Lithium Disilicate Glass-ceramics for dental applications

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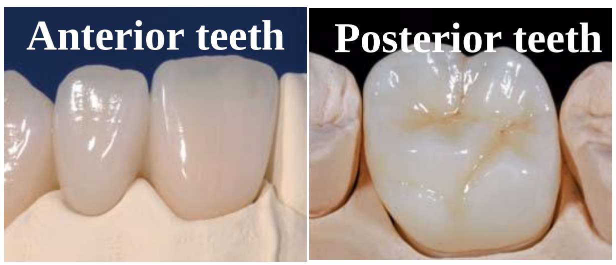
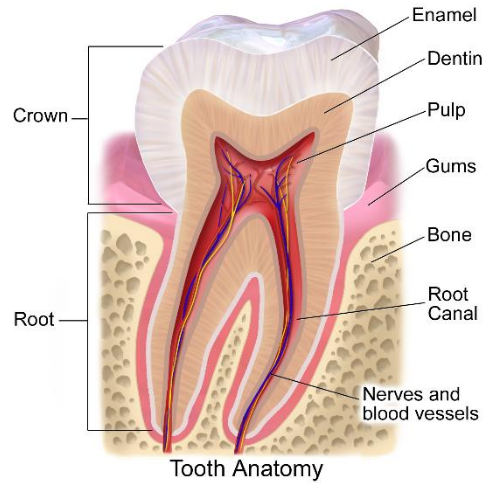
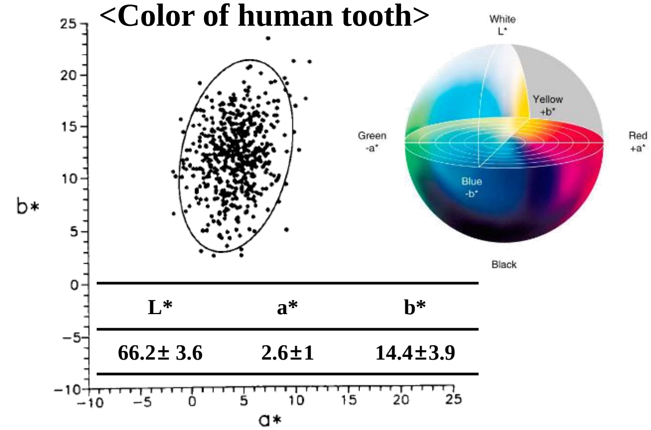
Introduction : Properties of Human teeth





Ref (https://en.wikipedia.org/wiki/Tooth_enamel

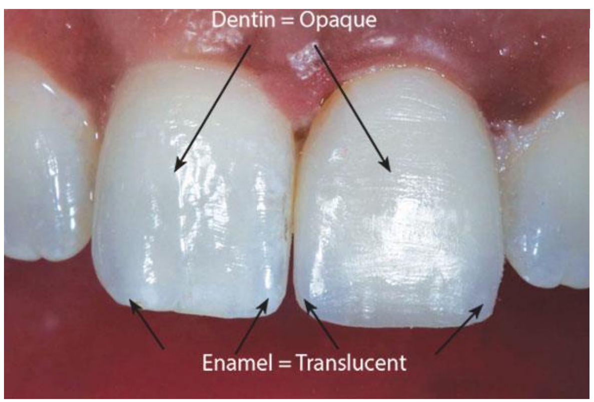
<Color of human tooth>



L*	a*	b*
66.2± 3.6	2.6±1	14.4±3.9

FIG. 1. Chromaticity coordinates in the CIELAB system for the 600 human tooth samples and ellipse containing 95% of the points.

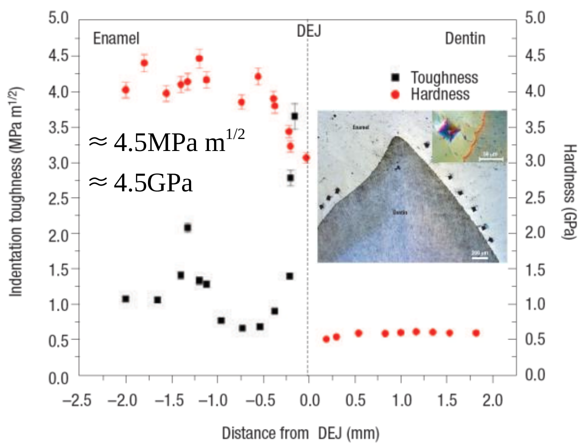
Ref) Rubino, M et al, Color Research & Application 19 (1994) 19-22



Enamel : Blue/White Opalesence & Fluorescence

http://www.glidewelldental.com/images/dentist/chairside/v7-4/articles/zirconia-veneer/lightbox/Fig18.jpg

<Toughness & Hardness of human teeth>



Ref) V.Imbeni, Nature. Mat. 4 (2005)

<Translucency of human tooth>

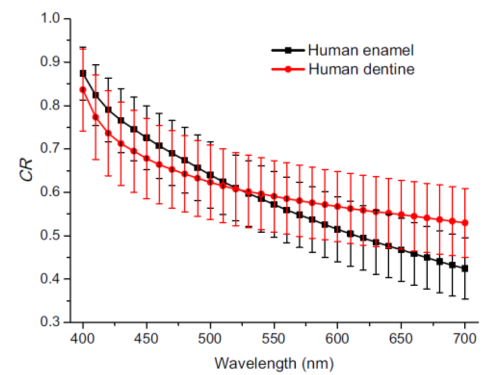


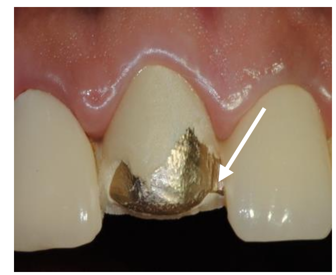
Fig. 2 Wavelength-dependent contrast ratio (CR) of human enamel and human dentine.[33]

Ref) Yong-Keun Lee, J. Biomed. Opt 20(4)

Introduction : Dental Materials

PFM(Porcelain Fused metal) crown

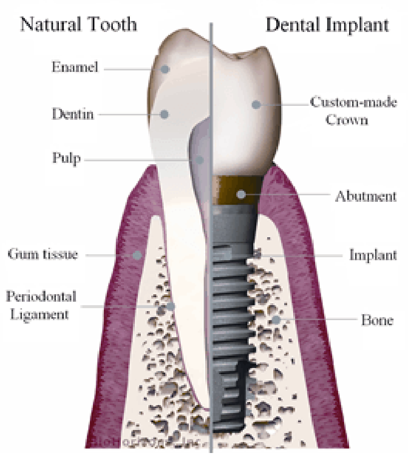
Fracture occured (Porcelain : 75~100MPa)

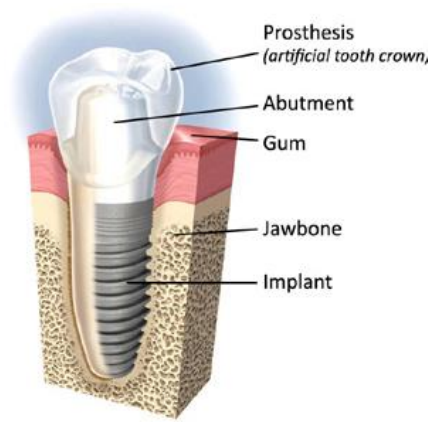


All-ceramic crown

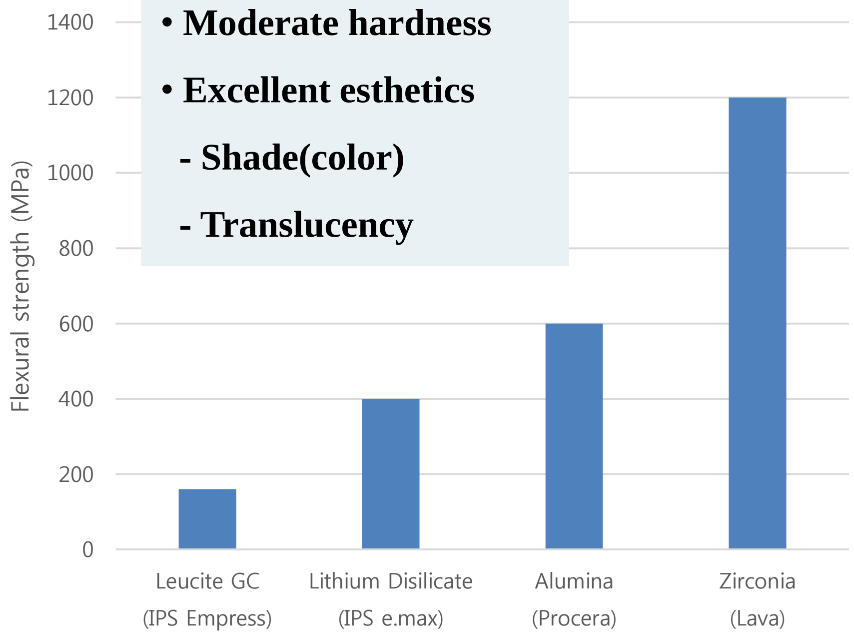
Introduction : Dental ceramics

<Dental Implant>

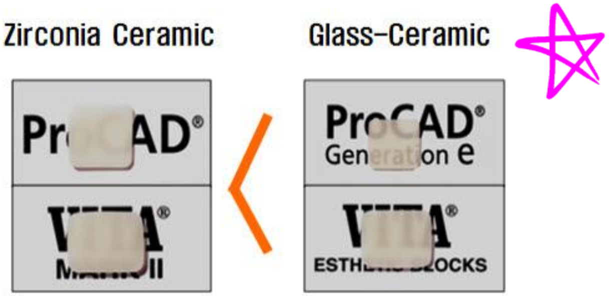




- **High strength**
- **Moderate hardness**
- **Excellent esthetics**
  - **- Shade(color)**
  - **- Translucency**



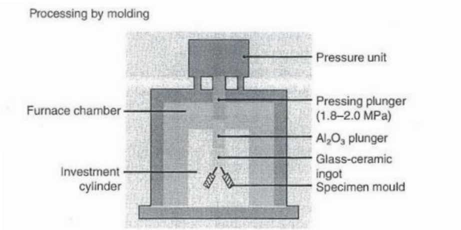
<Translucency>



Introduction : Manufacturing of Crown

<Hot-Pressing : LS2 GC>

Hot-pressing furnace



24.2 Moulding furnace for fabricating leucite-type dental restorations.

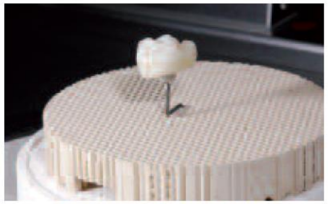
Plastic deformation of LS2 GC (softening)

Insert the cold IPS e.max Press ingot into the hot investment ring with the shade designation facing upward

Cut the sprues using a fine diamond disk

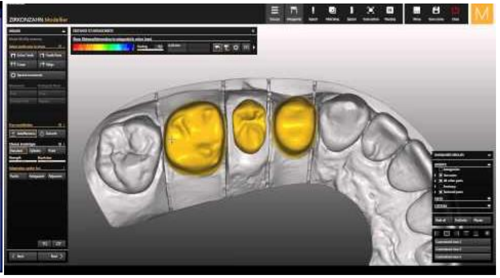
Apply a surface texture with suitable grinding instruments.

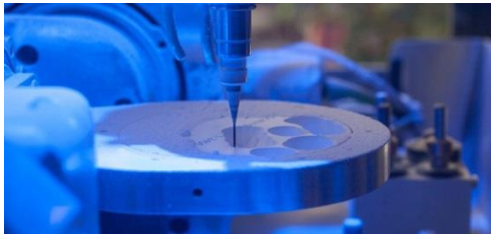
Apply an even layer of glazing material to the surface



Conduct the Glaze firing on a honey-comb firing tray with the respective parameters

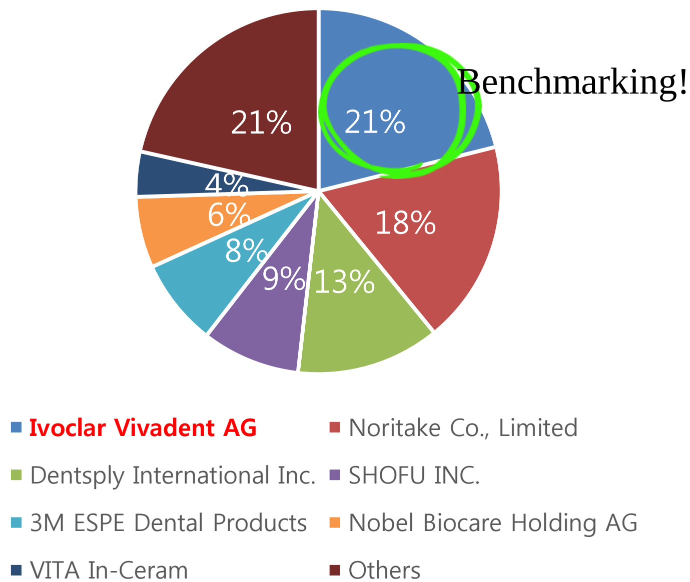
<CAD/CAM : Zirconia, Alumina, LS GC>

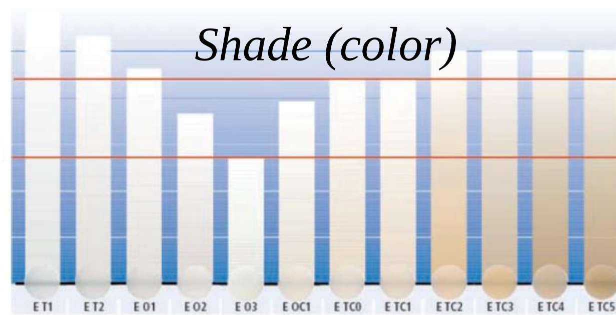


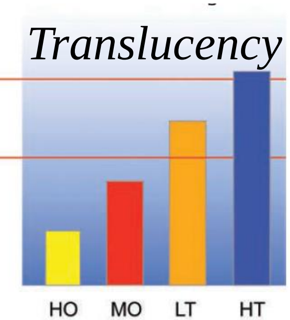


Introduction : Lithium disilicate glass-ceramics

Companies of Crowns and Bridge







CTE (100–400°C) [10^{-6}/K]	10.2
CTE (100–500°C) [10^{-6}/K]	10.5
Flexural strength (biaxial) [MPa]*	400
Fracture toughness [MPa $m^{0.5}$]	2.75
Modulus of Elasticity [GPa]	95
Vickers hardness [MPa]	5800
Chemical solubility [μg/cm^2]*	40
Press temperature [°C]	915–920

*according to ISO 6872

Table 2

Motivation & Objective

- Development of suitable composition design and estabilishment of heat-treatment condition to obtain ***400MPa*** flexural strength of lithium disilicate glass-ceramics with various color, translucency and feasibility of plastic deformation.

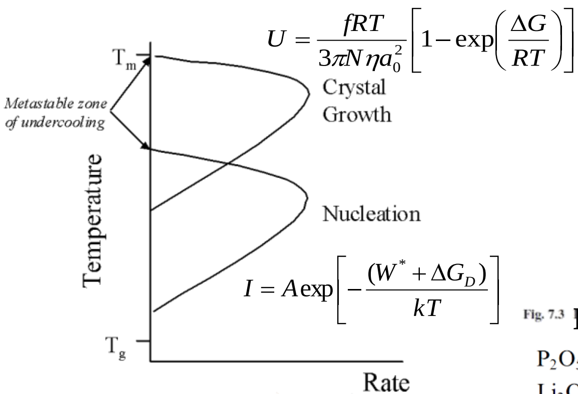
Optimal crystallization condition	Shade & Translucency	Plastic deformation (Softening) → Manufacturing condition
Part. I	**Part. II**	**Part. III**
To obtain optimal crystallization condition for LS2 GC by design of composition through mixture design. **To identify the appropriate heat-treatment condition.**	**To fit the shade and translucency of Benchmarking product. (Ivoclar vivadent)**	**To study about plastic deformation behavior of LS2 GC for hot-pressing condition.**

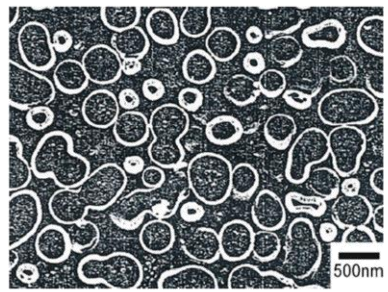
I-1. Crytallization of Lithium Disilicate Glass-Ceramics by Mixture Design

Part I-1. Motivation & Objective

- On the basis of mixture design (Design of experimental), ***the effect of additives ratio*** on crystallization of LS2($Li_2O \cdot 2SiO_2$) was studied.

<Crystallization of Lithium Disilicate(LS2) Glass>



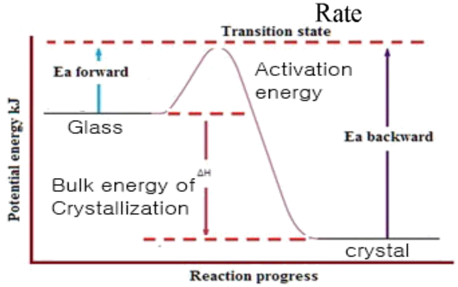


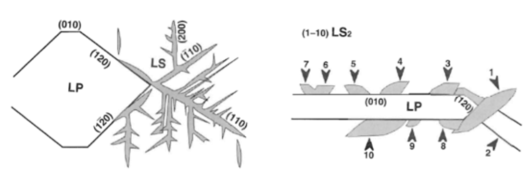
Liquid-liquid phase separation

$P_2O_5(glass) + 3Li_2O(glass) = 2Li_3PO_4(crystal)$

$Li_2O(glass) + SiO_2(glass) = Li_2SiO_3(crystal)$

$Li_2SiO_3(crystal) + SiO_2(glass) = Li_2Si_2O_5(crystal)$





Figures 1-30 and 1-31 Epitaxial growth of Li_2SiO_3 (LS) (Fig. 1-30) and $Li_2Si_2O_5$(LS_2) (Fig. 1-31) on Li_3PO_4 (LP), according to Headley and Loehmann (1984).

<Additives for LS2>

Roles	Additives	Details
Nucleation reagent	***P_2O_5***	***Bulk Crystallization***
	ZrO_2	Additives for mechanical strength
	TiO_2	Surface Crystallization
	Pt, Pd, Au, Ag	Surface/bulk Crystallization
Glass network Former & Modifier	K_2O	flux
	Na_2O	flux
	BaO	Increase of Li_2SiO_3 crystallization peak although lead to decrease of Volume fraction
	CaO	
Viscosity & chemical stability	La_2O_3 ,Al_2O_3	control viscosity and flow in plastic state
	MgO, ZnO, Nb_2O_3 ,B_2O_3, SrO	• Good chemical stability • Low viscosity to enhance Li_2SiO_3 crystal result in moderate fraction • Deteriorate crystal growth of Li_2SiO_5

Ref) Glass and Glass Ceramics for Medical Applications (Emad El-Meliegy) p212~214

Experimental

X - variation

1. Glass composition
2. Crystallization (Heat-treatment) — Nucleation / Crystal growth

Black box

1. Crystalline phase
2. Crystalline phase size

Y - Results

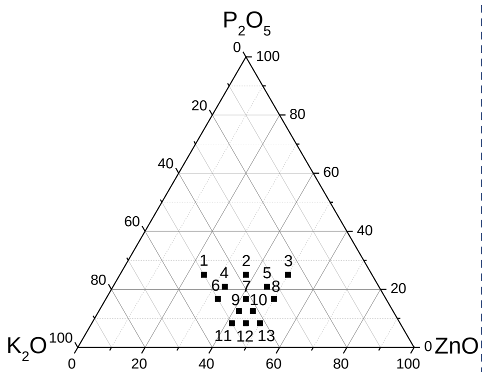
1. Bi-axial strength
2. Vickers hardness
3. Fracture toughness (K_{IC})

<Glass composition>

- Matrix $SiO_2/Li_2O=2.3$ (94mol% fixed)
- Total amount of additives : 6mol%

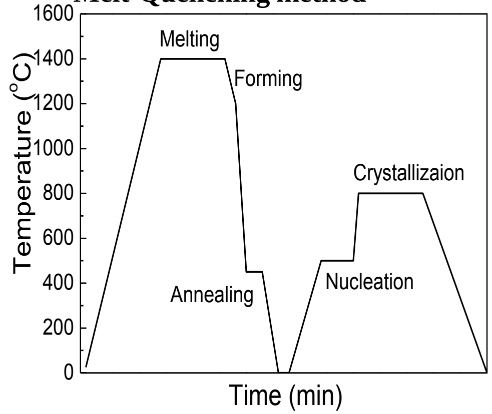
Additives	P_2O_5	ZnO	K_2O
Raw materials	$(NH_4)_2HPO_4$	ZnO	K_2CO_3
Role	Nucleation agent	Glass modifier	

Sample ID	Compositions of additives (mol%)			ZnO/K_2O
	P_2O_5	K_2O	ZnO	
#1	1.5	3	1.5	0.5
#2	1.5	2.25	2.25	1
#3	1.5	1.5	3	2
#4	1.25	2.75	2	0.727
#5	1.25	2	2.75	1.375
#6	1	3	2	0.667
#7	1	2.5	2.5	1
#8	1	2	3	1.5
#9	0.75	2.75	2.5	0.909
#10	0.75	2.5	2.75	1.1
#11	0.5	3	2.5	0.833
#12	0.5	2.75	2.75	1
#13	0.5	2.5	3	1.2



<Experimental>

Glass fabrication :
Melt-Quenching method



Batch → Mixing → Melting → Forming → Annealing → Glass → DTA → Heat –treatment (Nucleation) → Heat –treatment (Crystal Growth) →

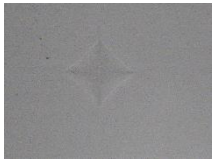
- XRD
- SEM
- Fracture toughness
- Strength
- Hardness

<Bi-axial strength>

- ISO 6872
- Piston on a 3-balls
- Sample size : 12.8mm(Dia), 1.2T

<Hardness : Vicker's >

- Indentation load: HV 0.5
- Duration time : 10s

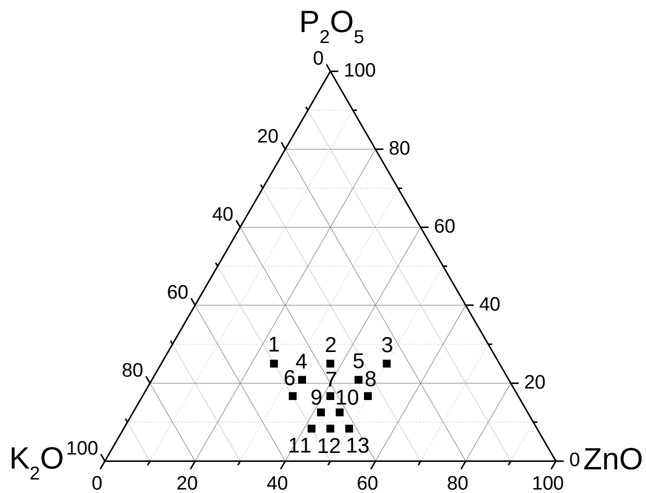


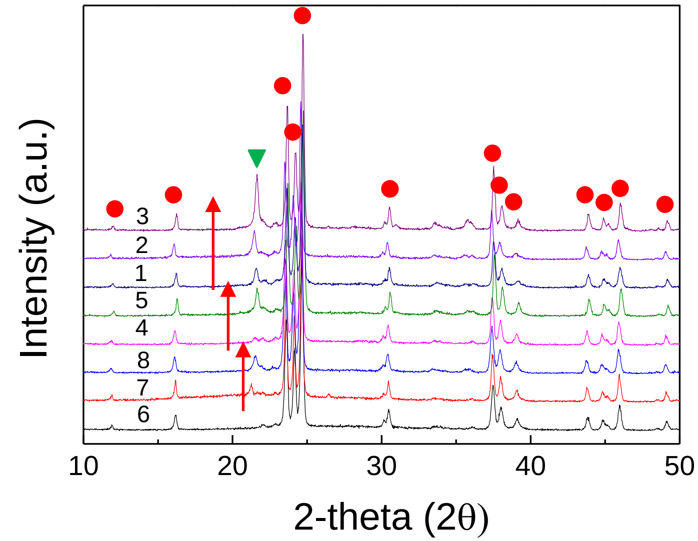
XRD

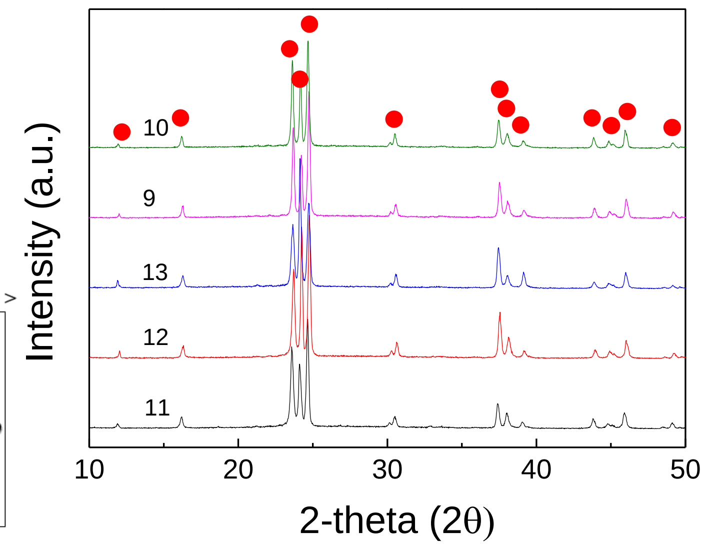
- ● Lithium Disilicate [01-072-0102]
- ▼ Cristobalite – SiO_2 [01-071-0785]

Composition	P_2O_5 (mol%)	ZnO/K_2O
1	1.5	0.5
2		1
3		2
4	1.25	0.73
5		1.38
6	1	0.67
7		1
8		1.5
9	0.75	0.9
10		1.1
11	0.5	0.83
12		1
13		1.2

Nucleation agent

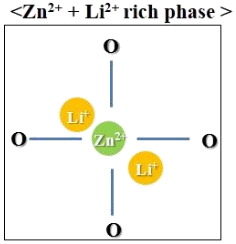






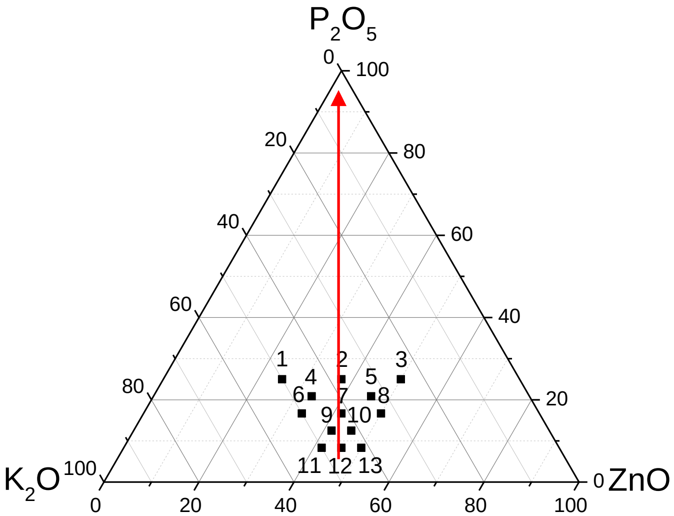
- The formation of secondary phase cristobalite is thought to be related to the Zn^{2+} ion
- The Zn^{2+} is thought to be located at tetrahedral sites since it prefers four coordination due to strong covalent boding via sp^3 hybridization
- It is assumed that Zn^{2+} ions behave as a glass former in the tetrahedral unit $(ZnO_4)^{2-}$ possessing Li^+ and K^+ to maintain neutrality in the glass, and therefore the Si-rich region increases near $(ZnO_4)^{2-}$ and is crystallized as cristobalite.

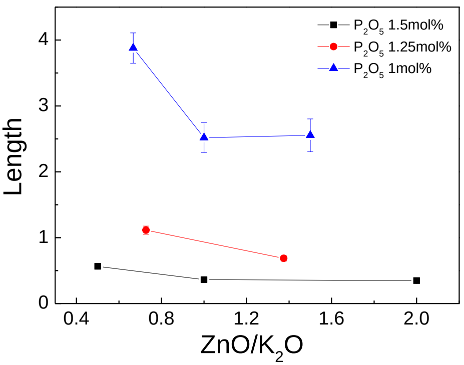
<Zn^{2+} + Li^{2+} rich phase>

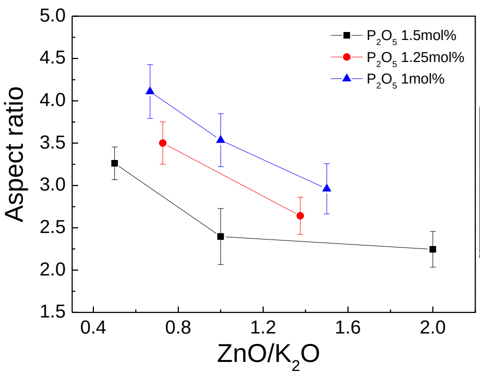


Microstructure : SEM

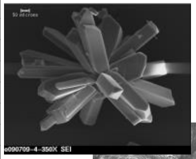
Nucleation agent

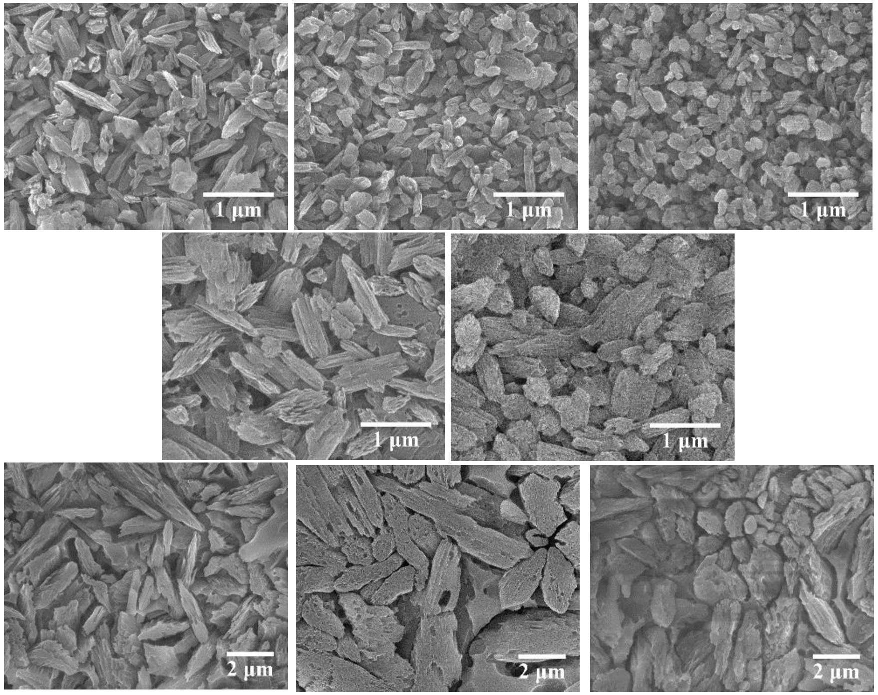


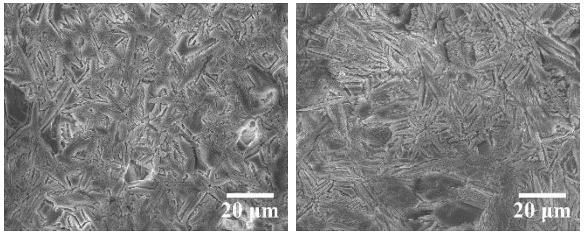


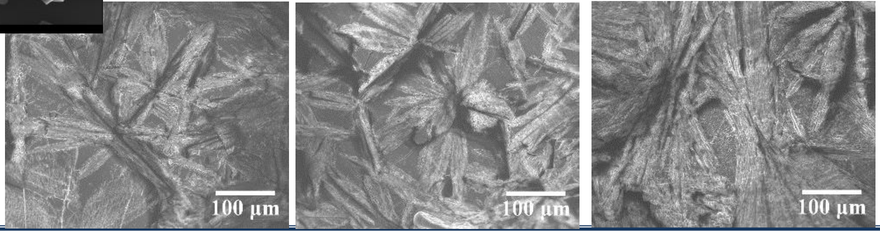


Spherulite

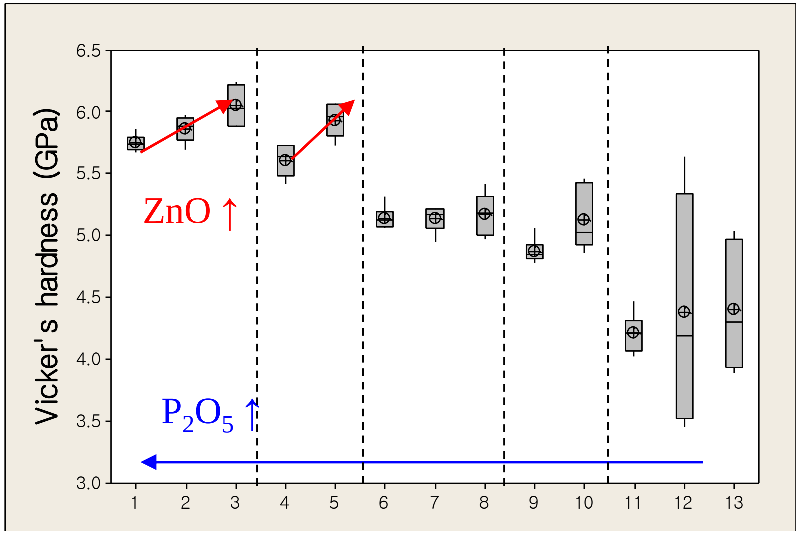


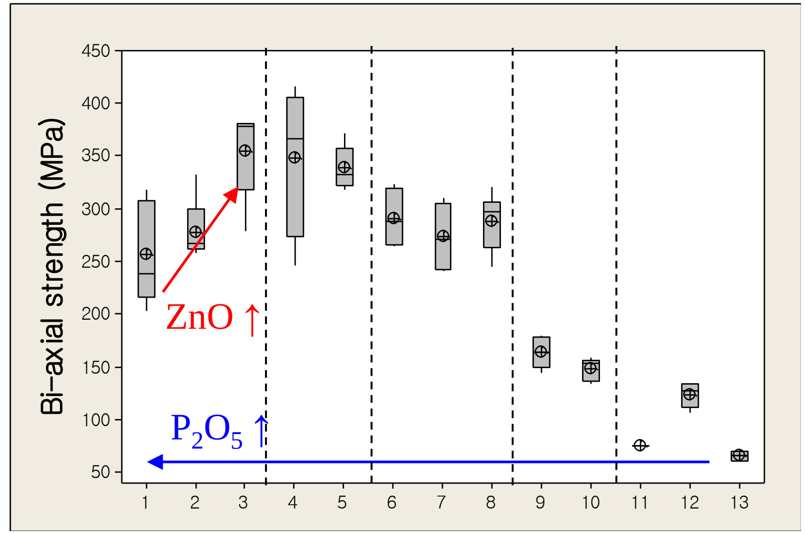




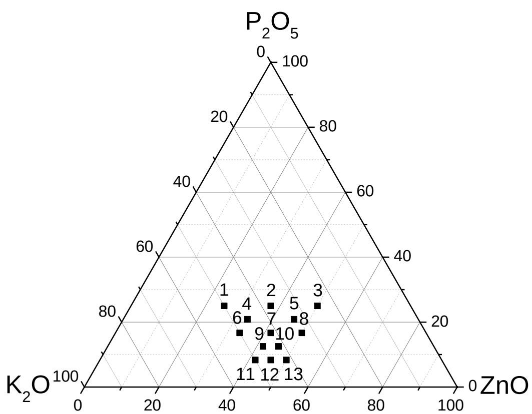


Strength & Hardness





Nucleation agent



- The Bi-axial strength and hardness increased as increase of P_2O_5.
- The hardness tend to increase by increase of ZnO.
- The strength and hardness prone to increase as decrease of grain size. It is thought that the addition of P_2O_5 provided many sites of crystalline phase, and the ZnO hinderd the growth of LS2 phase by consuming Li^+ Ion.

Surmmary

I-1. Crytallization of Lithium Disilicate Glass-Ceramics by Mixture Design

- The crystal size became small as increase of P_2O_5 due to its increase of heterogeneous nucleation sites and more spherical as increase of ZnO.

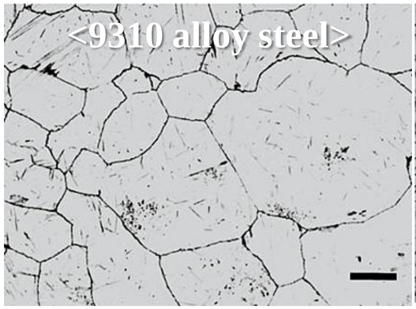
- The ZnO affected the formation of cristaobalite by consuming of Li^+ ion and the increase of SiO_2-rich phase fraction which is crystallized. Also, it impeded growth of LS2 crystalline phase.

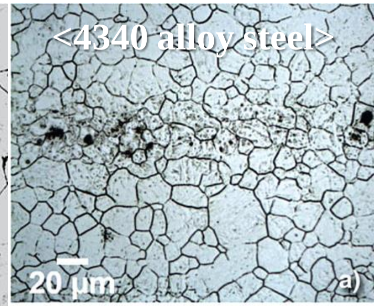
- The bi-axial strength and hardness increased as decrease of crystalline phase size.

I-2. Effect of crystallization on mechanical properties of lithium disilicate glass ceramics

Part I-2. Motivation & Objective

<Metal>





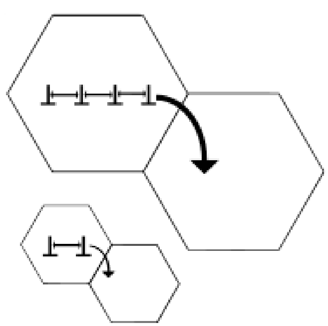
Ref) http://www.georgevandervoort.com/metallography/specific/iron-and-steel-specific/20001306-revealing-prior-austenite-grain-boundaries-in-heat-treated-steels-article.html

$$\sigma_f = \sigma_y + k_y d^{-1/2}$$

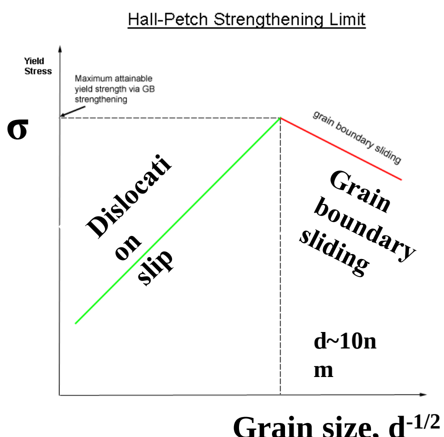
<Hall-Petch relation>

$$H = H_0 + k_h d^{-1/2}$$

- σ_f is the yield stress for the easiest slip system of a single crystal
- k_y is constant

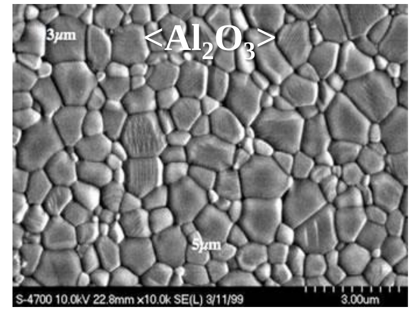


Dislocation Pile-up



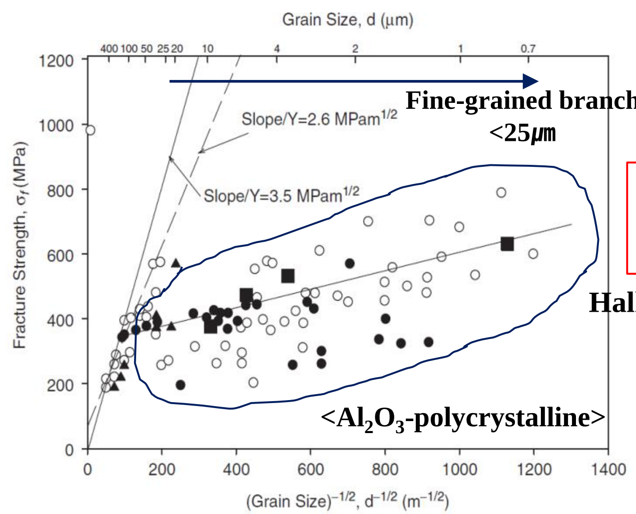
Ref) Wikipedia : Hall–Petch Strengthening

<Ceramics>



Ref) http://www.ceramtec.kr/ceramic-materials/aluminum-oxide/

<Glass Ceramics>



<Griffiths eq.>

$$K_I = Y\sigma c^{-1/2}$$

Y : Crack shape factor

Assumption)
Crack ≈ Grain size

Hall-Petch relation + Griffiths eq.

$$\sigma_f = \frac{K_{IC}}{Y} c^{-1/2} \approx \frac{K_{IC}}{Y} d^{-1/2}$$

Ref) Mechanical properties of ceramics (John. B. Wachtman) p215

1. **Does the strength and hardness of crystalline phase of LS2 glass-ceramics follows the Hall-Petch relation?**
2. **What factors would influence on the strength & hardness of LS2 glass-ceramics?**

Experimental

X - variation

1. Glass composition
2. Crystallization (Heat-treatment) — Nucleation / Crystal growth

Black box

1. Crystalline phase
2. Crystalline phase size

Y - Results

1. Bi-axial strength
2. Vickers hardness
3. Fracture toughness (K_{IC})

<Glass composition>

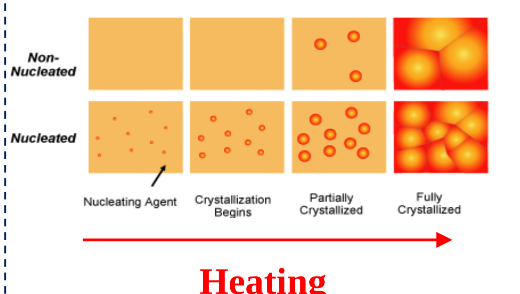
- SiO_2/Li_2O=2.3 (94mol% fixed)
- Additives total : 6mol%

Sample ID	Composition	SiO_2	Li_2O	P_2O_5	ZnO	K_2O
#3	P1.5Zn3	66.27	27.73	1.5	3	1.5
#4	P1.25Zn2.75	66.27	27.73	1.25	2.75	2
#7	P1.25Zn2	66.27	27.73	1.25	2	2.75
#12	P1Zn2.5	66.27	27.73	1	2.5	2.5

Additives	P_2O_5	ZnO	K_2O
Raw materials	$(NH_4)_2HPO_4$	ZnO	K_2CO_3
Role	Nucleation agent	Glass modifier	

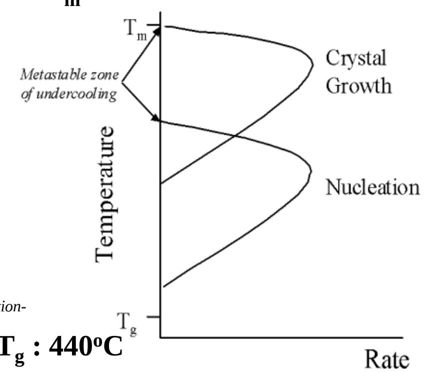
<Crystallization>

- Heat-treatment affects the number of nuclei, size of crystalline phase
- Nucleation temperature, time → The number of nuclei
- Crystal growth temperature, time→ Crystalline phase size



Ref) http://polymer-additives.specialchem.com/centers/polypropylene-nucleation-center/how-do-nucleating-agents-work

T_m : 990°C

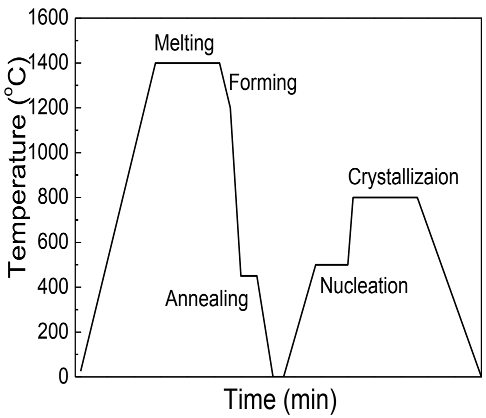


T_g : 440°C

Experimental

<Experimental>

Glass fabrication :
Melt-Quenching method



Batch → Mixing → Melting → Forming → Annealing → Glass

→ DTA → Heat –treatment (Nucleation) → Heat –treatment (Crystal Growth) →

- XRD
- SEM
- Fracture toughness
- Strength
- Hardness

<Maximum nucleation Temperature>

→ Marrota's DTA analysis

Ref) A. Marrota et al, J. Mat. Sci. 16 (1981) 341

$\ln(N_0 + N_n) = \frac{E_c}{R}\frac{1}{T_p} + const$ – for previously nucleated

N_0 = same surface & heating rate

$\ln N_0 = \frac{E_c}{R}\frac{1}{T_p^0} + const$ – for an as-quenched sample ($N_n = 0$)

$\ln(\frac{N_0 + N_n}{N_0}) = \frac{E_c}{R}\left(\frac{1}{T_p} - \frac{1}{T_p^0}\right)$

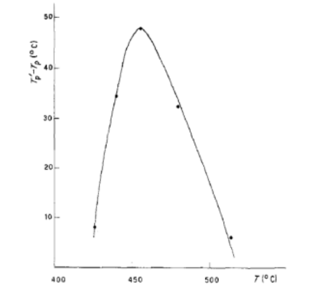


Figure 3 $T_p' - T_p$ plotted against temperature of heat-treatment for $Li_2O-2SiO_2$ glass.

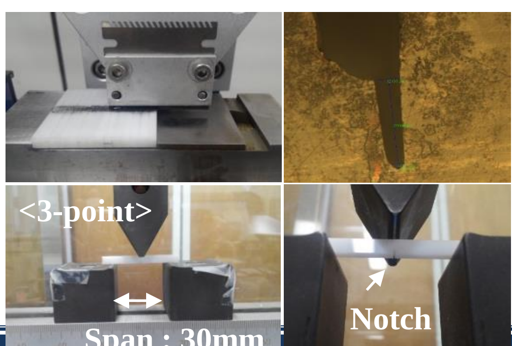
Isothermal : 1h
Heating rate : 15℃

$\Delta T = T_p' - T_p$ shift of the DTA peak temperature

→ Max. nucleation rate

<Fracture Toughness : SEVNB>

- **Single-Edge-V-Notch-Beam**
- **Notch depth : 1mm, Tip Radius: 15μm**
- **Sample size : 3 × 4 × 40 (mm)**



<Strength : Bi-axial >

- **ISO 6872**
- **Piston on a 3-balls**
- **Sample size : 12.8mm(Dia), 1.2T**

<Hardness : Vicker's >

- **Indentation load: HV 0.5**
- **Duration time : 10s**

<Crystal growth : Heat-treatment condition>

Factor	Name	Type	Levels	Level Values		
A	핵형성온도	Numeric	3	0	460	500
B	결정화온도	Numeric	2	800	850	
C	결정화시간	Numeric	2	2	4	

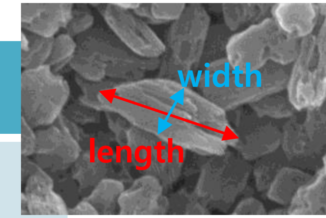
- **Nucleation duration: : 1h (fixed)**
- **Heating rate : 10℃/min**

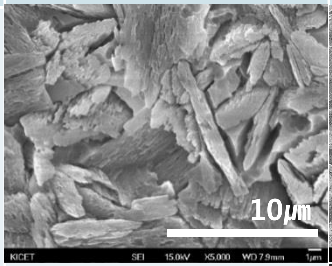
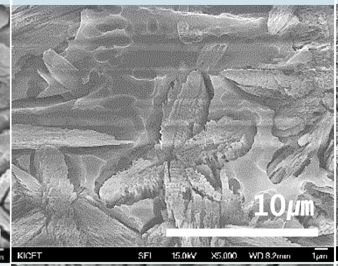
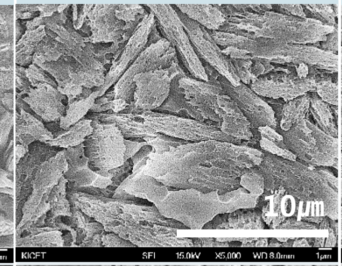
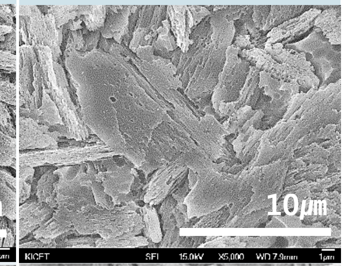
- **Crystal growth**
- **Heating rate : : 30℃ /min**

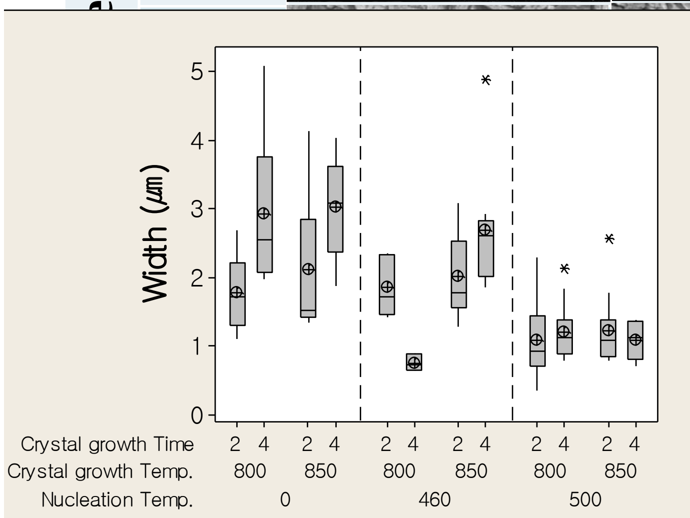
Max. Nucleation Temp. →

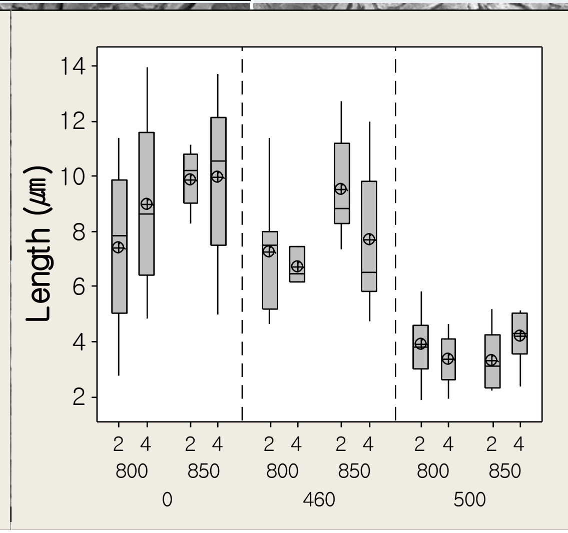
Nucleation Temp.	Crystal growth Temp.	Crystal growth Time
460	800	2
		4
	850	2
		4
500	800	2
		4
	850	2
		4
540	800	2
		4
	850	2
		4

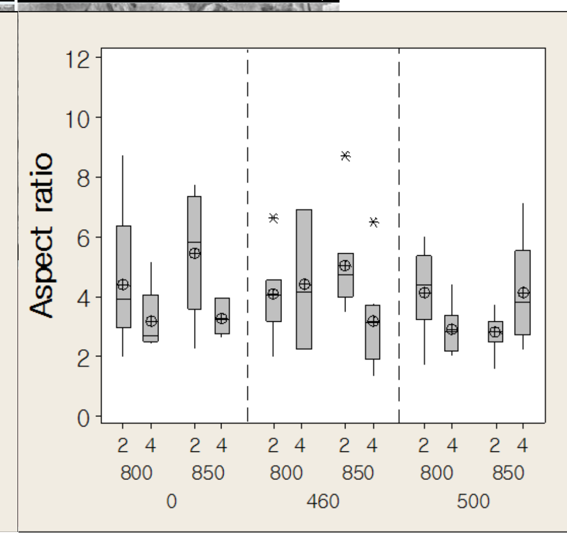
Crystalline phase size : P1Zn2.5



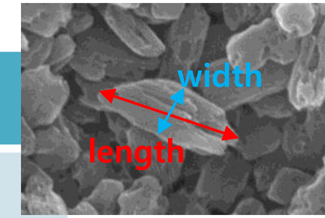
Crystal growth Temp.		800°C		850°C	
Crystal growth Time		2h	4h	2h	4h
emp.	0	 10μm	 10μm	 10μm	 10μm

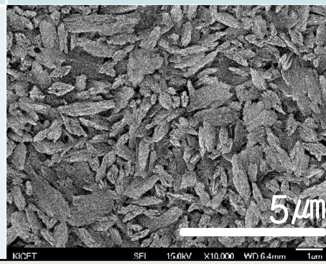
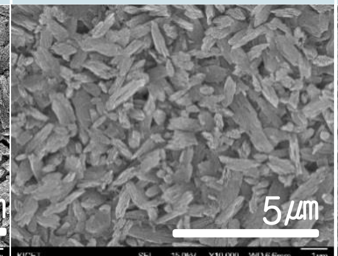
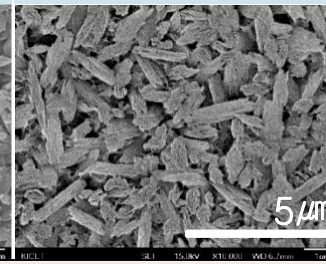
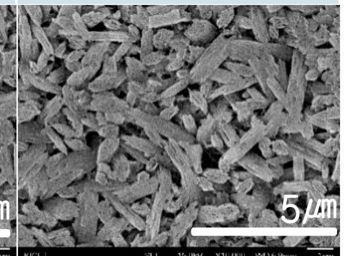


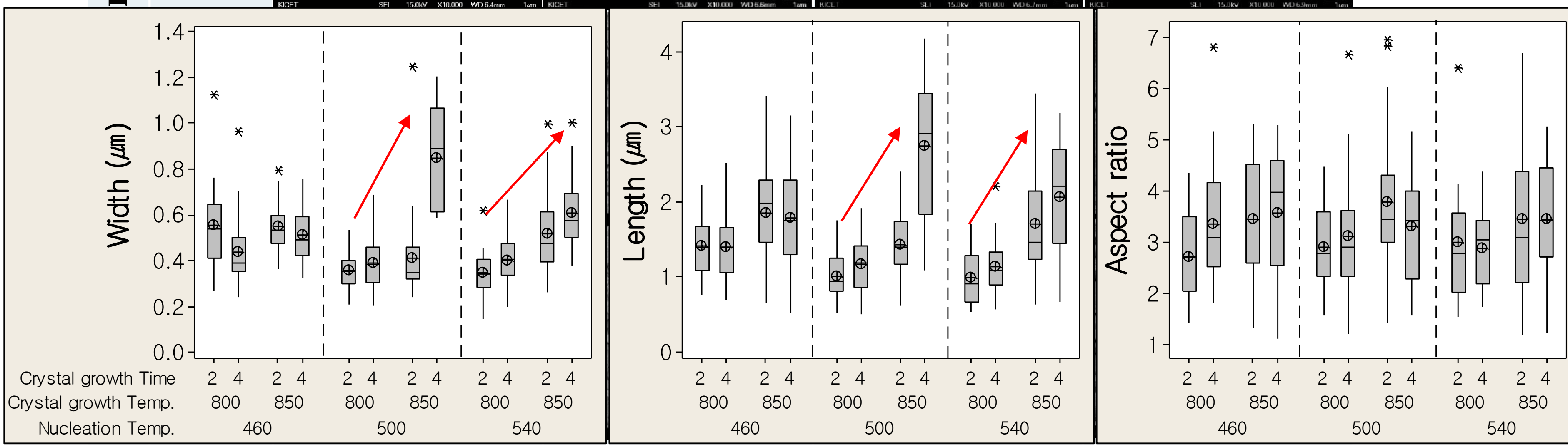




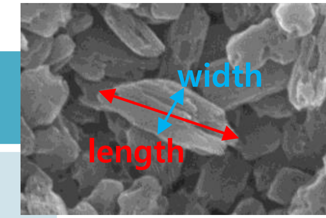
Crystalline phase size : P1.25Zn2

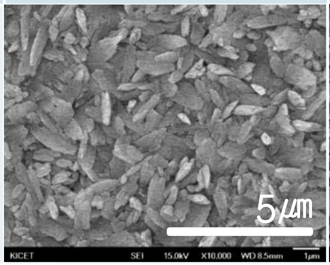
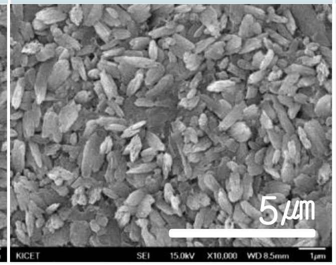


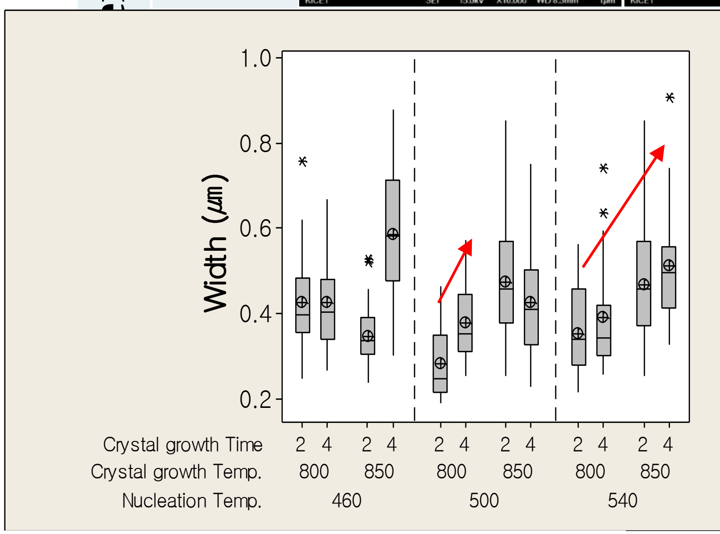
Crystal growth Temp.		800°C		850°C	
Crystal growth Time		2h	4h	2h	4h
mp.	460°C				

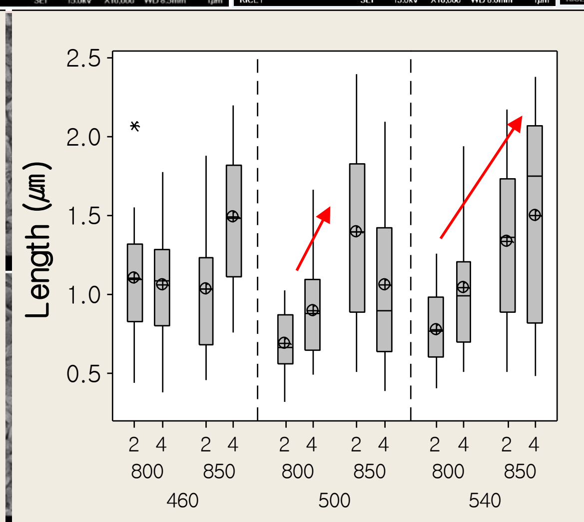


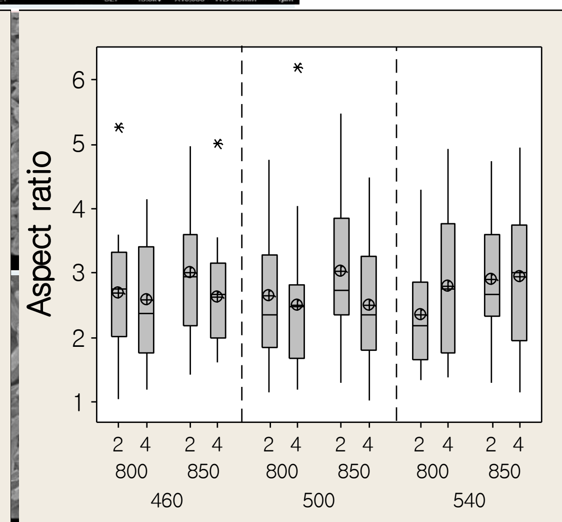
Crystalline phase size : P1.25Zn2.75



Crystal growth Temp.		800°C		850°C	
Crystal growth Time		2h	4h	2h	4h
mp.	460°C				

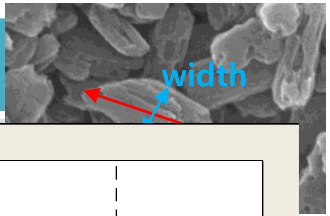


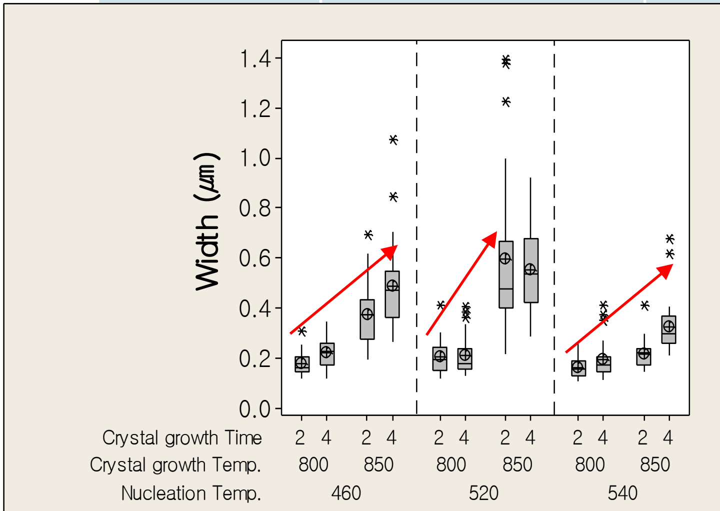


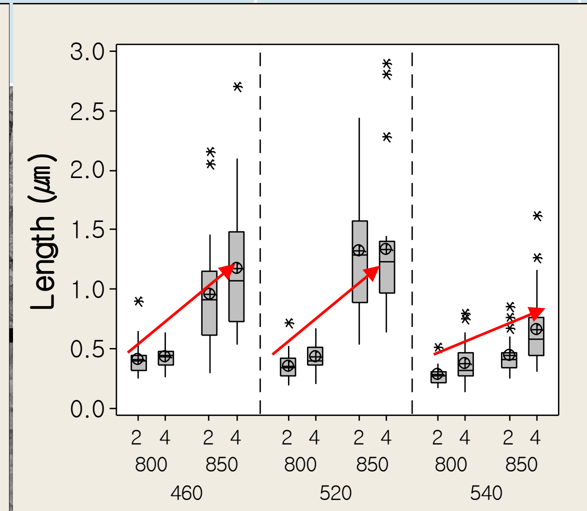


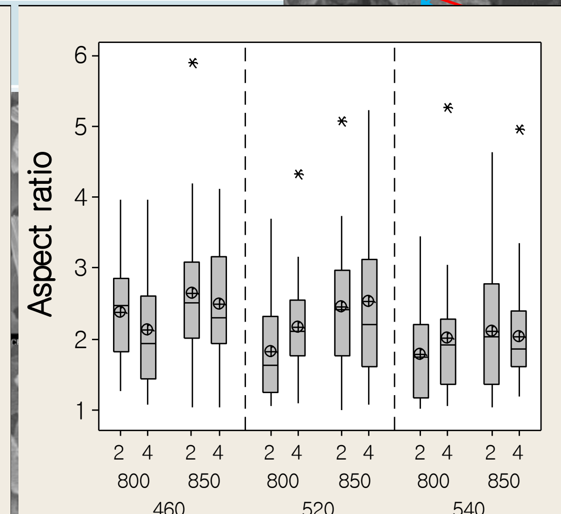
Crystalline phase size : P1.5Zn3

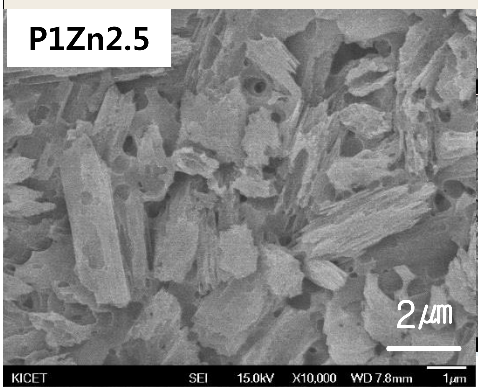
Crystal growth Temp.	800°C	850°C

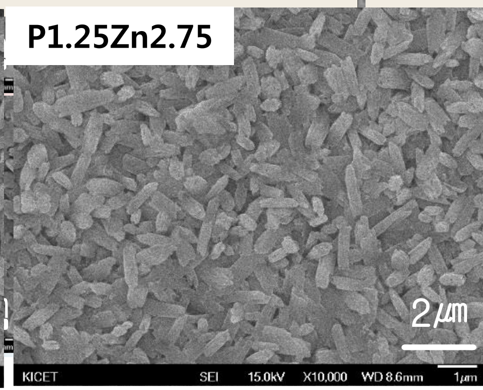


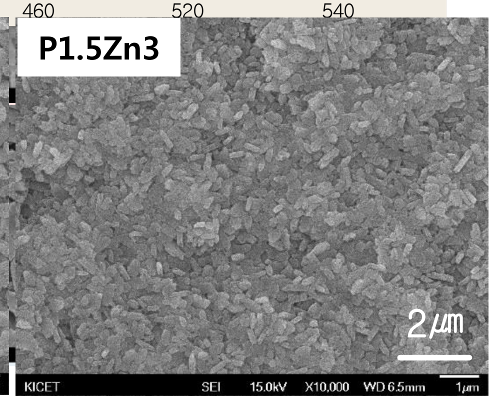






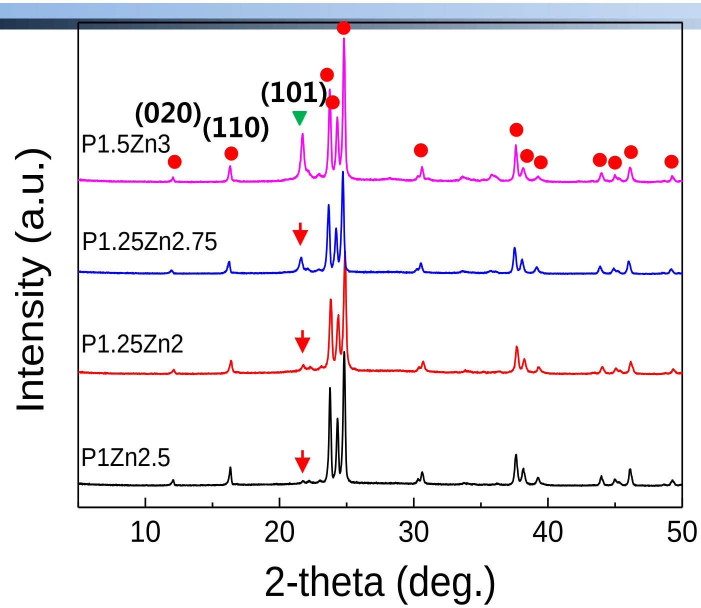






Heat treat-ment : 500°C, 800°C, 2h

Crystalline phase analysis : XRD



- ● Lithium Disilicate [01-072-0102]
- ▼ Cristobalite – SiO_2 [01-071-0785]

SiO_2/Li_2O=2.39

Composition	SiO_2	Li_2O	P_2O_5	ZnO	K_2O
P1.5Zn3	66.27	27.73	1.5	3	1.5
P1.25Zn2.75	66.27	27.73	1.25	2.75	2
P1.25Zn2	66.27	27.73	1.25	2	2.75
P1Zn2.5	66.27	27.73	1	2.5	2.5

- **Secondary phase cristobalite peak increased as increase of P_2O_5 and ZnO.**
- **P_2O_5 induced phase separation the Li_2O-rich region and SiO_2-rich region.**

<Phase separation>

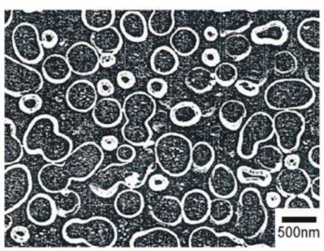
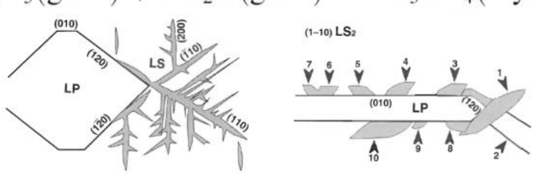


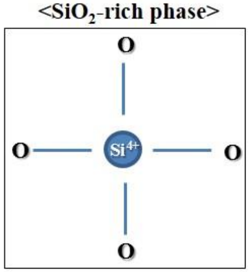
Fig. 7.3 Liquid–liquid phase separation

$$P_2O_5(\text{glass}) + 3Li_2O(\text{glass}) = 2Li_3PO_4(\text{crystal})$$

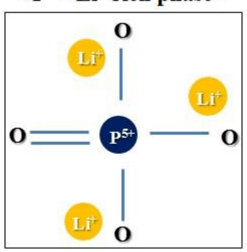


Figures 1-30 and 1-31 Epitaxial growth of Li_2SiO_3 (LS) (Fig. 1-30) and $Li_2Si_2O_5$(LS_2) (Fig. 1-31) on Li_3PO_4 (LP), according to Headley and Loehmann (1984).

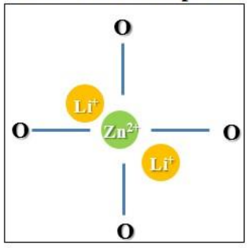
<SiO_2-rich phase>



<P^{5+}- Li^+ rich phase>



<Zn^{2+} + Li^{2+} rich phase >

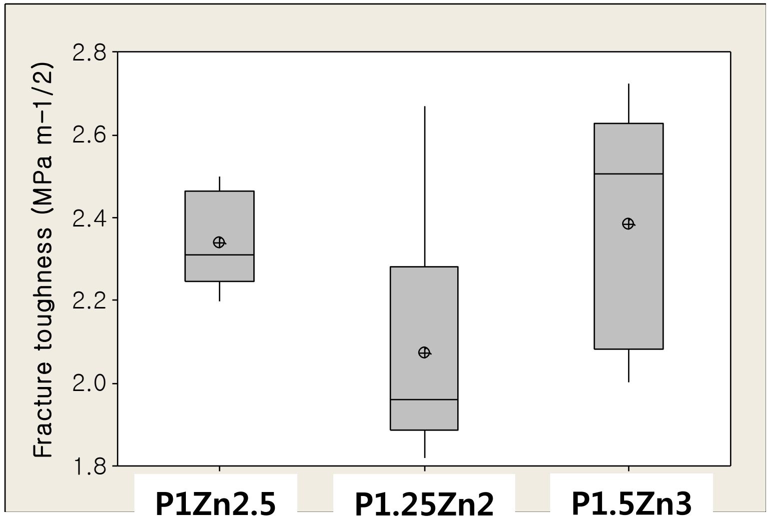


- **From the Li_2O-rich region, Li_3PO_4 was formed and it promoted the LS2 growth.**
- **<u>SiO_2-rich region may be left as increase of P_2O_5 and it formed cristobalite (SiO_2).</u>**
- **ZnO may consumed the Li^+ to maintain neutrality in the glass which result in increase of SiO_2-rich region leading the cristobalite (SiO_2) growth.**

Ref) Glass-ceramics technology (Wolfram Holnad) p50

Fracture toughness

<Fracture toughness. K_{IC}>

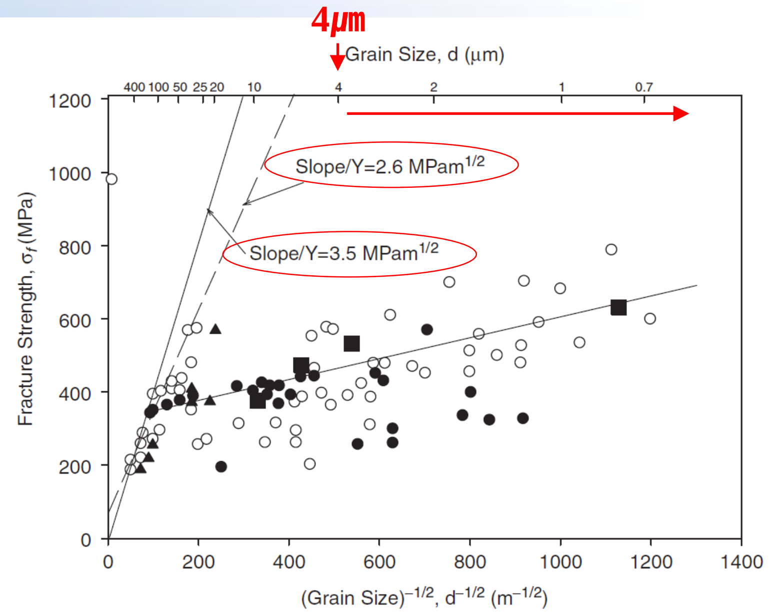


Composition	K_{IC}	Crystalline phase size (㎛)
P1.5Zn3	2.29±0.34	0.361
P1.25Zn2.75	-	0.962
P1.25Zn2	2.07±0.3	1.026
P1Zn2.5	2.34±0.11	3.878

Comparison	p-value
P1Zn2.5 vs P1.5Zn3	0.758
P1Zn2.5 vs P1.25Zn2	0.066
P1.25Zn2 vs P1.5Zn3	0.109

→ All K_{IC} of samples was identical

→ No significance



Hall-Petch relation + Griffiths eq.

Assumption)
Crack ≈ Grain size

$$\sigma_f = \frac{K_{IC}}{Y} c^{-1/2} \approx \frac{K_{IC}}{Y} d^{-1/2}$$

$$slope = \frac{K_{IC}}{1.12\sqrt{\pi}} \qquad Y = 1.12\sqrt{\pi}$$

Composition	K_{IC}	Slope
P1.5Zn3	2.29±0.34	1.15
P1.25Zn2	2.07±0.3	1.04
P1Zn2.5	2.34±0.11	1.18

Srength vs Crystalline phase size

Hall-Petch relation + Griffiths eq.

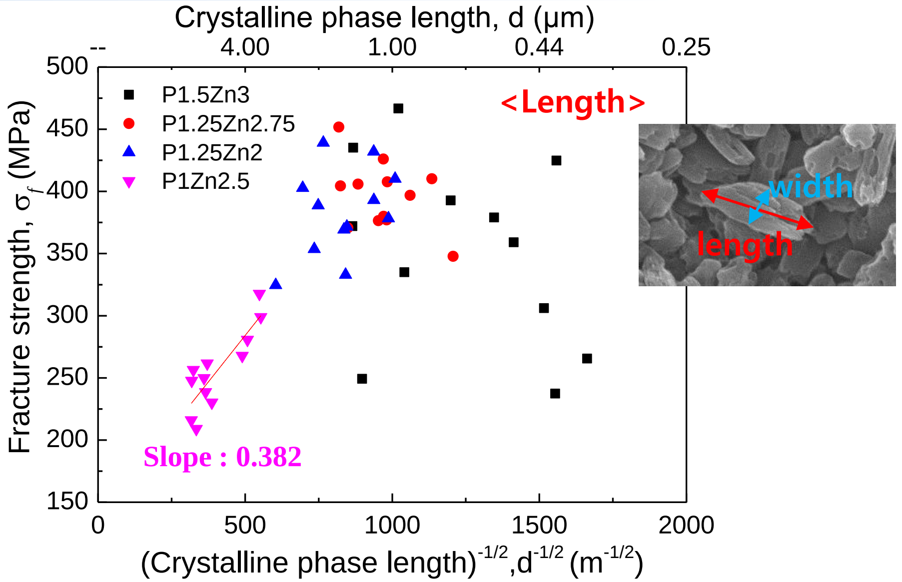
Assumption)
Crack ≈ Grain size

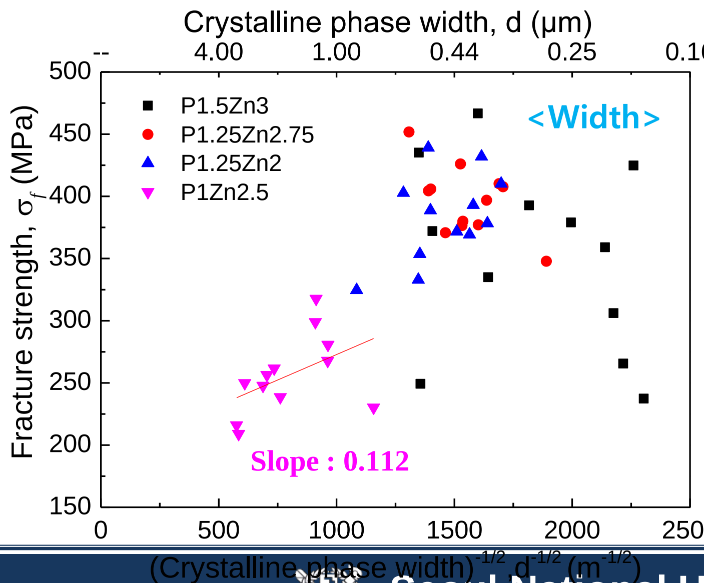
$$\sigma_f = \frac{K_{IC}}{Y} c^{-1/2} \approx \frac{K_{IC}}{Y} d^{-1/2} \quad slope = \frac{K_{IC}}{1.12\sqrt{\pi}}$$

Composition	K_{IC}	Slope (Calculated)	Slope (Measured)
P1Zn2.5	2.34±0.11	1.18	0.382

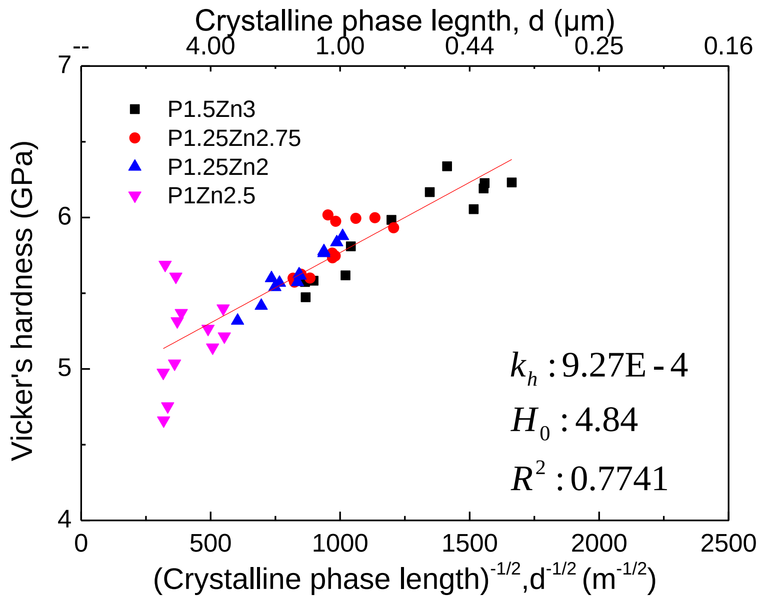
$$\sigma_f = \sigma_y + k_y d^{-1/2}$$

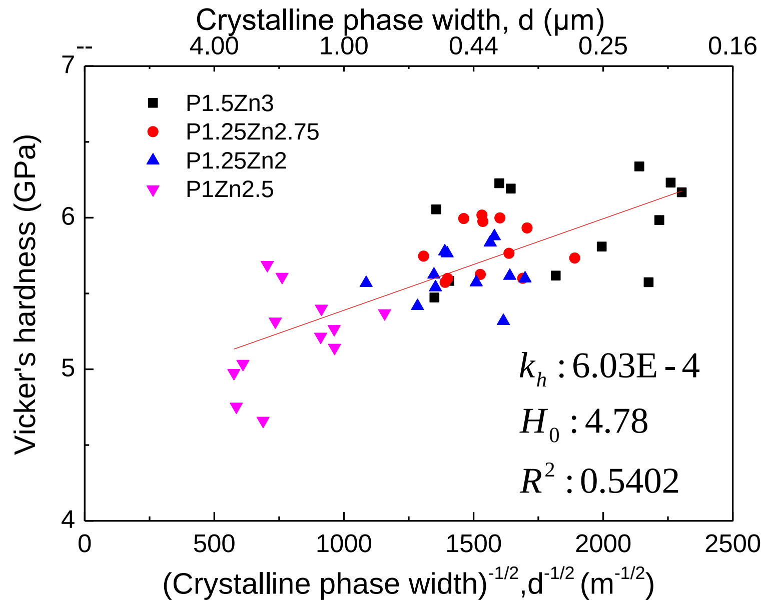
- The calculated slope from the crystalline phase size signified the relevance with K_{IC} showed very low value compared to the measurement → (P1Zn2.5 : 0.382 vs 1.18)
- This is explained that the crystalline phase size is too small(<4㎛), hence the only Hall-Petch corresponded.
- **Fracture strength increased as decrease of crystalline phase size** (length, width) until critical point **and it showed the deviation and decrease.** It could be attributed to the presence of secondary phase cristobalite (SiO_2).



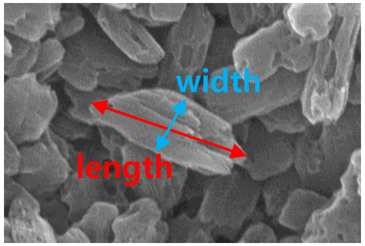


Hardness vs Crystalline phase size





$$H = H_0 + k_h d^{-1/2}$$



- Vickers hardness increased as decrease of crystalline phase size (length, width).
- **Even though fracture strength did not followed the Hall-Petch relation, the hardness coincided with it.**

Surmmary

Effect of crystallization on mechanical properties of lithium disilicate glass-ceramics

- Composition)

1) **The nucleation agent P_2O_5 promoted nucleation, therefore, crystalline phase became small.**
2) **As increase of P_2O_5 and ZnO, secondary phase cristobalite peak intensity increased.**

Why? : The Li^+ ion was consumed to form Li_3PO_4 crystal which promoted the LS2 growth, and to maintain the neutrality in Zn^{2+} tetrahedron.

- Crystallization) The crystalline phase grew as increase of crystal growth temperature and time.

Does the strength and hardness of crystalline phase of Lithium disilicate glass-ceramics follows the Hall-Petch relation?

- Fracture strength : No. It showed scattering and decrease and deviation at critical point.

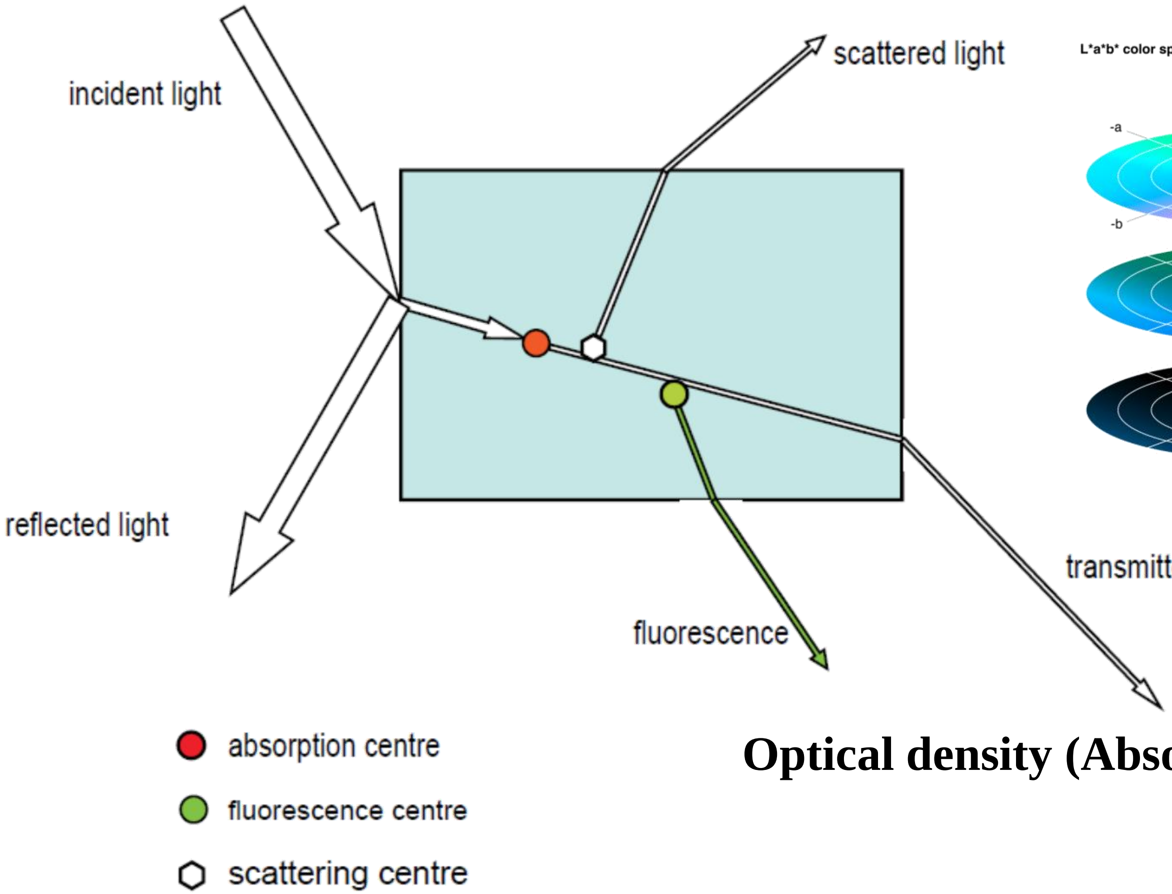
Why? : It is assumed that the secondary phase cristobalite(SiO_2) could affected fracture strength.

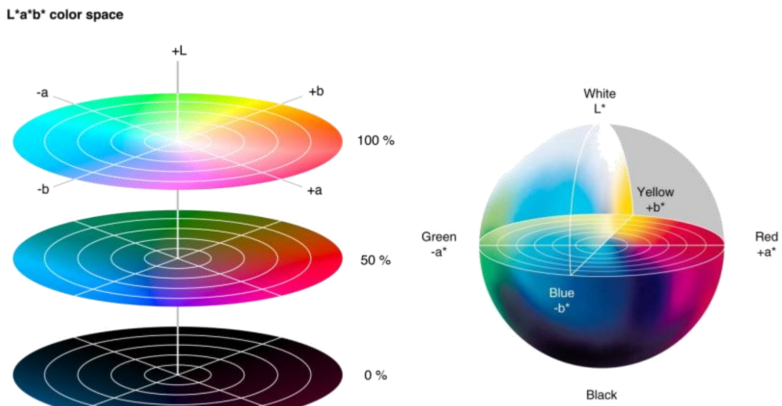
- Hardness : Yes. It followed the Hall-Petch relation.

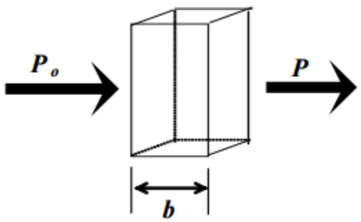
Why? : It will be studied further in future work.

II. Effect of the colorants on the color and translucency of lithium disilicate glass-ceramics

Principles of colour







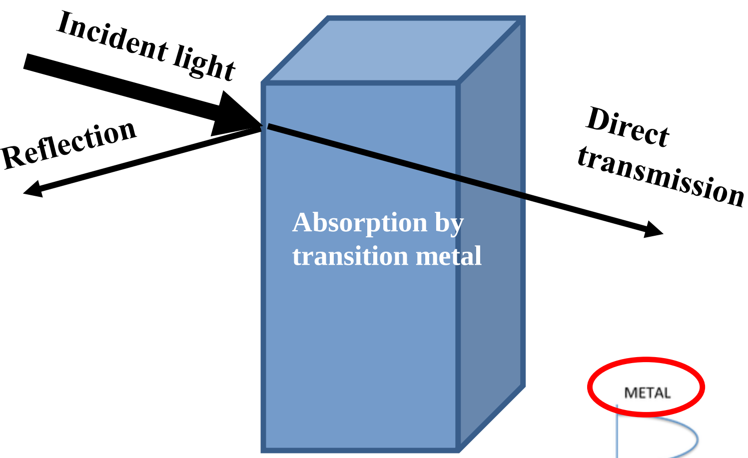
Optical density (Absorbance)

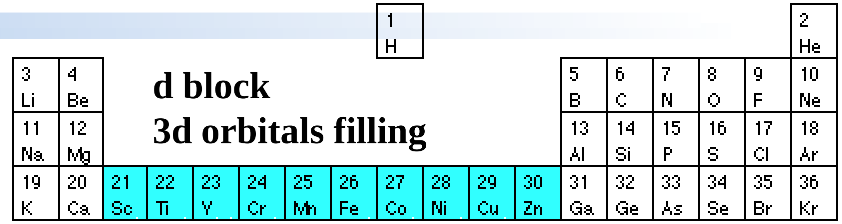
$$T\% = \frac{P}{P_0} \times 100$$

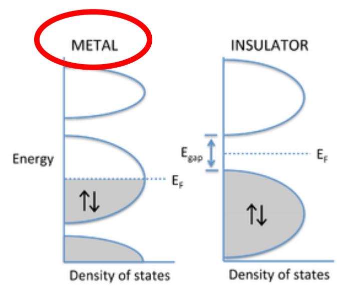
$$Absorbance = -\log T = \log \frac{P}{P_0}$$

- **Lambert's law : 흡광도는 cell의 길이에 비례 *A=ab*, a=constant, "absorptivity" [L/g cm or L/mole cm]**
- **Beer's law : 흡광도는 시료의 농도에 비례 *A=a`c*, c=concentration [g/L, mole/L]**
- **Lambert-Beer's law = *A=abc***

Absorption of light







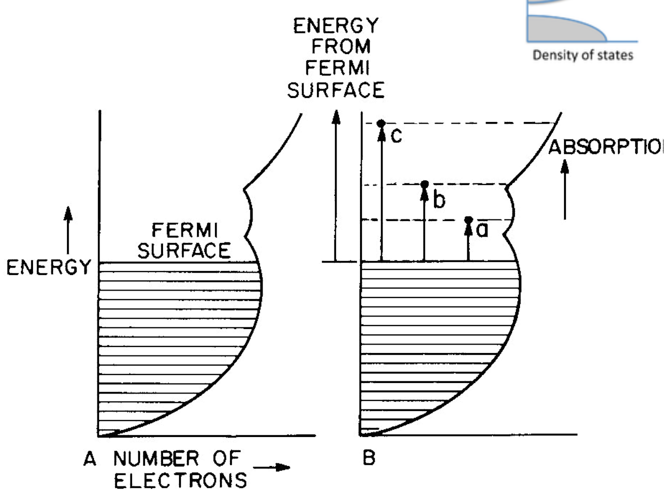
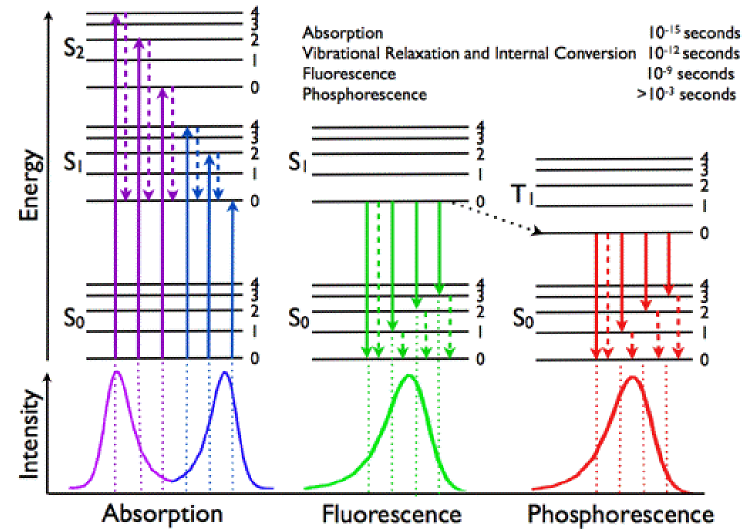


Fig. 6. Band diagram of a typical metal (A) showing light absorption transitions in

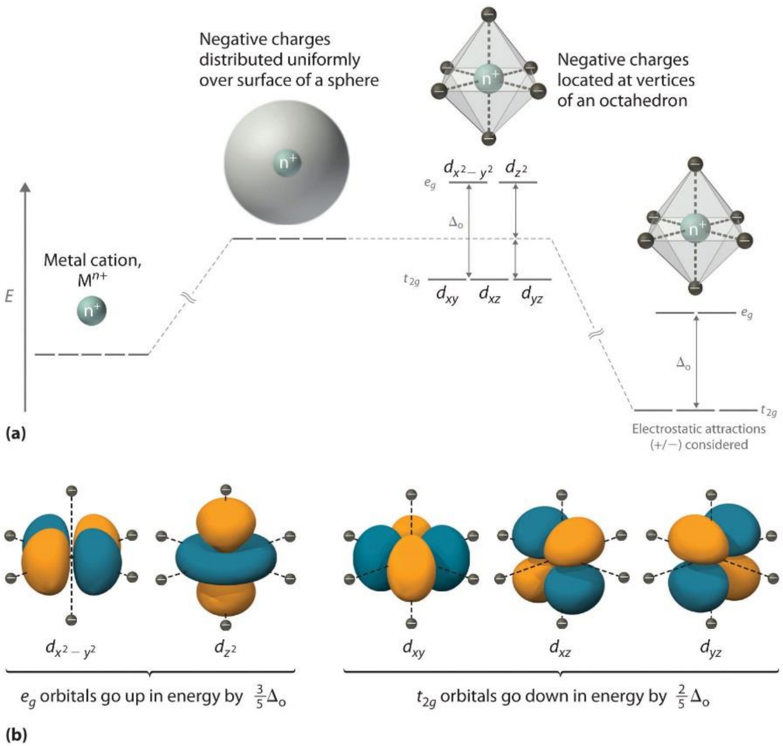


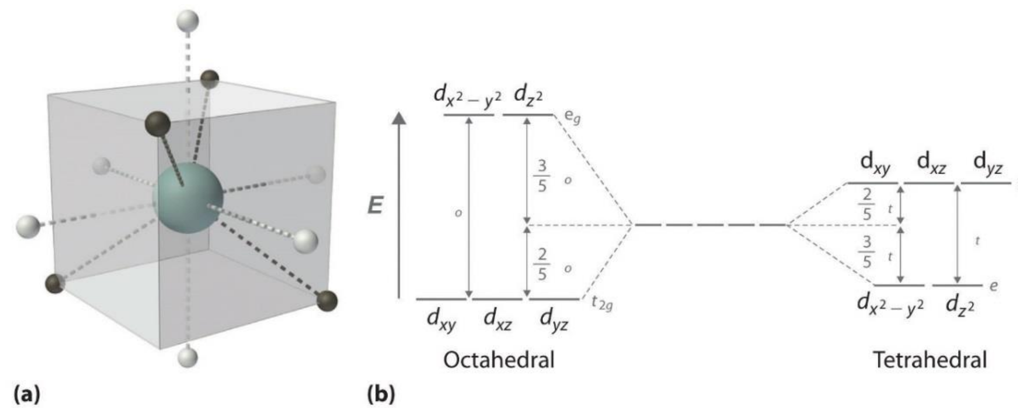
3d, 4f metal ion이 light을 선택적으로 흡수
(보색이 반사되어 색으로 나타남)

→ Metal 이기 때문에 emission이 아님.

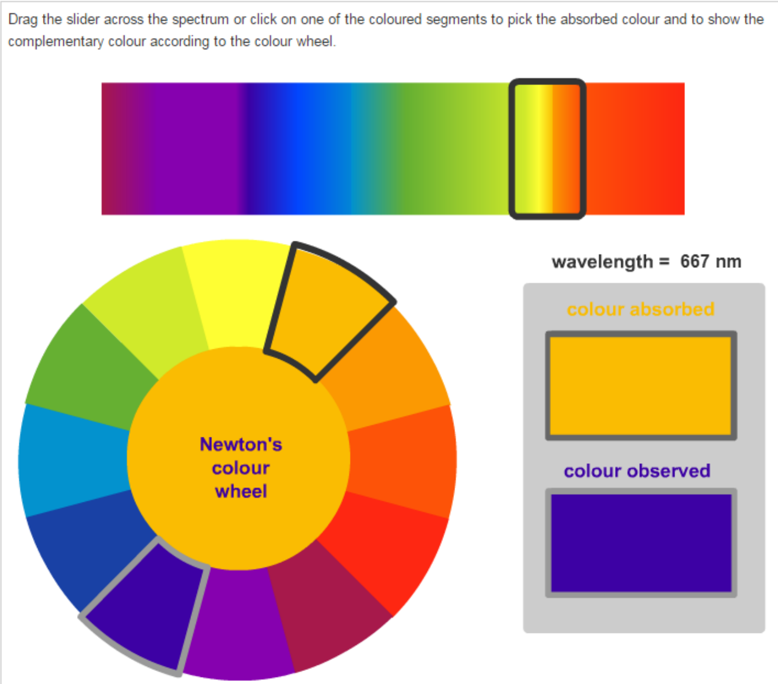
→ Metal 이온이 LS2 crystalline phase 혹은 이차상 (Cristobalite, quartz, LS, LP), 유리상에 위치 (확실한 위치는 알 수 없음 → 분석필요)

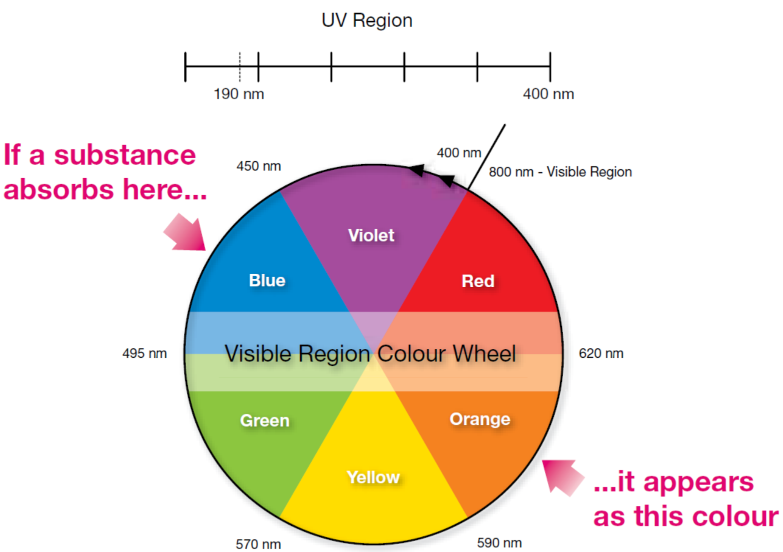
Crystal Field Theory

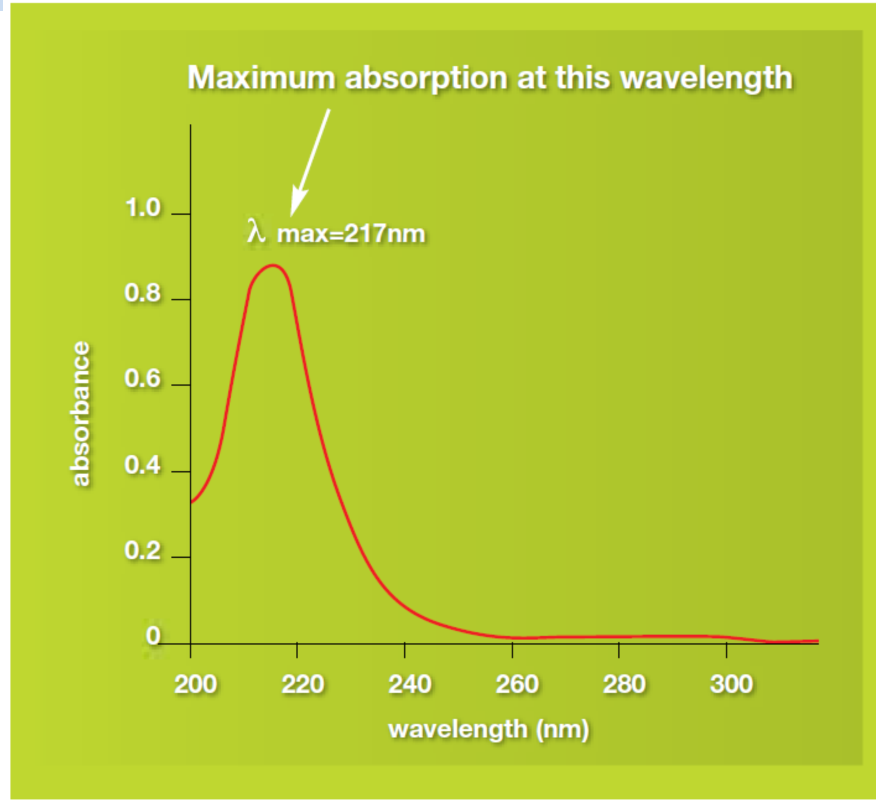




Complimentary colour







The absorption peak at a value of 217 nm, is in the ultra-violet region, and so there would be no visible sign of any light being absorbed making buta-1,3-diene colourless. The wavelength that corresponds to the highest absorption is usually referred to as "**lambda-max**" (λmax).

Red	620-750 nm
Orange	590-620 nm
Yellow	570-590 nm
Green	496-570 nm
Blue	450-495 nm
Violet	380-450 nm

Color generation in glass

Factors of color generation in glass

- Type and concentration of polyvalent ions
- Redox state of glass
- Oxygen pressure and so on

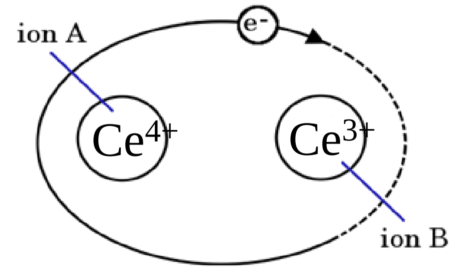
http://artglassdesigns.blogspot.kr/2014/12/colored-glass.html

<Colors generated by colorants in soda lime glass>

Transition metal ions			Rare earth ions		
Configuration	Ion	Color	Configuration	Ion	Color
	Ti^{4+}	Colorless	$4f^0$	La^{3+}	None
d^0	V^{5+}	Faint yellow to colorless		Ce^{4+}	Weak yellow
	Cr^{6+}	Faint yellow to colorless	$4f^1$	Ce^{3+}	Weak yellow
	Ti^{3+}	Violet-purple	$4f^2$	Pr^{3+}	Green
d^1	V^{4+}	Blue	$4f^3$	Nd^{3+}	Violet-pink
	Mn^{6+}	Colorless	$4f^4$	Pm^{3+}	None
d^2	V^{3+}	Yellow-green	$4f^5$	Sm^{3+}	None
d^3	Cr^{3+}	Green	$4f^6$	Sm^{2+}	Green
d^4	Cr^{2+}	Faint blue		Eu^{3+}	None
	Mn^{3+}	Purple	$4f^7$	Eu^{2+}	Brown
d^5	Mn^{2+}	Light yellow		Gd^{3+}	None
	Fe^{3+}	Faint Yellow to Colorless	$4f^8$	Tb^{3+}	None
d^6	Fe^{2+}	Blue-green	$4f^9$	Dy^{3+}	None
	Co^{3+}	Faint Yellow to Colorless	$4f^{10}$	Dy^{2+}	Brown
d^7	Co^{2+}	Blue-pink		Ho^{3+}	Yellow
d^8	Ni^{2+}	Brown-purple	$4f^{11}$	Er^{3+}	Weak pink
d^9	Cu^{2+}	Blue-green	$4f^{12}$	Tm^{2+}	None
d^{10}	Cu^{+}	Colorless	$4f^{13}$	Yb^{3+}	None
			$4f^{14}$	Lu^{3+}	None

Ref) Fundamentals of Inorganic Glasses, Arun K. Varshneya

<Redox in soda lime glass>



$$Ce^{4+} + Sb^{3+} \rightarrow Ce^{3+} + Sb^{4+}$$

Yellow → Weak yellow

<Redox potential series in soda lime glass>

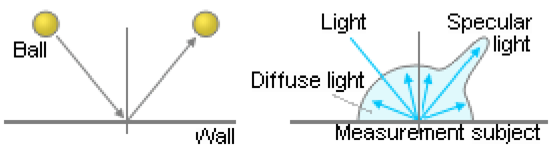
High oxidation potential →

Cr_2O_3-Mn_2O_3-CeO_2-V_2O_5-CuO-As_2O_3-Sb_2O_3-Fe_2O_3

Ref) Chemical approach to Glass, Milos Bohuslav Volf

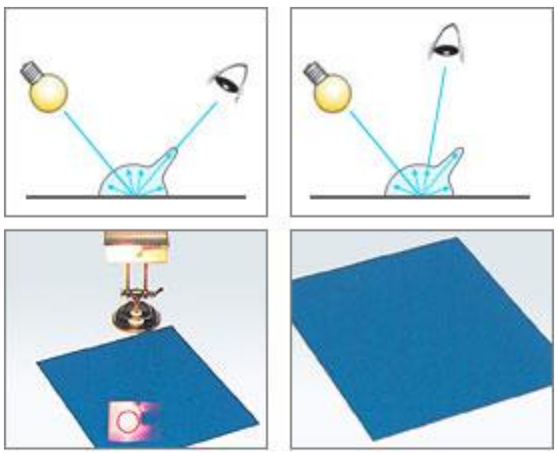
L* (Lightness)

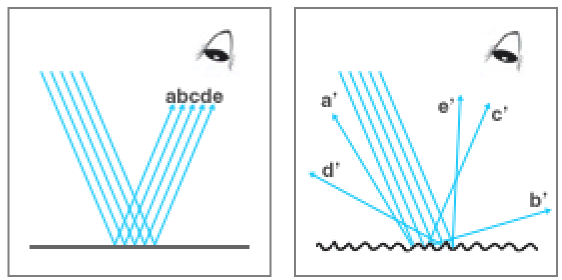
Brightness, lightness, luminance, or value, which describes the intensity of the colour, the number of photons reaching the eye.



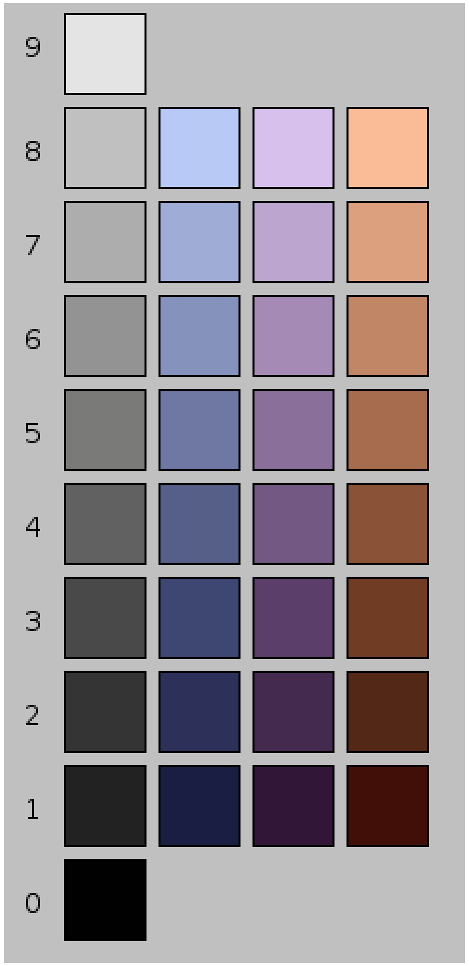
SCE (Specular Component Excluded)

SCI (Specular Component Included)





These figures indicate that a + b + c + d + e = a' + b' + c' + d' + e'.

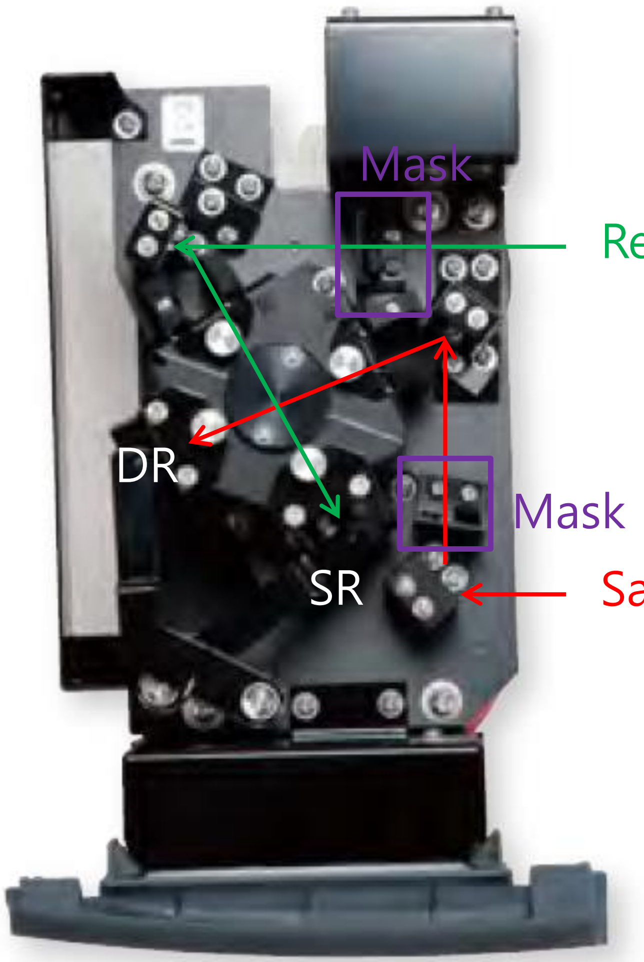


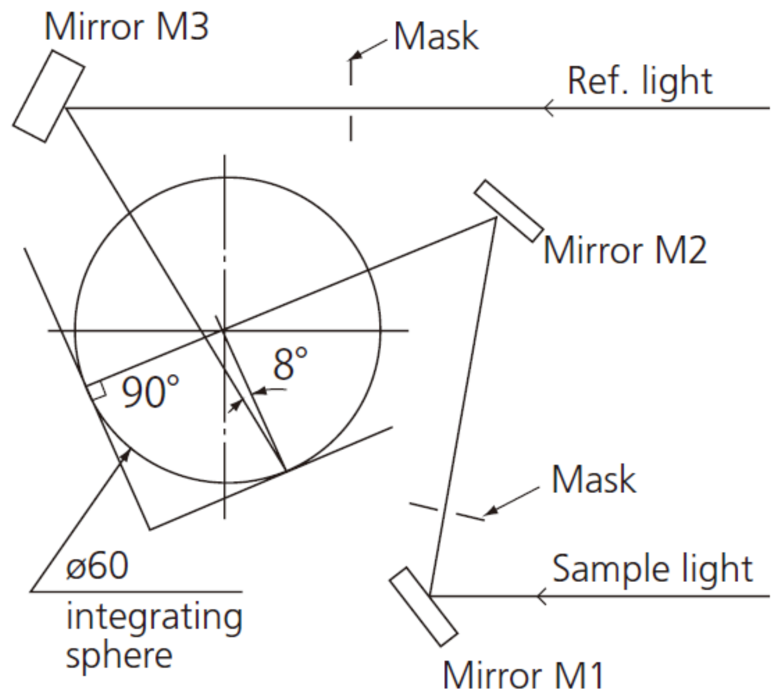
Usually, a person looks at the color of the object and ignores the specular reflection of the light source. → SCE mode would be sufficient to express colour

Ref) http://www.konicaminolta.com/instruments/knowledge/color/part3/02.html

Uv-vis spectrometer

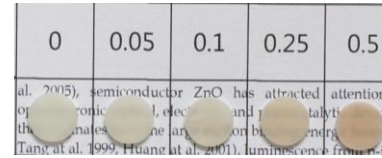
- **Shimadzu UV-2600**
- **Integrating sphere for diffuse reflectance**
- **240~1400nm**



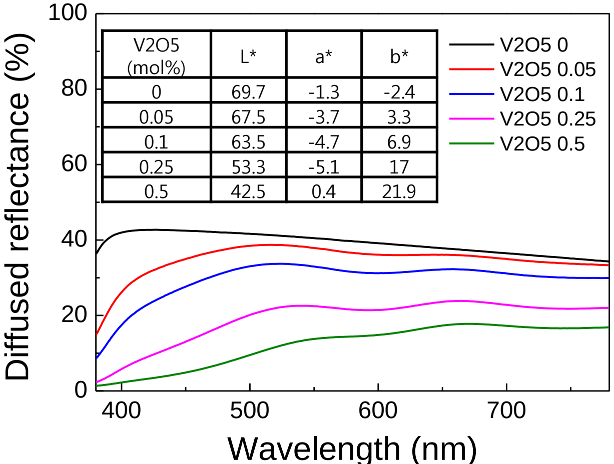


When the specular reflectance is measured, the samples locates in SR position which is tilted 8 degree.

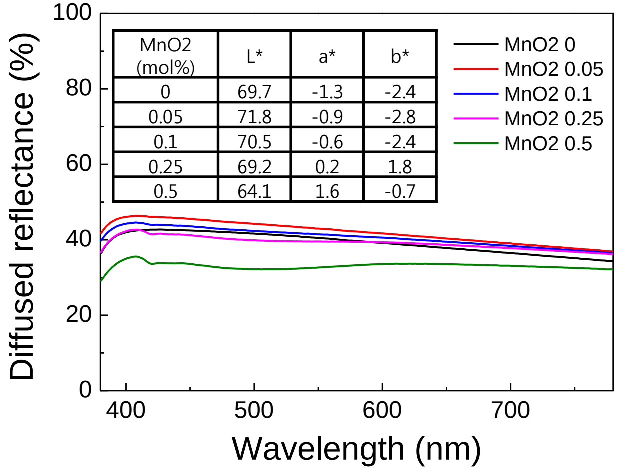
Diffused reflectance, L*a*b*



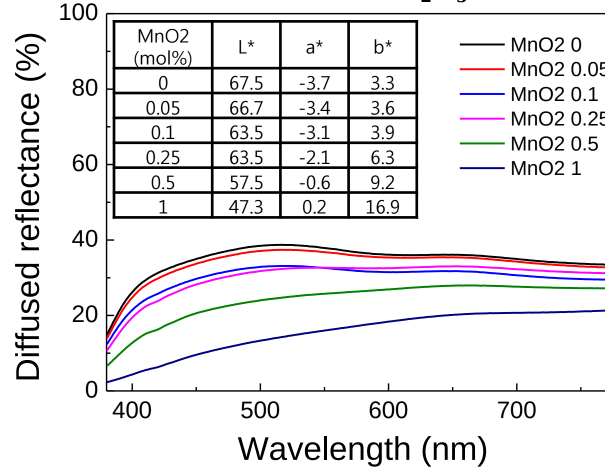
+V_2O_5 0.05mol%



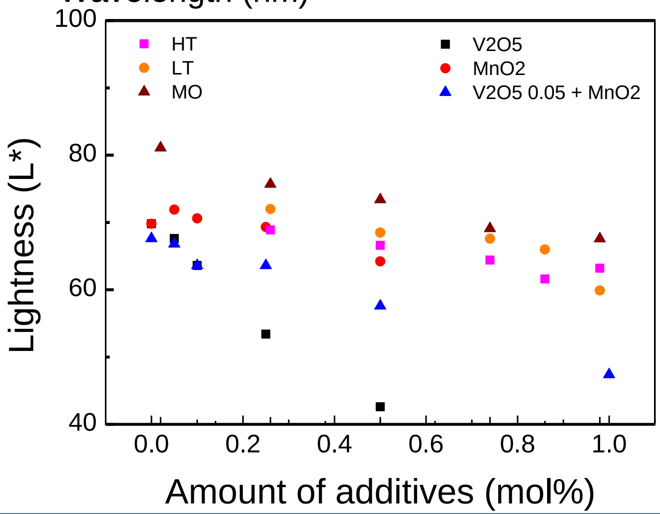
V2O5 (mol%)	L*	a*	b*
0	69.7	-1.3	-2.4
0.05	67.5	-3.7	3.3
0.1	63.5	-4.7	6.9
0.25	53.3	-5.1	17
0.5	42.5	0.4	21.9

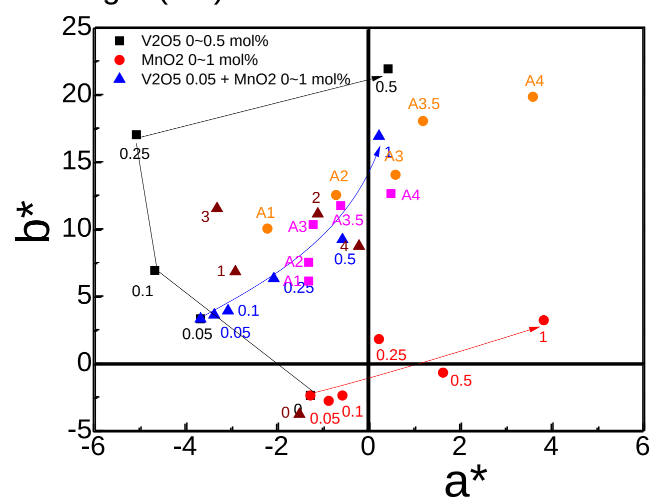


MnO2 (mol%)	L*	a*	b*
0	69.7	-1.3	-2.4
0.05	71.8	-0.9	-2.8
0.1	70.5	-0.6	-2.4
0.25	69.2	0.2	1.8
0.5	64.1	1.6	-0.7

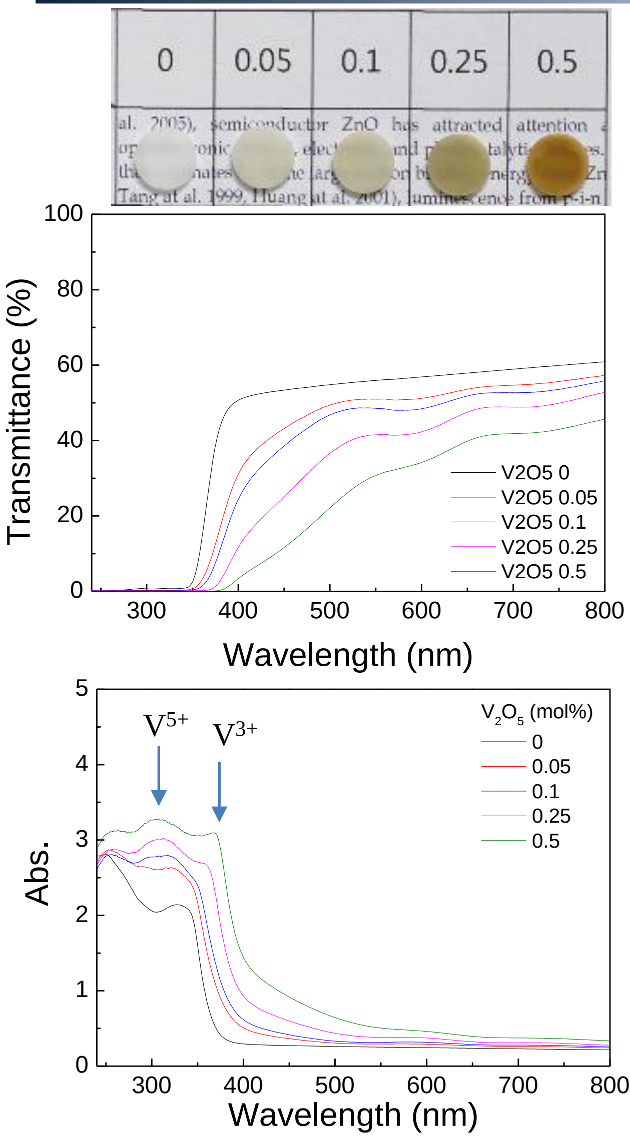


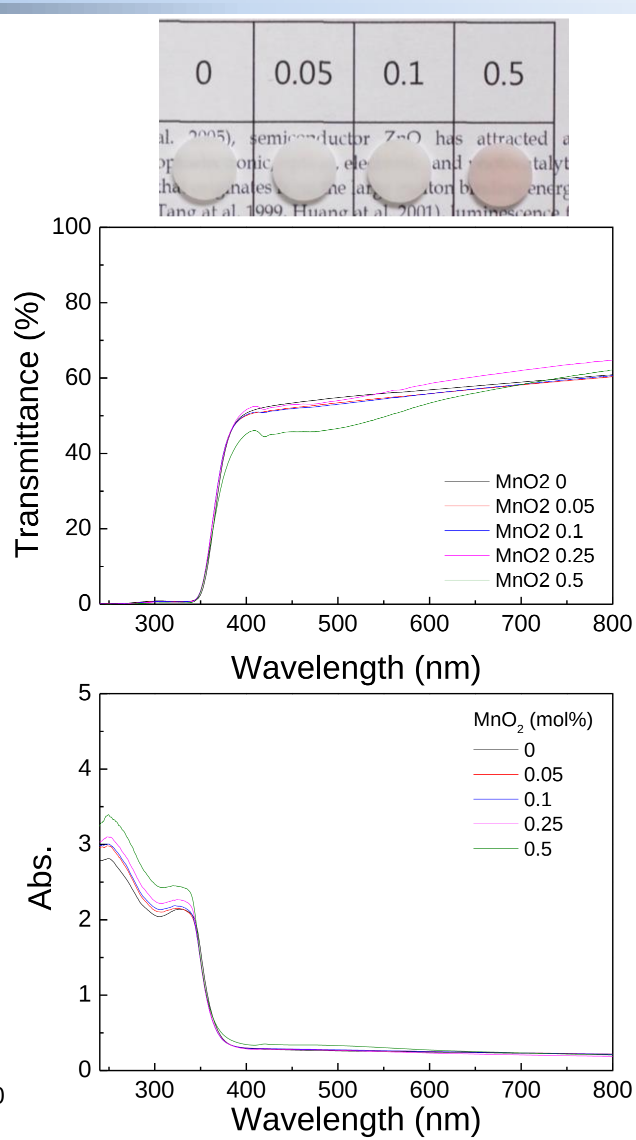
MnO2 (mol%)	L*	a*	b*
0	67.5	-3.7	3.3
0.05	66.7	-3.4	3.6
0.1	63.5	-3.1	3.9
0.25	63.5	-2.1	6.3
0.5	57.5	-0.6	9.2
1	47.3	0.2	16.9

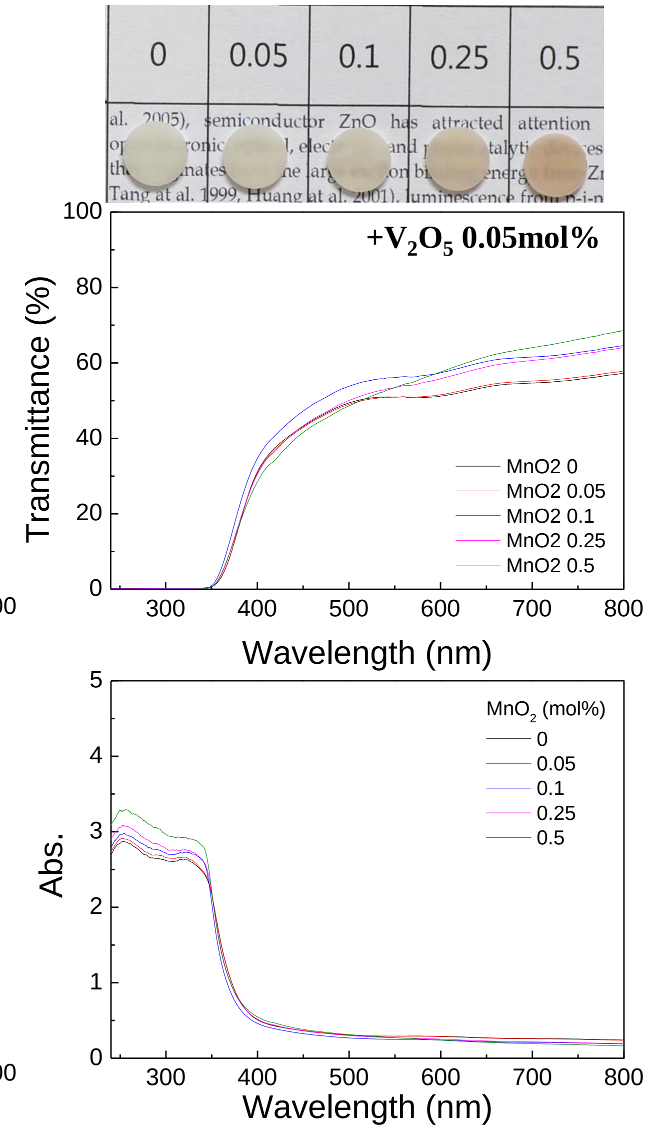




T%, Abs.


0
0.05
0.1
0.25
0.5
Transmittance (%)
Wavelength (nm)
V2O5 0
V2O5 0.05
V2O5 0.1
V2O5 0.25
V2O5 0.5
Abs.
Wavelength (nm)
V^{5+}
V^{3+}
V_2O_5 (mol%)
0
0.05
0.1
0.25
0.5


0
0.05
0.1
0.5
Transmittance (%)
Wavelength (nm)
MnO2 0
MnO2 0.05
MnO2 0.1
MnO2 0.25
MnO2 0.5
Abs.
Wavelength (nm)
MnO_2 (mol%)
0
0.05
0.1
0.25
0.5


0
0.05
0.1
0.25
0.5
$+V_2O_5$ 0.05mol%
Transmittance (%)
Wavelength (nm)
MnO2 0
MnO2 0.05
MnO2 0.1
MnO2 0.25
MnO2 0.5
Abs.
Wavelength (nm)
MnO_2 (mol%)
0
0.05
0.1
0.25
0.5

Literature survey

Structure–property correlations in highly modified Sr, Mn-borate glasses

A. Winterstein-Beckmann [a], D. Möncke [a], D. Palles [b], E.I. Kamitsos [b], L. Wondraczek [a,*]

[a] Otto-Schott-Institute, Friedrich-Schiller-University Jena, Fraunhoferstr.6, 07743 Jena, Germany
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Borate;
Strontium borate;
Manganese borate;
Structure

ABSTRACT

Highly modified borate glasses with the composition (1 − 2x)MnO–x(SrO–B_2O_3) (x = 0.46, 0.42, 0.36, 0.25, and 0.20) were prepared and investigated by Raman, infrared (IR), and electron paramagnetic resonance (EPR) spectroscopy. Optical properties were studied in regard to photoluminescence, optical absorption, and refractive index. The Mn^{2+}/Mn^{3+} equilibrium was shifted towards the divalent manganese ion as a result of the strongly reducing melting conditions employed in this work, which facilitate the preparation of transparent glasses with up to 80 mol% total SrO and MnO content. Changes in the optical and physical properties within this glass series were related to structural variations. The structure of glasses with relatively low MnO content was found to involve mainly trigonal $[BØ_2O]^-$ and tetrahedral $[BØ_4]^-$ metaborate groups, which are replaced progressively by pyroborate $[B_2O_5]^{4-}$ and orthoborate $[BO_3]^{3-}$ triangular units upon increasing MnO content. At the highest modification level (x = 0.20) the structure is built of orthoborate isomeric species in triangular $[BO_3]^{3-}$ and tetrahedral
cies form $[B_3O_9]^{9-}$ rings, which reestablish some degree of network
ing and six non-bridging oxygen atoms, and this is reflected
temperature for x = 0.25 over x = 0.20. Micro-Raman measurem
in these glasses due to chemical isomerization processes involvin
tures. Also, increasing MnO content was shown to cause MnO-clust
nescence and EPR measurements.

UV–Vismeasurementswere obtained in the transmission mode in the
range from 200–1200 nm. The spectra were converted into absorbance
and normalized to the sample thickness (optical density in cm–1).

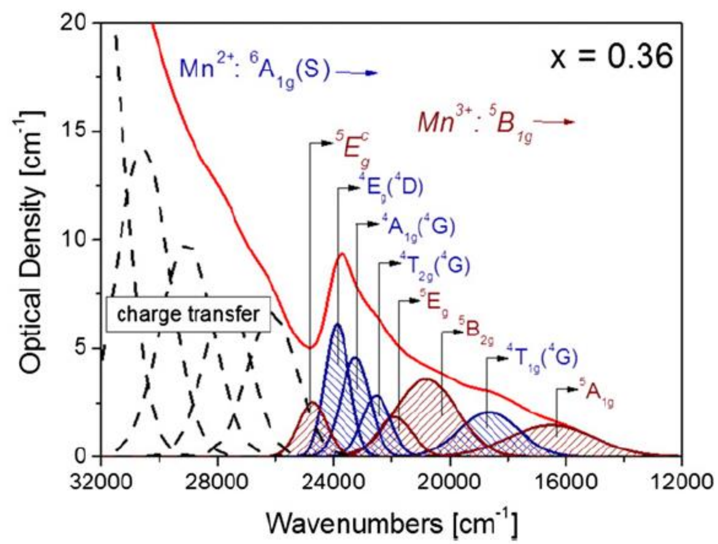
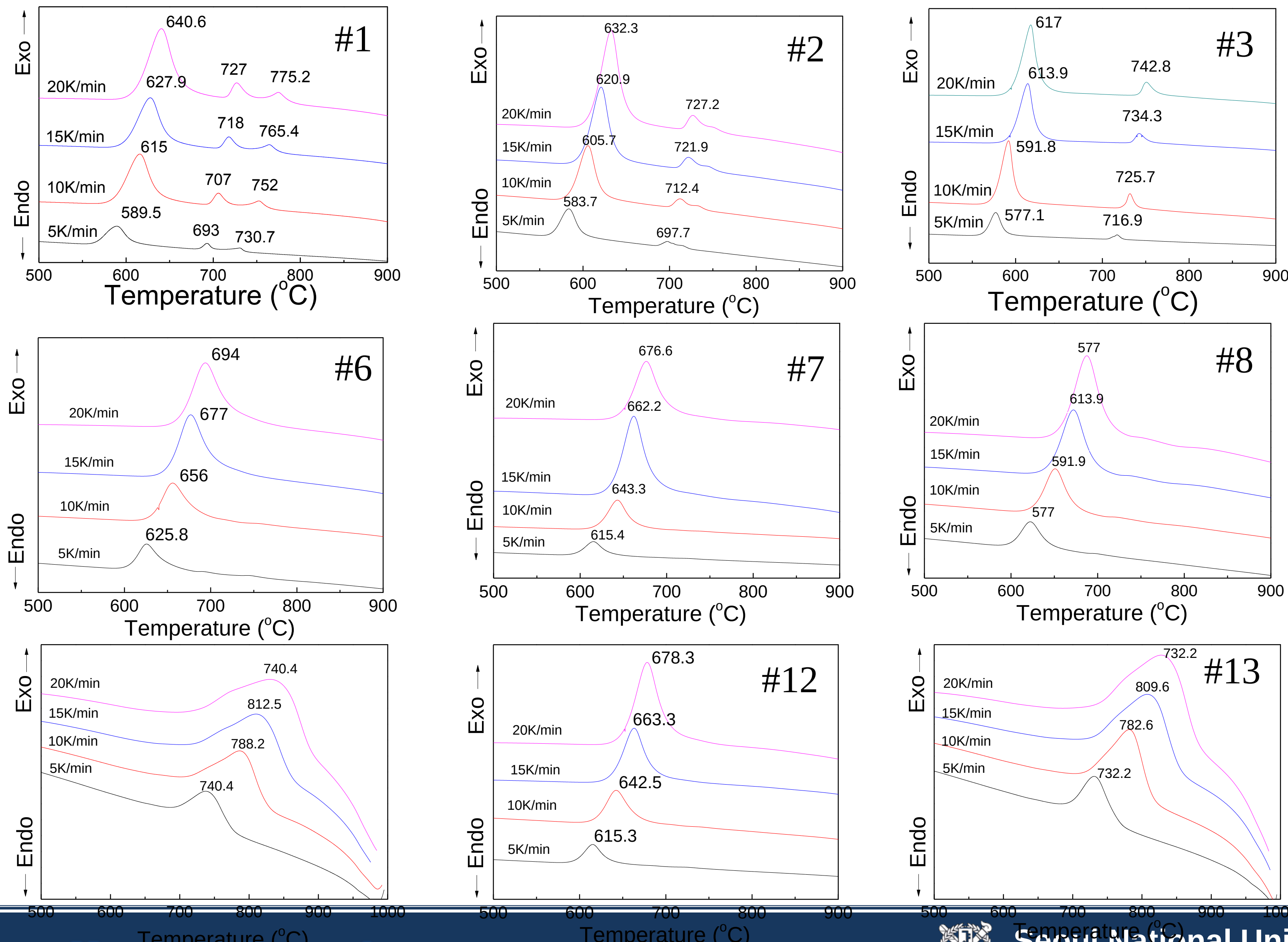


Fig. 3. Deconvolution of the optical spectrum for the sample x = 0.36. Above 25,000 cm^{-1} CT transitions are dominating and no deconvolution is possible (original thickness 1.49 mm).

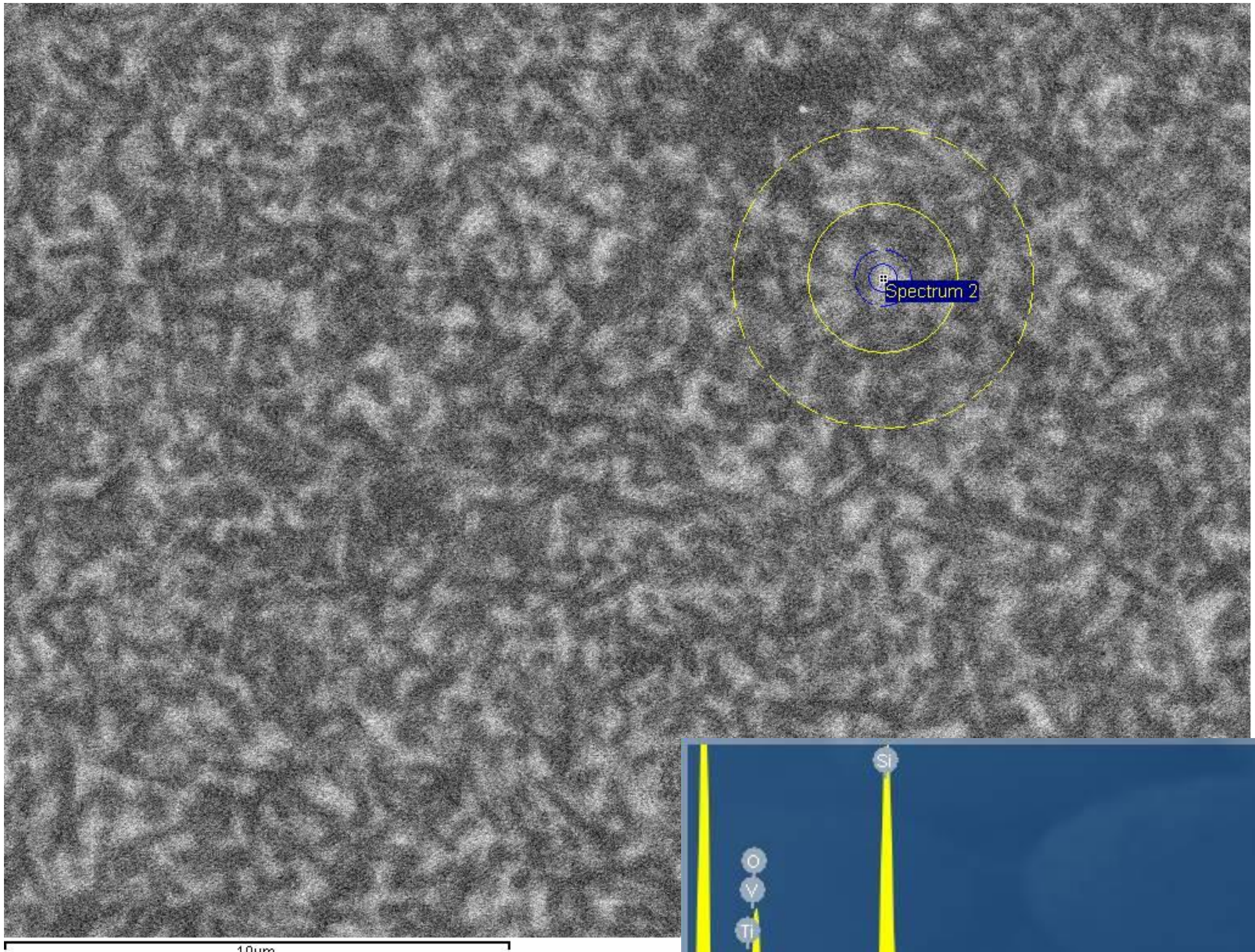
Thank you!

Discussion : Differential Scanning Calorimeter

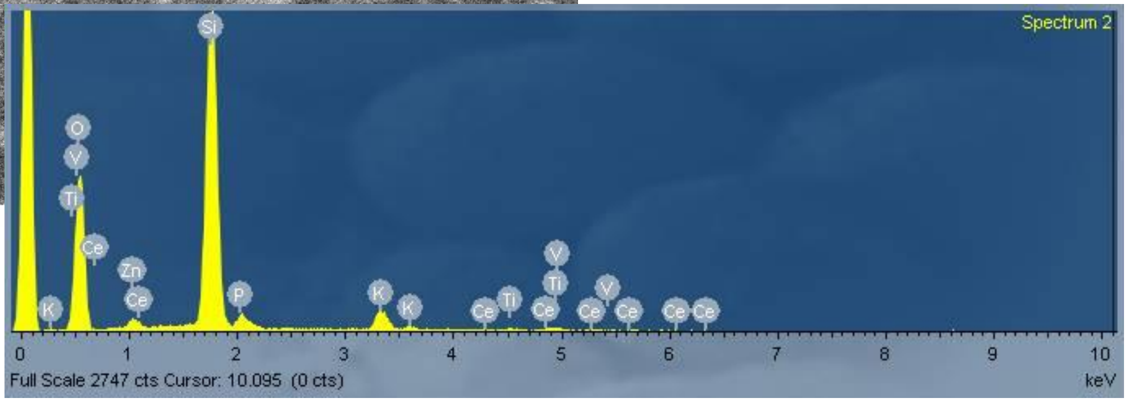


FE-SEM EDS Mapping

분석처 : KICET JEOL 6701F
Sample : 1) CeO2 0.5 TiO2 0.5 V2O5 0.5 (HF Etching X)



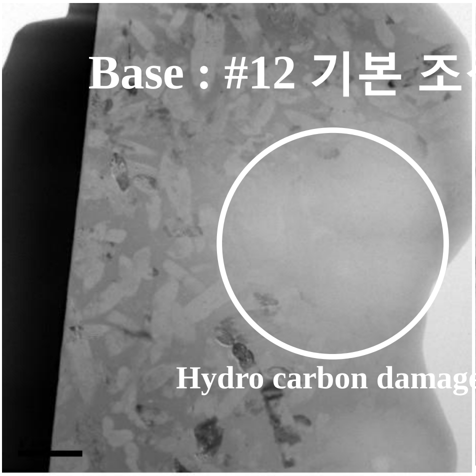
Element	Weight %	Atomic %	실투입 (mol%)
O K	17.13	68.98	
Si K	11.38	26.10	
P K	0.53	1.09	
K K	1.28	2.11	
Ti K	0.15	0.20	
V K	0.34	0.43	
Zn L	0.88	0.86	
Ce L	0.52	0.24	
Totals	32.18		



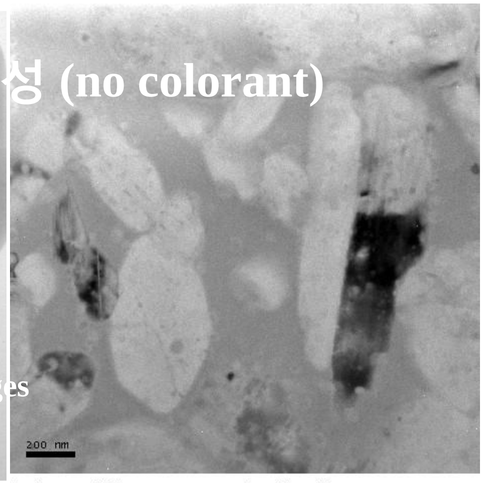
EDS resolution 작음
→ point로 찍으면 다른 부분까지 나옴

TEM (FIB) : Base(#12), CeO2 0.5 V2O5 0.5

분석처 : 가천대 Tecnai G2 F30 (300kV)
FIB : 가천대 나노기술혁신센터 FIB-STEM FEI Nova 200

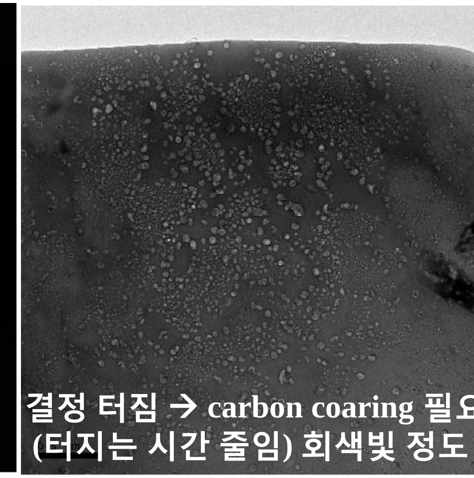


Specimen : cross S106
Operator : DC
Voltage : 300 kV
Microscope Name : D342
Name : CCD
Total Magnification : X22700
Image Name : 1-1
Resolution : 2048 x 2048 pixels
Acquisition Date : 12/17/2015
Acquisition Time : 1:27:21 PM
Collection Number :
Exposure Time : 0.512 s

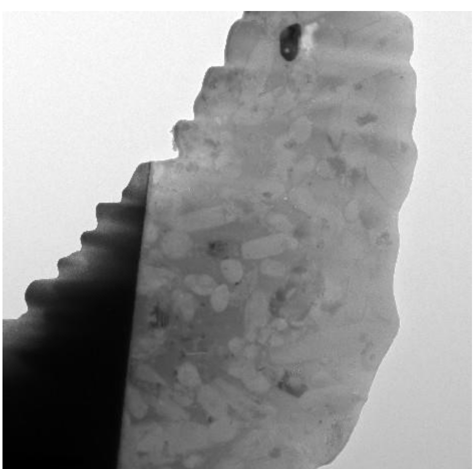


Specimen : cross S106
Operator : DC
Voltage : 300 kV
Microscope Name : D342
Name : CCD
Total Magnification : X86400
Image Name : 1-2
Resolution : 2048 x 2048 pixels
Acquisition Date : 12/17/2015
Acquisition Time : 1:29:03 PM
Collection Number :
Exposure Time : 0.512 s

Specimen : cross S106
Operator : DC
Voltage : 300 kV
Microscope Name : D342
Name : CCD
Camera Constant : 17 mmÅ
Image Name : 1-5
Resolution : 2048 x 2048 pixels
Acquisition Date : 12/17/2015
Acquisition Time : 1:37:19 PM
Collection Number :
Exposure Time : 0.512 s

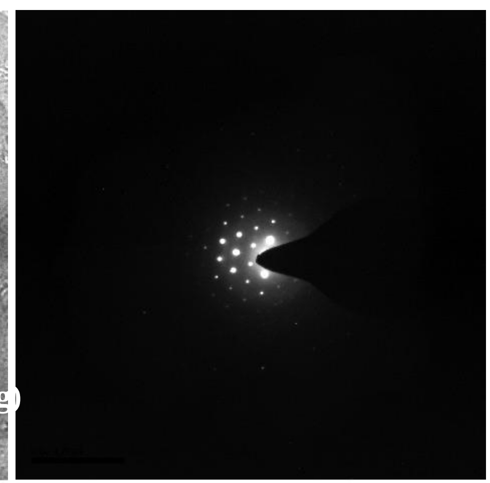


Specimen : cross S106
Operator : DC
Voltage : 300 kV
Microscope Name : D342
Name : CCD
Total Magnification : X44100
Image Name : 1-6
Resolution : 2048 x 2048 pixels
Acquisition Date : 12/17/2015
Acquisition Time : 1:43:05 PM
Collection Number :
Exposure Time : 0.512 s

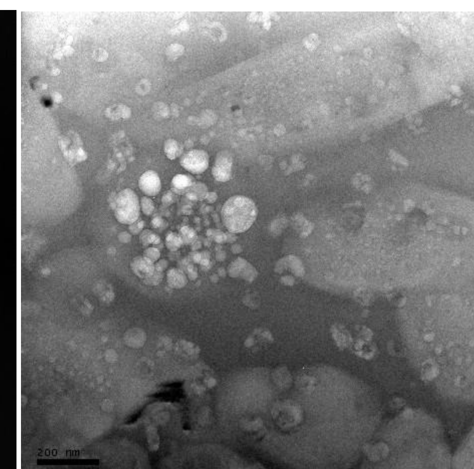


Specimen : cross S106
Operator : DC
Voltage : 300 kV
Microscope Name : D342
Name : CCD
Total Magnification : X22700
Image Name : 2-1
Resolution : 2048 x 2048 pixels
Acquisition Date : 12/17/2015
Acquisition Time : 1:48:39 PM
Collection Number :
Exposure Time : 0.512 s

Specimen : cross S106
Operator : DC
Voltage : 300 kV
Microscope Name : D342
Name : CCD
Total Magnification : X86400
Image Name : 2-2
Resolution : 2048 x 2048 pixels
Acquisition Date : 12/17/2015
Acquisition Time : 1:49:09 PM
Collection Number :
Exposure Time : 0.512 s



Specimen : cross S106
Operator : DC
Voltage : 300 kV
Microscope Name : D342
Name : CCD
Camera Constant : 17 mmÅ
Image Name : 2-6
Resolution : 2048 x 2048 pixels
Acquisition Date : 12/17/2015
Acquisition Time : 1:53:52 PM
Collection Number :
Exposure Time : 0.512 s



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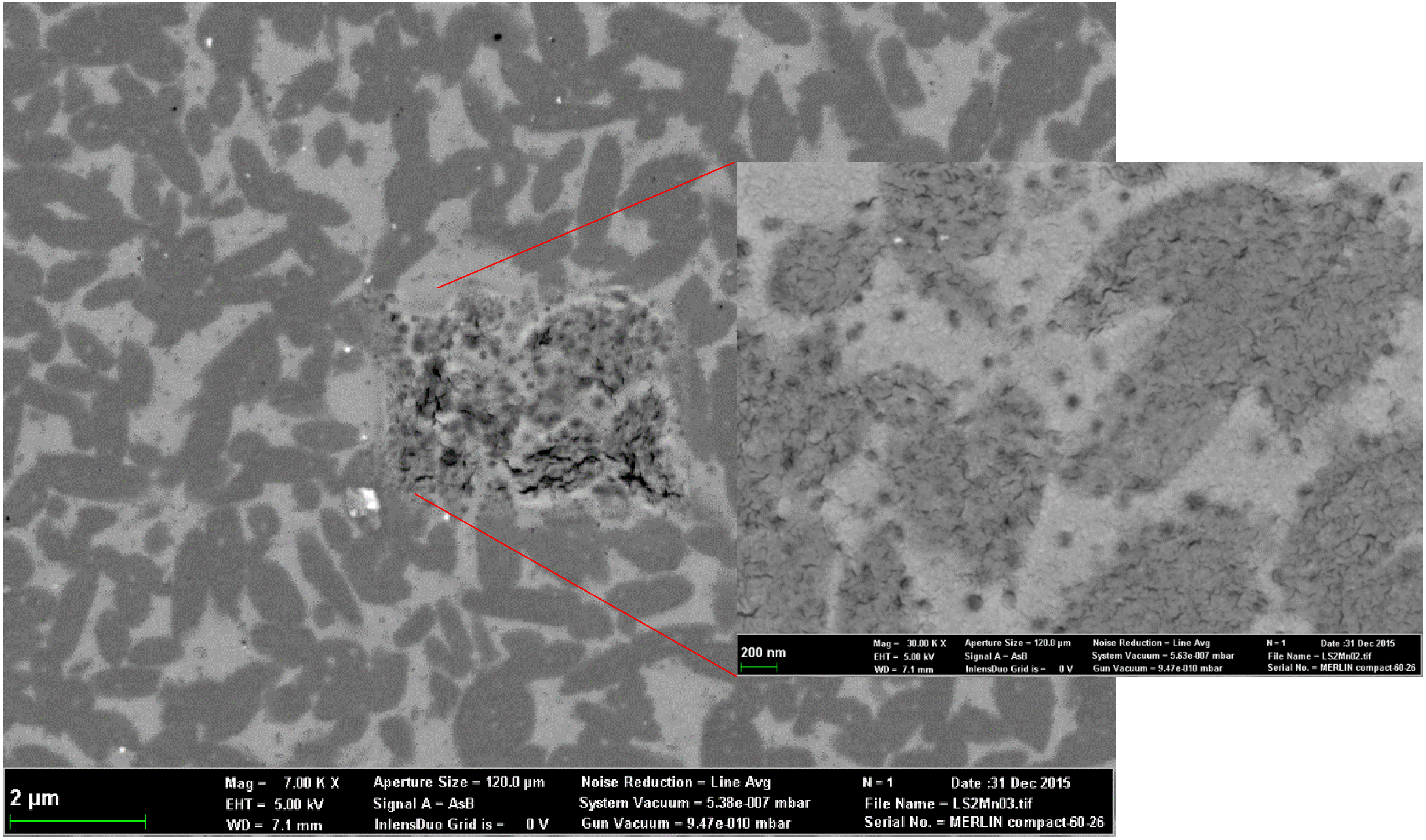
Operator : DC
Voltage : 300 kV
Microscope Name : D342
Name : CCD
Total Magnification : X110000
Image Name : 2-7
Resolution : 2048 x 2048 pixels
Acquisition Date : 12/17/2015
Acquisition Time : 1:56:21 PM
Collection Number :
Exposure Time : 0.512 s

FE-SEM EDS Mapping

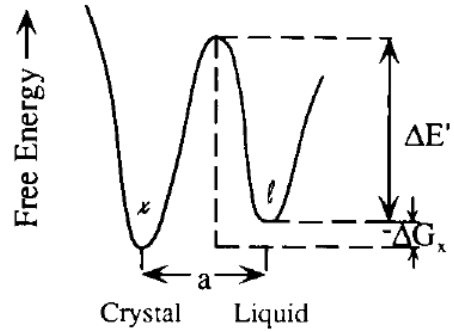


- **5kV에서 Aperture Size 가 120 µm 경우 damage 발생 → EDS Mapping 중 damage 발생 가능**
- **KICET JEOL 6701F 에서는 15kV 15 current 맞춰도 damage 발생 X**

Crystal growth rate

- υ frequency with which atoms are transported across the interface
- a_0 : distance the crystal advances for a layer of attached molecules
- ΔG_x : free energy of crystallization

According to Turnbull(1960) : reaction-rate theory,



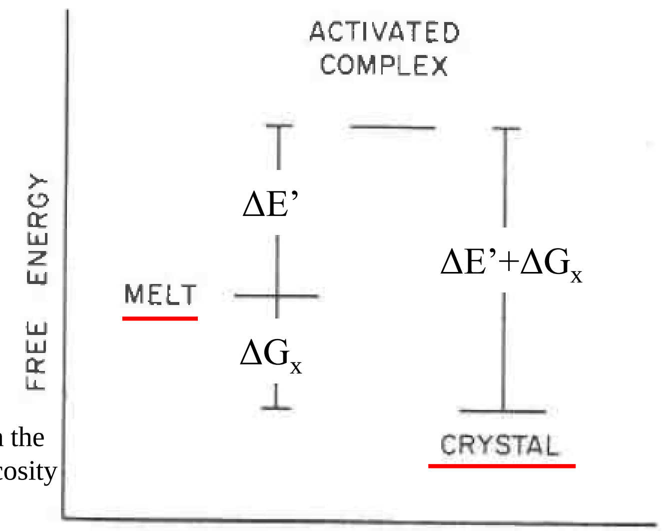


FIG. 1. Free energy relationships during the attachment process at the crystal-melt interface.

$$v1 = \upsilon \exp\left[-\frac{\Delta E'}{RT}\right]$$

$$v2 = \upsilon \exp\left[-\frac{(\Delta E' - \Delta G_x)}{RT}\right]$$

$$a_0(v1 - v2) = U = a\upsilon \exp\left[-\frac{\Delta E'}{RT}\right]\left[1-\exp\left(\frac{\Delta G_x}{RT}\right)\right]$$

$$D = a_0^2 \upsilon \exp\left[-\frac{\Delta E'}{RT}\right]$$

Stokes-Einstein relation between the diffusion coefficient and the viscosity

$$D = \frac{RT}{3N\pi a\eta}$$

$$U = \left(\frac{D}{a}\right)\left[1-\exp\left(\frac{\Delta G_x}{RT}\right)\right]$$

$$U = \left(\frac{fRT}{3N\pi a_0^2\eta}\right)\left[1-\exp\left(\frac{\Delta H_f \Delta T}{RT\cdot T_m}\right)\right]$$

Wilson-Frenkel theory

Crystal growth velocity is ~ 10^5cm/sec

$$U \approx \upsilon a_0\left(\frac{\Delta H_f \Delta T}{RT\, T_m}\right)$$ ΔG_m<<RT, Small undercooling

과냉각이 작을 때 성장율은 ΔH, ΔT에 비례!

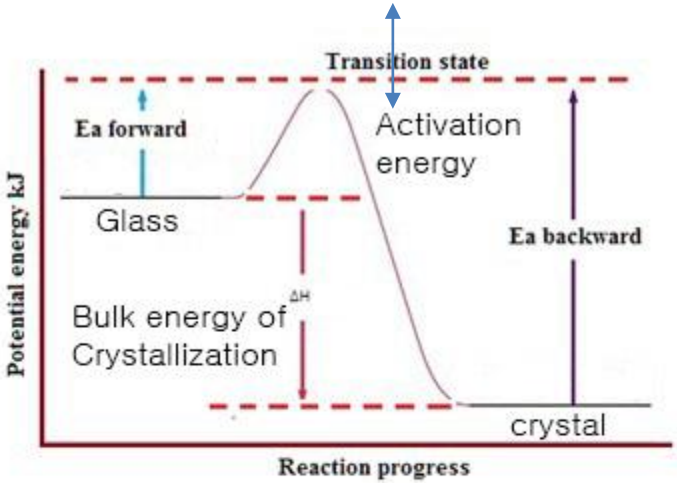
$U \approx \upsilon a_0$ ΔG_m>>RT Large undercooling

과냉각이 클 때는 한계값 도달! (점도가 높아짐)

Fundamentals of inorganic glasses, A. K. Varshneya , Physical ceramics, Yet-Ming Chaing, Dunbar Birnie III, W. David Kingery, (p437-)

Crystal growth rate

1) The irregular glass structure can be re-arranged into the periodic lattice of the growing crystal
2) Energy released in the phase transformation process can be eliminated by the heat flow away from the crystal-glass interface



Energy barrier i.e. activation energy

Bulk free energy of crystallization

$$U = a_0 \upsilon \left[\exp\left(-\frac{\Delta E'}{RT} \right) \right] \left[1 - \exp\left(\frac{\Delta G_x}{RT} \right) \right]$$

a_0 : interatomic seperation
υ : vibrational frequency at the crystal-glass interface

$$D = a_0^2 \upsilon \left[\exp\left(-\frac{\Delta E'}{kT} \right) \right]$$

$$D = \frac{RT}{3\pi N \eta a_0^2}$$

$$U = \frac{fRT}{3\pi N \eta a_0^2} \left[1 - \exp\left(\frac{\Delta G_x}{RT} \right) \right]$$

$$U_R = \frac{U\eta}{T\left[1 - \exp\left(\frac{\Delta G_x}{kT} \right) \right]} = \frac{fR}{3\pi a_0^2 N_0}$$

Reduced growth rate U_R

$$U = \frac{fD_u}{a_0} \left[1 - \exp\left(\frac{\Delta G_x}{kT} \right) \right]$$

Negligibly small compared with D_u

$$D_u = D_0 \exp\left(-\frac{E}{RT} \right)$$

$$U = \frac{fD_0}{a_0} \exp\left(-\frac{E}{RT} \right)$$

Matusita
J. Mat. Sci, 10 (1975) 961

$$U = U_0 \exp\left(-\frac{E}{RT} \right)$$

Vogel

Glass-Ceramics, P. W. Mcmillan 2nd edition