Borate glasses with high lanthanide oxides solubility for the cold crucible induction melter (CCIM) applications

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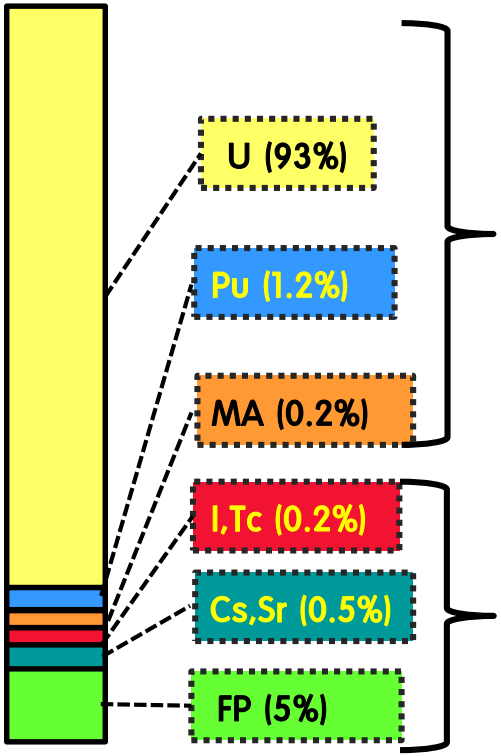
Introduction – Pyro-processing

MA: Minor Actinide
FP : Fission Product
TRU : TRans Uranic wastes (Pu + MA)

Spent Fuel



Pyro-processing

To recover U and TRU from spent fuels of pressurized water reactors

Reuse

U + Pu + MA → 94.4%

Disposal

I,Tc + Cs,Sr + FP(RE) → 5.4%

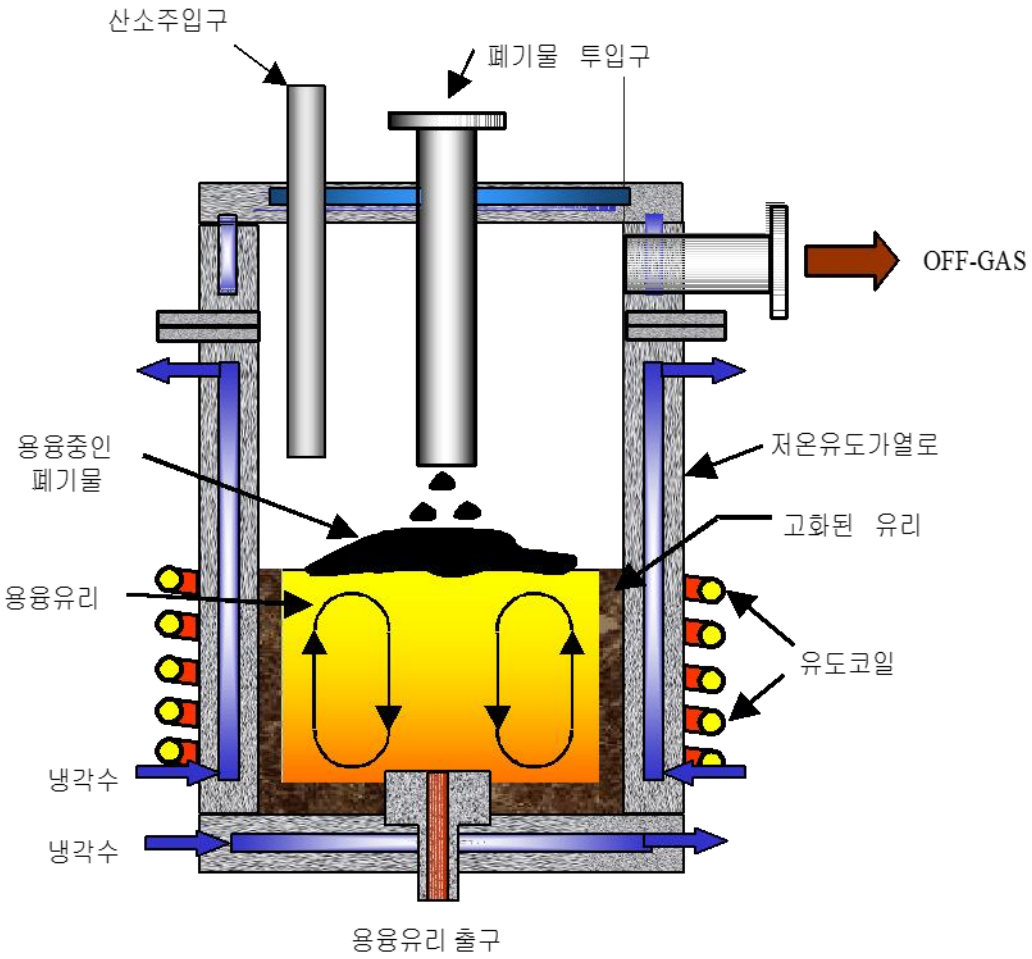
I,Tc	Cs,Sr	RE	Total
3.18	9.36	87.8%	100%

RE waste composition

	Mol%
Nd_2O_3	39.22
CeO_2	22.69
La_2O_3	11.72
PrO_2	10.86
Sm_2O_3	8.13
Y_2O_3	4.80
Eu_2O_3	1.30
Gd_2O_3	1.28

- The composition is different from radioactive mixed wastes
  –> needs for development of new specified wasteforms

Introduction : Cold Crucible Induction Melter (CCIM)



울진에 건설 완료 후 운영허가 승인 받아 시운전 중

1) 유도가열 방식으로 유리를 용융

2) 전극의 부식을 고려할 필요가 없으므로, 수명 길고 고온공정가능

3) Crucible을 냉각수로 식혀주어 100도 정도의 온도 유지

요구되는 유리 spec.

→ 전기전도도 : 0.1~1 S/cm

→ 점도 : 10~100 poise

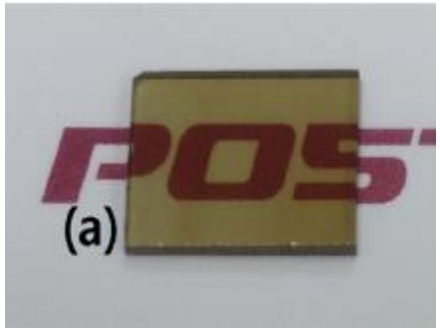
→ 침출(r) : $2 g/m^2$ 이내

1) K.H. Yang, et. al, NETEC-KHNP , 2001, win korea

Introduction – Previous researches for rare-earth wastes

- **Leached values of RE ions from glasses are very low.**

$46SiO_2 - 12Na_2O - 12B_2O_3 - 24CaO - 3CeO_2 - 3Nd_2O_3$ (mol%)



1300 °C / 30 min
23.5 wt% loading

Normalized released value, r ($g \cdot m^{-2}$).

	Element					
	Ce	Nd	B	Si	Na	Ca
PCT-A (7days)	$3.30 \cdot 10^{-6}$	$3.58 \cdot 10^{-6}$	0.072	0.039	0.167	0.028
MCC1 (35days)	LoD < 0.1 ppb	LoD < 0.1 ppb	15.6	8.38	18.6	

LoD :Limit of detection

- This glass contained only 6 mol% of RE
- We focused on high loadings of RE wastes

M. Kim, et al. *J. Nucl. Mat.* 467 (2015): 224-228.

Objectives

- Fabricate glasses wasteform

  to immobilize Nd_2O_3 wastes

  from pyro-processing

  1. with high waste loading

  2. with acceptance to CCIM

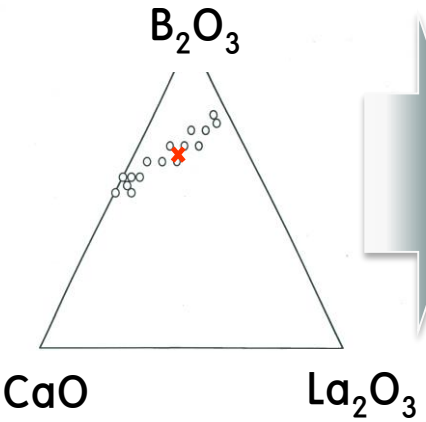
조성 탐색 및 선정 – Borate glasses

1300도/30분 용융조건

Borate glasses are known for high RE solubility [1]

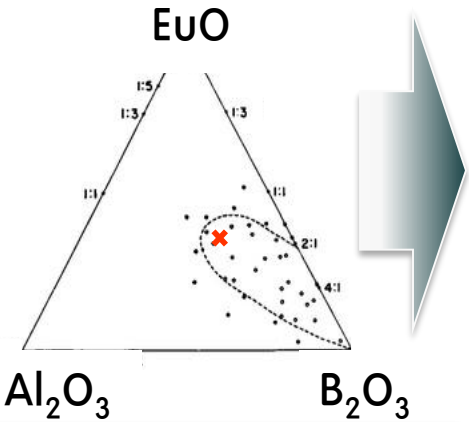
Two candidates of RE-rich borate composition

$RO-B_2O_3$ glass [2] (R=Ca,Cd,Ba,Zn..)



Mol%	Ca_1차
Nd_2O_3	20
CaO	30
B_2O_3	50
Total	100
	제조성공

Alumino-borate glass [2]



Mol%	Al_1차	Al_2차
Nd_2O_3	30	20
Al_2O_3	30	35
B_2O_3	40	45
Total	100	100
	결정화	고점성

Chemical durability (PCT) test

Ca_1차유리	Nd	Ca	B
C_i [ppm]	LoD	36.72	16.99

➢ 균질유리 형성. 결정형성 안됨

Al_2차유리	Nd	Al	B
C_i [ppm]	LoD	0.02	6.36

➢ 화학적 내구성이 ~3배 좋음 (Al 영향)

Nd 담지량은 유지하되, 두 유리의 단점을 보완하고자
Ca_1차유리에서 (Ca+B)일부를 Al으로 치환하여, 최종조성 선정

[1] K. Terashima et al. J. Am. Ceram. Soc., 80 [11] 2903–909 (1997)

Experimental procedures

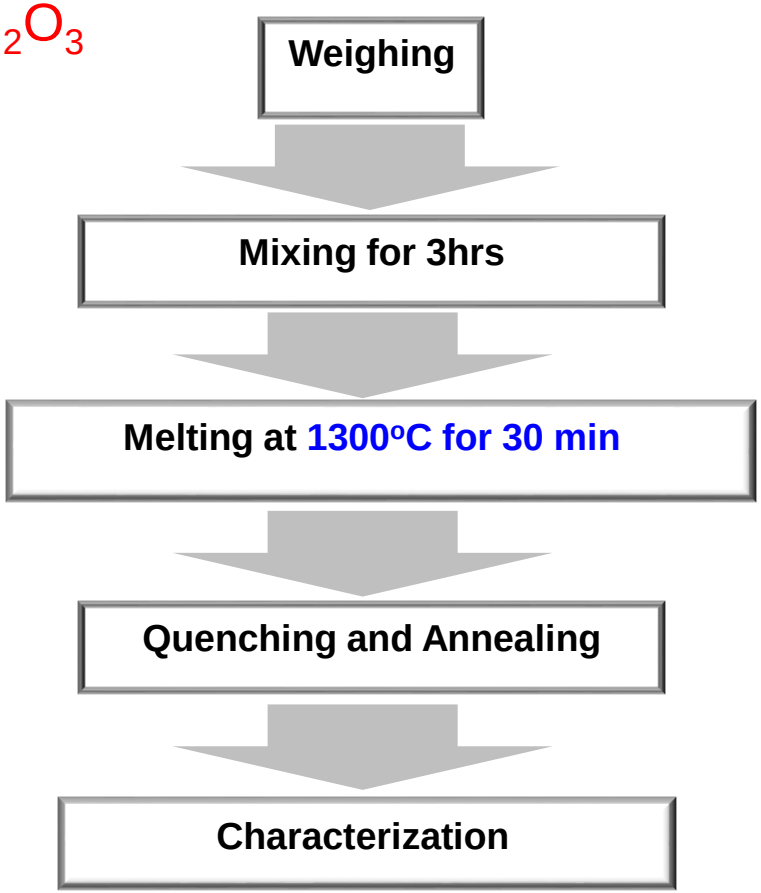
➢ Final batch composition (mol%)

(100-x) (0.25 CaO - 0.19 Al_2O_3 - 0.56 B_2O_3) - x Nd_2O_3
(x=0, 10, 20, 30)

	Mol %			
CaO	25.0	22.5	20.0	17.5
Al_2O_3	18.8	16.9	15.0	13.1
B_2O_3	56.2	50.6	45.0	39.4
Nd_2O_3	**0**	**10**	**20**	**30**
Total	100	100	100	100

changing Nd_2O_3 concentration : 0 - 30 mol%

< Experimental procedure >



Results- appearance of glasses

$(100-x)\,(0.25\,CaO - 0.19\,Al_2O_3 - 0.56\,B_2O_3) - x\,Nd_2O_3$

(x=0, 10, 20, 30)

➢ Appearance

0% 10% 20% 30%

Homogeneous glasses

➢ Characteristics

	20 % 유리
Density	2.124 g/cm^3
T_g	679 °C
Hardness	5.72 Gpa

Formation of crystalline phases in the glasses containing

RE > (20+△) mol% (0<△<10)

Results- maximum RE loading

Evaluation of Nd_2O_3 loading between 20 -30 mol%

Condition: 1300 °C/ 30min (at atmosphere),
air quenching , 15 grams-batch

RE addition (mol%)	Homogeneous glass with no crystals
20	O
22	O
25	X
28	X
30	X

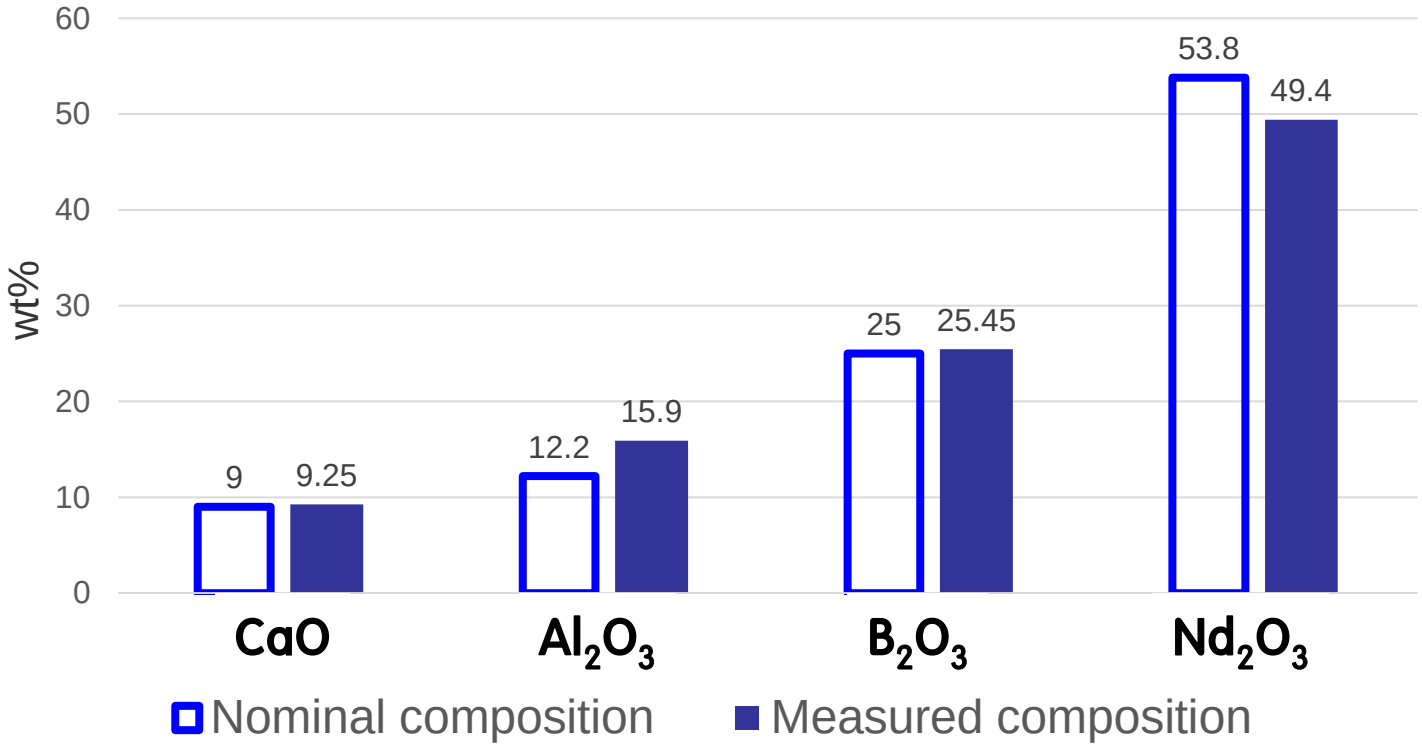
Between 22~25mol%

We succeeded fabrication of the glass containing 22mol% (56.8wt%) without crystallization

Waste loading & composition analyses - ICP-AES

- Compositions of Nd_2O_3 and other components in specimens

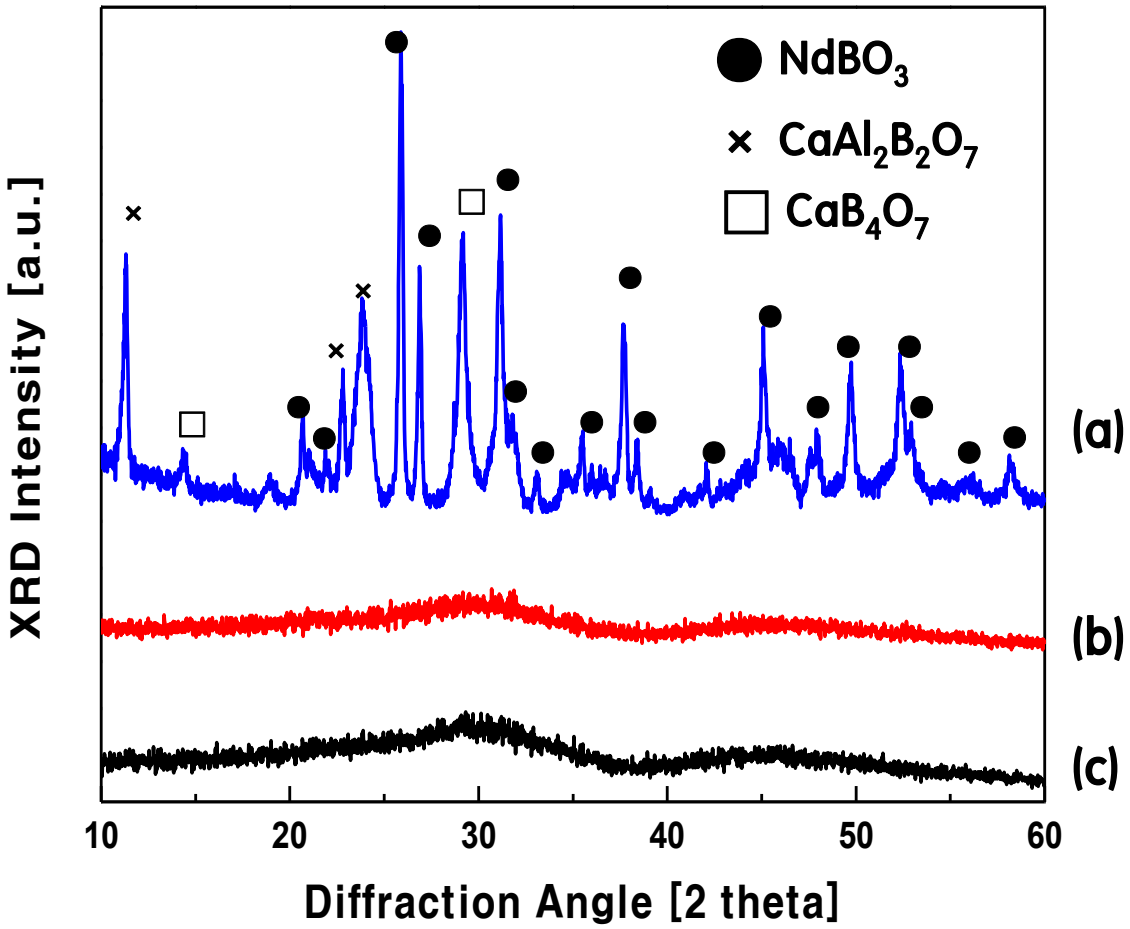
(80) (0.25 CaO - 0.19 Al_2O_3 - 0.56 B_2O_3) – 20 Nd_2O_3

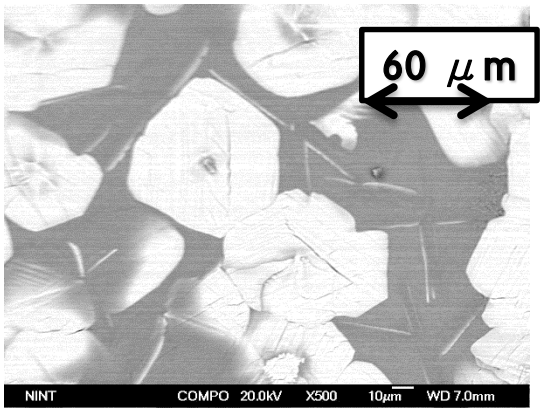


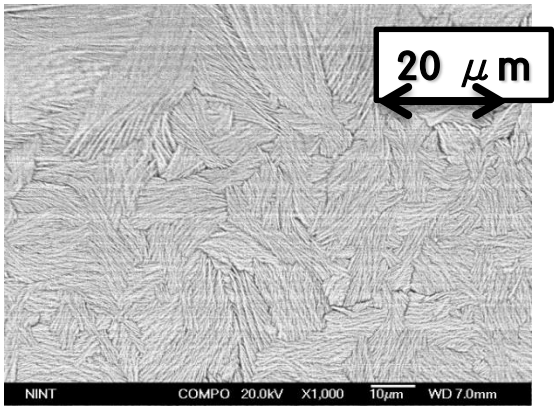
- Most components in the specimens are similar to nominal composition
- Change between nominal and real Nd_2O_3 concentration is within 4 wt%

Glass phase stability – crystallization

(80) (0.25 CaO - 0.19 Al_2O_3 - 0.56 B_2O_3) – 20 Nd_2O_3







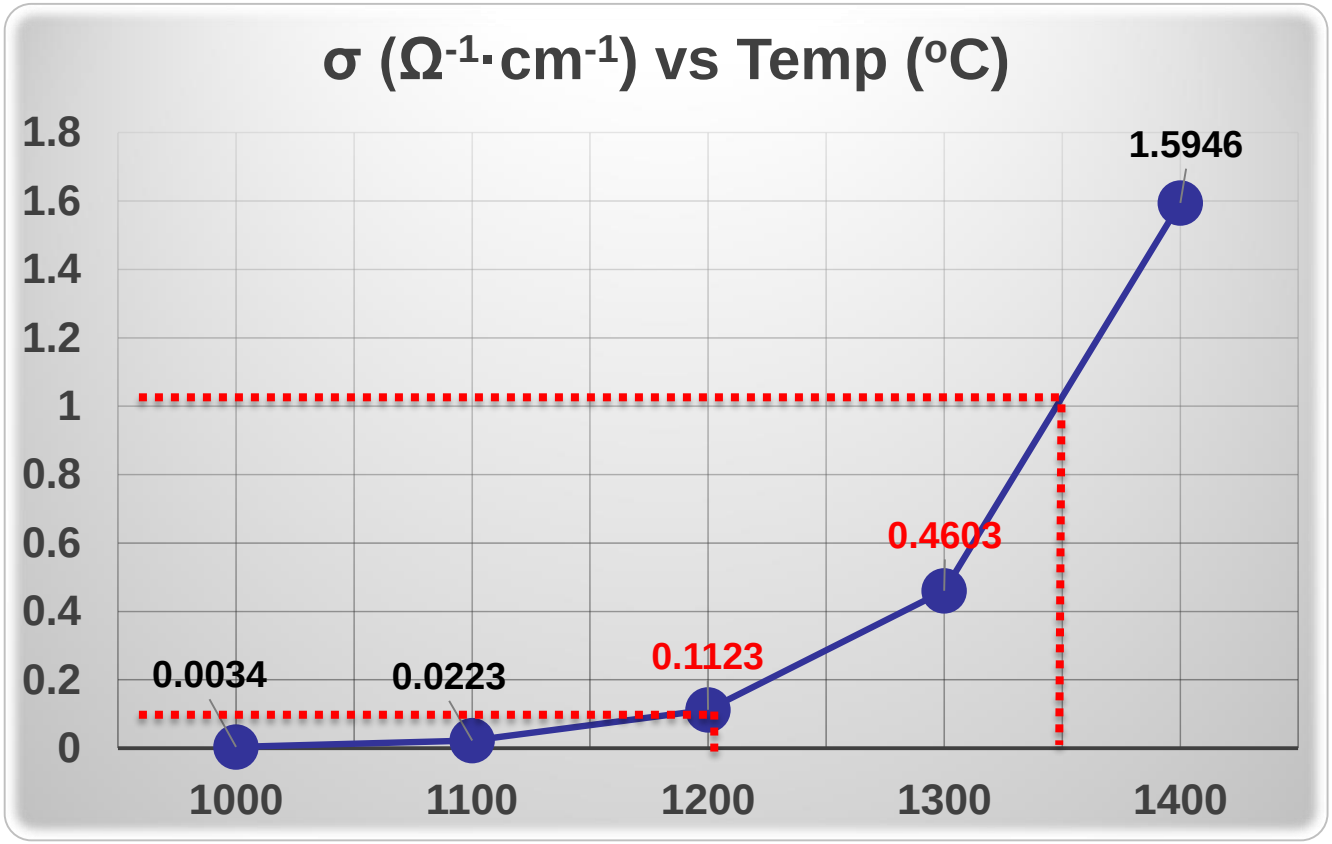
(a) HT : 800℃ / 5h
(b) HT : 700℃ / 5h
(c) HT : 600℃ / 5h

- Crystallization doesn't occur at the temp. below 700°C.
- 처분장 온도(동굴처분 시 20도)에 비해 높아, 본 유리는 열적으로 안정

Results- Electrical conductivity

(80) (0.25 CaO - 0.19 Al_2O_3 - 0.56 B_2O_3) – 20 Nd_2O_3

$\log\sigma = A - B/T(K)$



- CCIM에 적용하기 위해 허용되는 전기전도도 (0.1~1 S/cm) 이에 대응하는 온도 범위는 약 1200~1350 도

Chemical durability test - Product Consistency Test (PCT)

(100-x) (0.25 CaO - 0.19 Al_2O_3 - 0.56 B_2O_3) - x Nd_2O_3 (powder, 90도, 7일)

(x=0, 10, 20, 30)

(장점) 파우더 사용하여 침출 반응을 가속화 // 단기간 평가/비교 기준이 명확

(PCT 분석법) 파우더를 DIW 내에 7일(90도)간 보관 후 탈이온수에 누출된 이온 농도 측정

Normalized concentrations, r_i [g/m²]

$$r_i(\mathrm{g/m^2}) = \frac{C_i}{f_i(A/V)}$$

r [g/m^2]	Ca	B	Al	Nd
0%	0.469	0.677	0.002	-
10%	0.473	0.406	0.016	Lod (< $5.00 \cdot 10^{-5}$)
20%	0.073	0.067	0.009	Lod (< $3.62 \cdot 10^{-5}$)

- 모든 유리에서 Nd 의 Released concentrations : < 0.1 ppm
- 모든 원소가 US 기준 (r < 2g/m²) 만족
- 유리 망목 형성제인 B의 침출량은 Nd 증가에 따라 1/10 정도 감소

  -> RE 첨가 시 matrix 결합 강화

Chemical durability test – Materials characterization center (MCC)

(100-x) (0.25 CaO - 0.19 Al_2O_3 - 0.56 B_2O_3) - x Nd_2O_3

(x=0, 10, 20, 30)

MCC1 test (bulk, 90도, 20일)

Bulk 시편을 사용하여 거시적 유리구조의 영향을 고려 (ex, surface)

(MCC1 분석법)

Bulk 시편을 DIW 내에 20일(90도) 보관

- 탈이온수에 누출된 이온 농도 측정
- 표면 morphology 관찰

Normalized concentrations, r_i [g/m^2]

r [g/m^2]	Ca	B	Al	Nd
0%	20.25	25.91	1.57	-
20%	0.83	0.19	0.16	Lod

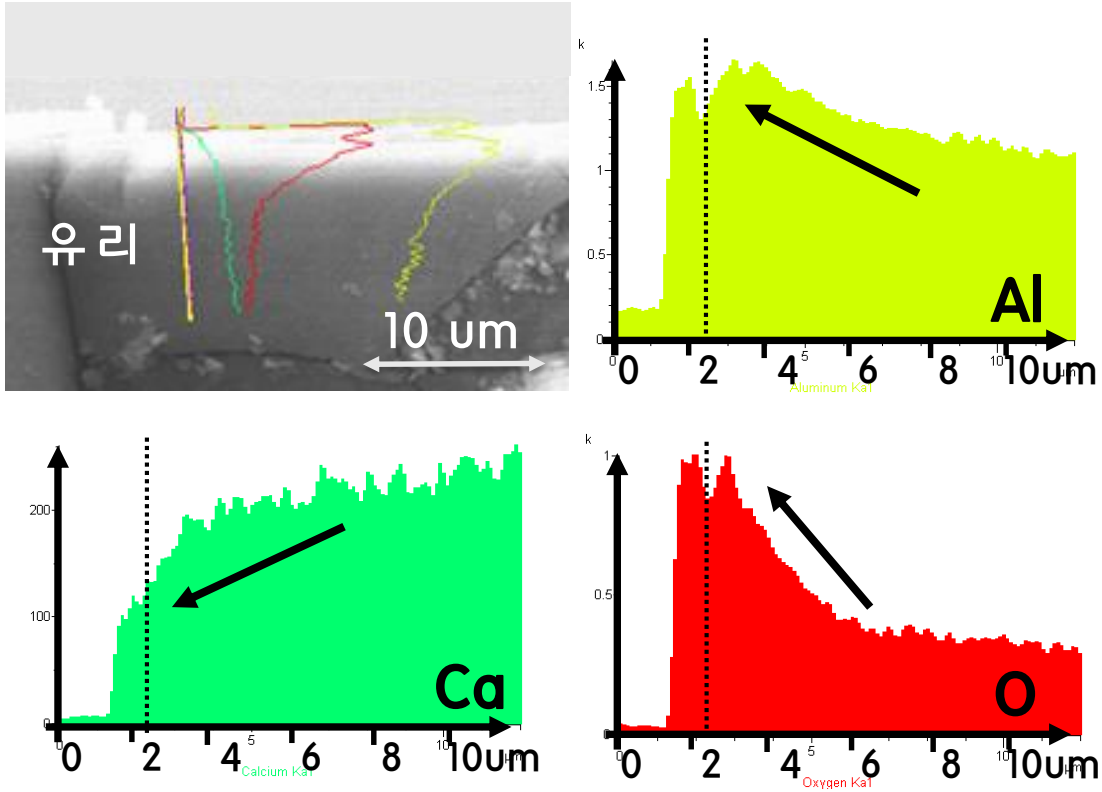
- 모든 유리에서 Nd 의 Released concentrations : < 0.1 ppm
- 희토류 첨가량 증가 시 1/10~ 1/100 정도로 감소

Elemental distribution at surface after dissolution

Bulk 침출 분석 (MCC) 후 표면의 침출층에서의 원소분포 규명

25 CaO - 19 Al_2O_3 - 56 B_2O_3) – 0 Nd_2O_3

(EDS : Line scanning)



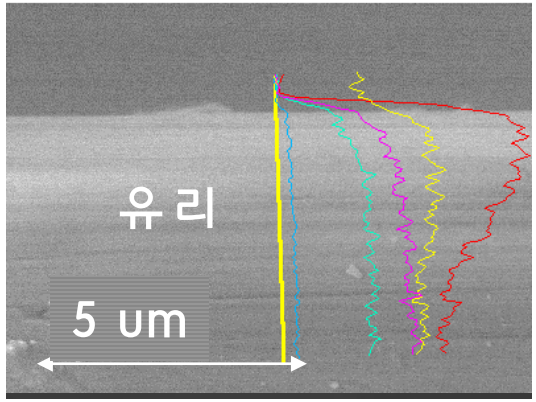
- Ca 는 표면의 농도 감소 -> 유출
- Al, O는 표면 함유량 높음 -> Ca에 비해 유출이 지연됨 (Al은 유리 형성제)
- B은 EDS로 측정불가

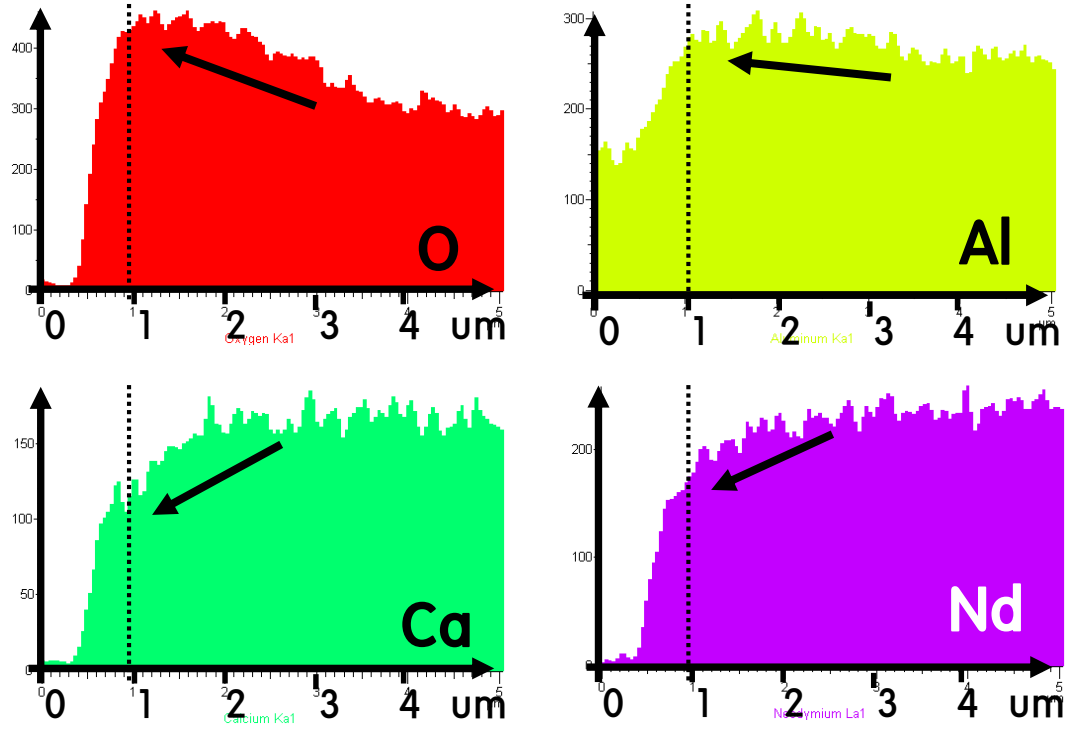
- Ca 등 수식제가 먼저 침출/ 유리구조 형성에 관여하는 원소 침출지연
- Silicate 유리와 유사

Elemental distribution at surface after dissolution

Bulk 침출 분석 (20일) 후 표면의 원소성분 분석 (EDS : Line scanning)

(80) (0.25 CaO - 0.19 Al_2O_3 - 0.56 B_2O_3) – 20 Nd_2O_3





- Al, O (표면농축), Ca (표면결핍) 은 Nd 첨가하지 않은 borate 유리와 거동 유사
- Nd은 Ca과 유사.
  - : Nd 도 유리수식제(modifier)로 존재하며 matrix보다 앞서 용출될 가능성
  - : 침출 후 Nd의 표면 재응축 여부 검증 필요

Summary

- Borate glasses containing 0 - 30 mol% Nd_2O_3 were fabricated.
  - at 1300 ^{O}C for 30 min.
  - Maximum loading was 56.8wt% (22mol%)

- The suitability as a wasteform was evaluated.
  - Crystallization didn't occur at the temperature below 700 ^{O}C
  - The released concentration of Nd were < 0.1 ppm.
  - After dissolution, Al, O were enriched at surface and Ca, Nd were depleted at surface.
  - Nd may exist as modifier in borate glasses and dissolve in a similar way with other modifiers.