

Advanced Glass Science

(4016101)



Instructor: Asst.Prof.Dr. Jakrapong Kaewkhao

Course Outline:

Week 5: Luminescence properties and advanced measurement/calculation analysis

+

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*

Luminescence

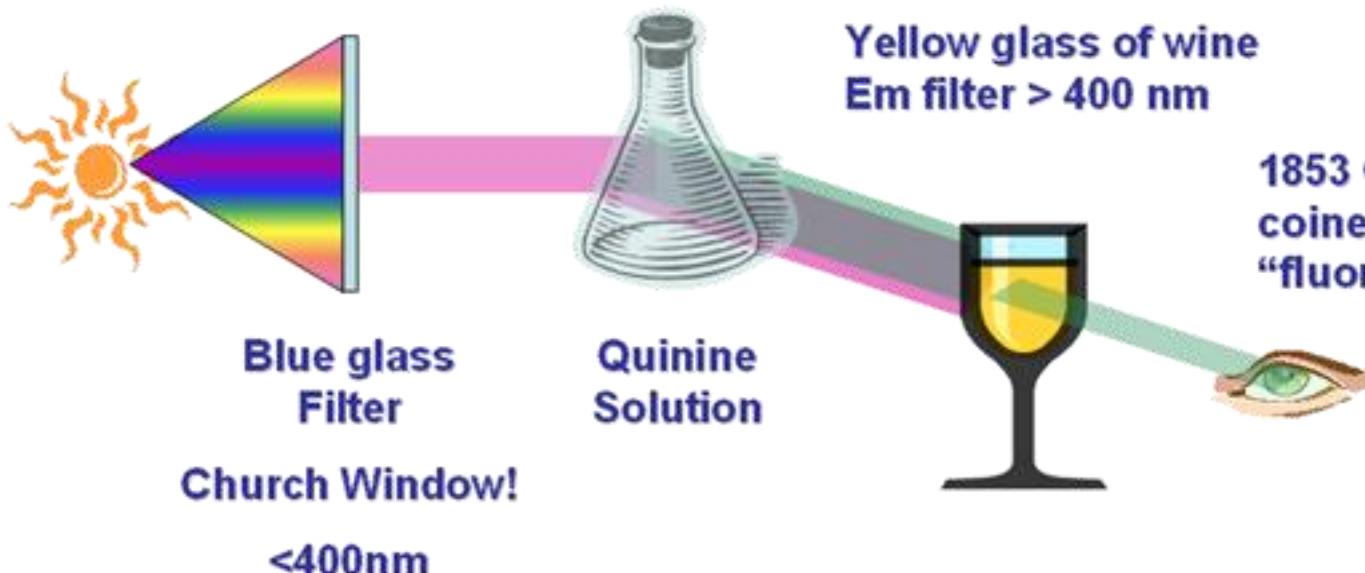


Fluorescence: a type of light emission

- First observed from quinine by Sir J.F.W. Herschel in 1845

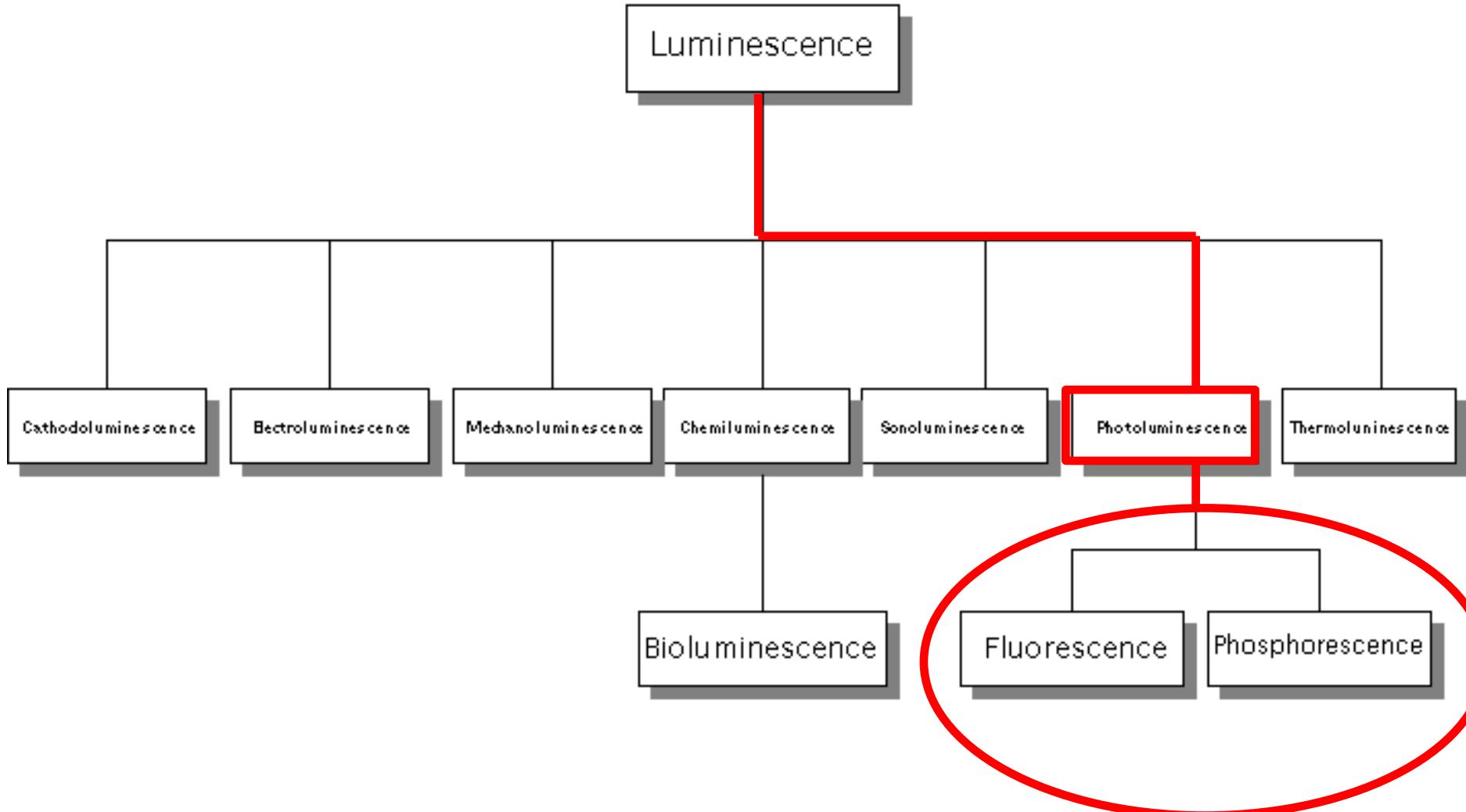


John Herschel
(1792-1871)



1853 G.G. Stokes coined term “fluorescence”

Type of Luminescence



Principle of Photoluminescence



➤ Chemiluminescence — *excitation resulting from a chemical reaction*

➤ Phosphorescence — *excitation by absorption of photons:*

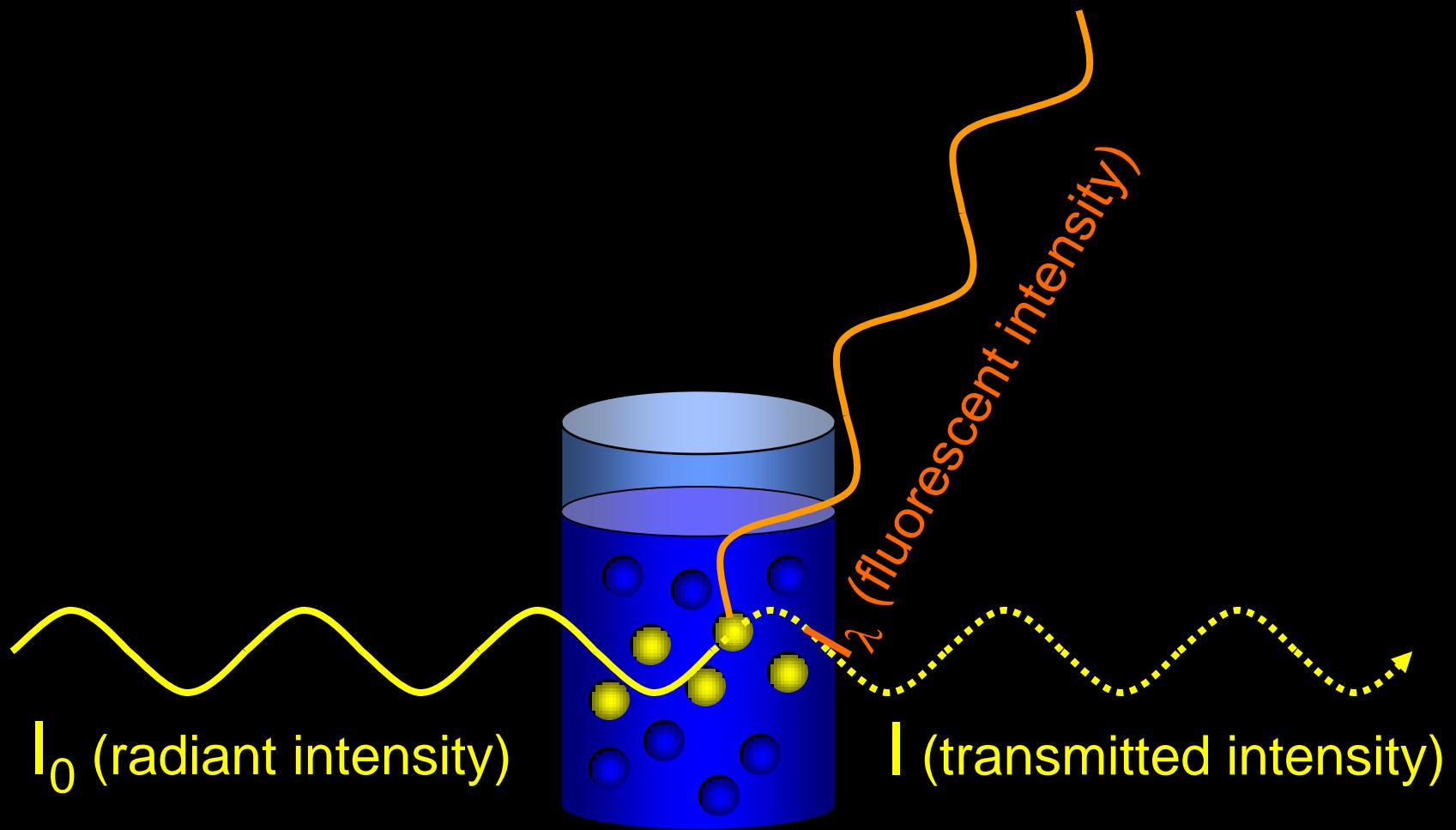
➤ BASIC PRINCIPLE: **PHOTOLUMINESCENCE**

1st: molecules are excited (outer shell electrons like in absorbance phenomenon)

2nd: excited species give an emission spectrum that provides information for quantitation and qualification

Fluorescence is short-lived, with luminescence ceasing almost immediately ($<10^{-5}$ sec), while phosphorescence features luminescence from 10^{-4} to several seconds.

What Do We Make Use Of?



Principle of Photoluminescence



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M X J



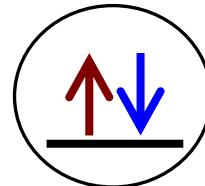
$$M = 2S + 1$$

M = Multiplicity or orbital angular momentum
S = Spin quantum number



Pair electron;

$$S = (+1/2 - 1/2) = 0$$



$$\text{So, } M = 2(0) + 1 = 1$$

But, while the molecules in the excited state, an electron has a chance to change reverse spin.

$$S = (+1/2 + 1/2) = 1$$

$$\underline{\hspace{1cm}} \quad \uparrow$$

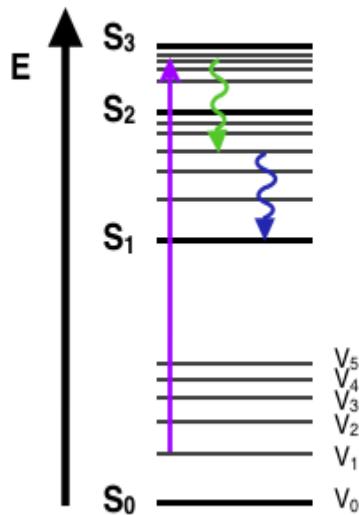
$$\text{So, } M = 2(1) + 1 = 3$$

$$\underline{\hspace{1cm}} \quad \uparrow$$

Principle of Photoluminescence

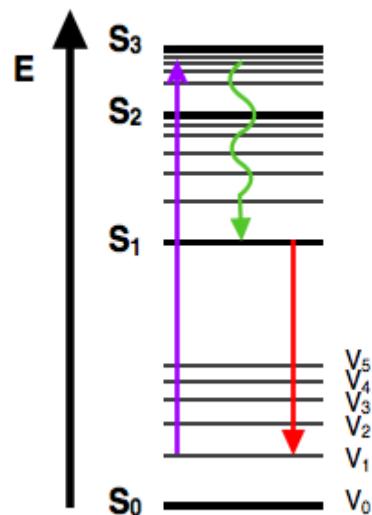


Possible scenario with absorbance, internal conversion, vibrational relaxation shown.



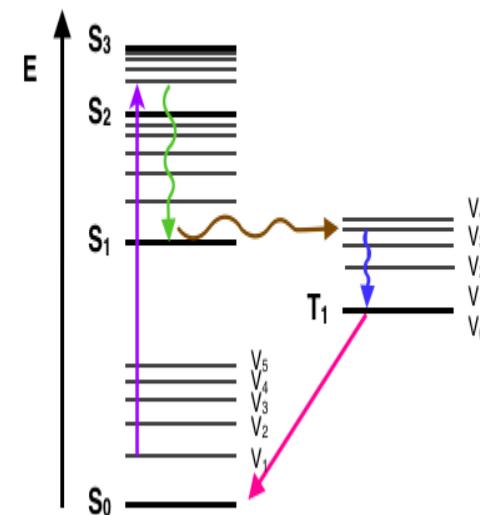
Absorbance

Possible scenario with absorbance, internal conversion, and fluorescence shown.



Fluorescence

A possible phosphorescence pathway: absorbance, internal conversion, intersystem crossing, vibrational relaxation, phosphorescence



Phosphorescence

Fig. 1 Jablonski diagram

Time Scale



Transition	Time Scale (sec)	Radiative process
Absorption	10^{-15}	Yes
Internal conversion	$10^{-14} - 10^{-11}$	No
Vibrational relaxation	$10^{-14} - 10^{-11}$	No
Fluorescence	$10^{-9} - 10^{-7}$	Yes
Intersystem crossing	$10^{-8} - 10^{-3}$	No
Phosphorescence	$10^{-4} - 10^{-1}$	yes

Factors Influencing Photoluminescence



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Solvent effects

→ Frank-Condon principle



Effect of pH

→ - Different molecule and ion
- Resonance



Temperature effect

→ Internal conversion



Effect of hydrogen bonding

→ - Reduce Quantum efficiency
- Internal conversion



Effect of dissolved oxygen

→ - Oxidation with fluorescence mat.
- Intersystem crossing



Effect of impurity

→ Inner filter effect



Effect of concentration

→ Concentration quenching effect

Effect of Concentration



$$I_f \propto \Delta I \propto (I_o - I_T)$$

$$I_f = \Theta_f(I_o - I_T)$$

- I_f = Intensity of fluorescence
 I_o = Intensity of initial light
 I_T = Intensity of transmittance
 Θ_f = Quantum efficiency

From Lambert-Beer law; $I_T = I_o e^{-2.303\epsilon bc}$

$$\text{So, } I_f = \Theta_f(I_o - I_o e^{-2.303\epsilon bc})$$

$$I_f = \Theta_f I_o (1 - e^{-2.303\epsilon bc})$$

Distribution equation

$$\text{So, } e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots + \frac{x^n}{n!}$$

Effect of Concentration



$$\text{So, } I_f = \Theta_f I_o \left[1 - 1 + 2.303\epsilon bc - \frac{(2.303\epsilon bc)^2}{2!} + \frac{(2.303\epsilon bc)^3}{3!} + \dots + \frac{(2.303\epsilon bc)^n}{n!} \right]$$

$$I_f = \Theta_f I_o \left[2.303\epsilon bc - \frac{(2.303\epsilon bc)^2}{2!} + \frac{(2.303\epsilon bc)^3}{3!} + \dots + \frac{(2.303\epsilon bc)^n}{n!} \right]$$

If the solution dilution, $\epsilon bc \leq 0.05$

$$\text{So, } I_f = \Theta_f I_o 2.303\epsilon bc \quad \text{or} \quad I_f = KC$$

Where K = Constant for the equipment used
C = Concentration

Effect of Concentration

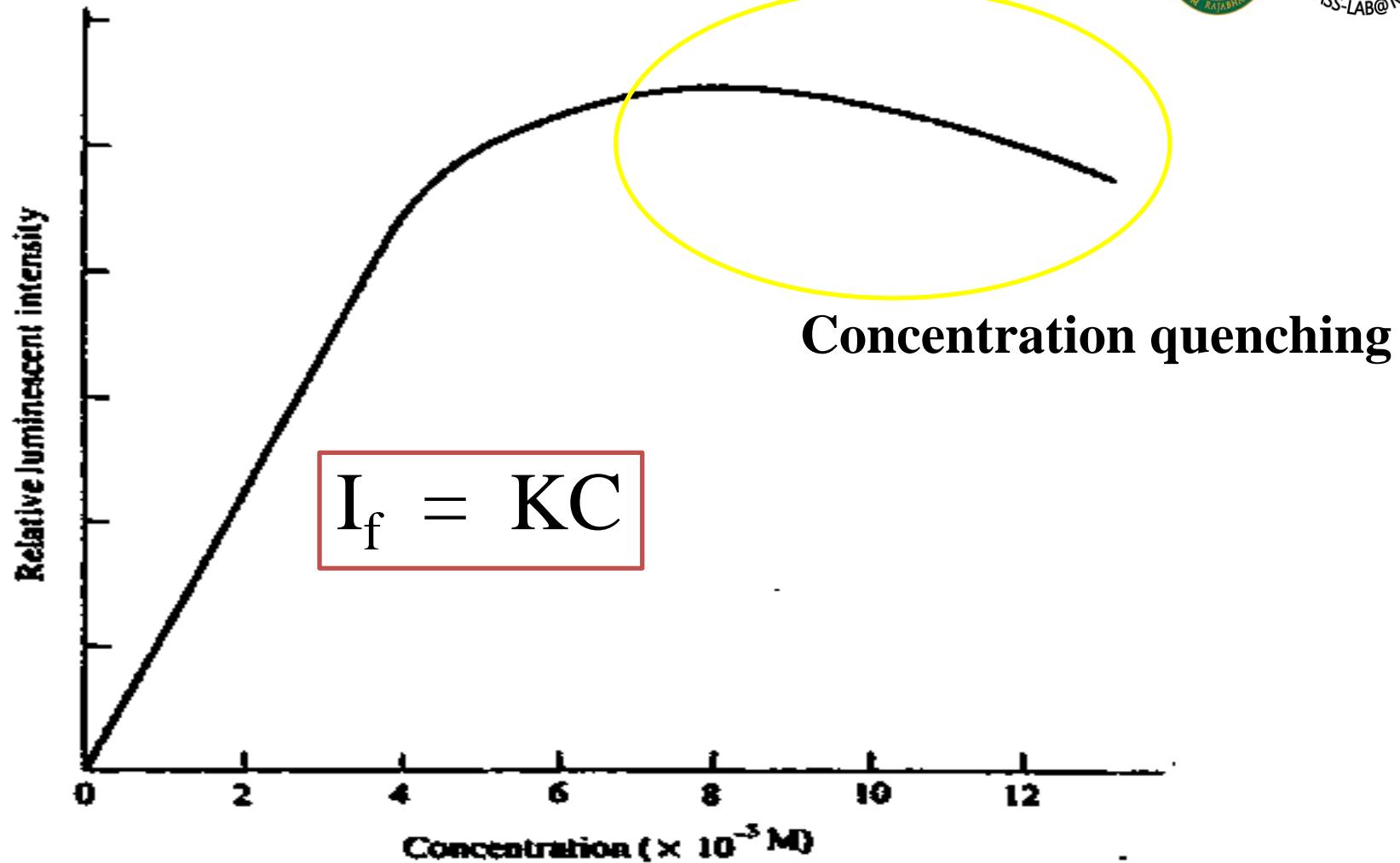


Fig. 2 Relation of concentration and luminescence intensity

Luminescence Measurement

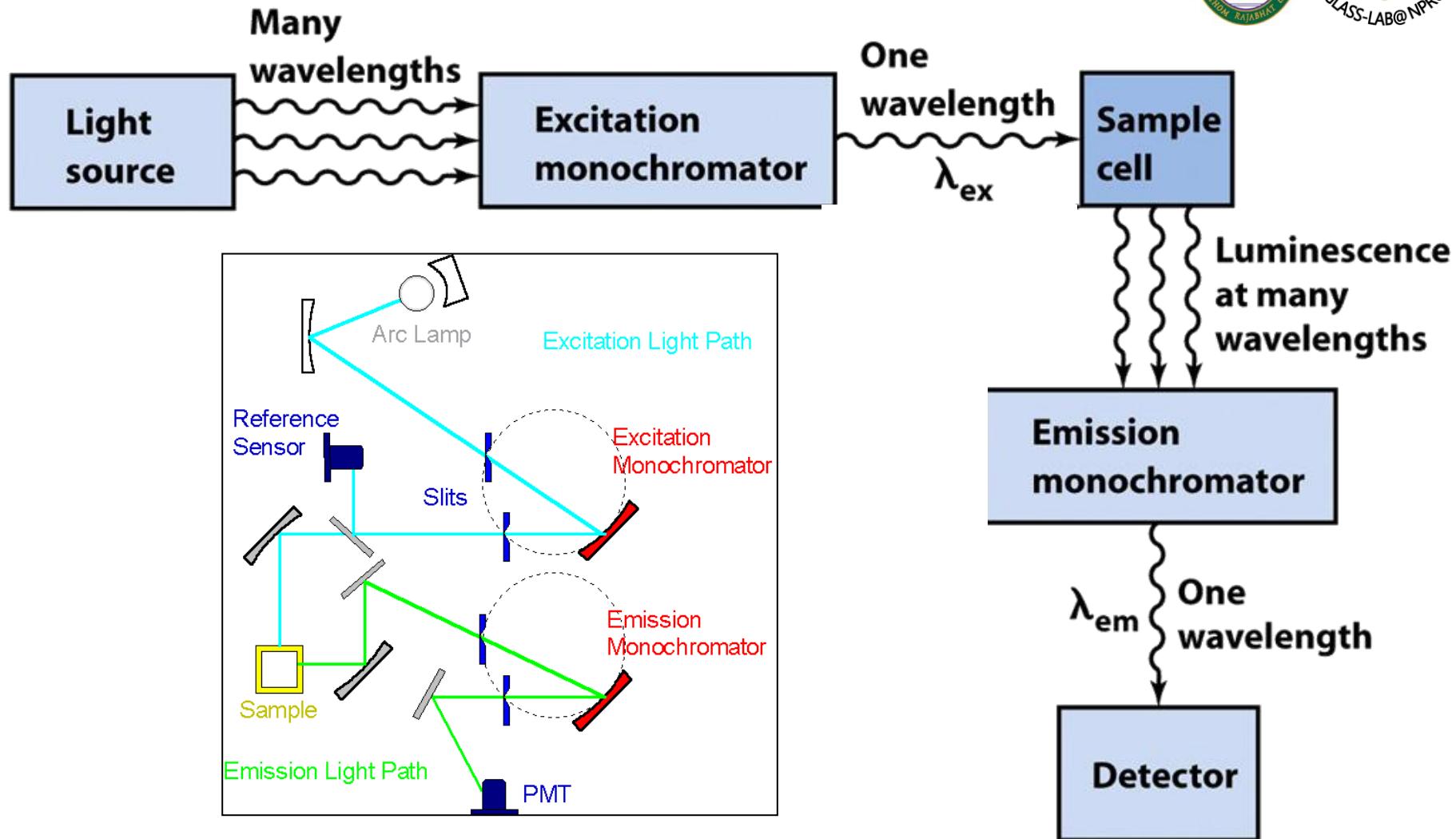


Fig. 3 Luminescence measurement diagram

The Photoluminescence and Physical Properties of Eu³⁺ Ions in Li₂O-Y₂O₃-B₂O₃ 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*}

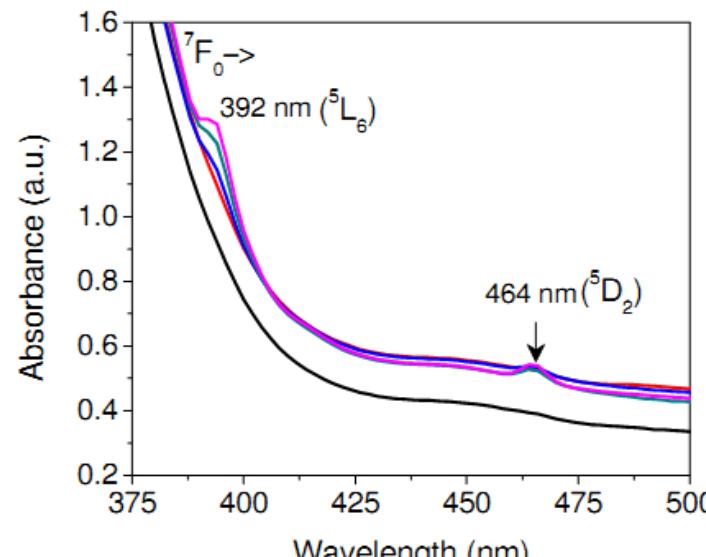


Fig. 4 The optical absorption spectra of LiYBO:Eu³⁺ glass samples

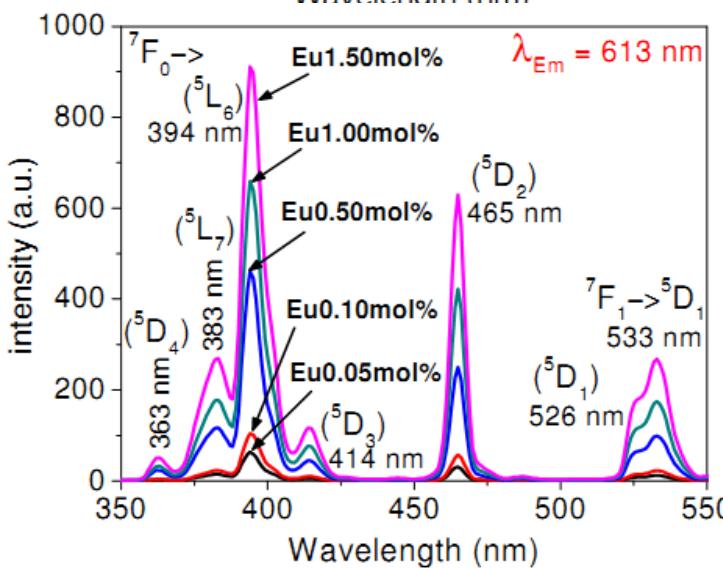


Fig. 5 The excitation spectra of LiYBO:Eu³⁺ glass samples

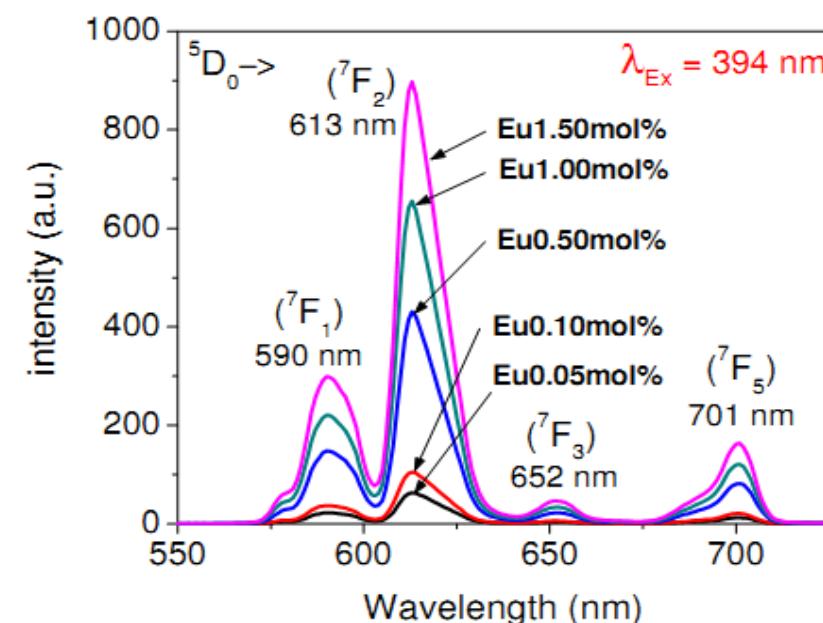


Fig. 6 The emission spectra of LiYBO:Eu³⁺ glass samples

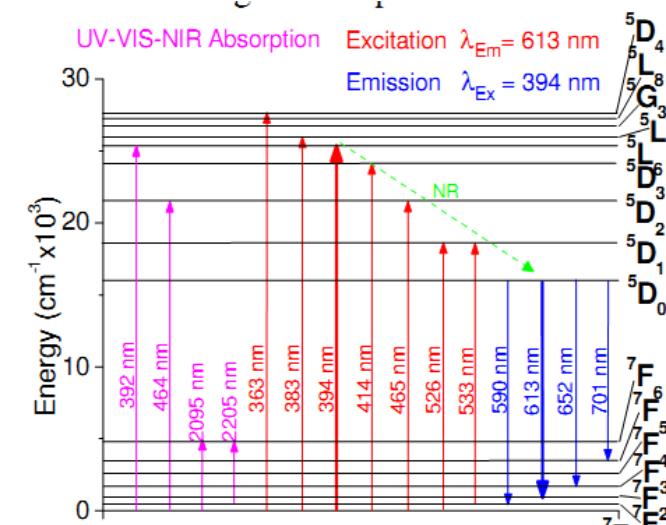


Fig. 7 Energy level of LiYBO:Eu³⁺ glass samples

The Photoluminescence, Optical Absorption and Physical Properties of Dy³⁺ Ions in Li₂O-La₂O₃-B₂O₃ 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*}

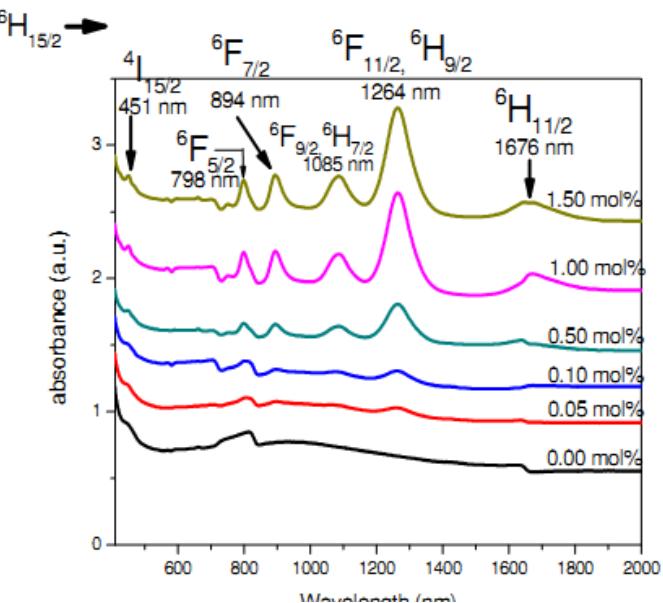


Fig. 8 The optical absorption spectra of LiLaBO:Dy³⁺ glass samples

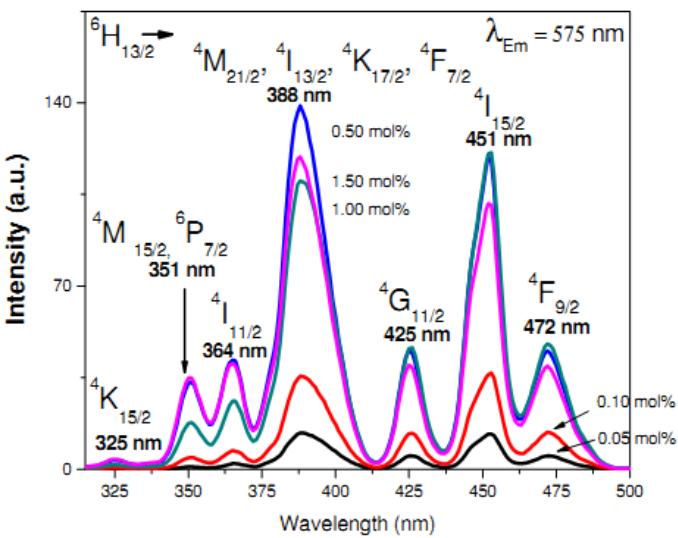


Fig. 9 The excitation spectra of LiLaBO:Dy³⁺ glass samples

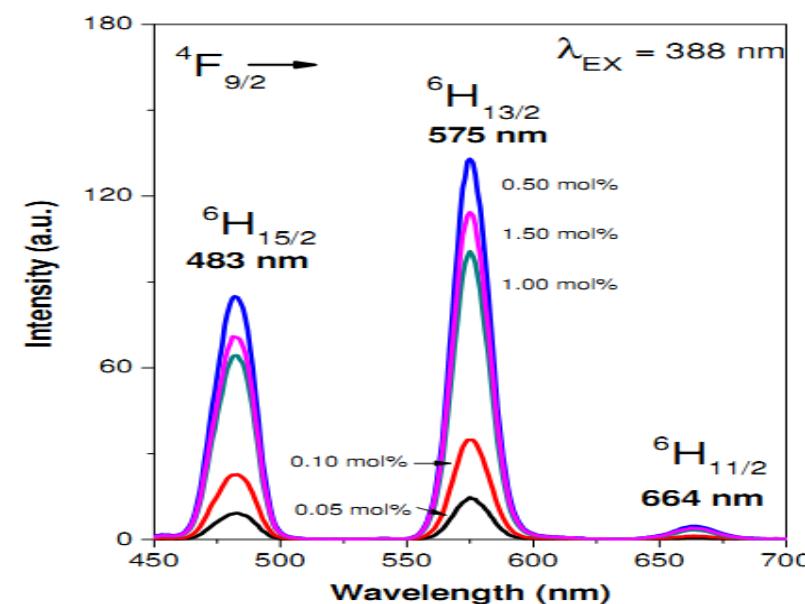


Fig. 10 The emission spectra of LiLaBO:Dy³⁺ glass samples

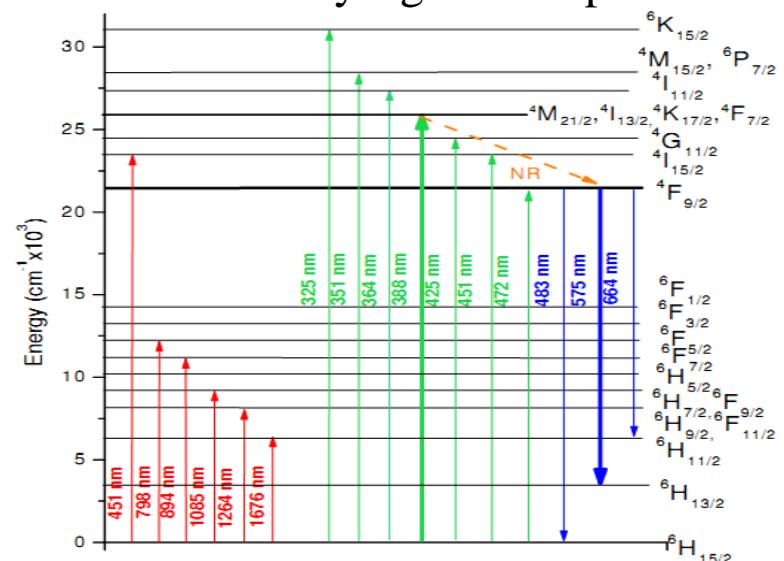


Fig. 11 Energy level of LiLaBO:Dy³⁺ glass samples

Optical Absorption and Photoluminescence Properties of Dy³⁺ Ions in Bi₂O₃-SiO₂-B₂O₃ Glass System

N. Sangwananatee^{1,a}, Y. Tariwong^{1,a}, S. Sarachai^{1,a},
 J. Kaewkhao^{2,3,b}, N. Chanthima^{2,3,c*}

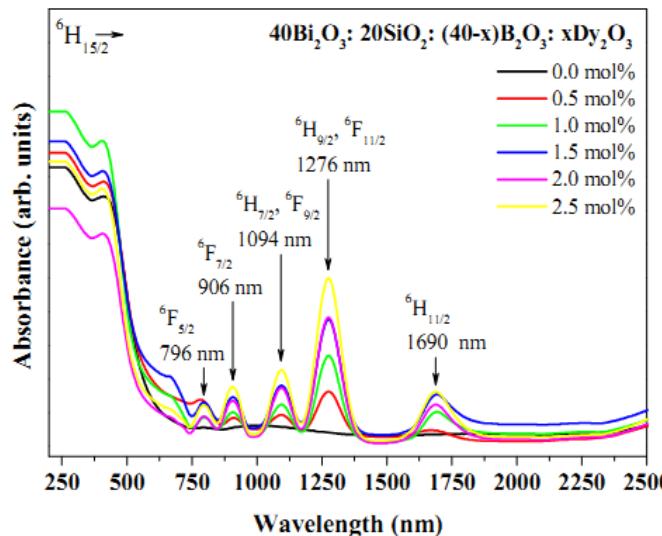


Fig. 12 The optical absorption spectra of Dy³⁺ doped in bismuth borosilicate glasses

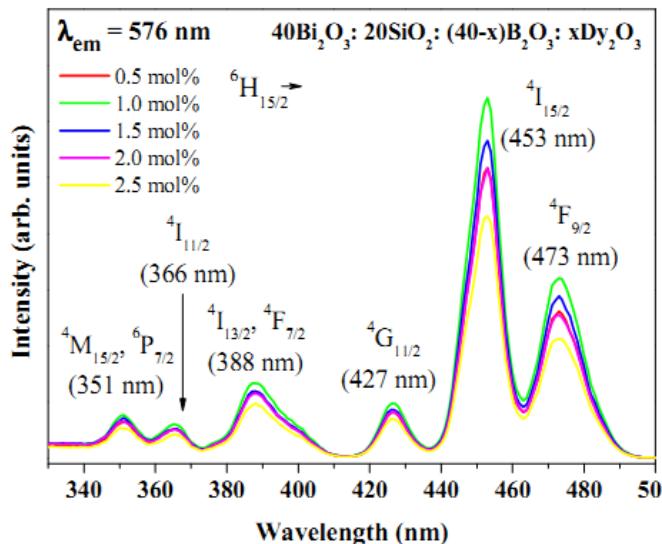


Fig. 13 The excitation spectra of Dy³⁺ doped in bismuth borosilicate glasses

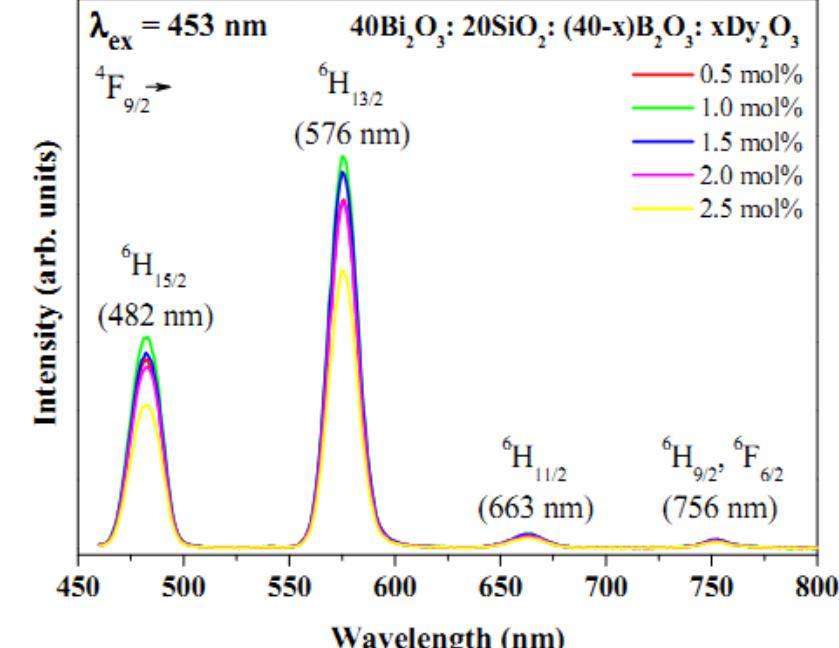


Fig. 14 The emission spectra of Dy³⁺ doped in bismuth borosilicate glasses

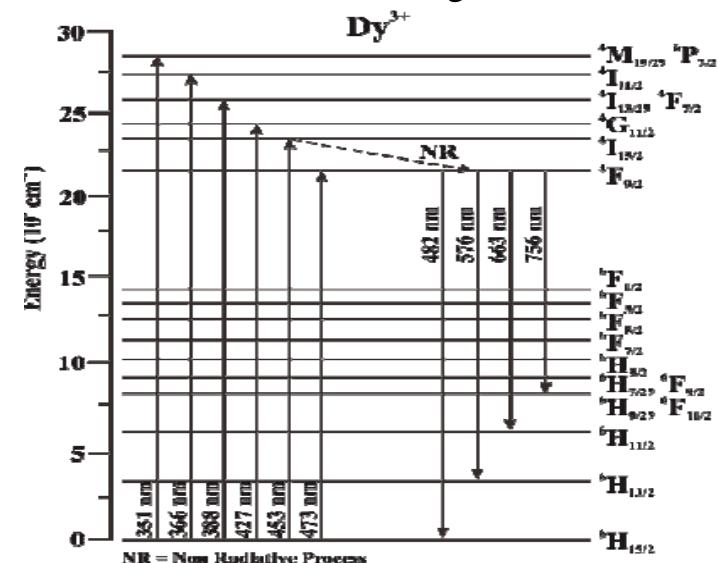


Fig. 15 Energy level of LiLaBO:Dy³⁺ doped in bismuth borosilicate glasses

Luminescence and Optical Properties of $\text{Li}_2\text{O}_3:\text{Gd}_2\text{O}_3:\text{B}_2\text{O}_3:\text{Sm}_2\text{O}_3$ Glasses System

W. Sa-arbsin^{1,a}, P. Yasaka^{2,b}, J. Kaewkhao^{1,2,c}, K. Boonin^{1,2,d*}

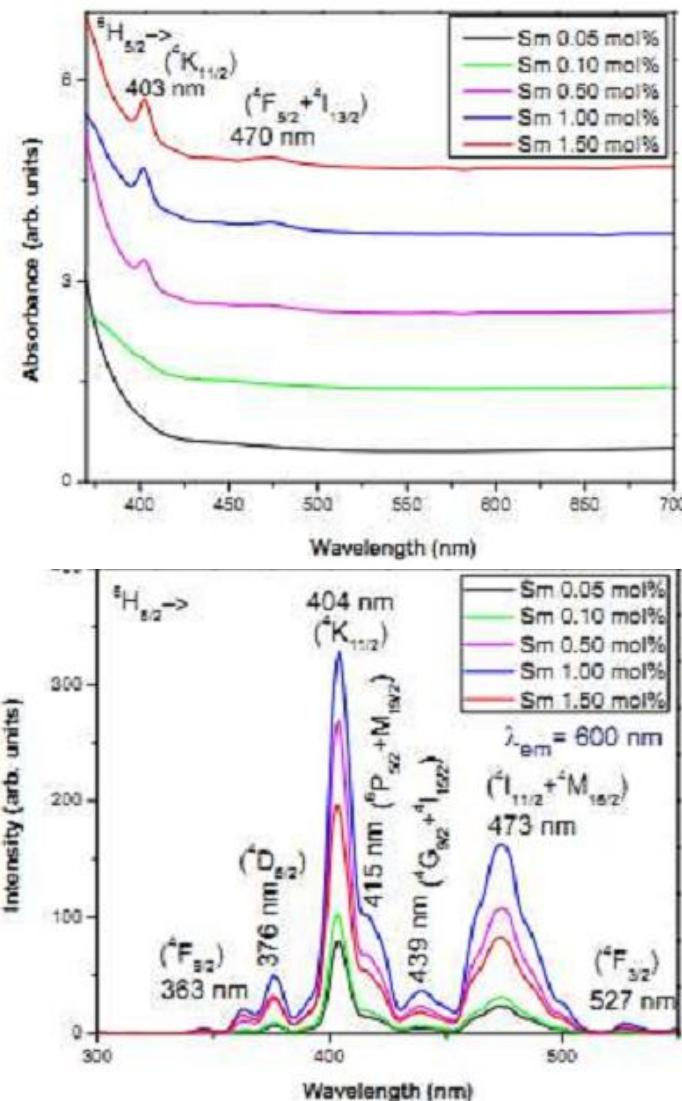


Fig. 16 The optical absorption spectra of LGOBO:Eu³⁺ glass samples
Fig. 17 The excitation of LGOBO:Eu³⁺ glass samples

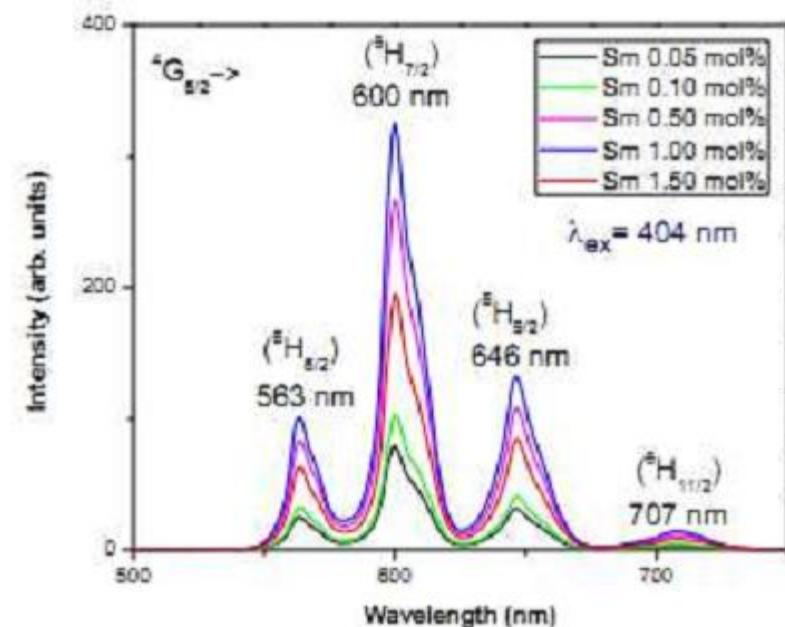


Fig. 18 The emission spectra of LGOBO:Sm³⁺ glass samples

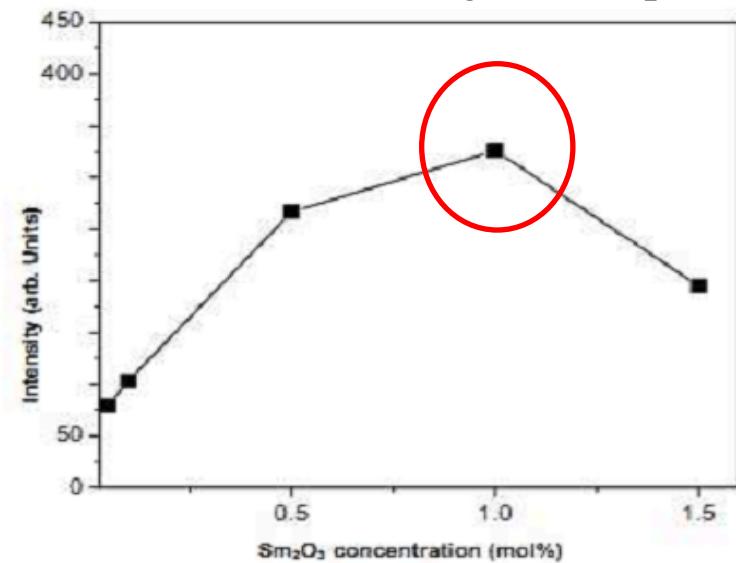


Fig. 19 Concentration quenching of LGOBO:Sm³⁺ glass samples

Research Article

Up- and Downconversion Luminescence Properties of Nd³⁺ Ions Doped in Bi₂O₃-BaO-B₂O₃ Glass System

R. Ruamnikhom,¹ P. Limsuwan,¹ M. Horprathum,² N. Chanthima,³
H. J. Kim,⁴ S. Ruengsri,⁵ and J. Kaewkhai³

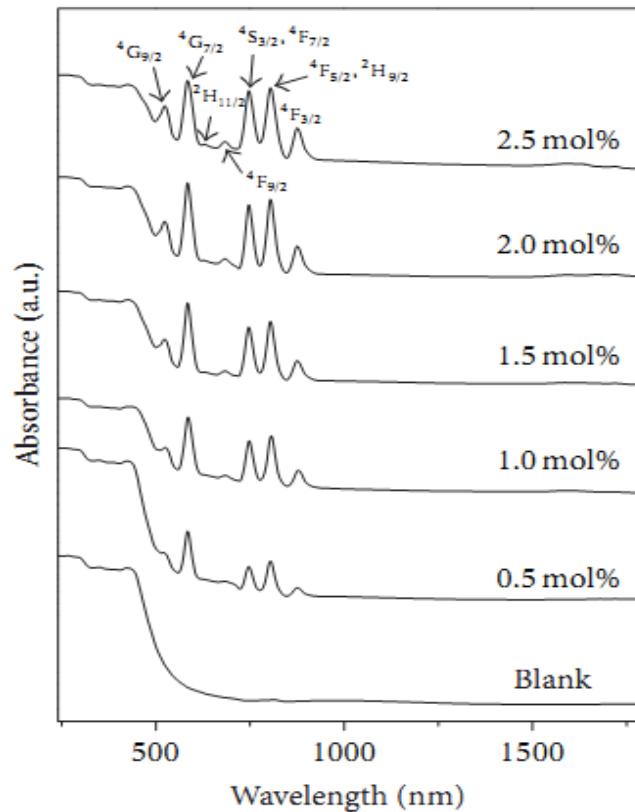
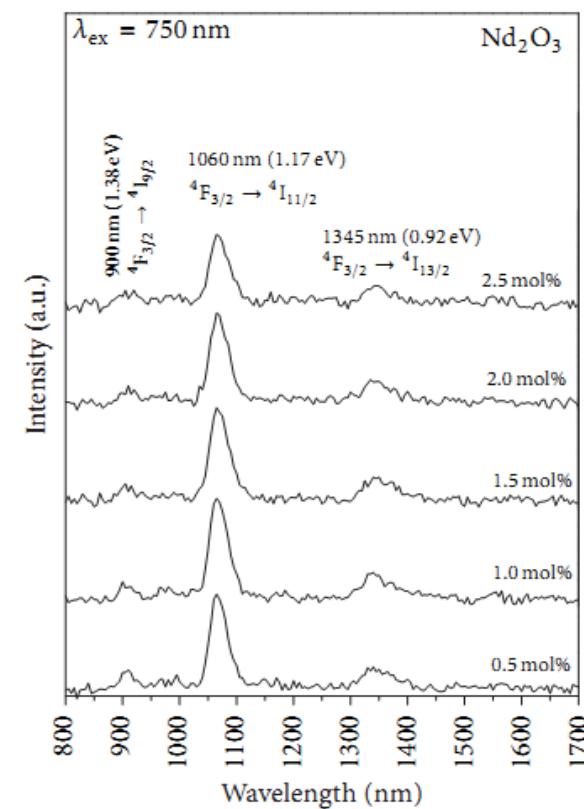


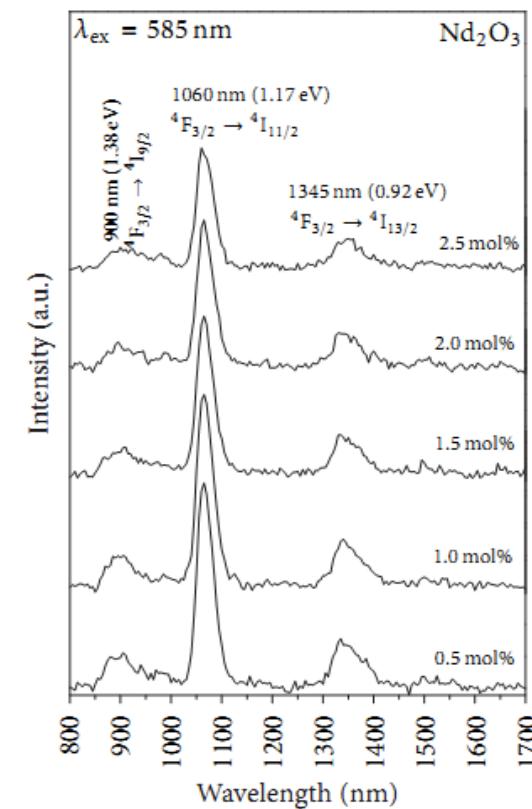
Fig. 20 The optical absorption spectra of Nd³⁺-doped BiBaBo glass samples

Nd ₂ O ₃ (mol%)	Glass system
0.00	40.00Bi ₂ O ₃ :20.00BaO:40.00B ₂ O ₃
0.50	40.00Bi ₂ O ₃ :20.00BaO:39.50B ₂ O ₃ :0.50Nd ₂ O ₃
1.00	40.00Bi ₂ O ₃ :20.00BaO:39.00B ₂ O ₃ :1.00Nd ₂ O ₃
1.50	40.00Bi ₂ O ₃ :20.00BaO:38.50B ₂ O ₃ :1.50Nd ₂ O ₃
2.00	40.00Bi ₂ O ₃ :20.00BaO:38.00B ₂ O ₃ :2.00Nd ₂ O ₃
2.50	40.00Bi ₂ O ₃ :20.00BaO:37.50B ₂ O ₃ :2.50Nd ₂ O ₃



(a)

Fig. 21 The NIR emission spectra of Nd³⁺-doped BiBaBo glass samples when excited by 585 and 750 nm



(b)

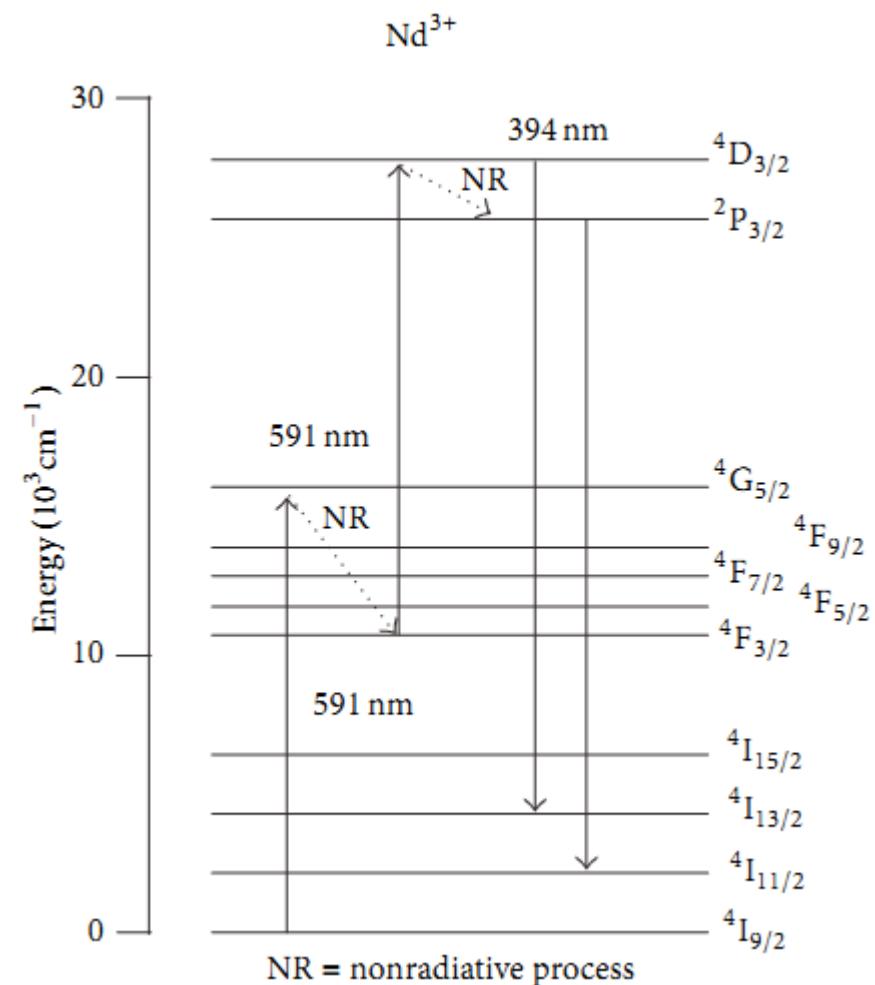
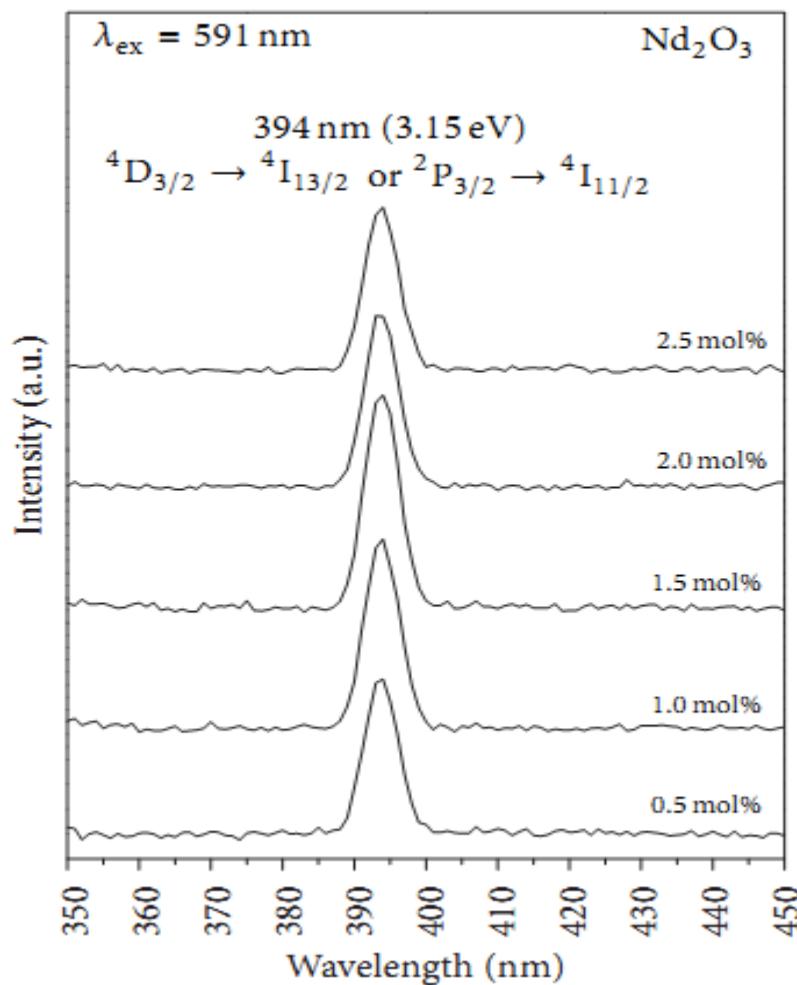


Fig. 22 The upconversion luminescence spectra of Nd^{3+} -doped BiBaBo glass samples when excited by 591 nm

Fig. 23 Energy level of Nd^{3+} -doped BiBaBo glass samples

Next week

Course Outline:

- Week 6:**
- *Transition element in glass*
 - *Glass color*
 - *Oxidation/Reduction equilibrium in glass*
- Case studies from international publications*

