Advanced Glass Science
(4016101)

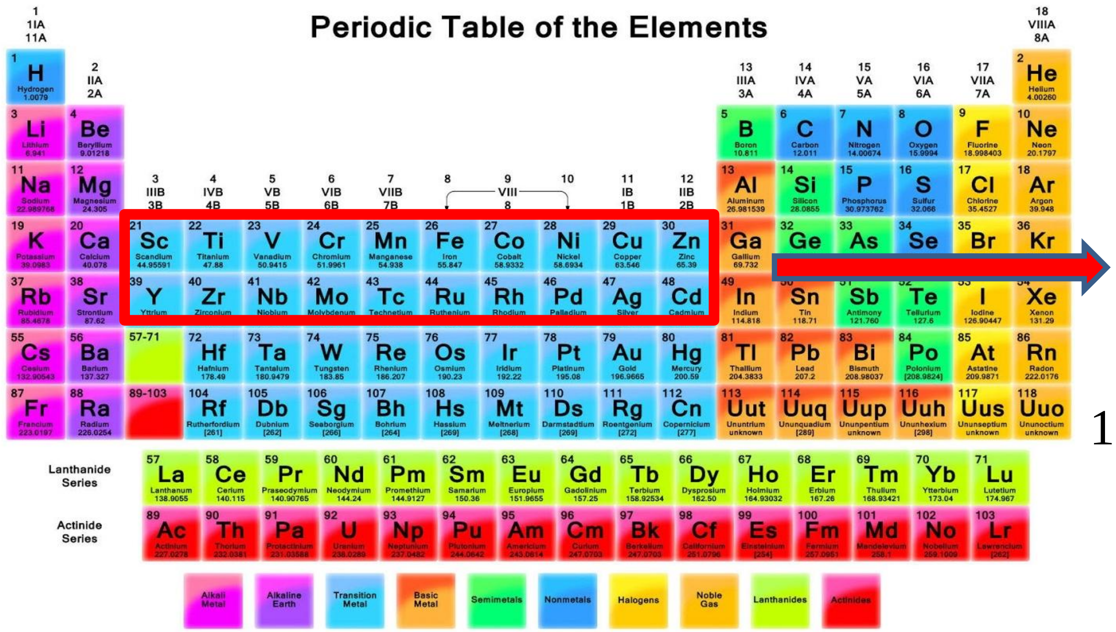
Instructor: Asst.Prof.Dr. Jakrapong Kaewkhao

Course Outline:

Week 6: *- Transition element in glass*
- Glass color
- Oxidation/Reduction equilibrium 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***

Transition Group



Sc to Ni 1^{st} series

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^n}\ 4s^2$

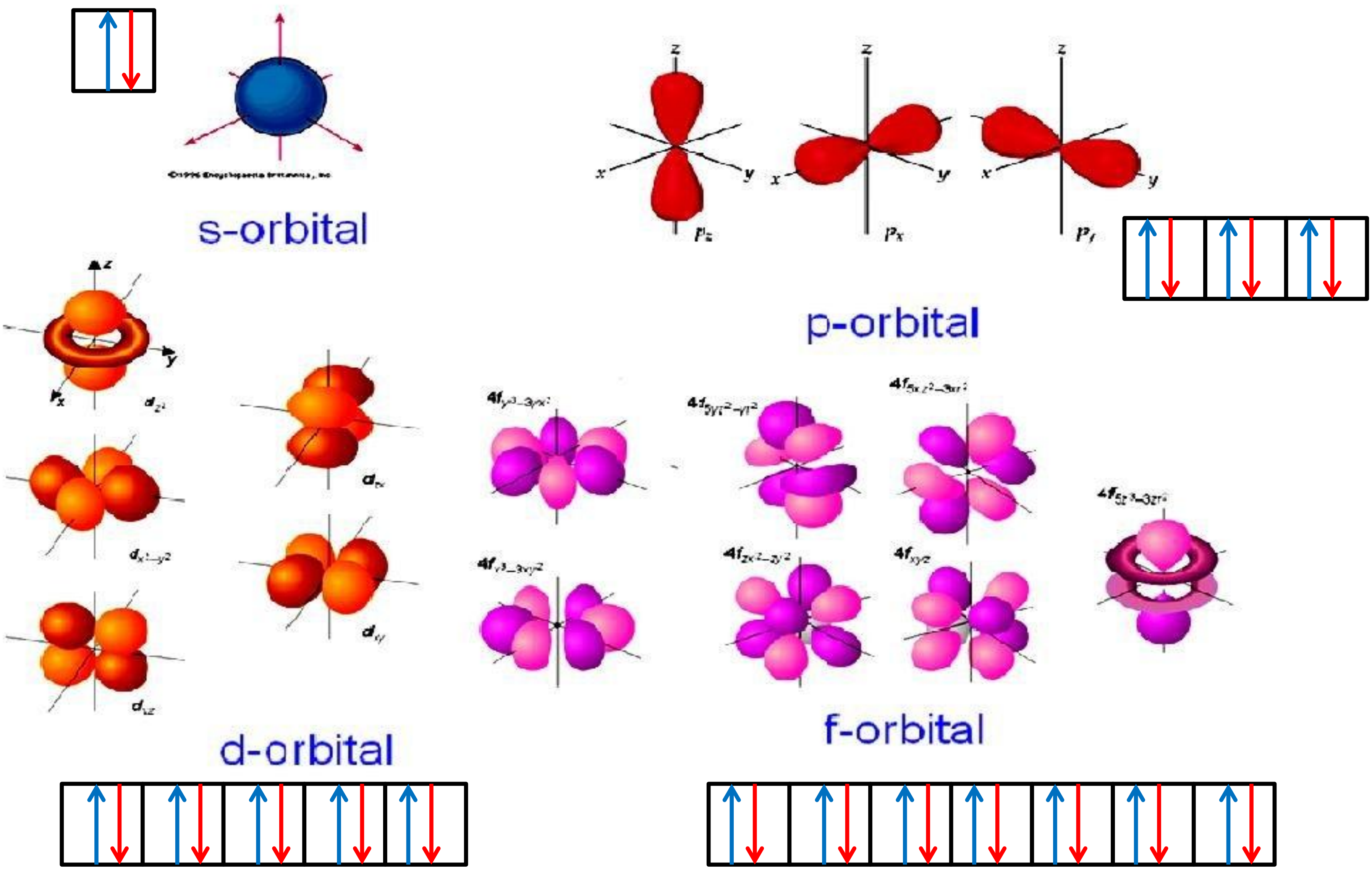
Y to Pd 2^{nd} series

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ \mathbf{4d^n}\ 5s^2$

There are three major approaches to the study of bonding in transition metal complexs:

1. Ligand field theory, which is a modified form of crystal field theory in which allowance is made for orbital overlap.
2. Valency bond theory
3. Molecular orbital theory

Ligand Field Theory



Ligand Field Theory

Consider transition metal ions:

There are five hybrid orbitals for **3d electrons** with distinct spatial orientations.

Electron energy distributions for the five *d* orbitals

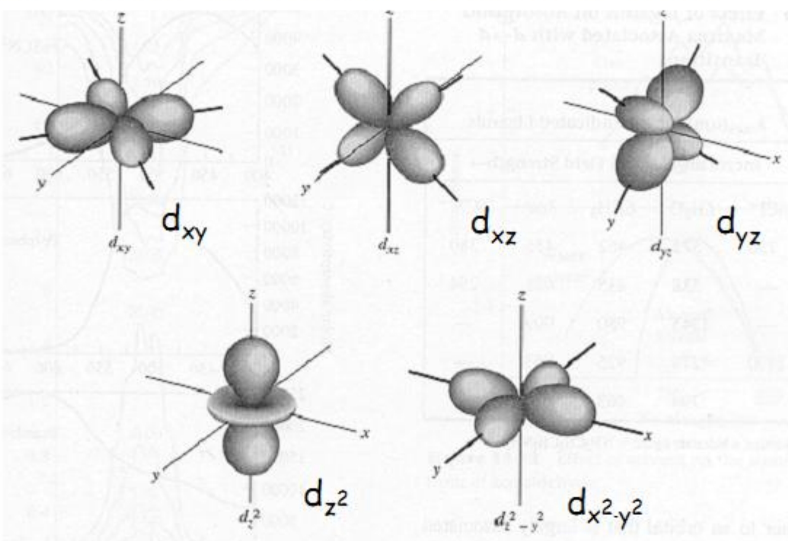


Figure 14-8 Electron-density distribution in the five *d* orbitals.

- Energies of d orbitals in transition-metal ions in different hosts are not identical

- In the absence of an electric or magnetic field (as in dilute gaseous state), the energies of the five orbitals are identical and so the absorption of a photon is not required for an electron to move from one orbital to another.

- In the presence of a field (e.g., when the transition metal cation is coordinated by anions) splitting of the d-orbitals energies results.

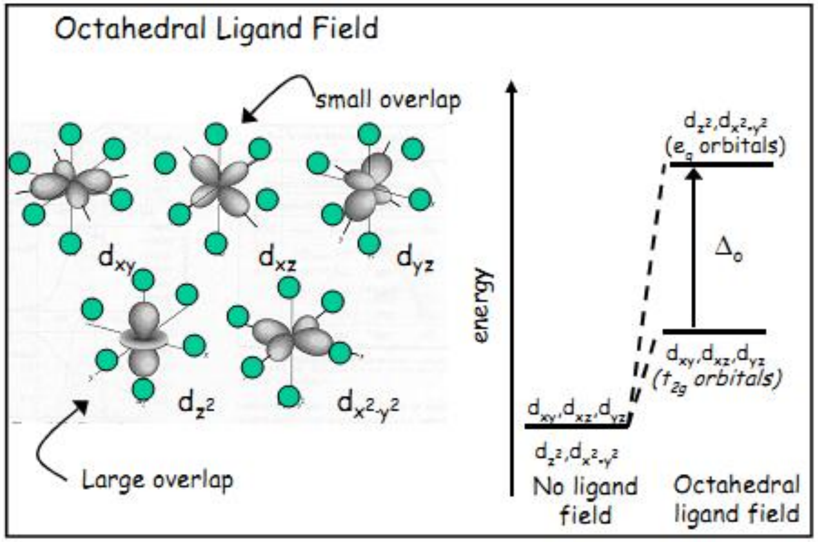
- Electrostatic repulsion between electron pairs from the host (donor) and from the 'central' TM ion.

Ligand Field Theory

Splitting of d^n terms in an octahedral field

Term	Components in an octahedral field
S	A_{1g}
P	T_{1g}
D	$\mathbf{E_g + T_{2g}}$
F	$A_{2g} + T_{1g} + T_{2g}$
G	$A_{1g} + E_g + T_{1g} + T_{2g}$
H	$E_g + T_{1g} + T_{1g} + T_{2g}$
I	$A_{1g} + A_{2g} + E_g + T_{1g} + T_{2g} + T_{2g}$

Ligand Field Theory

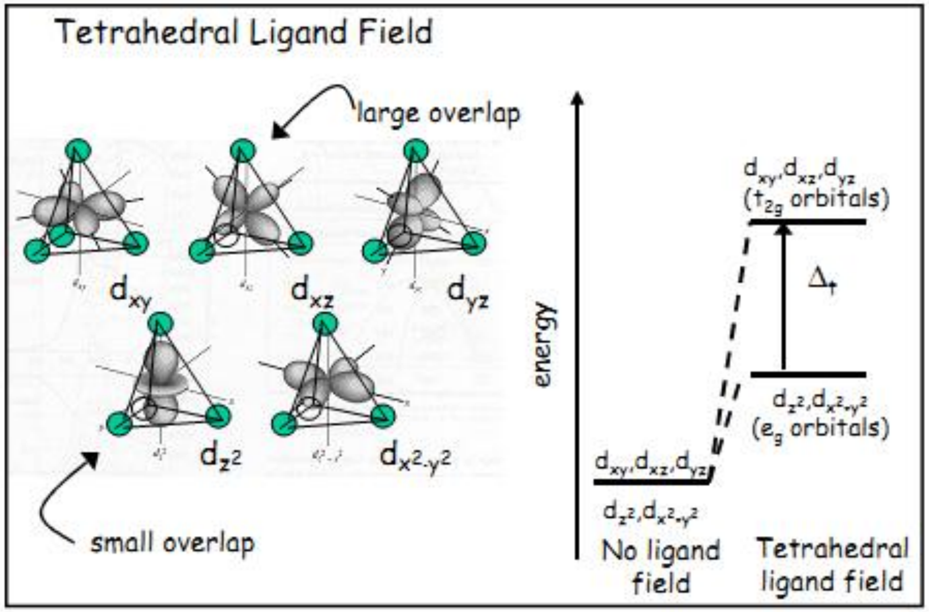


• In an octahedral ligand field, there is a greater overlap of the d_{x2} and d_{x2-y2} orbitals (the e_g orbitals- so-named from group theory) with the ligand orbitals, and so these will have greater energies than the d_{xy}, d_{xz}, and d_{yz} orbitals (the t_{2g} orbitals).

• Photons that possess the gap energy (the energy difference between the different d-orbitals, Δ_o) will be absorbed as they excite electrons from the lower energy orbitals to the higher energy orbitals.

• Ti^{3+}/octahedral CN: [Ar]3d1: $t^1_{2g}e^0_g \rightarrow t^0_{2g}e^1_g$ transition: Purple color in phosphate glass

Ligand Field Theory

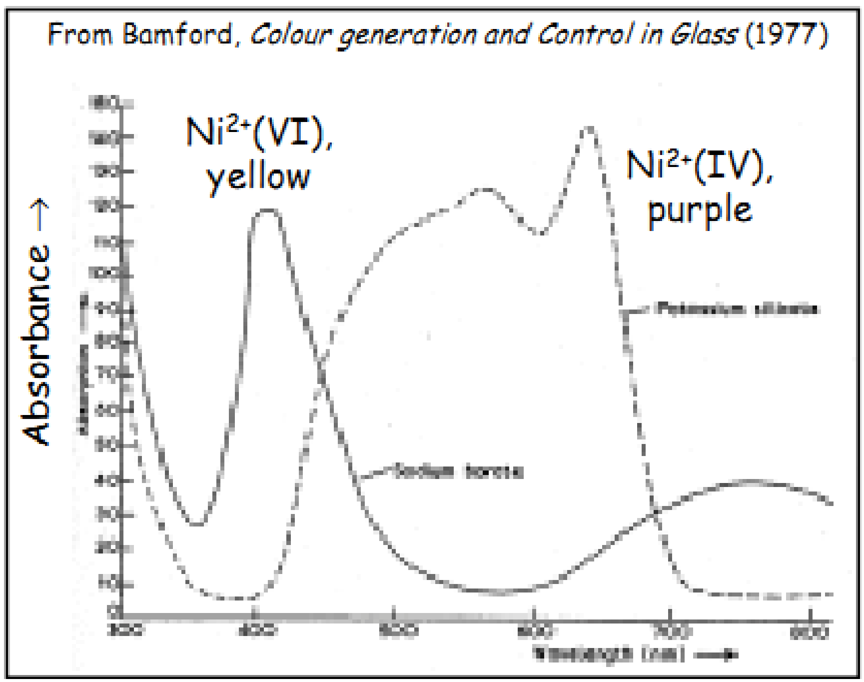


• In a tetrahedral ligand field, there is a greater overlap of the d_{xy}, d_{xz}, and d_{yz} orbitals with the ligand orbitals, and so these will have greater energies than the d_{x2} and d_{x2-y2} orbitals.

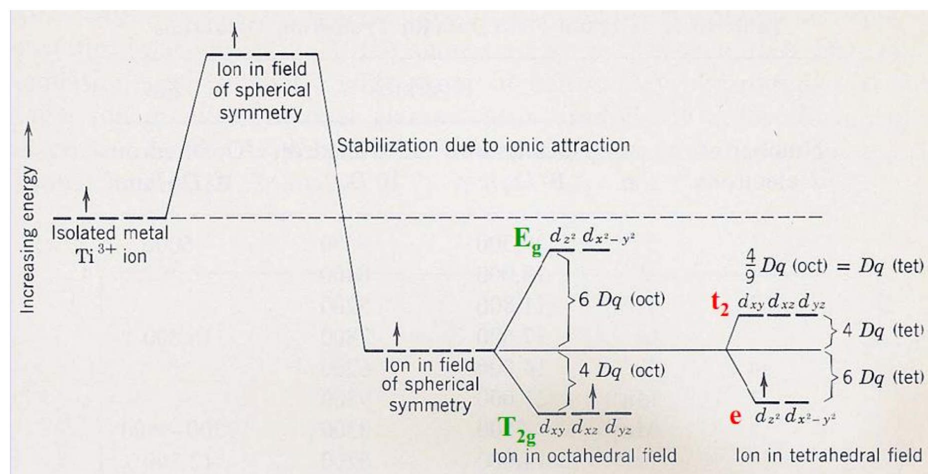
• Photons that possess the gap energy (the energy difference between the different d-orbitals, $\Delta\tau$) will be absorbed as the excite electrons from the lower energy orbitals to the higher energy orbitals

Glass Color

1. The color is due to absorption of light.
   - Environment in glass structure
   - Oxidation state
2. Solid colloid
3. The color is due to differences in particle size.

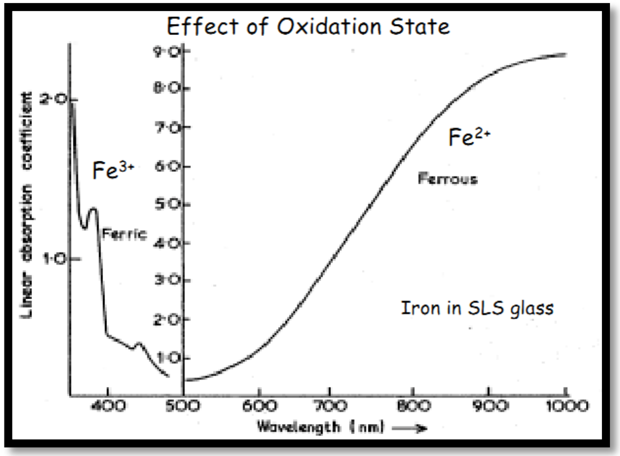


- Consider Ni^{2+}: ([Ar]3d8)
- Na-Ca-silicate: Ni^{2+}(VI): $t^6_{2g}e_{2g} \rightarrow t^5_{2g}e^2_g$: pale yellow glass
- K-Ca-silicate: Ni^{2+}(IV): $e^4_g t^4_{2g} \rightarrow e^3_g t^5_{2g}$: purple glass



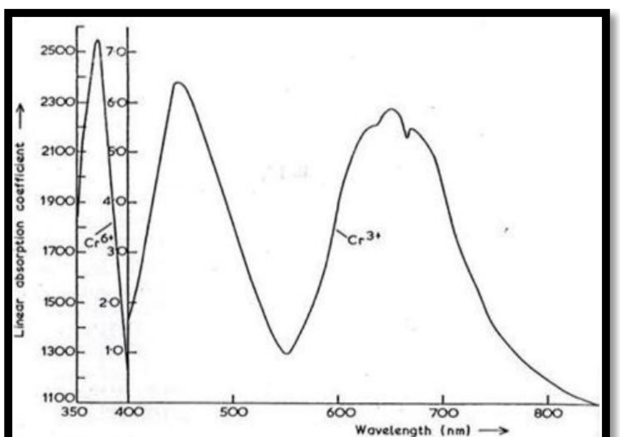
Crystal field energy relationships for Ti^{3+} ion in an octahedral and tetrahedral field.

Oxidation/Reduction Equilibrium in Glass



$$4Fe^{2+} + O_2 \rightarrow 4Fe^{3+} + 2O^{2-}$$

Green Yellow



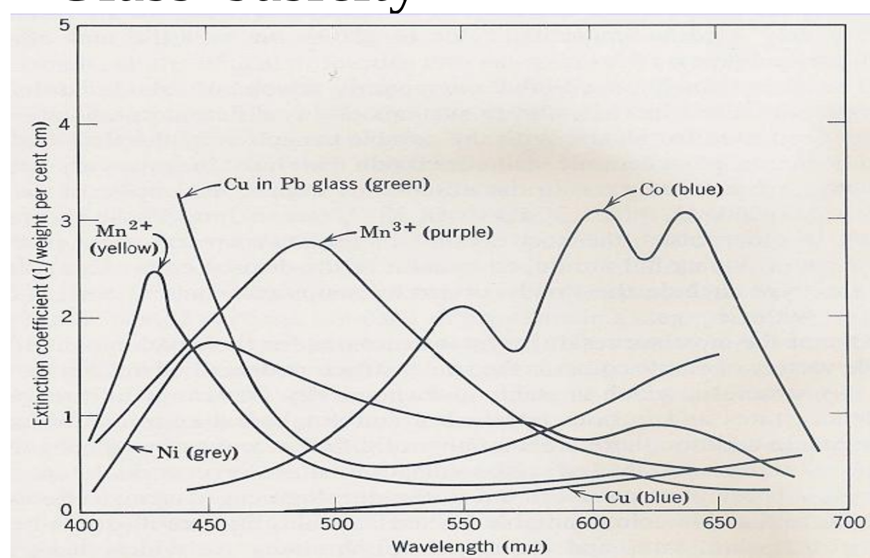
$$4Cr^{6+} + 3O_2 \rightarrow 4Cr^{6+} + 6O^{2-}$$

Green Yellowish

$$A^{(n-z)+} + \frac{z}{4}O_2 \underset{}{\overset{K'_A(T)}{\rightleftharpoons}} A^{n+} + \frac{z}{2}O^{2-}$$

[O2-] depends on

- P_{O2} over the melt
- Melt temperature
- $[M^{x+}]$ concentration
- Glass 'basicity'



Oxidation/Reduction Equilibrium in Glass

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
				7					
			6	6	6				
		5	5	5	5	5			
	4	4	4	4	4	4	4		
3	3	3	3	3	3	3	3		
	2	2	2	2	2	2	2	2	2
	1	1	1	1	1	1	1	1	

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Optical Characterization of Soda Lime Borosilicate Glass Doped with TiO_2

S. Ruengsri[a*], J. Kaewkhao[b,c], P. Limsuwan[c,d]

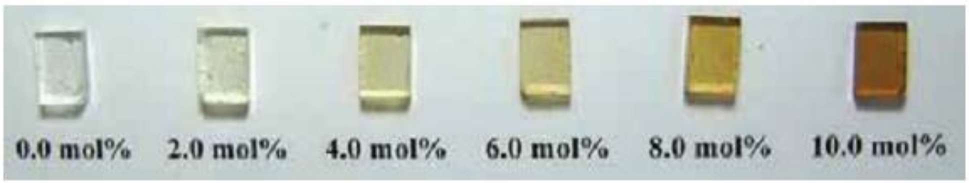

Fig. 1 Photograph of TiO_2 doped glass

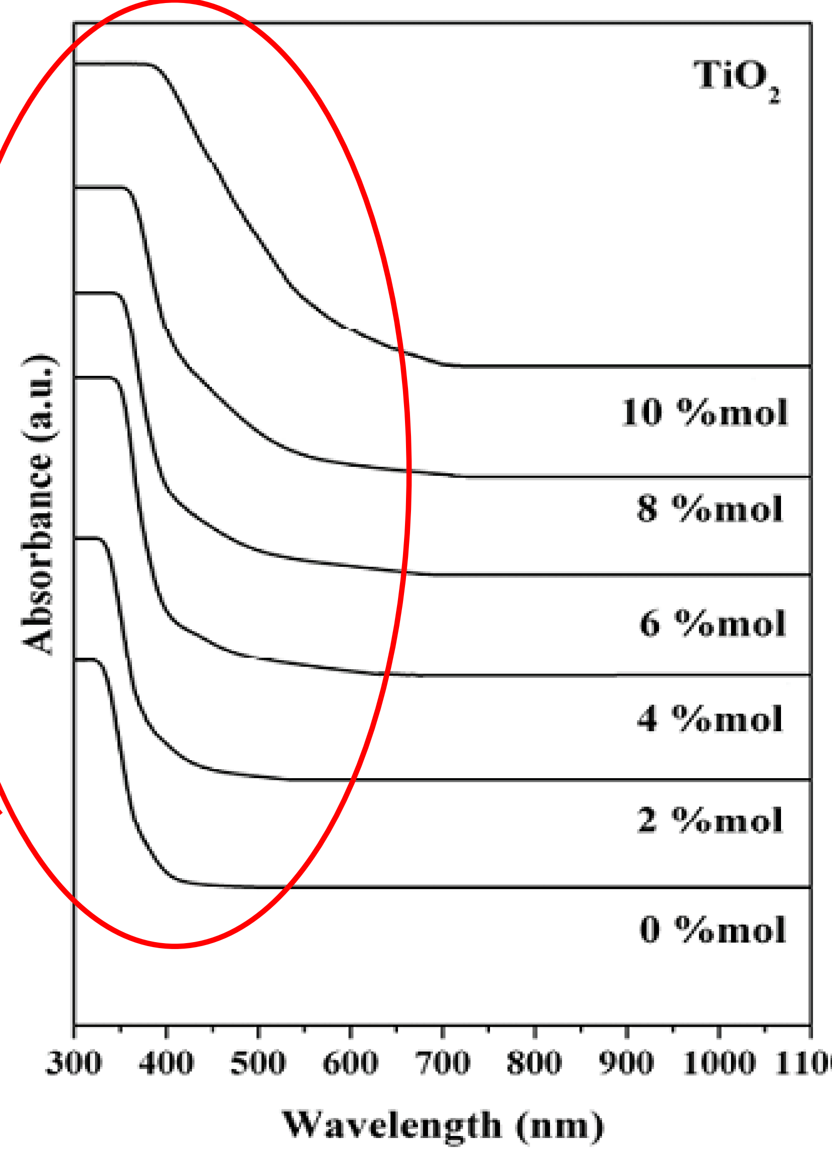

Fig. 2 The optical spectra of TiO_2-doped glass

- Absorb in UV region
- Showed colorless

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Investigation on Physical and Optical Properties of Vanadium Oxide in Soda Lime Borate Glasses

Y. Ruangtaweep[1,2,a*] and J. Kaewkhao[1,2,b]

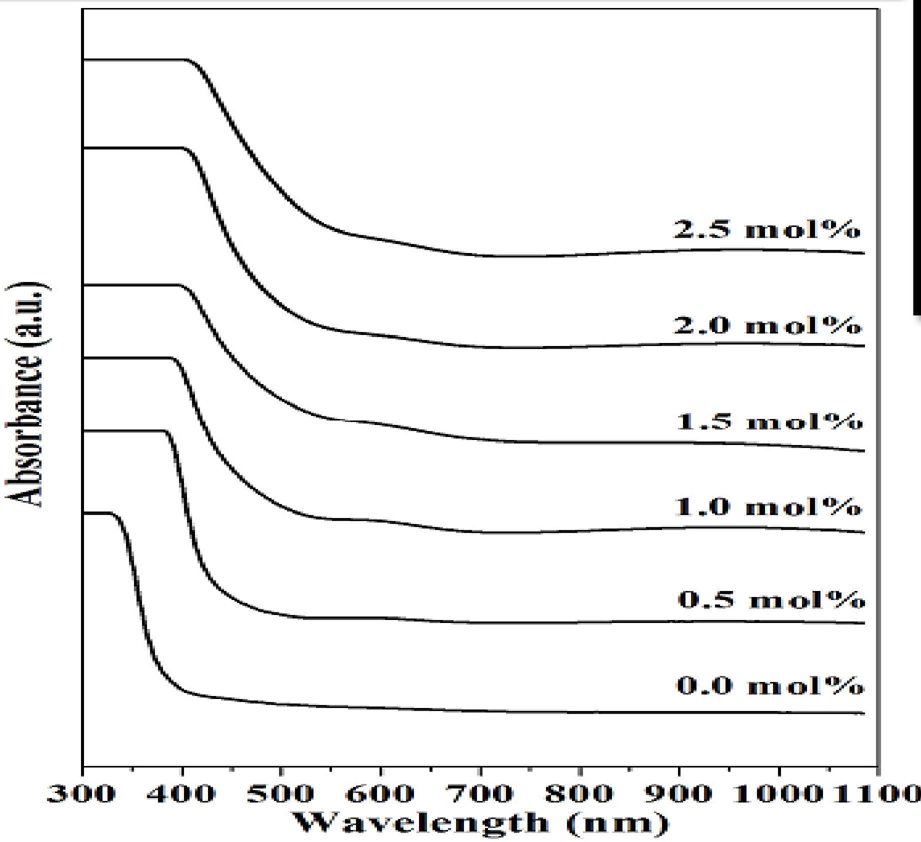

Fig. 3 The optical spectra of V_2O_5-doped glass

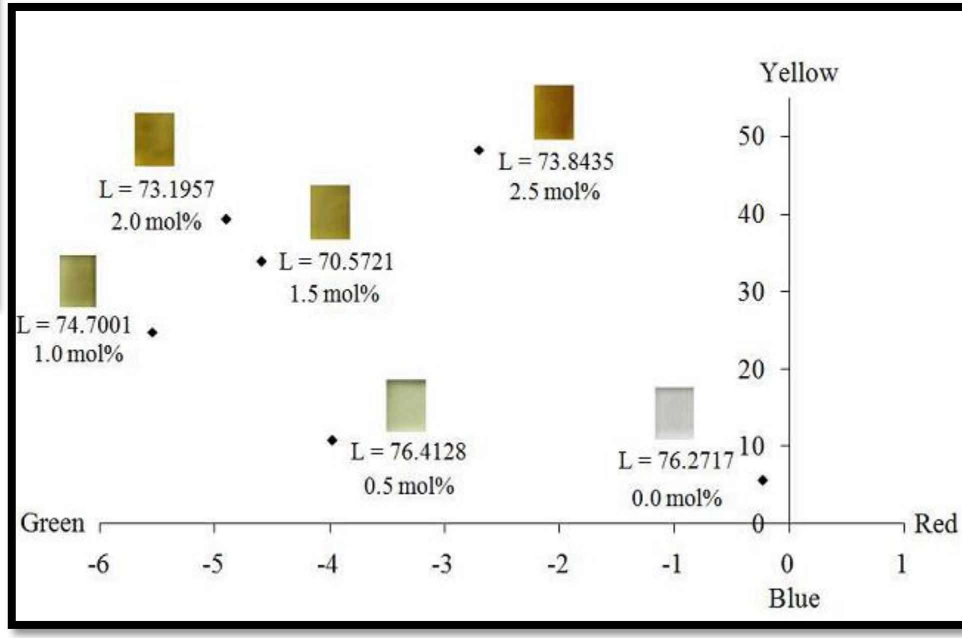

Fig. 4 The CIE L*a*b* color scale of V_2O_5-doped glass

- Band at 380-420 nm for V^{5+}
- Band at 650, 960 for V^{4+}
  $^2B_{2g} \rightarrow {}^2B_{1g}$, $^2B_{2g} \rightarrow {}^2E_g$
- Showed dark yellow

$$4V^{4+} + O_2 \rightarrow 4V^{5+} + 2O^{2-}$$

Blue Yellow

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Physical and optical properties of the SLS glass doped with low Cr_2O_3 concentrations

P. Meejitpaisan[a*], J. Kaewkhao[b,c], P. Limsuwan[a,c], C. Kedkaew[a]

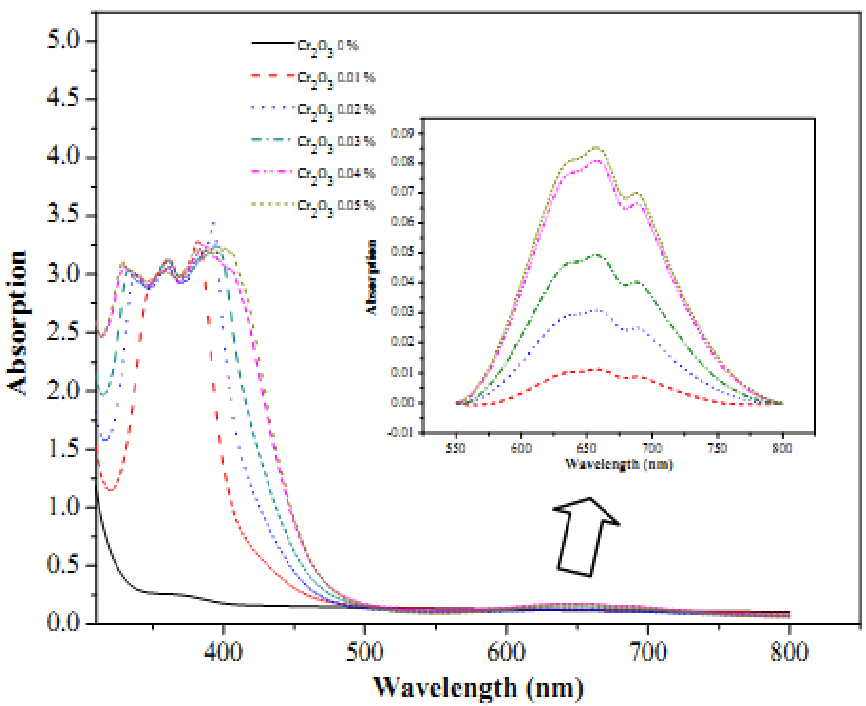

Fig. 5 The optical spectra of Cr_2O_3-doped glass

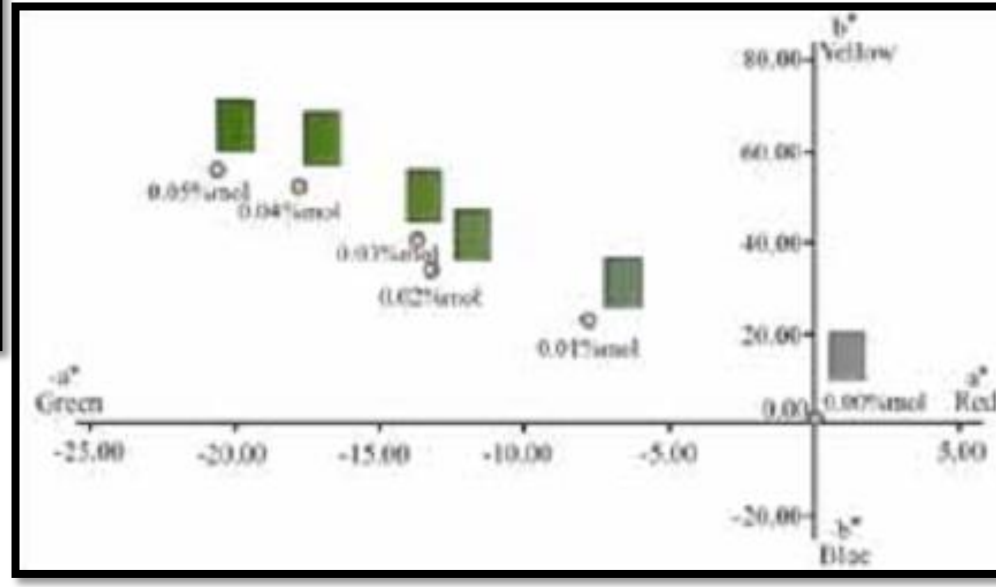

Fig. 6 The CIE L*a*b* color scale of Cr_2O_3-doped glass

- Band at 330, 350, 370 nm for Cr^{6+}
- Band at 650 for Cr^{3+}
- Cr^{6+}/Cr^{3+} = 60 times
- Showed yellow-green color

$$4Cr^{6+} + 3O_2 \rightarrow 4Cr^{6+} + 6O^{2-}$$

Green Yellowish

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Coloration in Soda-Lime-Silicate Glass System Containing Manganese

N. Srisittipokakun[1,a], C. Kedkaew[1,b], J. Kaewkhao[2,c] and P. Limsuwan[1]

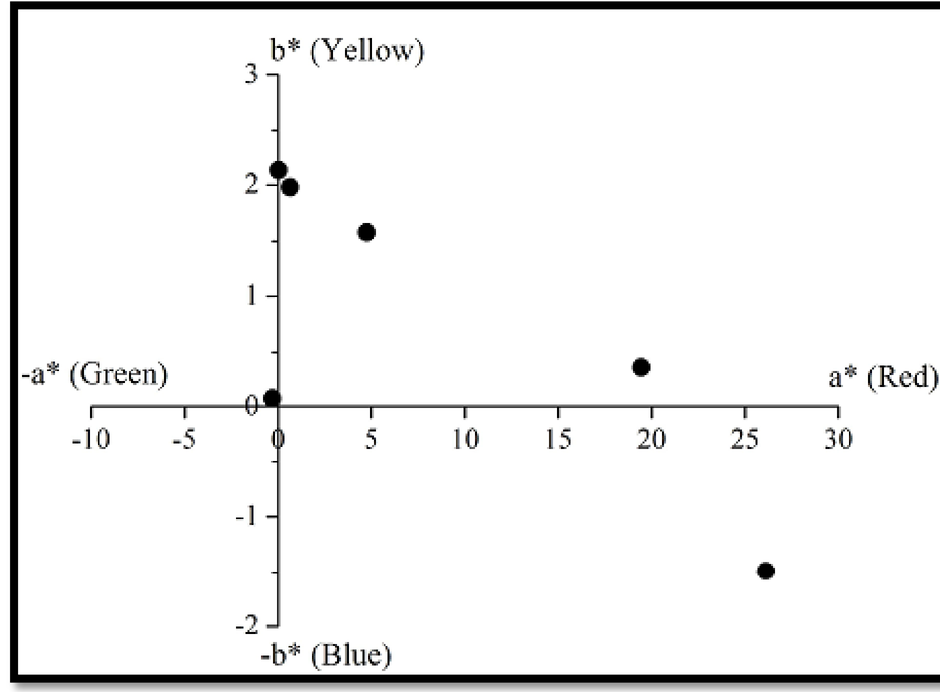

Fig. 8 The CIE L*a*b* color scale of MnO_2-doped glass

- Band at 500nm for Mn^{3+}: $^5E_g \rightarrow {}^5T_{2g}$ Octahedral
- Showed dark purple color

$$4Mn^{3+} + O_2 \rightarrow 4Mn^{4+} + 2O^{2-}$$

Purple Brown

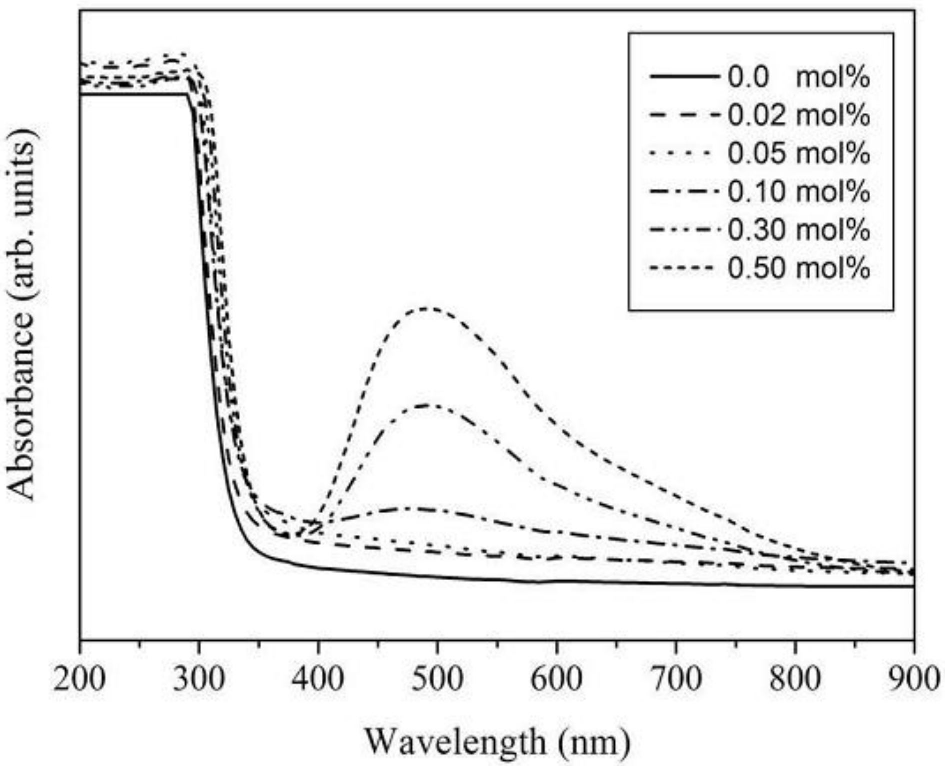

Fig. 7 The optical spectra of MnO_2-doped glass

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The Spectroscopic Analysis of Iron-Doped Soda-Lime-Silica Glass by Spectrophotometer and ESR Spectrometer

Y. Ruangthaweep[1,a], T. Kittiauchawal[2], J. Kaewkhao[3], K. Thamaphat[1] and P. Limsuwan[1]

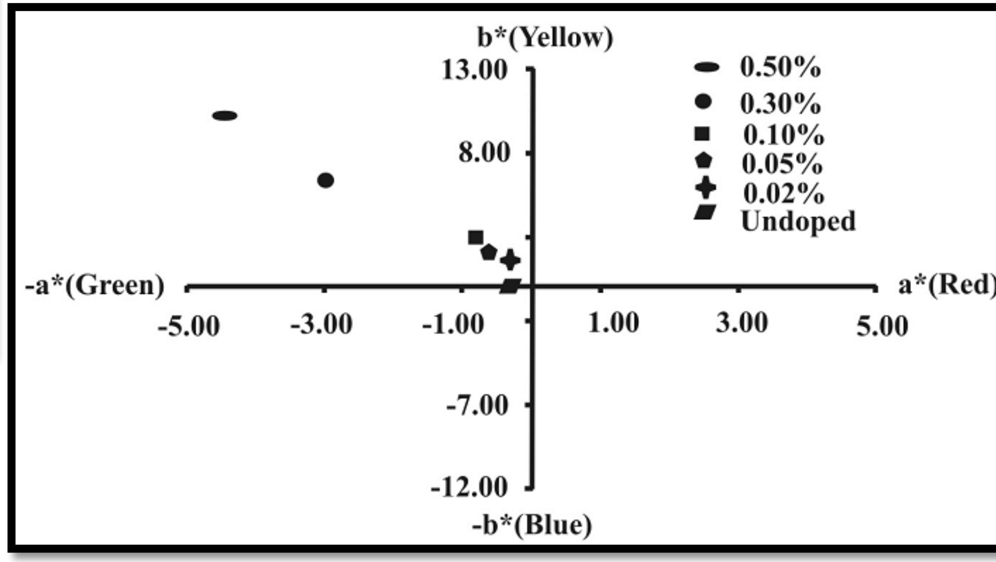

Fig. 10 The CIE L*a*b* color scale of Fe_2O_5-doped glass

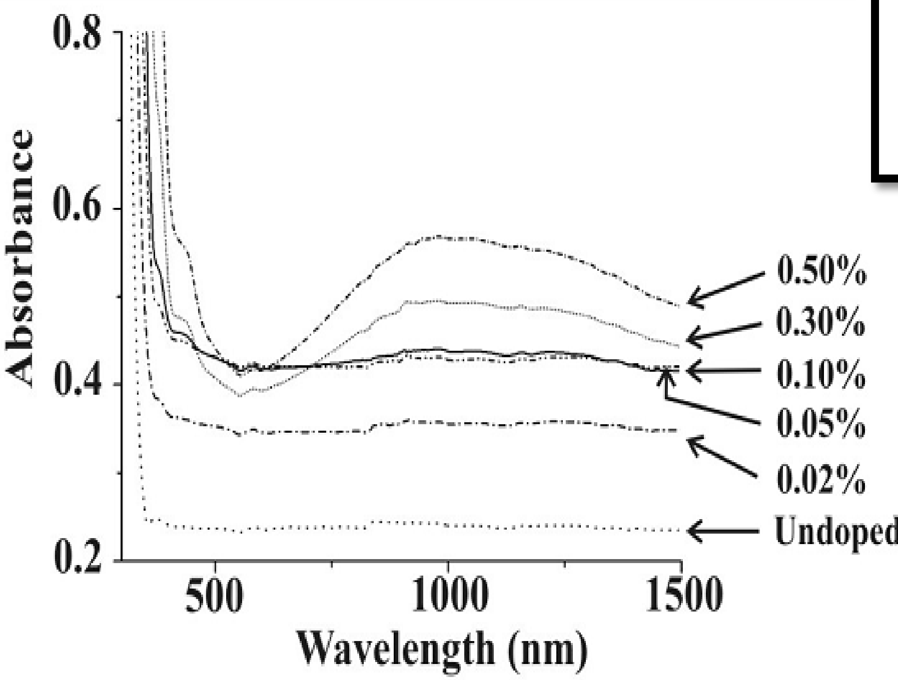

Fig. 9 The optical spectra of Fe_2O_5-doped glass

- Bands at 380, 420, 435 nm for Fe^{3+}
- 380 nm: $^6A_{1g}(^6S) \rightarrow {}^4A_{1g}, {}^4E_g(^4G)$
- 420 nm: $^6A_{1g}(^6S) \rightarrow {}^4T_{2g}(4D)$
- 435 nm: $^6A_{1g}(^6S) \rightarrow {}^4E_g(4D)$
- Band at 1050 nm for Fe^{2+}
- Showd yellow-green

$$4Fe^{2+} + O_2 \rightarrow 4Fe^{3+} + 2O^{2-}$$

Green Yellow

Journal of Solid Mechanics and Materials Engineering
Vol. 1, No. 4, 2007

Effects of Glass Structure on the Optical Absorption of Transition Ions in Industrial Soda-Lime-Silica Glasses*

- Bands at 525, 595, 650 nm for Co^{2+}
- Tetrahedral site
- Showed dark blue

$$4Co^{2} + O_2 \rightarrow 4Co^{3+} + 2O^{2-}$$

Blue Yellow

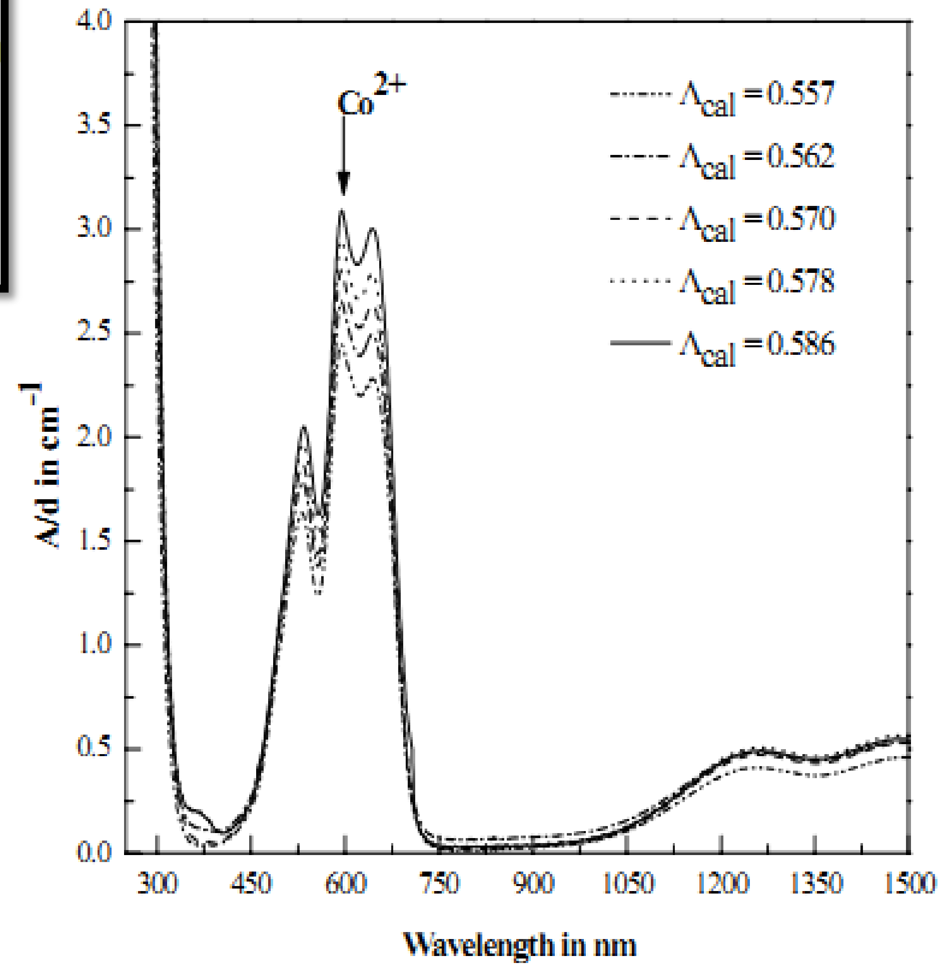

Fig. 11 The optical spectra of CoO-doped glass

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Fabrication and Investigation Some Properties of NiO Doped Borosilicate Glasses

K. Kirdsiri[1,2, a*], N. Srisittipokakun[1,2,b], J. Kaewkhao[1,2,c], P. Limsuwan[3,d]

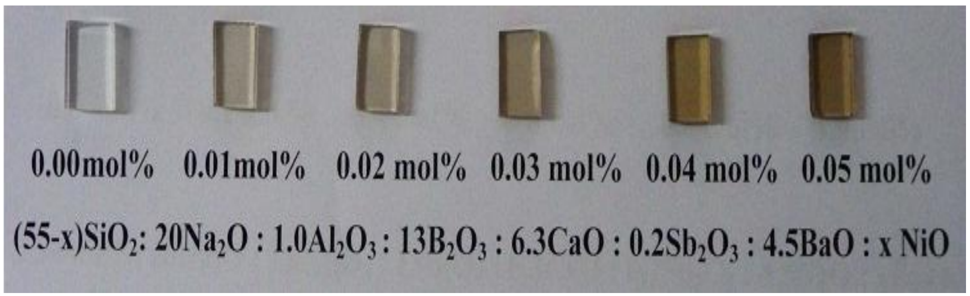

Fig. 12 Photograph of NiO doped glass

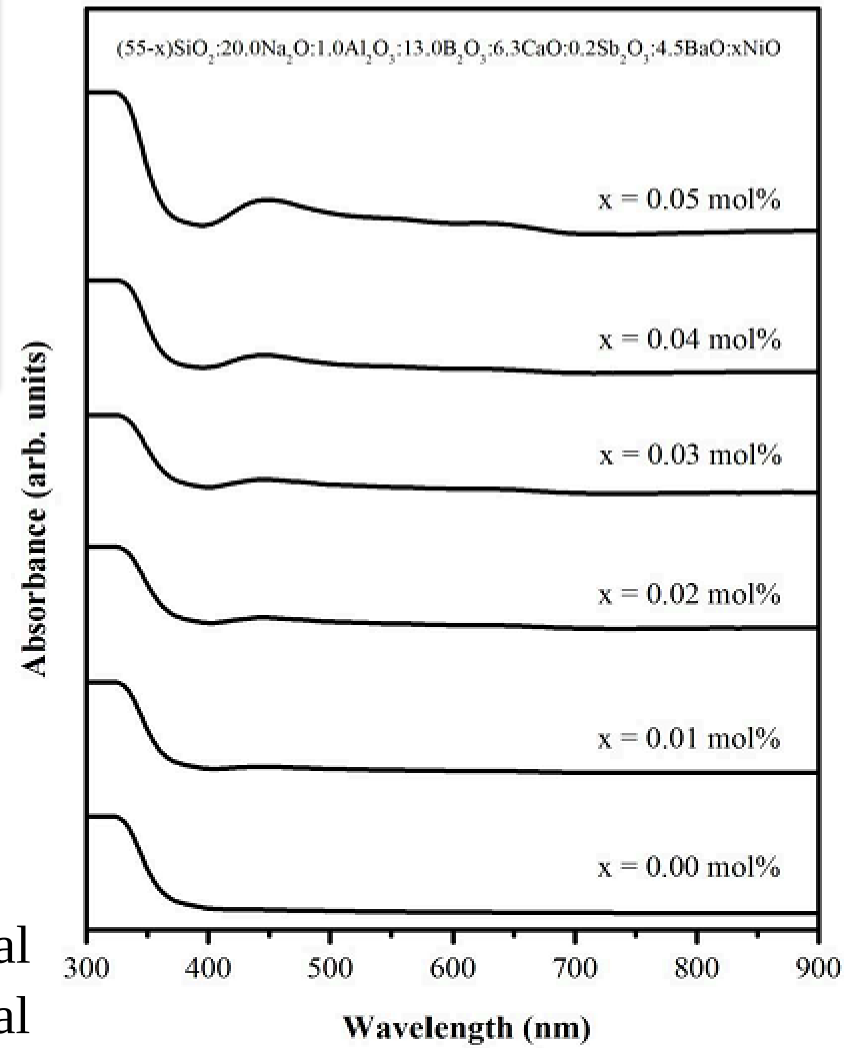

Fig. 13 The optical spectra of NiO-doped glass

- Band at 450 nm: ${}^3A_2(F) \rightarrow {}^1T_{2g}(D)$ octahedral
- Band at 625 nm: ${}^3T_1(F) \rightarrow {}^3T_1(P)$ tetrahedral
- Showed dark yellow in borosilicate glasses
- Environment in glass structure

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Formation and Optical Absorption of CuO-Doped SLS System

T. Wongsing[a], J. Kaewkhao[b,c], P. Limsuwan[a,c], C. Kedkaew[a*]

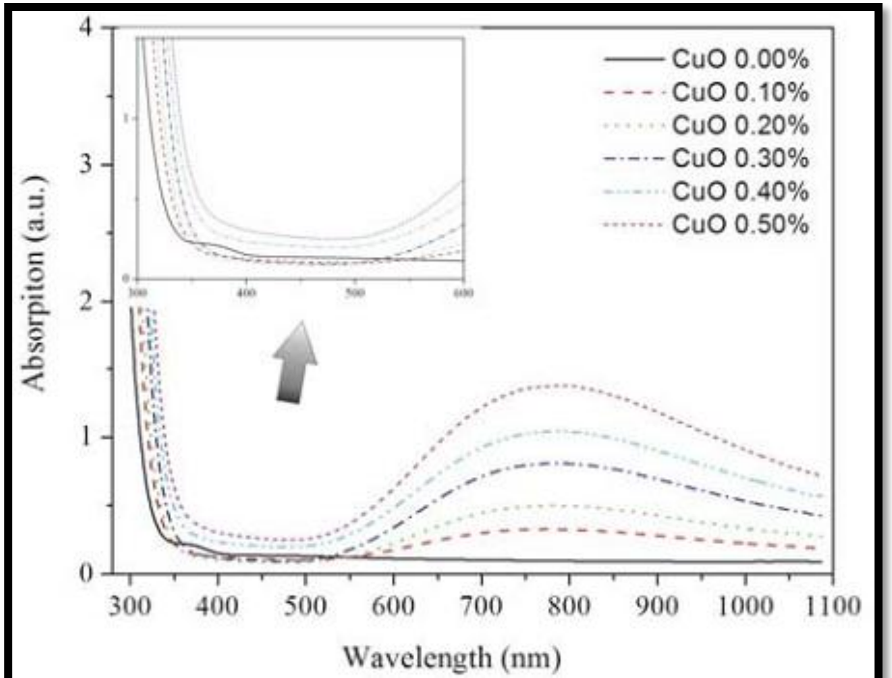

Fig. 14 The optical spectra of CuO-doped glass

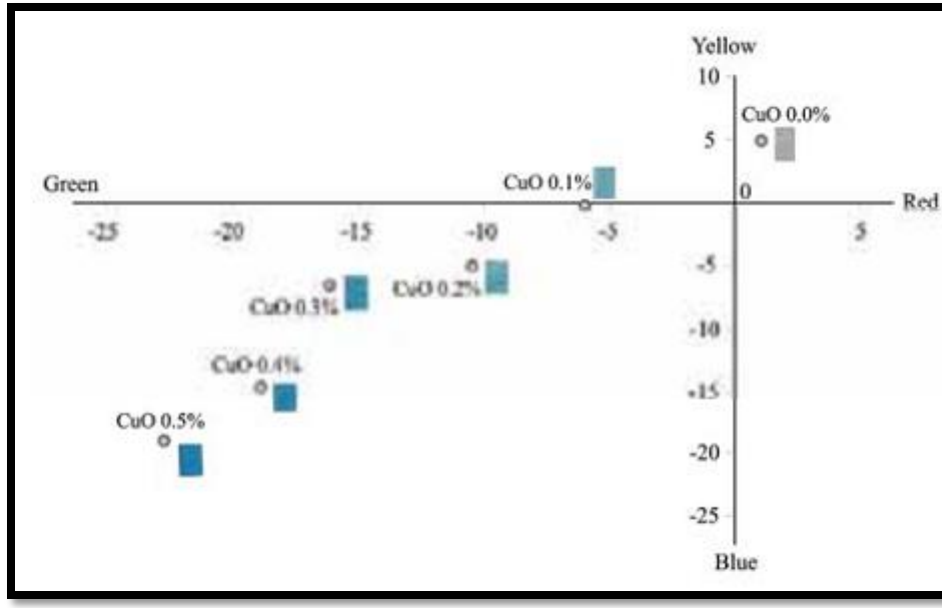

Fig. 12 The CIE L*a*b* color scale of CuO-doped glass

- Boardband at 600-1100 nm for Cu^{2+}
- $^2E_g(D) \rightarrow {}^2T_{2g}(D)$
-Showed blue-green color

$$4Cu^0 + 2O_2 \rightarrow 4Cu^{2+} + 4O^{2-}$$

Coloeless Blue-Green

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Article

Effect of ZnO on the Physical Properties and Optical Band Gap of Soda Lime Silicate Glass

Mohd Hafiz Mohd Zaid [1], Khamirul Amin Matori [1,2,*], Sidek Hj. Abdul Aziz [1], Azmi Zakaria [1,2] and Mohd Sabri Mohd Ghazali [1,3]

- Absorb in UV region
- Showed colorless

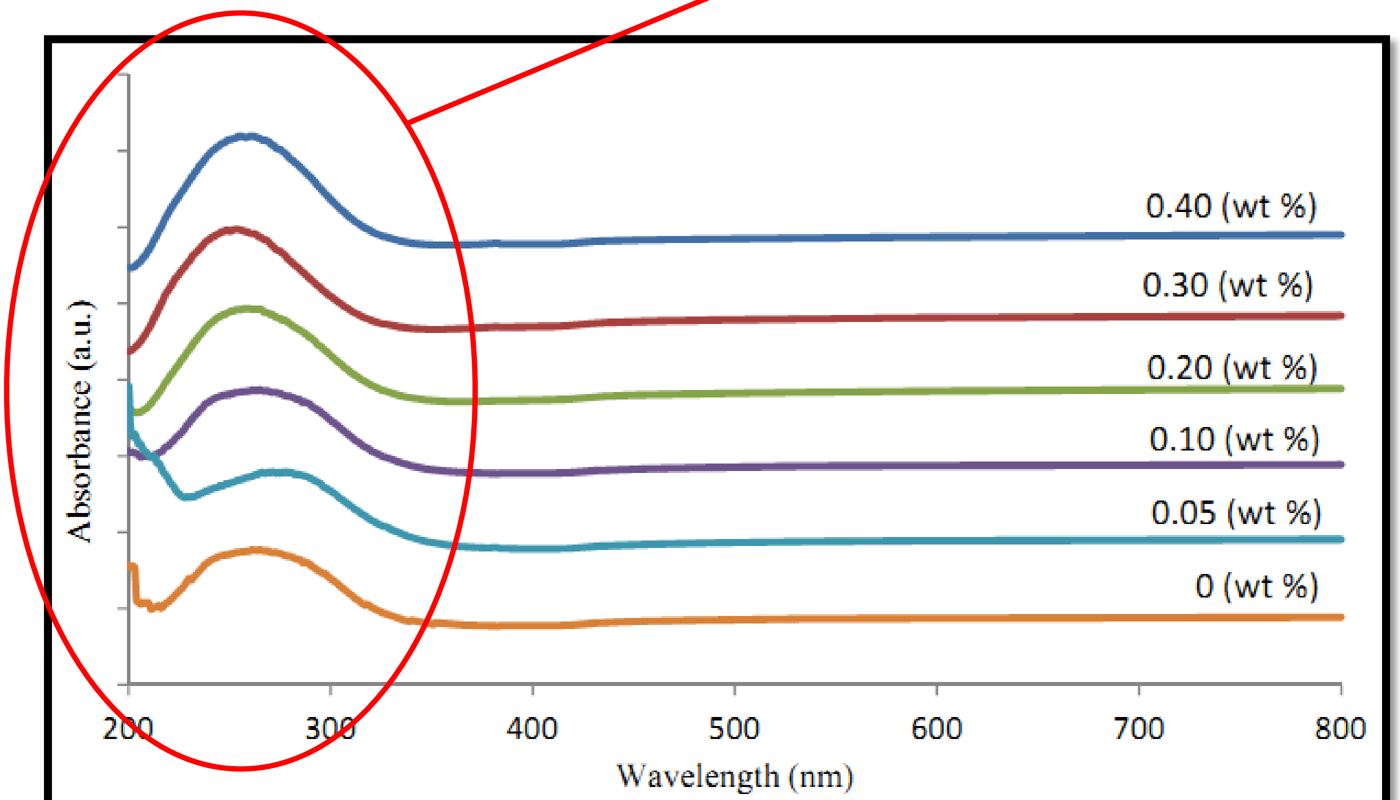

Fig. 16 The optical spectra of ZnO-doped glass

Conclusion (Glass Color)

Transition ion	Color
Cu^{+}, Zn^{2+}, Sc^{3+}, Ti^{4+}	Colorless
Cr^{2+}, Cu^{2+}, V^{4+}, Co^{2+}	Blue
Fe^{2+}, Ni^{2+}, V^{3+}, Cr^{3+}, Mn^{6+}	Green
Mn^{2+}	Pink
Mn^{7+}	Violet
Fe^{3+}, Co^{3+}, V^{5+}, Cr^{6+}	Yellow
Mn^{4+}	Brown

APPENDIX

ช่วงความยาวคลื่น (nm)	การดูดกลืนสี	การส่งผ่านสี
380-420	ม่วง	เหลือง-เขียว
420-440	น้ำเงิน-ม่วง	เหลือง
440-470	น้ำเงิน	ส้ม
470-500	เขียว-น้ำเงิน	แดง
500-520	เขียว	ม่วง
520-550	เขียว-เหลือง	ม่วง
550-580	เหลือง	น้ำเงิน-ม่วง
580-620	ส้ม	น้ำเงิน
620-680	แดง	เขียว-น้ำเงิน
680-780	ม่วง	เขียว

Next week

Course Outine:

Week 7: - Lanthanide element in glass

- *Case studies from international publications*