Advanced Glass Science (4016101)

Instructor: Asst.Prof.Dr. Jakrapong Kaewkhao

Course Outline:

Week 4: Optical properties and advanced measurement/ calculation analysis

- Refractive index
- Dispersion
- Absorption

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*





Reference to the second second

Refractive Index ~ (velocity of light in vacuo, or air)/(velocity of light in medium)

Snell's Law:

$$n = \frac{\sin \theta_i}{\sin \theta_r} = \frac{v_1}{v_2} = \frac{n_2}{n_1}$$



Reflectance:



*note: n, unitless quantity

n (air)	=	1.0003
water	=	1.33
sapphire	=	1.77
diamond	=	2.42
f-SiO ₂	=	1.458



The light travel from <u>less</u> to <u>more</u> density $(n_2 > n_1)$

- Refracted ray <u>convergent</u> with perpendicular ray (normal line) $\theta_2 < \theta_1, v_2 < v_1, \lambda_2 < \lambda_1$

The light travel from <u>more</u> to <u>less</u> density $(n_2 < n_1)$

- Refracted ray *divergent* with perpendicular ray (normal line)

 $\theta_2 > \theta_1, \, v_2 > v_1, \, \lambda_2 > \lambda_1$

 $n_1 \sin \theta_1 = n_2 \sin \theta_2$

Normal Normal Incident Reflected Refracted ray ray $\theta_1 | \theta$ Air $(n_1 = 1.00)$ Air $(n_2 = 1.00)$ Water $(n_1 = 1.33)$ Water $(n_2 = 1.33)$ Incident Refracted **Reflected** ray ray ray



Total internal refrection

- Refractive angle can't more than 90°
- $-n_1 \sin \theta_{1(\max)} = n_2 \sin 90^{\circ}$
- $\theta_{1(\max)}$ is *critical angle*
- If incident more than $\theta_{1(max)}$
- Not refracted but refrected
- Critical angle (Brewster's angle) below which light is totally reflected:

$$\sin \theta_c = \frac{1}{n}$$

- Total internal refrection:

The light travel from <u>more</u> to <u>less</u> density only!!!







Refractive Index and polarizability



When light interact with the transparent material

- a) Molecules with permanent dipoles will align in the field as much as the structure will allow.
- b) Ion which are evenly spaced tend to be displaced in the field so as to create a net dipole moment
- c) The uniform electron cloud around an atom or ion tends to distort so as to produce a dipole.

The effect of an external electric field, E, on the components of a solid



Refractive Index and polarizability

The bulk polarization;

$$P = \varepsilon_0 \chi E$$

where ε_0 is the permittivity of free space, χ is the dielectric susceptibility and *E* is the applied electric field.

The refractive index of a material, n, is actually a reflection of its electronic polarizability. The relation ship between the two is given by

$$n \sim \sqrt{\varepsilon_{\rm r}}$$

where $\varepsilon_r = \chi + 1$

and ε_r is the relative permittivity of material (*dielectirc constant*)

Refractive index represents the interaction of light with electrons of the constituent atoms in a glass.

- 'n' increases with electron density or polarizability.
 - Low 'n': low atomic ions: BeF₂ glasses, $n \sim 1.27$; SiO₂, B₂O₃: $n \sim 1.46$ low polarizable ions (F^{-} for O^{2-}) bridging oxygen for nonbridging oxygens; NBO's increase 'n'
- increasing $R_2O \rightarrow$ increase in 'n'
 - 'n' increases even when smaller atomic# ions (Li, Na) replace Si⁴⁺ because of the greater polarizability of NBO's
- note that 'n' increases in the series Na < K < Li < Rb < Cs



Effect of composition on the refractive index of alkali silicate g







- Refractive index is sensitive to other network structural changes
 - replacing Na_2O with Al_2O_3 in aluminosilicate glasses decreases 'n' because polarizable NBO's are replaced by less polarizable Al-O-Si bridging oxygens

-High index glasses contain heavy, polarizable ions: Pb, Bi, Ti, etc.

- PbO•Bi₂O₃•Ga₂O₃ glasses: visible light 'n'~2.7
- S²⁻ for O²⁻ also increases 'n'

- Asymmetric ions also contribute to large 'n'

Current Control Contro

Molar Refractivity: measure of the contribution of constituent ions in a glass to the overall refractive index; dependent on ion polarizability.

Molar refractivity is the sum of the individual ionic refractivities (RI): for $A_x B_y$, $R_m = x R_A + y R_B$

- Increasing ion size, increasing ionic refractivity: Li⁺<Na⁺<K⁺; Mg²⁺<Ca²⁺<Ba²⁺
- Small, highly charged glass-forming ions (Si⁴⁺, P⁵⁺) contribute less to the index of refraction than the larger modifiers

*Note: The ionic refractivity are used to predict the molar refractivity (and so the refractive index) of a glass with a known composition.

(from W. Vogel, Chemistry of Glass, 1985)				
Cation	Ionic Refraction			
Li ⁺	0.2			
Na^+	0.5			
\mathbf{K}^+	2.2			
Mg ²⁺	0.28			
Ca^{2+}	1.33			
Ba ²⁺	4.3			
Pb ²⁺	3.1			
B ³⁺	0.05			
Al ³⁺	0.17			
Si ⁴⁺	0.1			
P ⁵⁺	0.07			

Molar electronic polarizability

The relation between the refractive indices of the material and its molar refraction (R_m) is given by

$$R_m = \frac{(n^2 - 1)}{(n^2 + 2)} V_m,$$

where $(n^2-1)/(n^2+2)$ is known as the reflection loss (R_{loss})

The molar refraction is proportional to the molar electronic polarizability of the material, a_m , by the relation

$$\alpha_m = \left(\frac{3}{4\pi N}\right) R_m,$$

where *N* is the number of polarizable ions per mole.

**Note:* The increase in molar refraction and increase refractive index accompany the increase in polarizability.



The factors affecting refractive-index of the glass

1. Polarizability of the first neighbor ions coordinated with it (anion).

2. Field intensity Z/a^2 (i.e., polarization power), where Z is the valence of the ion (ionic charge) and a is the distance of separation (ionic radius).

3. Coordination number of the ion.

4. Non-bridging oxygen bonds (NBO's).

5. Electronic polarizability of the oxide ion.

6. Optical basicity of the glasses.





Dispersion

- Refractive index depends on wavelength.
- -This dependence is call *dispersion*
- So, refractive index should be quoted at a specific wavelength:

Abbe number;
$$v_{d}$$
: $v_{d} = (n_{d} - 1) / (n_{F} - n_{C})$

n_D, 589.3 nm, Na-D line emission (yellow) n_F, 486.1 nm, H-F line emission (blue) n_C, 656.3 nm, H-C line emission (red)









Dispersion

Dispersion: the variation in index with wavelength: $dn/d\lambda$

- Associated with the oscillation of electron couple to light

- At short wavelengths, 'n' increases because the photons are absorbed by the promotion of electrons across the optical band-gap;

UV-absorption

- At longer wavelengths, 'n' increases because photons are absorbed by phonons associated with molecular scale vibrations;

IR-absorption

- $dn/d\lambda$ varies as the λ approaches either the UV- or IR-edges.



ISS-LAB@

Wavelength, λ (micrometer) (from Fleming, in Experimental Techniques of Glass Science, 1993)



Fig. 2 The energy level from ground to excited state

Absorption

1. Lambert's law

 $\frac{dI}{dt} = I$ $-\frac{dI}{dt} = kI$ $-\frac{dI}{I} = kdt$ $\ln \frac{I_0}{I_t} = kt$

- $\frac{I_0}{I_t} = e^{kt}$ $I_t = I_0 x 10^{-0.4343kt}$ $I_t = I_0 x 10^{-kt}$
- I_0 = Intensity of incident ray
 - = Intensity of light-transmitting
 - = Mean free path (cm)
- k = Proportion of mean free path



Absorption

2. Beer's law



$$I_t = I_0 x 10^{-kc}$$

; C = concentration of medium

When combining equation of Lambert and Beer, so

 $I_t = I_0 x 10^{-\varepsilon ct}$

Where *transmittance* (T) is I_t/I_0 and *absorbance* (A) is $log(I_t/I_0)$

$$A = \varepsilon ct = -\log T = 2 - \log(\% T)$$

- A = Absorbance
- C = concentration (mol/L)
- ϵ = Absorbance coefficient

- T = Transmittance
- t = mean free path (cm)



Table 1 The relation between of color and absorbance

ช่วงความยาวคลื่น (nm)	การดูดกลื่นสี	การส่งผ่านสี
380-420	ม่วง	เหลือง-เขียว
420-440	น้ำเงิน-ม่วง	เหลือง
440-470	น้ำเงิน	ส้ม
470-500	เขียว-น้ำเงิน	แคง
500-520	เขียว	ม่วง
520-550	<mark>เขี</mark> ยว-เหลือง	ม่วง
550-580	เหลือง	น้ำเงิน-ม่วง
580-620	ส้ม	น้ำเงิน
620-680	แดง	เขียว-น้ำเงิน
680-780	ม่วง	เขียว

小学的影响	Available online at www.sciencedirect.com								
	SciVerse ScienceDirect Procedia Engineering		Glass ID Cr ₂ O ₃ (mol%)) (Glass composition (mol%)			
FI SEVIER			S65Cr0		0	65SiO2	65SiO ₂ -25Na ₂ O-10CaO		
		www.elsevier.com/locate/procedia	S	65Cr1	0.01	64.99Si	O2-25Na2O-1	0CaO-0.01Cr	$_{2}O_{3}$
	I-SEEC2011		S	65Cr2	0.02	64.98Si	02-25Na2O-1	0CaO-0.02Cr	$_{2}O_{3}$
Physical and optical properties of the SLS glass doped with low Cr ₂ O ₂ concentrations		S65Cr3		0.03	64.97Si	64.97SiO ₂ -25Na ₂ O-10CaO-0.03Cr ₂ O ₃			
		ped with	S65Cr4		0.04).04 64.96SiO ₂ -25Na ₂ O-10CaO-0.04C			r_2O_3
P Meeiitnaisan ^{a*} I Kaewkhaq ^{b,c} P Limuwan ^{a,c} C Kedkaew ^a		S65Cr5 0.05 64.95SiO ₂ -25Na ₂ O-10Ca		0CaO-0.05Cr	² 03				
	Parameters		Cr_2O_3 concentration (mol%)						
			0	0.01	0.02	0.03	0.04	0.05	
	Density, p (g/cm ³)		2.5498	2.5531	2.5579	2.5594	2.5637	2.5672	
	Molar volume, V _m (cm ³ /mol)	2	23.5931	23.5658	23.5252	23.5153	23.4797	23.4510	
	Refractive index, np (589.3 n	m)	1.5269	1.5272	1.5277	1.5279	1.5282	1.5285	
	Molar refractivity, R _m (cm ⁻³)		7.2524	7.2479	7.2407	7.2400	7.2331	7.2273	
	Refraction losses, R (%)		0.3073	0.3075	0.3077	0.3078	0.3080	0.3081	
	Molar electronic polarizabilit	$y, \alpha_m (Å^3)$	2.8775	2.8757	2.8725	2.8726	2.8698	2.8675	



The relation between molar electronic polarizability and refractive index



The CIE L*a*b* color scale of undoped and doped Cr2O3 in soda lime silicate glass samples

CASE 1(con't)

64.4SiO₂: 10.0CaO: 25.0Na₂O: 0.6Fe₂O₃



J. Kaewkhao^{*1,2,3}, N. Srisittipokakun^{1,3}, K. Kirdsiri^{1,3}, C. Kedkaew⁴ and P. Limsuwan^{2,4}



Table 1 Various physical and optical properties of SiO ₂ -Na ₂ O-CaO- Fe ₂ O ₃ glasses						
	Melting Temperature (°C)					
Physical property	1200	1300	1400	1500		
Average molecular weight, <i>M</i> (g/mol)	60.6592	60.6592	60.6592	60.6592		
Density, ρ (g/cm ³)	2.5519	2.5765	2.5778	2.5655		
Thickness of the glass, d (cm)	0.3500	0.3500	0.3500	0.3500		
Refractive index, n_o (589.3 nm)	1.5307	1.5311	1.5317	1.5324		
Dielectric constant (ε)	2.3430	2.3444	2.3462	2.3484		
Optical dielectric constant $(P\partial t/\partial P)$	1.3430	1.3444	1.3462	1.3484		
Molar volume, V_M (cm ³ /mol)	23.7698	23.5434	23.5311	23.6439		
Molar refractivity, R_m (cm ³ /mol)	7.3506	7.2855	7.2886	7.3316		
Refraction losses, R (%)	4.3976	4.4033	4.4112	4.4203		

$$R_{m} = \frac{(n^{2} - 1)}{(n^{2} + 2)} V_{m},$$

$$R_{m} = (\frac{1.5307^{2} + 1}{1.5307^{2} + 2})(23.7698)$$

$$R_{m} = (\frac{1.3430}{4.3430})(23.7698)$$

$$R_{m} = 7.3506 cm^{3} / mol$$

$$\alpha_{\rm m} = \left(\frac{3}{4\pi \rm N}\right) R_{\rm m}$$

$$\alpha_{\rm m} = \left(\frac{3}{4\times\pi\times6.02\times10^{23}}\right) (7.3506)$$

$$\alpha_{\rm m} = 2.91$$

 J. Kaewkhao, et al., 2008, "Effect of Copper (ll) Oxide to Glass Properties from Local Sand in Nakorn Pathom Province",
 Thai Journal of Physics, Vol.3, pp.152-153. $20Na_2O : 1.0Al_2O_3 : 13B_2O_3 : 6.3CaO :$ $0.2Sb_2O_3 : 1.5PbO_2 : (58-x)SiO_2 : x CuO$ (where x = 0.0, 0.2, 0.4, 0.6 and 0.8)

- It has been found that refractive index and density values increased for all the glasses, with the substitution of CuO in the place of SiO_2 due to higher molecular weight of CuO compare to that of SiO_2 .

- Theoretically, the refractive index is a function of density and mean polarisability of the medium.

- The prepared glass samples show the refractive index is a function of glasses density at different CuO content and it has been found that the refractive index could be increased linearly with glass density.



P. Chimalawong, et al., 2010, "*Optical properties of the SiO2-Na2O-CaO-Nd2O3 glasses*" **American Journal of Applied Sciences**, 7(4), pp.584-589.

$(65-x)SiO_2 : 25Na_2O : 10CaO : xNd_2O_3$ (where x = 0.0-5.0 mol%)

Table 2: Various physical properties of SiO2-Na2O-CaO-Nd2O3 glasses

	Nd ₂ O ₃ (mol %)							
Parameters	0.0	1.0	2.0	3.0	4.0	5.0		
Average molecular weight, M(g)	60.1573	62.9212	65.6852	68.4491	71.2130	73.9770		
Density, (g.cm ⁻³)	2.5314	2.6175	2.7031	2.7789	2.8526	2.9194		
Thickness of the glass, d (cm)	0.3880	0.3580	0.3550	0.3680	0.3630	0.3530		
Refractive index nd (589.3 nm)	1.5247	1.5350	1.5444	1.5542	1.5601	1.5709		
Molar volume V_M (cm ³ mol ⁻¹)	23.7644	24.0387	24.2999	24.6317	24.9643	25.3398		
Molar refractivity, R _m (cm ⁻³)	7.2793	7.4840	7.6758	7.8965	8.0031	8.3246		
Molar polarizability, α _m (ų)	2.8858	2.9669	3.0429	3.1304	3.1727	3.3001		
Refraction losses, R (%)	4.3192	4.4540	4.5779	4.7079	4.7865	4.9312		
Indirect optical band gab, Eg (eV)	3.5673	3.3357	3.2376	3.2343	3.1720	2.9548		
Glass optical basicity, (Λ)	0.6288	0.6430	0.6571	0.6710	0.6847	0.6982		
Glass oxide polarizability, α_{o2-} (Å ³)	1.6544	1.6629	1.6682	1.6803	1.6820	1.7009		



The refractive index is a function of density and mean polarisability of the medium. <u>J. Kaewkhao</u> et al., 2009, "Optical Absorption Study of CoO in glass Prepare from Local Sand ", **The Proceedings of 47th Kasetsart University Annual**

Conference, March 17 - March 20, pp.374-379.

 $20Na_2O : 1.0Al_2O_3 : 13B_2O_3 : 6.3CaO :$ $0.2Sb_2O_3 : 1.5PbO_2 : (58-x)SiO_2 : x CoO$ (where x = 0.00-0.05)

-- The main absorption bands of Co^{2+} in tetrahedral symmetry from the ground state ${}^{4}A_{2}(F)$, to the ${}^{4}T_{2}(F)$, ${}^{4}T_{1}(F)$ and ${}^{4}T_{1}(P)$ states.

-- The very intense absorption band centered about 600 nm was assigned to the spin- and electricdipole-allowed ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(P)$ transition, the spin-orbit coupling causes the splitting of this band. --The absorption intensities of Co²⁺ in tetrahedral symmetry are about 100 times that of Co²⁺ in octahedral symmetry. The absorption bands in the visible region, due to octahedral and tetrahedral Co^{2+,} occur closely and overlap considerably.

-- The high intensity of the tetrahedrally co-ordinated band is a consequence of the mixing of the 3dorbitals with 4p-orbitals and ligand orbitals. Moreover, the peak intensity was increase with increasing of the CoO concentration.



P. Chimalawong, et al., 2010, "Optical and Electronic Polarizability Investigation of Nd3+ Doped Soda-Lime-Silicate Glasses"

Journal of Physics and Chemistry of Solids, 71 (7), pp.965-970.

It is observed that the absorption intensity of the observed bands increase with the increase of Nd_2O_3 concentration. The spectra consists of various absorption peaks corresponding to the transitions between the and higher energy ground states inside the $4f^3$ electronic configuration of the Nd^{3+} ions. The transitions were assigned by comparing the band positions in the absorption spectra with those reported in literatures

 $(65-x)SiO_2 : 25Na_2O : 10CaO : xNd_2O_3$ (where x = 0.0-5.0 mol%)



CASE 5

Next week



Course Outine: Week 5: Luminescence properties, advanced measurement/calculation analysis Case studies from international publications