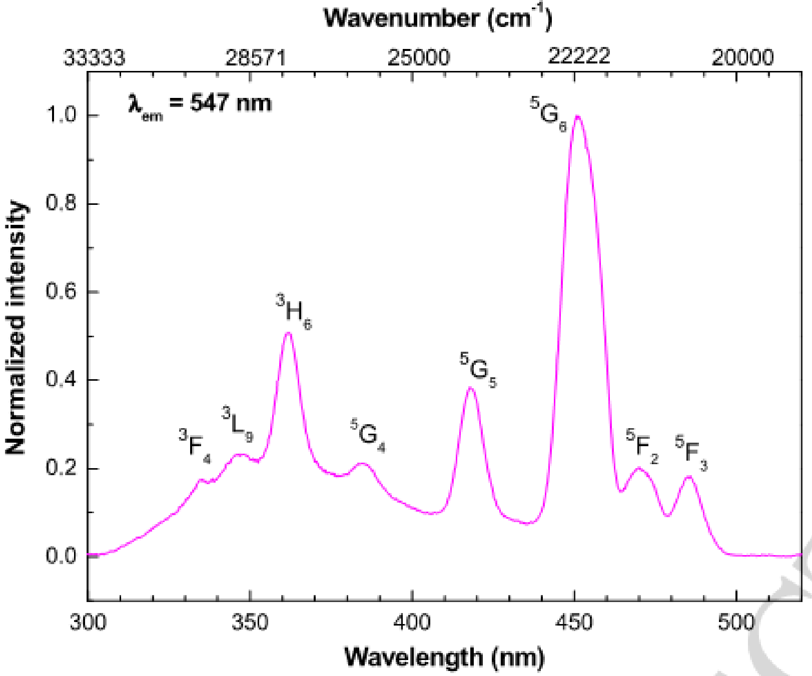


Fig. 28 The excitstion spectra of Ho^{3+}-doped glass samples

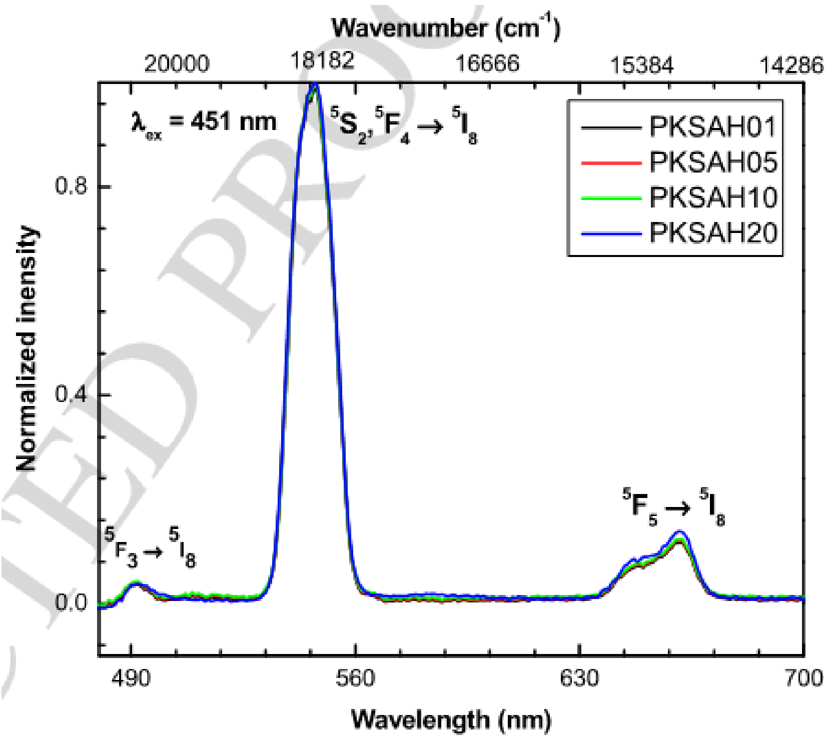


Fig. 29 The emission spectra of Ho^{3+}-doped glass samples

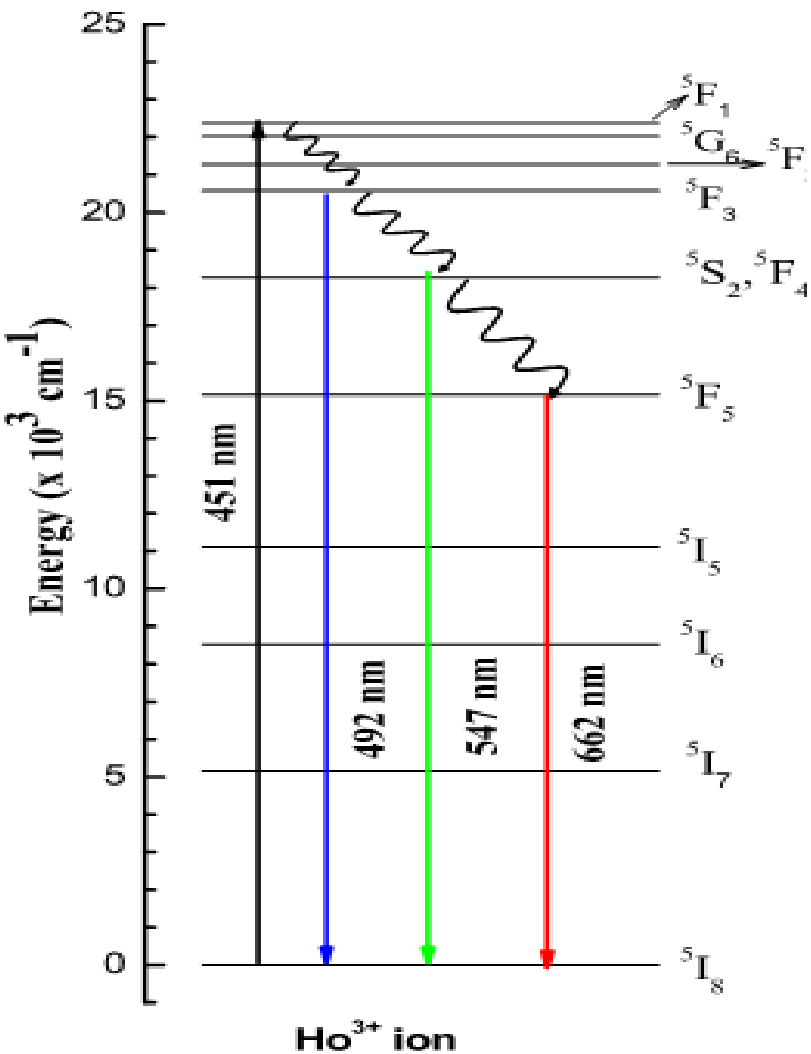


Fig. 30 Energy level of Ho^{3+} -doped glass samples

Next week

Course Outine:

Week 8: Midterm Exam