August 8, 2017_@Missouri University of S&T, Rolla, MO, USA

Durability Studies of Phosphate Glasses

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Outline

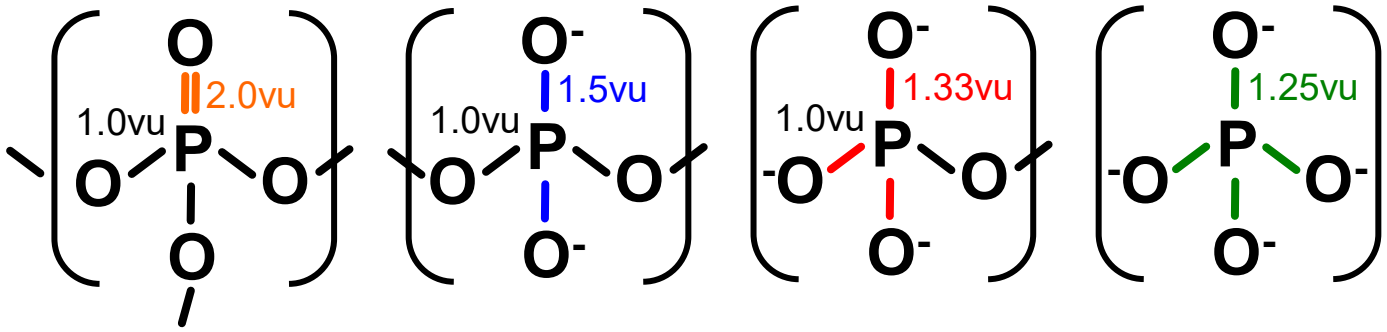
1. Binary phosphate glasses
2. Barium iron phosphate (IP) glasses
3. R_2O-, R'O-doped IP glasses
   (R=Li, Na, K; R'=Ca, Ba)
4. ZrO_2-doped IP glasses

1. Binary Phosphate Glasses

Water & chemical durability

- One of dispensable properties for practical applications, e.g., nuclear waste immobilization, high-durable glass for alkali and acidic solutions (silicate-based glasses)
- Basic data for biomedical applications

Basic tetrahedral units of phosphate glasses

PO_4 tetrahedral unit				
$[Q^n]$	Q^3	Q^2	Q^1	Q^0
[O/P]	2.5	3	3.5	4
Ideal composition (mol%)	$100P_2O_5$	$50R_2O–50P_2O_5$ $50R'O–50P_2O_5$	$67R_2O–33P_2O_5$ $67R'O–33P_2O_5$	$75R_2O–25P_2O_5$ $75R'O–25P_2O_5$

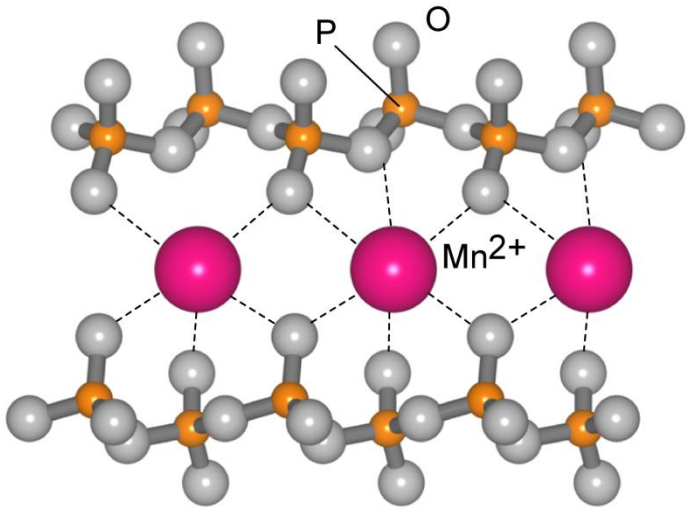
R: Monovalent metal, R': Divalent metal

$\diagdown O \diagup$: Bridging oxygen O^- : Non-bridging oxygen

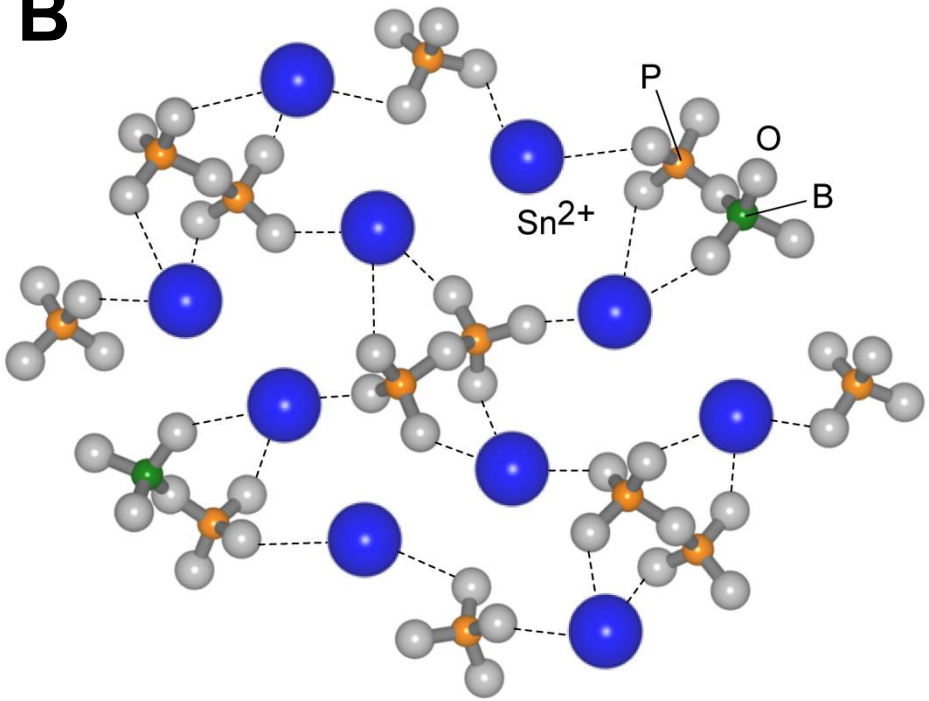
R. Brow, J. Non-Cryst. Solids, **263&264** (2000) 1–28.

Type A&B Phosphate Glasses

A



B

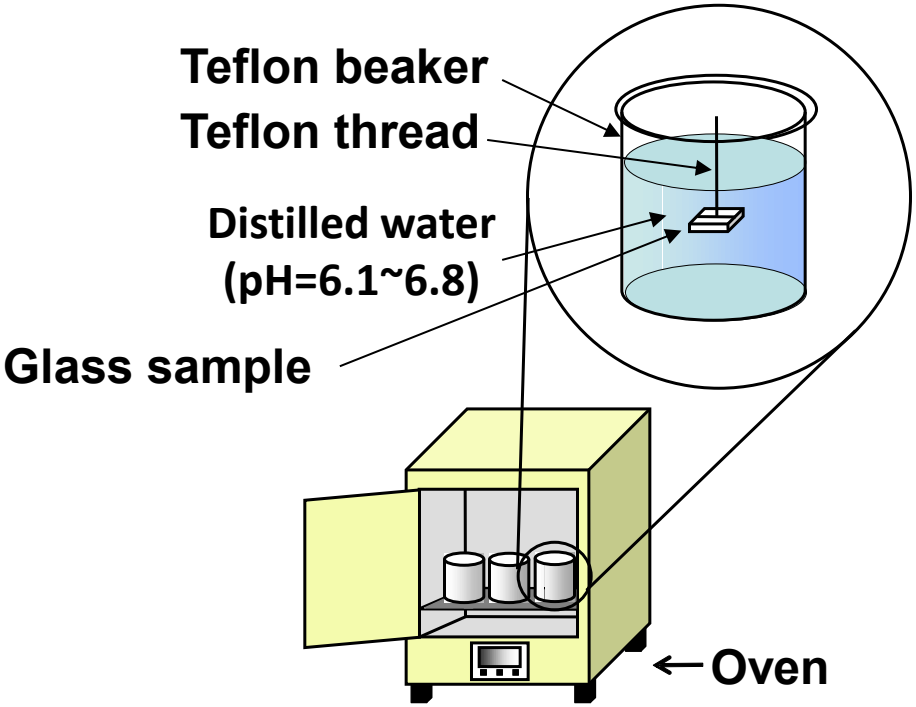


[Type A]
~2.63 < [O/P] < 3.25
- Poor durability
- Q^2 chain structure

[Type B]
[O/P] ≥ 3.25
- Better durability
- Q^1 and/or Q^0 structure connected with other components

MCC-1 Static Leaching Test

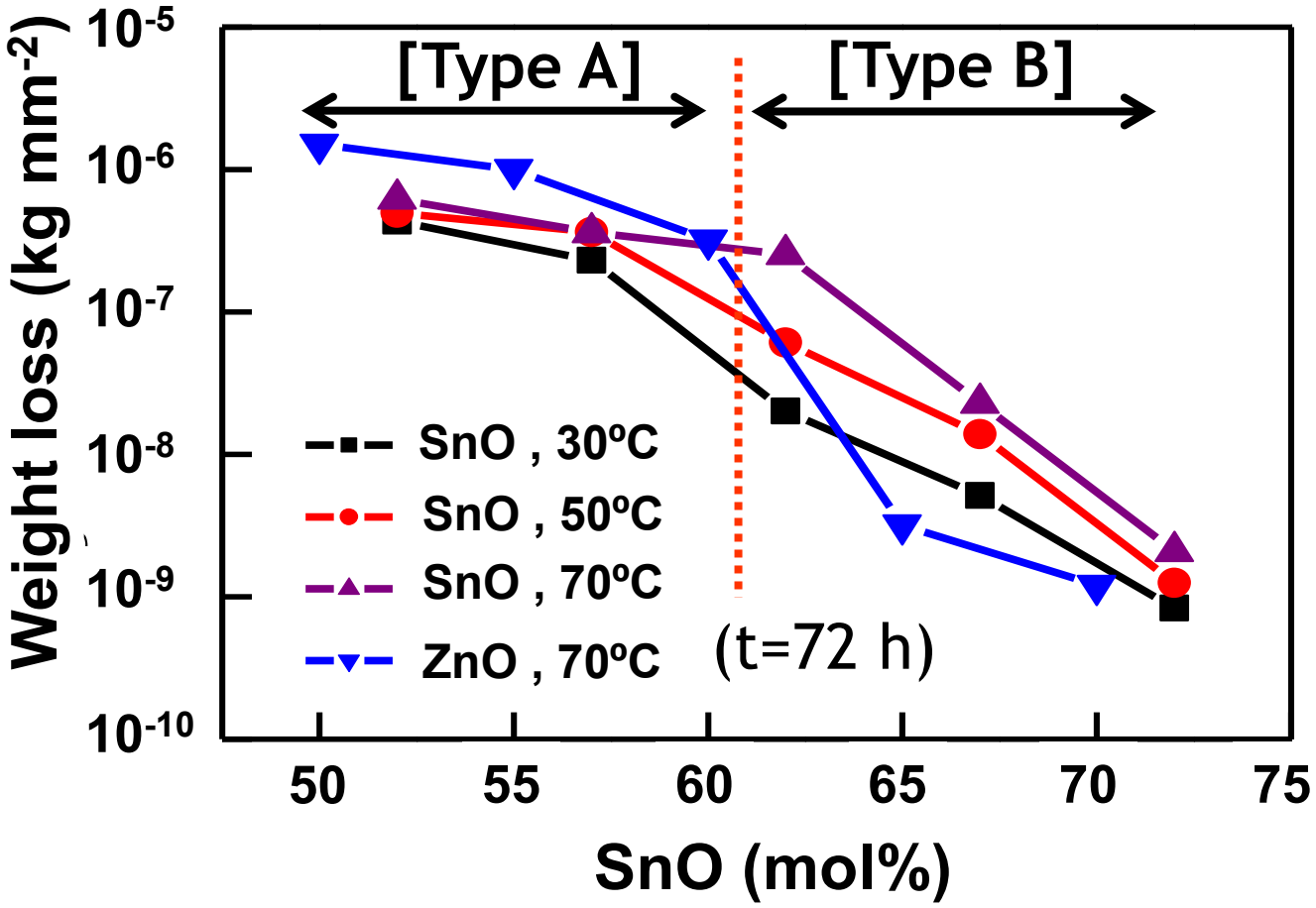
Water durability of bulk glass samples at < 100 ºC



H. Takebe, Y. Baba, M. Kuwabara, J. Non-Cryst. Solids, **352** [28-29], 3088-3094 (2006).

P_2O_5 concentration dependence

SnO-P_2O_5 and ZnO-P_2O_5 binary glasses



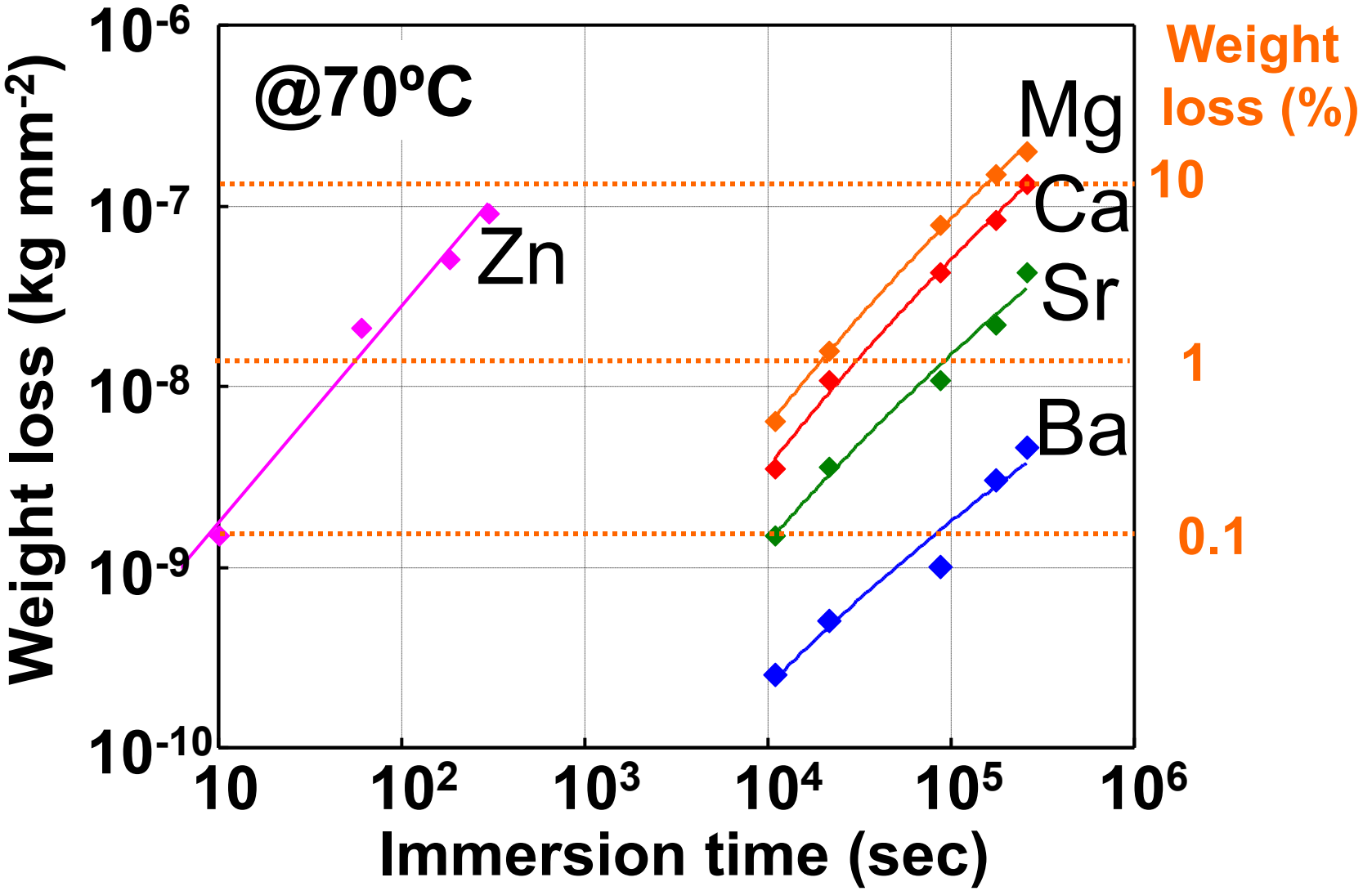
• H. Takebe, Y. Baba, M. Kuwabara, J. Non-Cryst. Solids, **352** [28-29], 3088-3094 (2006).

•J. Cha, T. Kubo, H. Takebe, M. Kuwabara, J. Ceram. Soc. Japan, **116** [8], 915–919 (2008).

Fig. Relationships between weight loss and SnO/ZnO concentration in water durability experiments.

NWM type dependence

50R'O–50P_2O_5 (mol%)(R'=Zn, Mg, Ca, Sr, Ba)

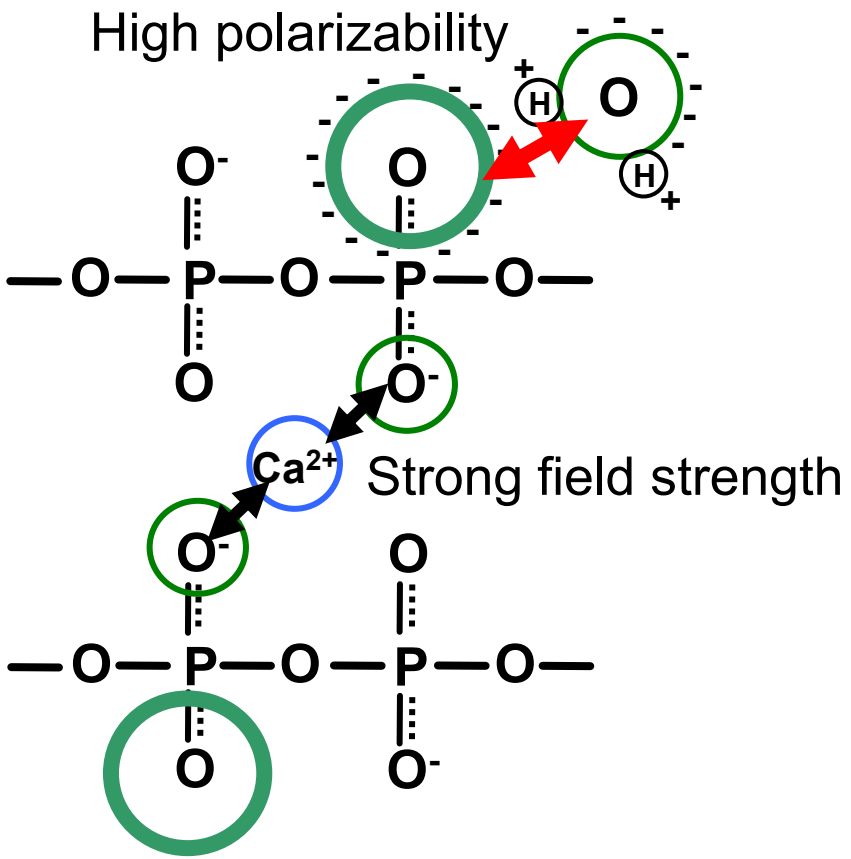


H. Takebe, Y. Baba, M. Kuwabara, "Compositional Dependence of Water Durability in Metaphosphate Glasses", ICG Procs., (2007) Z10, Strasbourg, France.

Interaction between PO_4 network and H_2O molecule

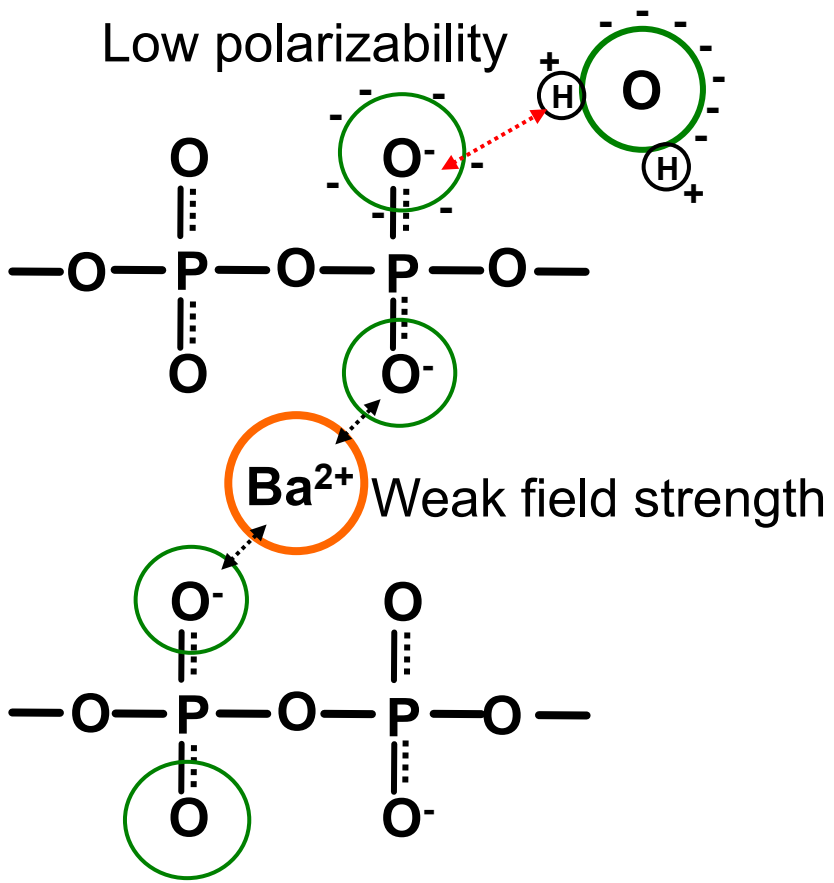
〔Poor durability〕

R = Mg, Ca

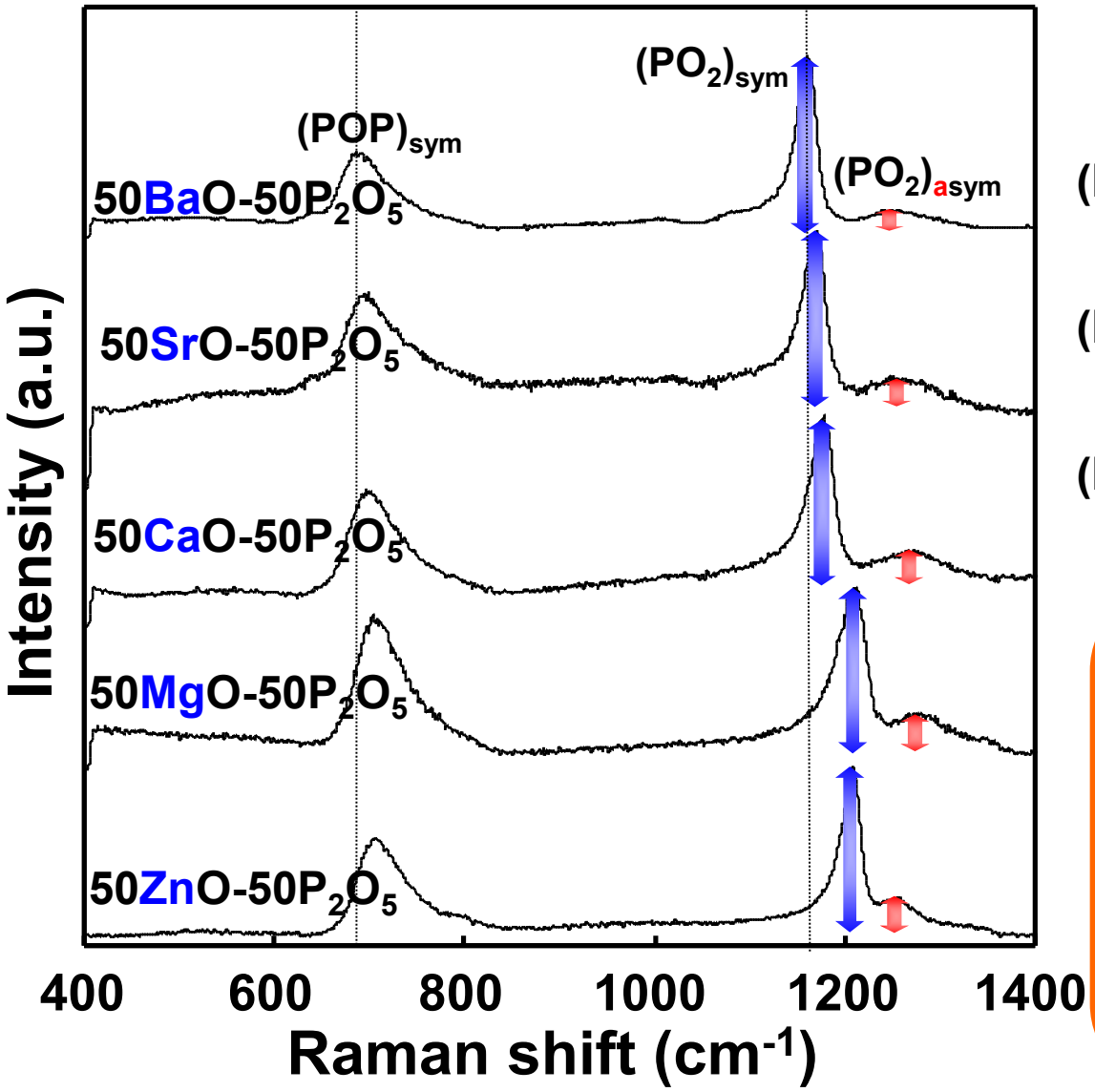


〔Good durability〕

R = Ba, Sr



Raman spectra of meta-phosphate glasses



[Meta-phosphate glasses, Q^2 chain structure]

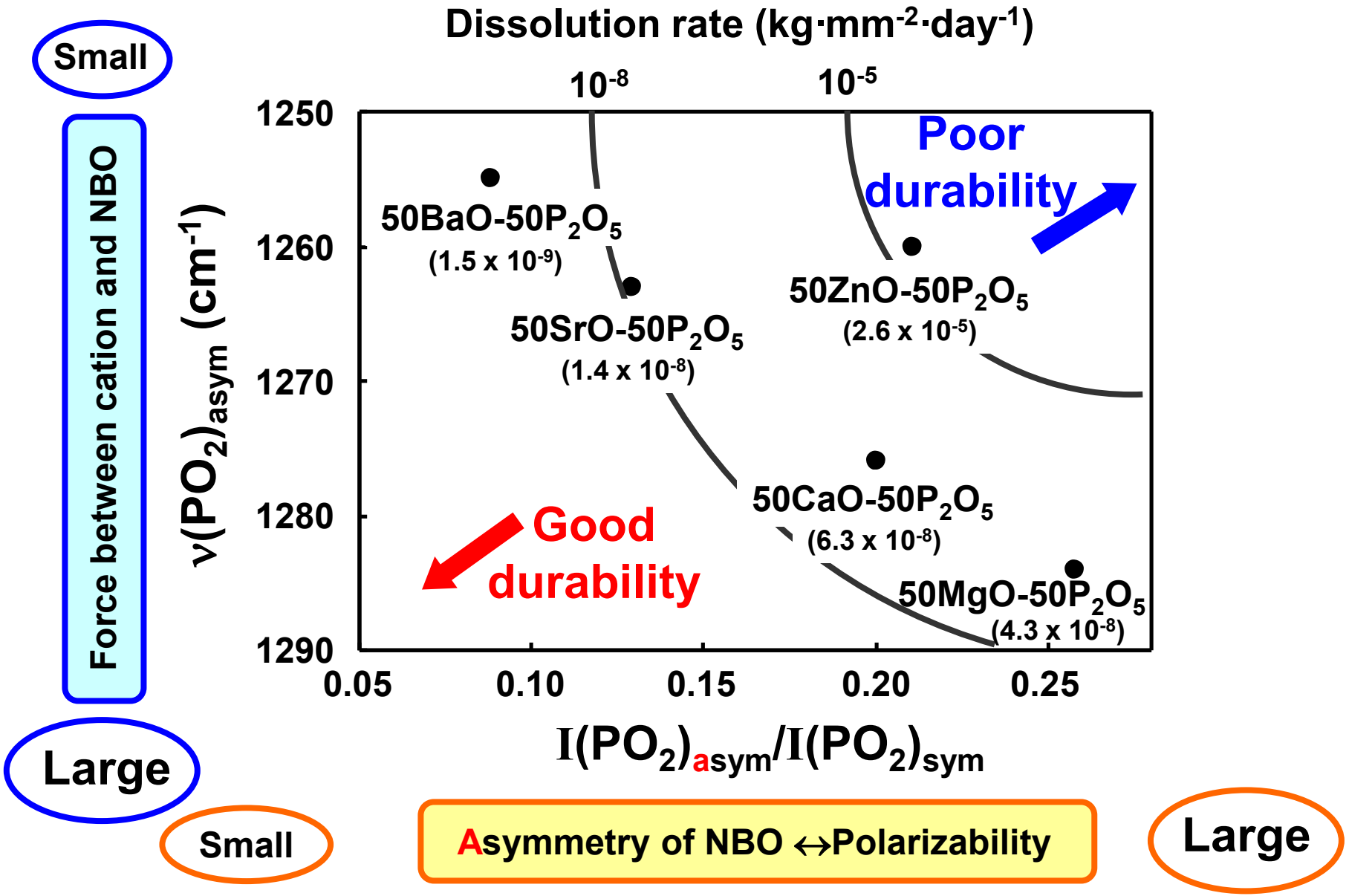
$(POP)_{sym}$: Bridging oxygen, Symmetric stretching

$(PO_2)_{sym}$: Non-bridging oxygen, Symmetric stretching

$(PO_2)_{asym}$: Non-bridging oxygen, Asymmetric stretching

- $I(PO_2)_{asym}/I(PO_2)_{sym}$ → Asymmetry of NBO
- $\nu(PO_2)_{asym}$ → Bonding force between cation and NBO

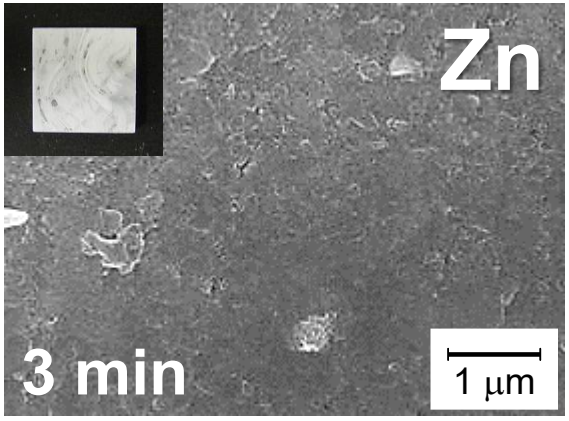
Factors affecting dissolution rate

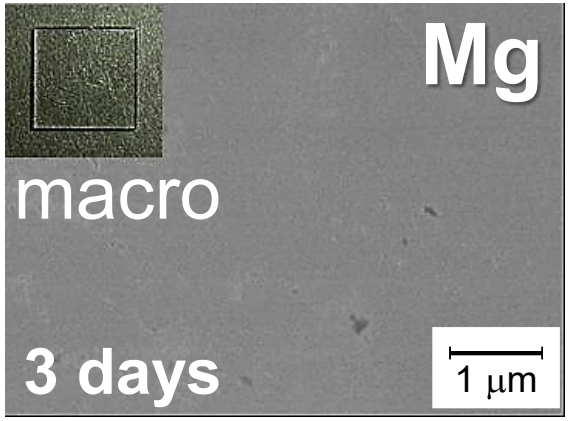


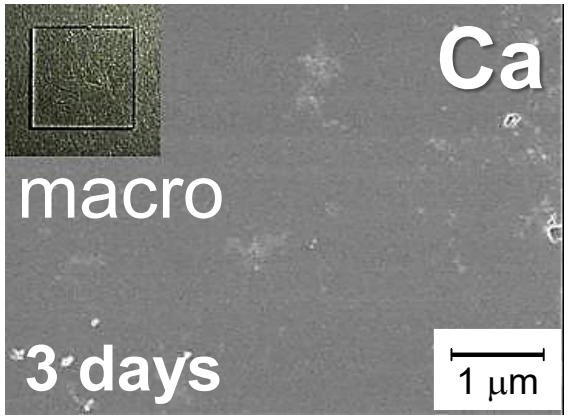
Appearance & microstructure

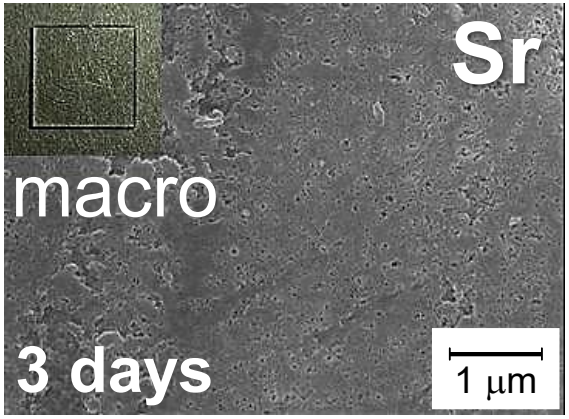
50R'O–50P_2O_5 (mol%)
(R'=Zn, Mg, Ca, Sr, Ba)

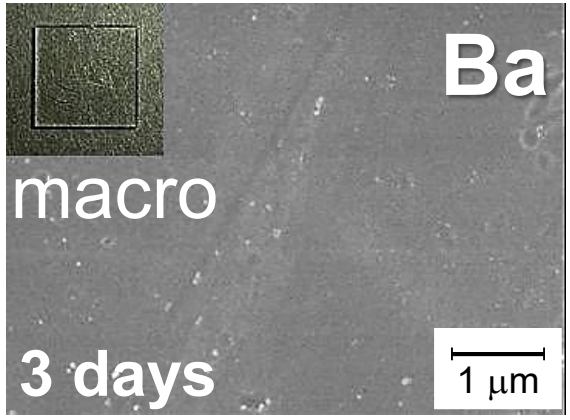
After immersion test @70ºC by MMC-1 static leaching method









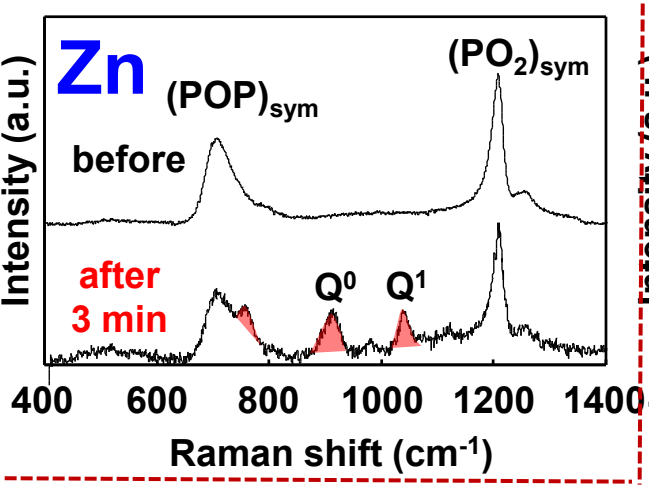


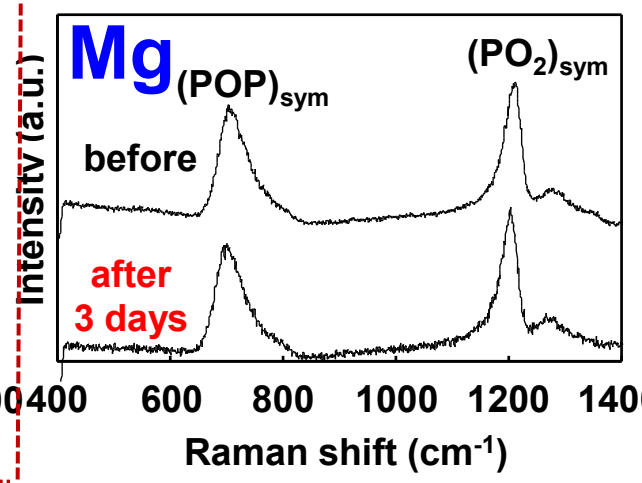
- **[Type a]**
  Zn
- **[Type b]***
  Mg, Ca, Sr, Ba

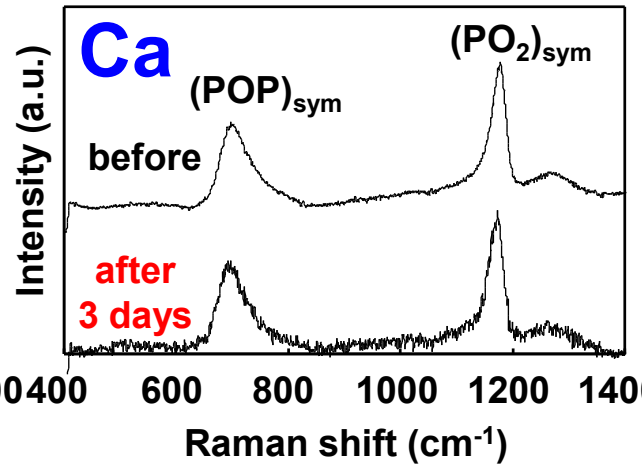
* Bunker et al. (JNCS, 1984): "The dissolution mechanism involves hydration of entire chains rather than cleavage of P–O bonds by hydrolysis reactions in R_2O–CaO–P_2O_5 glasses (R=Li, Na)."

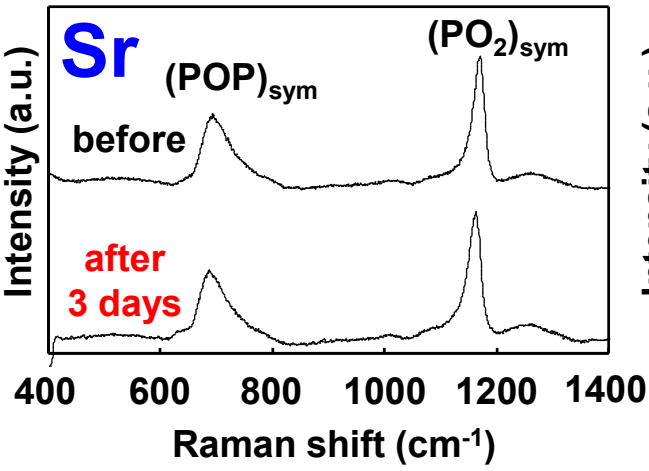
Raman spectra of $50RO–50P_2O_5$ glass before and after immersion test

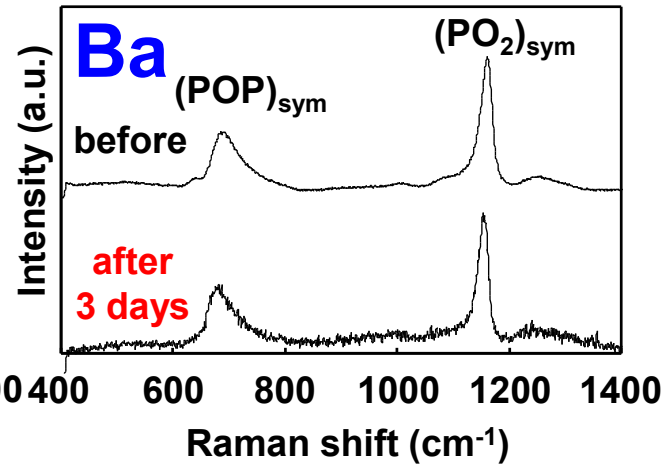
R=

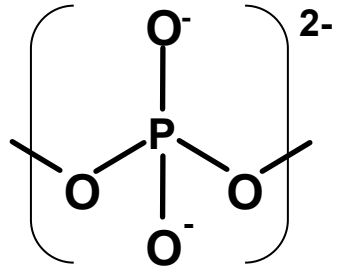












Meta-phosphate,
Chain structure

Summary 1

- Water durability of meta-phosphate glasses (type A phosphate glass) depends on modifier type in the order of Ba >Sr > Ca > Mg as an opposite order of silicate glasses.
- The order of water durability is related to the polarizability of oxygen ions in PO_4 Q^2 networks.
- We classify meta-phosphate glasses into two types: **a**: Zn and **b**: Mg, Ca, Sr, Ba systems due to dissolution behavior into water.

What's next?

How many types of modifier cations are there in terms of dissolution behavior?

- Alkali and alkaline-earth ions
- Zn^{2+} (Cd^{2+}, Hg^{2+}, a similarity of electronic structure)
- p-block ions, e.g., Sn^{2+}, Pb^{2+}
- Transition metal ions
- and …

To control the ion releasing rate for biomedical applications

2. Barium Iron Phosphate Glasses

Introduction

Iron phosphate ($FeO–Fe_2O_3–P_2O_5$) glass

- Good chemical durability [1]
- High loading capacity [2]

[1] X. Yu et al., J. Non- Cryst. Solids 215, 21 (1997).
[2] D.E. Day et al., J. Non- Cryst. Solids 241, 1 (1998).

➡ **For vitrified radioactive wastes**

[Our research background]

[March 11, 2011]

The contaminated water generated by cooling the Fukushima Daiichi reactor.

↳ Decontamination by co−precipitation (AREVA process)
June–September, 2011

➡ **Radioactive sludge** (Total amount: 597 m^3)

Main components

- **$BaSO_4$**
- ppFeNiK (Ferrocyanide nickel potassium)

It is difficult to prepare durable borosilicate glasses with $BaSO_4$.

Optimization the composition of iron phosphate glasses including $BaSO_4$ [3]

[3] H. Takebe et al., Phys. Chem. Glasses 57, 5, 213 (2016).

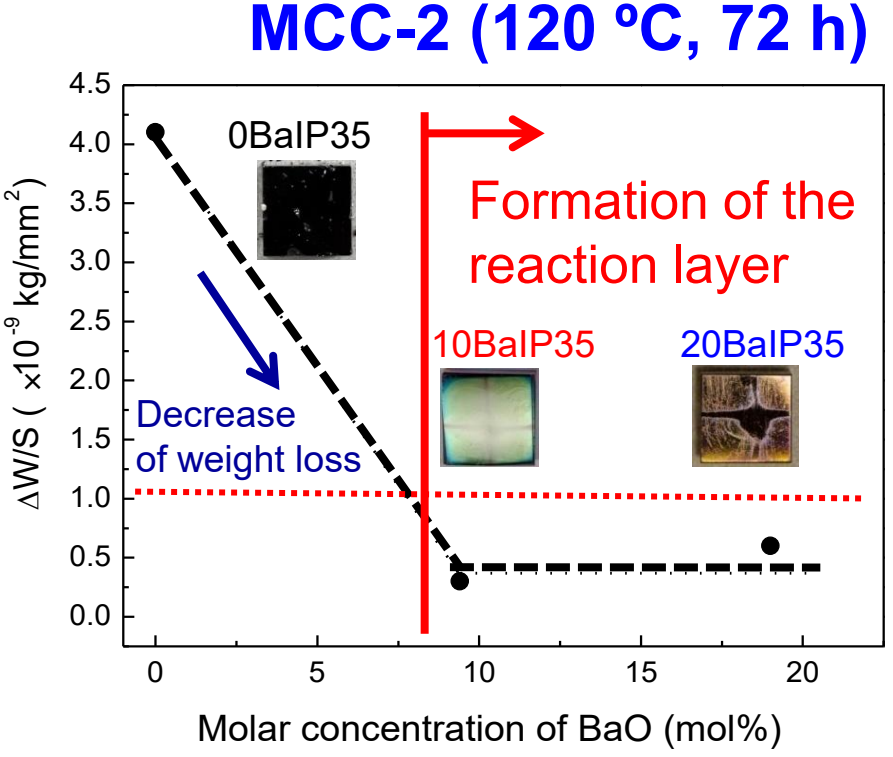
Purpose of this study

Water durability of BaO*–FeO–Fe_2O_3–P_2O_5 (BaIP) glasses

*$BaSO_4$ decompose into BaO during melting process.

BaO addition

Significant improvement of water durability[3], [4]



[3] H. Takebe et al., Phys. Chem. Glasses **57** [5], 213 (2016).
[4] P.A. Bingham et al., J. Non-cryst. **355**, 1526 (2009).

What is the role of the reaction layer?

Glass composition

Samples（Abbreviation: xBaIP35）

$$x\mathrm{BaO} - \frac{(100 - x)}{100}\{35\mathrm{FeO}_y - 65\mathrm{P_2O_5}\} \quad \begin{cases} x = 0, 10, 20 \text{ mol\%} \\ y = 1-1.5 \end{cases}$$

The compositions were selected from our previous study [3].

☐ Calculated sample composition

Sample	Analyzed composition (mol%)				O/P (±0.04)
	BaO	FeO	Fe_2O_3	P_2O_5	
0BaIP35	---	8	29	63	3.25
10BaIP35	10	7	27	56	3.38
20BaIP35	19	7	23	51	3.43

Calculated by cation ratio (by SEM−EDS) and Fe^{2+} ratio (by titration method).

Experimental

Water durability tests

MCC−2 static leach test method

Leaching condition

- Leachate: ultrapure water at 120ºC
- Immersion time: 24, 72, 120, 168 h

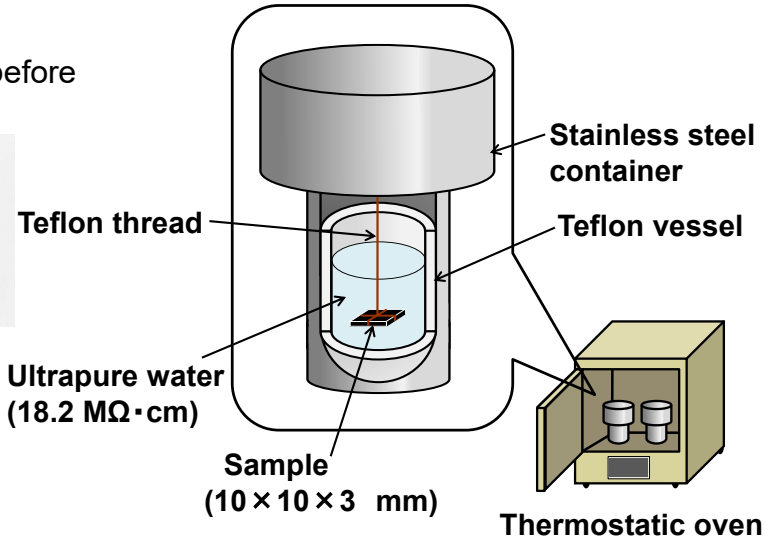
Evaluation

- **ΔW/S** (Weight loss per surface area)
- Change in appearance

The sample appearance before the tests



5 mm



Characterization of the reaction layer

FE−SEM

A sectional view of the 20BaIP35 glass (Immersion time: 24−168 h)

Evaluation methods

- **Change in microstructure**
- **Thickness of the reaction layer**

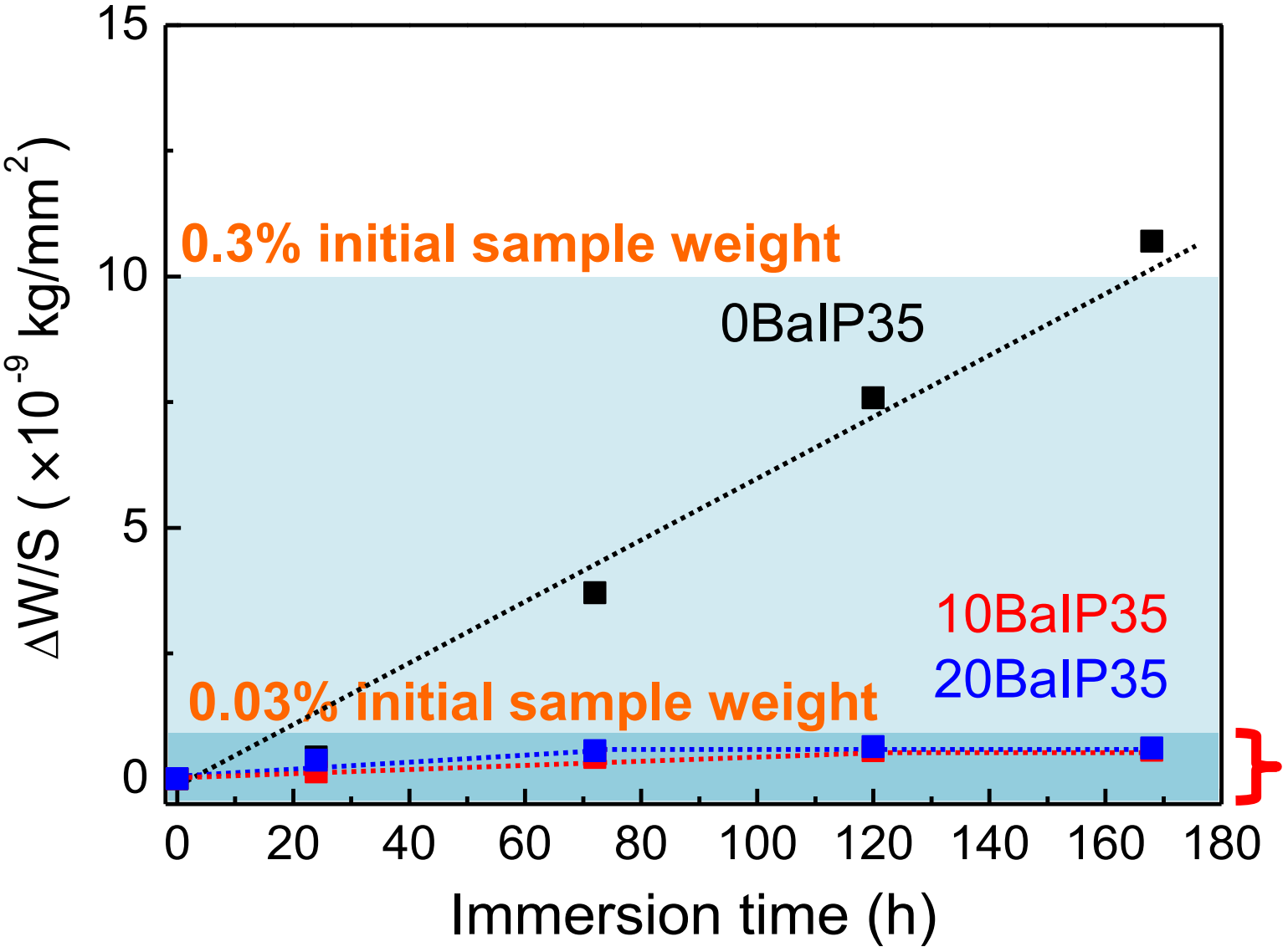
200 kV TEM

The stripped reaction layer fragments (Immersion time: 168 h)

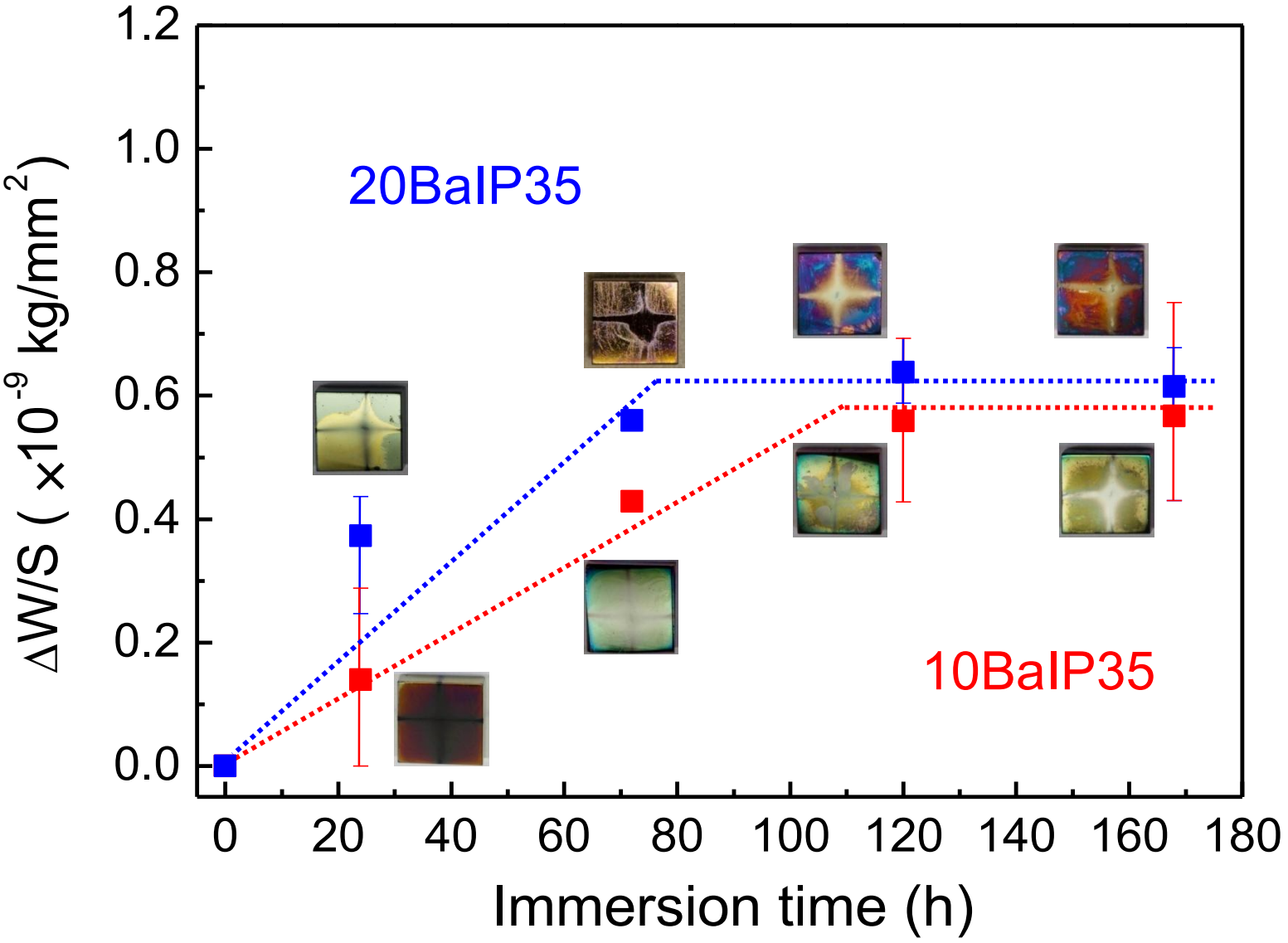
Evaluation methods

- **TEM−EDS**
- **Electron beam diffraction**

Water durability vs immersion time



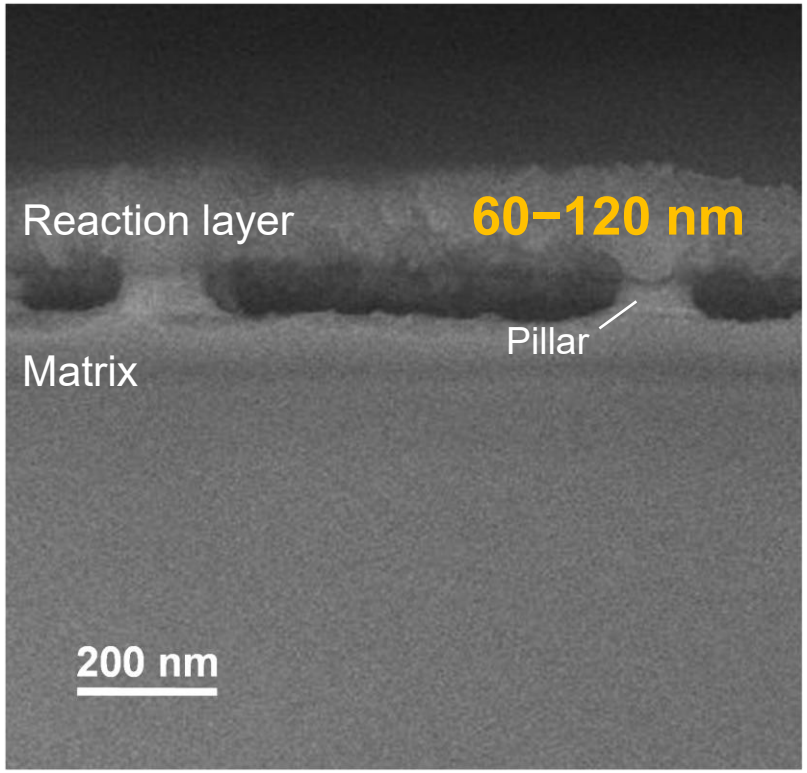
Water durability vs immersion time for $BaO–FeO–Fe_2O_3–P_2O_5$ glasses



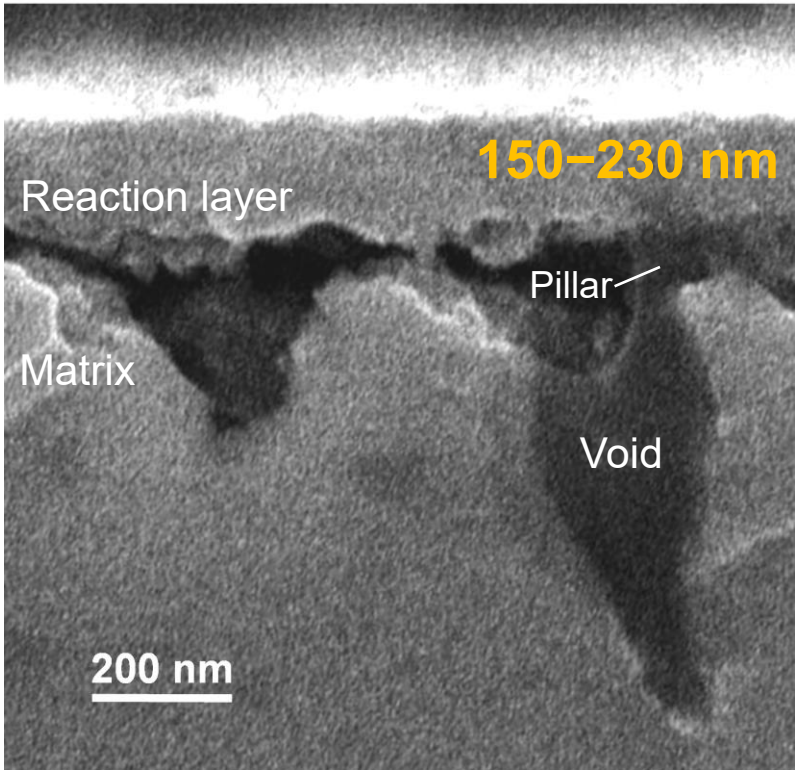
FE−SEM micrographs

- Cross section view of the 20BaIP35 glass

Immersed for 24 h



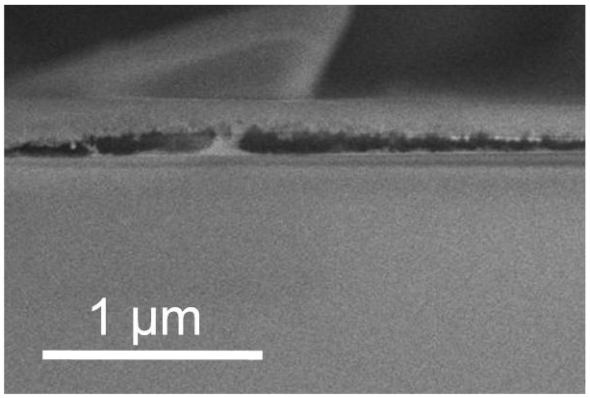
Immersed for 168 h



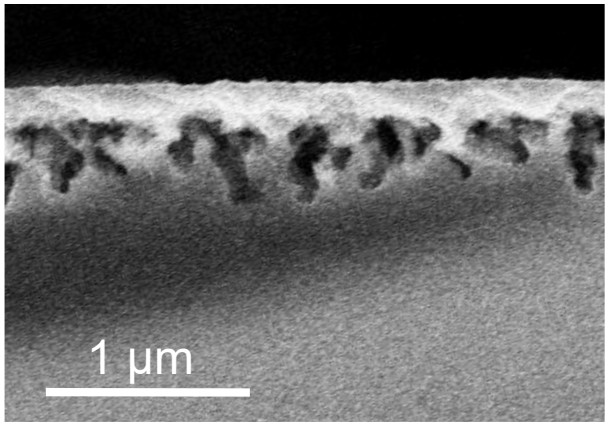
Focused on the thickness of the reaction layer

Microstructure of reaction layer

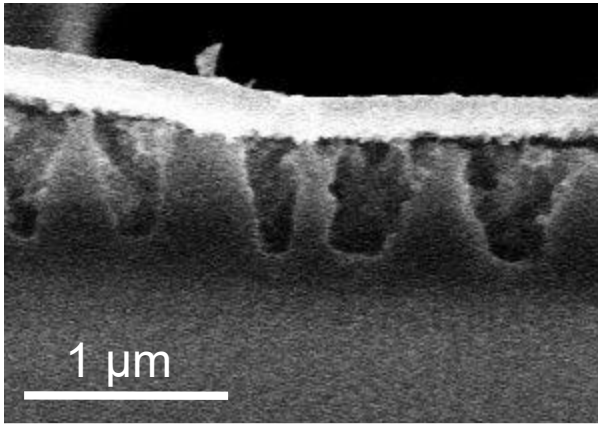
20BaIP35 glass



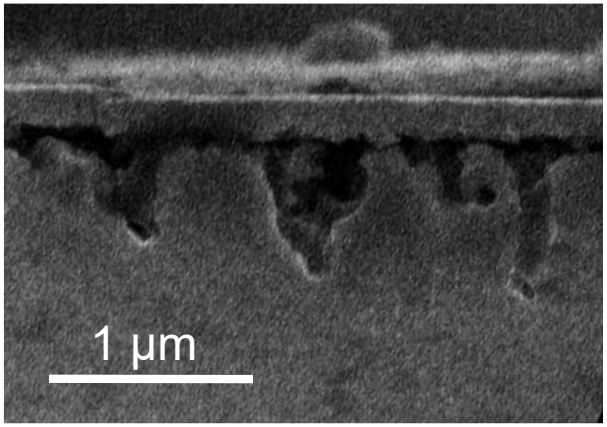
24 h



72 h



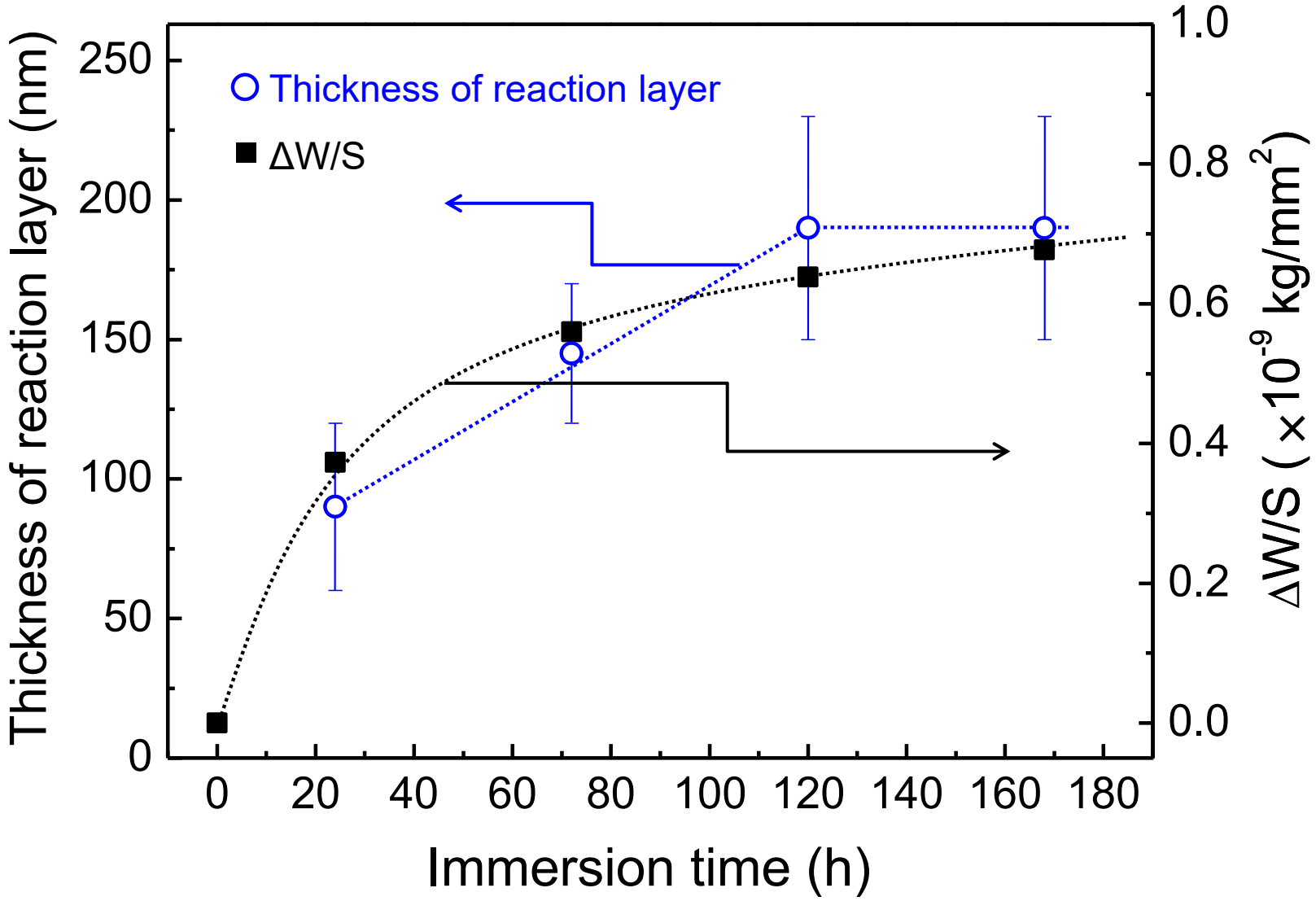
120 h



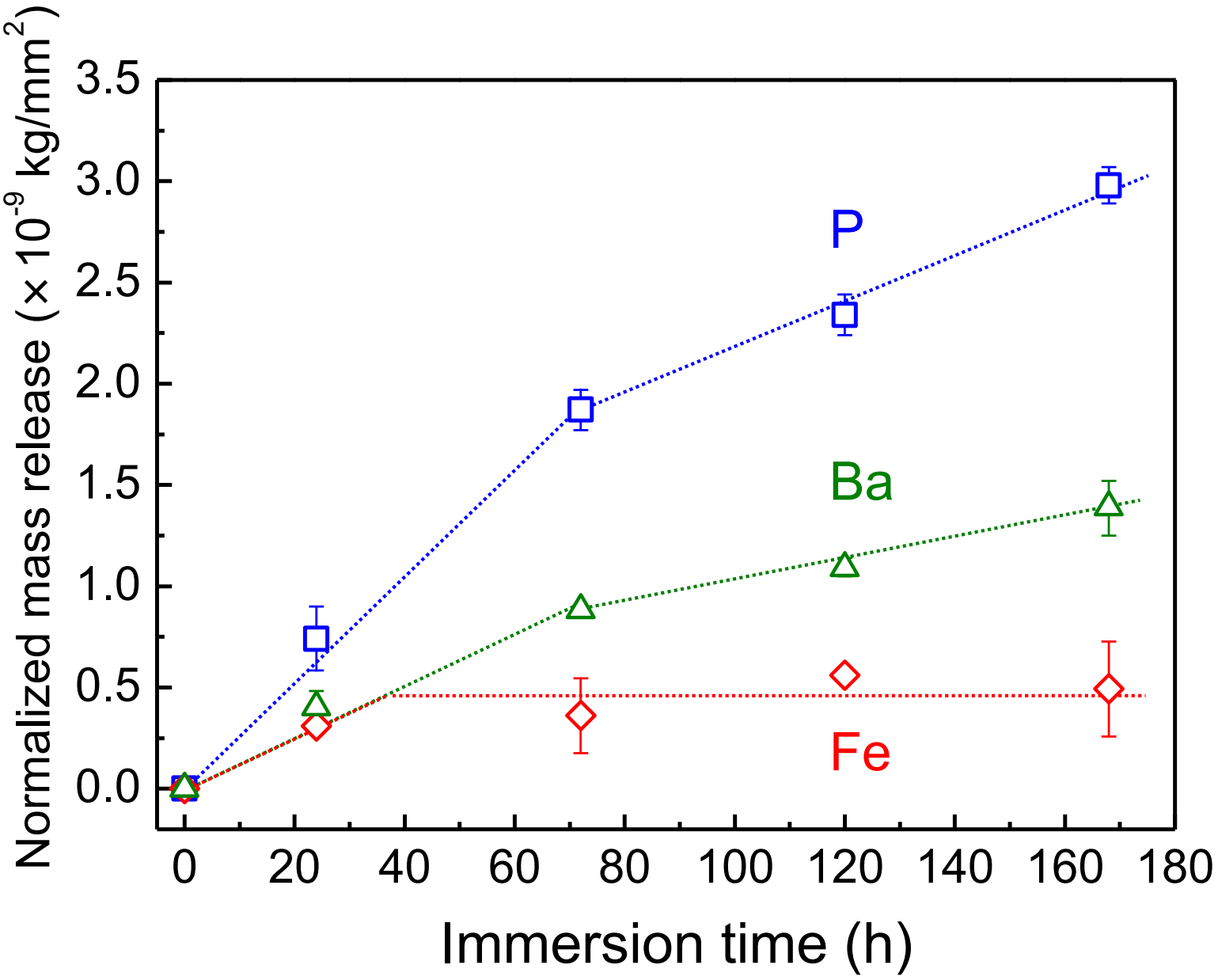
168 h

Reaction layer thickness

Variations of reaction layer thickness and weight loss with immersion time in 20BaIP35 glass

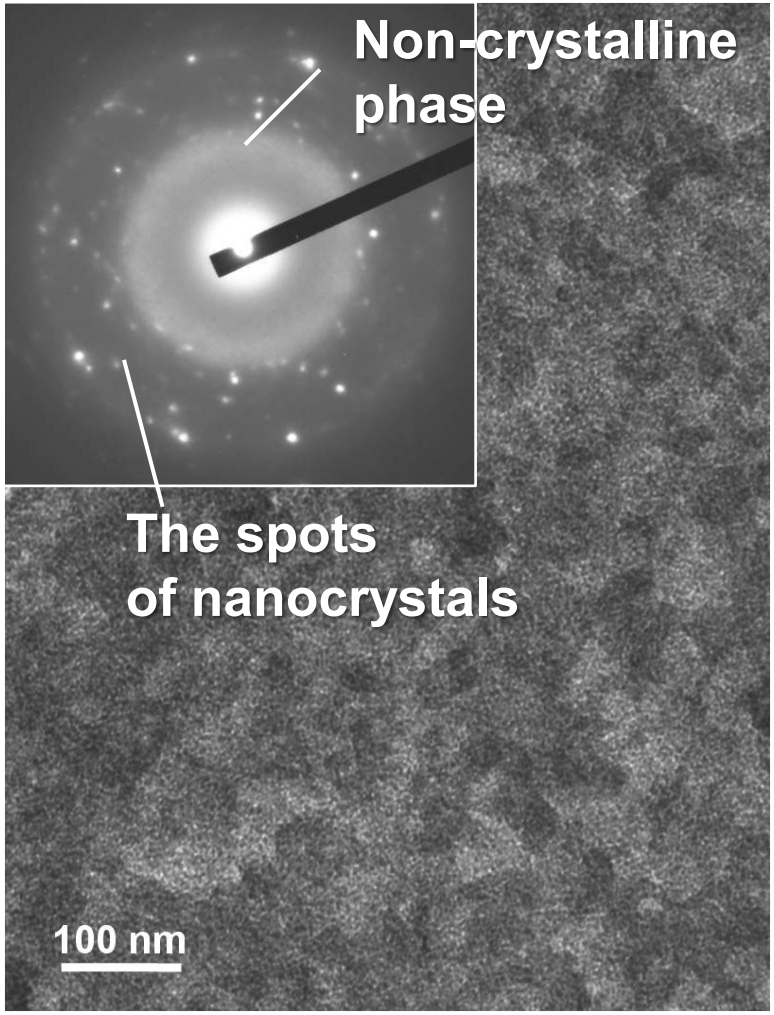


Cations released to solution



Phase and composition

The TEM bright field image and SAED pattern



Cation ratios of the reaction layer calculated by TEM−EDS *

Samples	Ba	Fe	P
20BaIP35 glass (Before the test)	11	30	59
Reaction layer	---	91	9

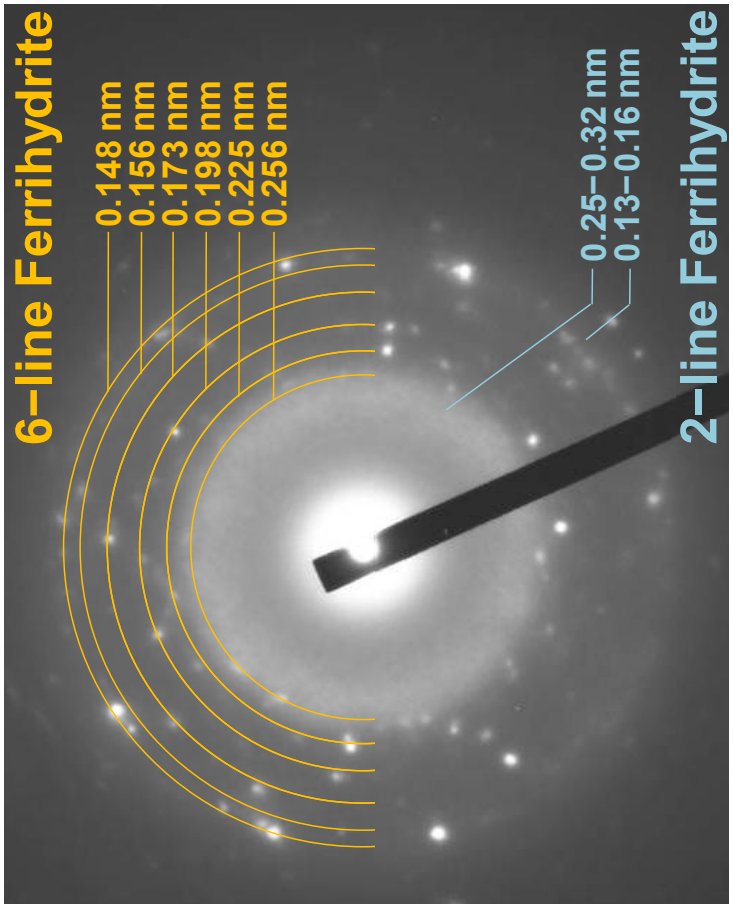
* Cation ratio of the glass before the test and the reaction layer was calculated by the results of SEM−EDS and TEM−EDS.

The reaction layer has a FeO_x−rich composition.

P and Ba components eluted into the leachate.

Phase and composition

The SAED pattern



The reaction layer consists of 6−line ferrihydrite and 2−line ferrihydrite.

Ferrihydrite:
a kind of ferric hydroxide
(Nominal composition: $5Fe_2O_3 \cdot 9H_2O$)

Cation ratio of the reaction layer

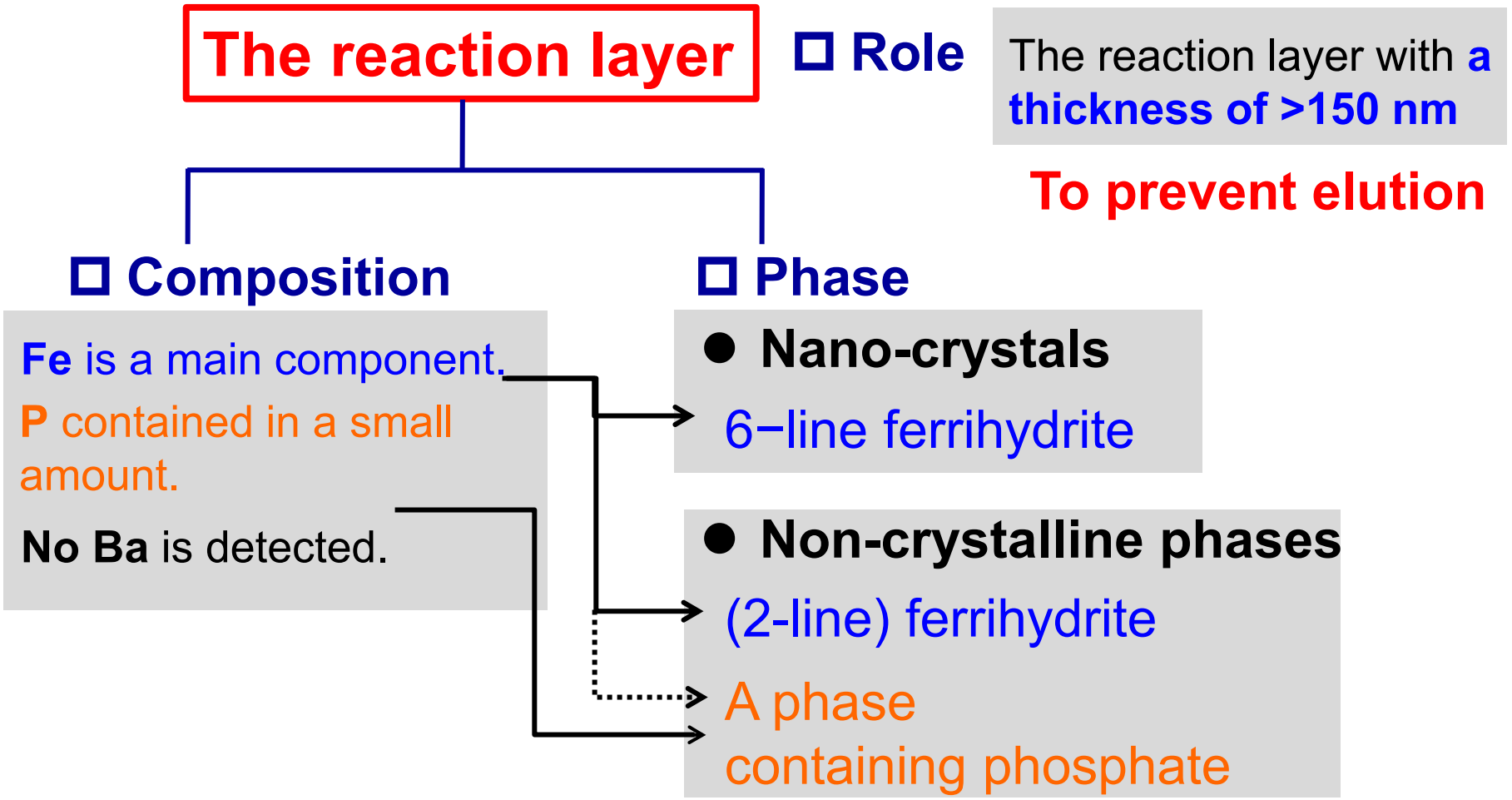
Sample	Ba	Fe	P
Reaction layer	---	91	**9**

➡ **A non-crystalline phase containing PO_x probably exists.**

The reaction layer consists of **6−line ferrihydrite** nanocrystal, **2−line ferrihydrite**, and **a non-crystalline phase containing phosphate**.

Summary 2

- **Characterization of the reaction layer**

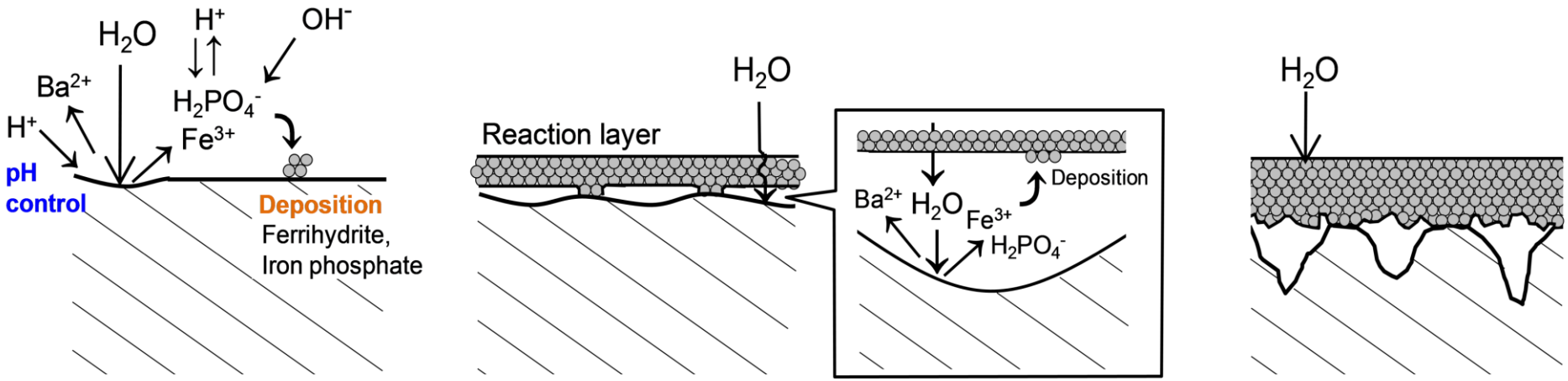


Discussion

A proposed formation process of the reaction layer

- **Phosphate ion produces decrease of pH value.** (Proton evolution by dissociation)

➡ Deposition of ferrihydrite and iron phosphate is inhibited.



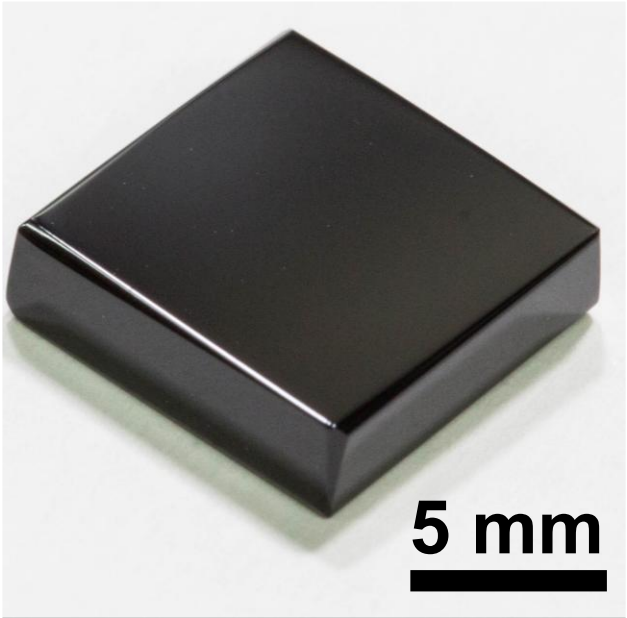
There is no Ba in the reaction layer. However, BaO addition probably promotes the formation of the reaction layer by the increase of local pH. ➡ **Other cations?**

3. R_2O-, R'O-doped iron phosphate glasses (R=Li, Na, K; R'=Ca, Ba)

Basic Classification by Appearance

After @120 ºC for 72 h by MCC-2 static leaching method

Before



*Iron phosphate glass

- **[Type I]**
  Standard IP* glass, fractured
  ZrO_2-IP glass, Low MoO_3-IP glass
- **[Type II]**
  BaO-IP glass, protective layer
  K_2O, CaO-IP glass
- **[Type II']**
  Na_2O-IP glass, protective layer with cracks
- **[Type III]**
  High MoO_3-IP glass, Dissolution

Macroscopic appearance

After @120 ºC for 72 h by MCC-2 static leaching method

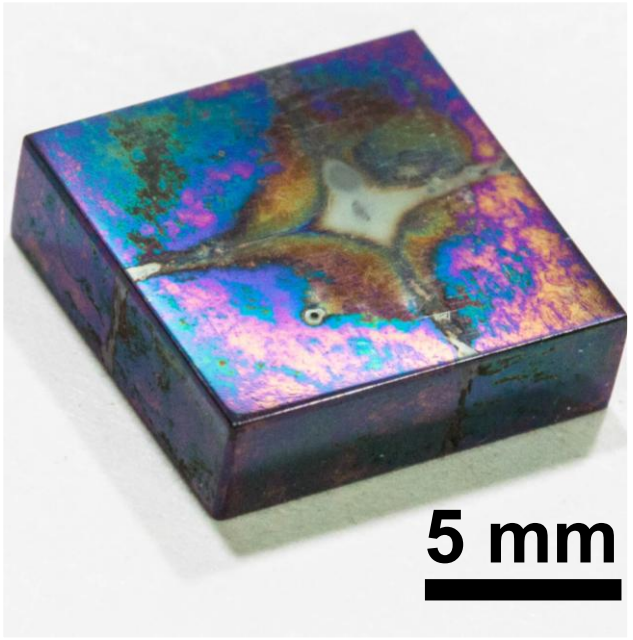
[Type I]

IP35 glass



[Type II]

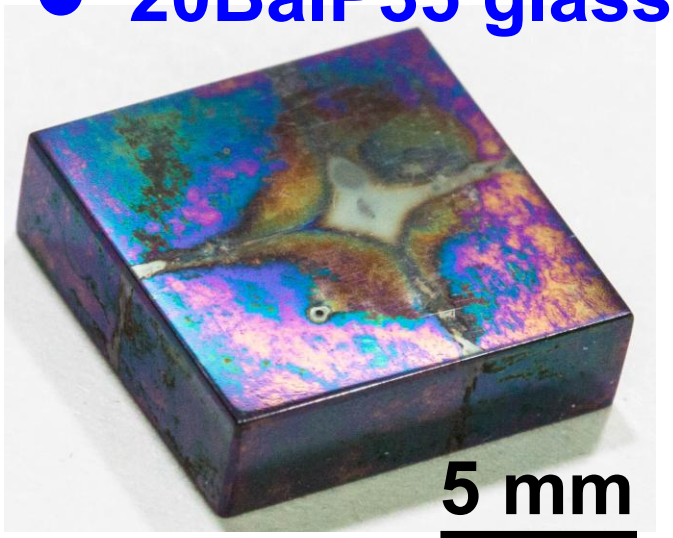
20BaIP35 glass



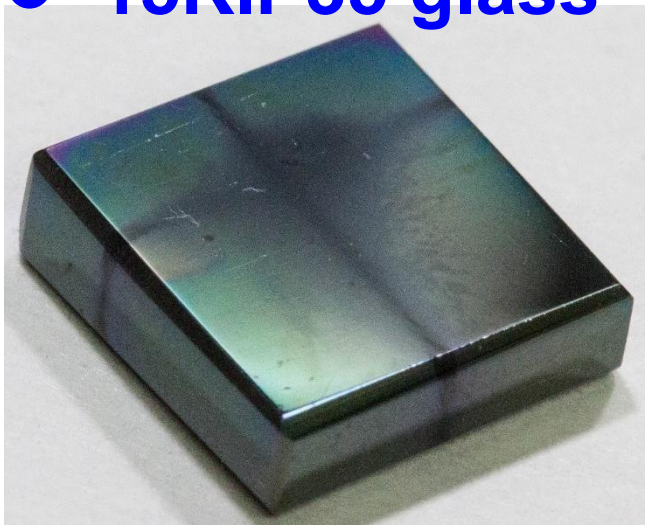
Macroscopic appearance

[Type II]

- 20BaIP35 glass

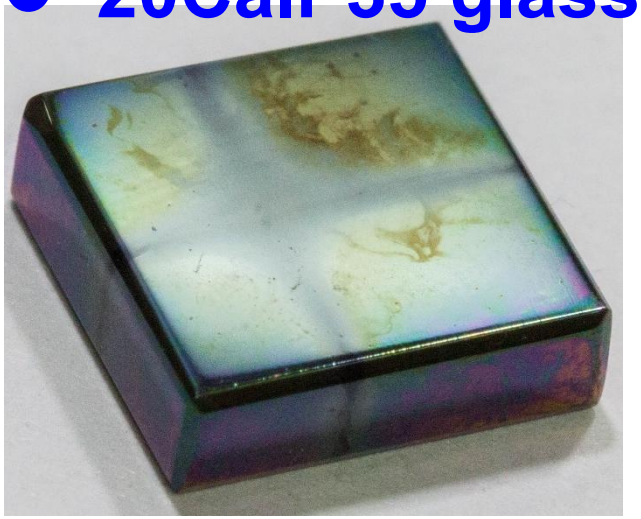


- 15KIP35 glass



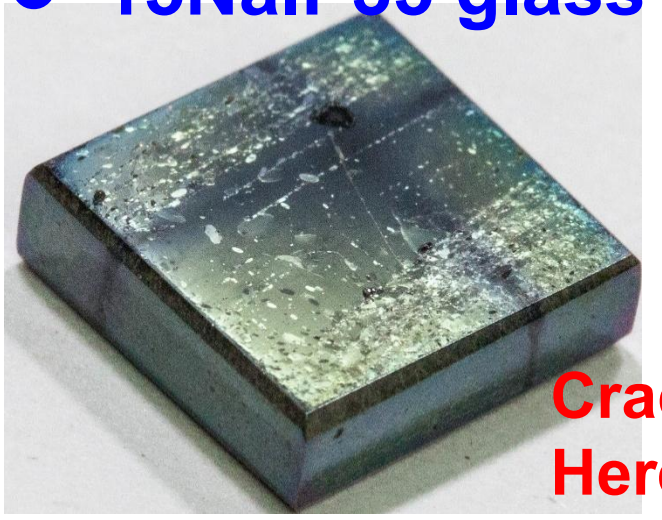
After MCC-2 static leaching test @120 ºC for 72 h

- 20CaIP35 glass



[Type II']

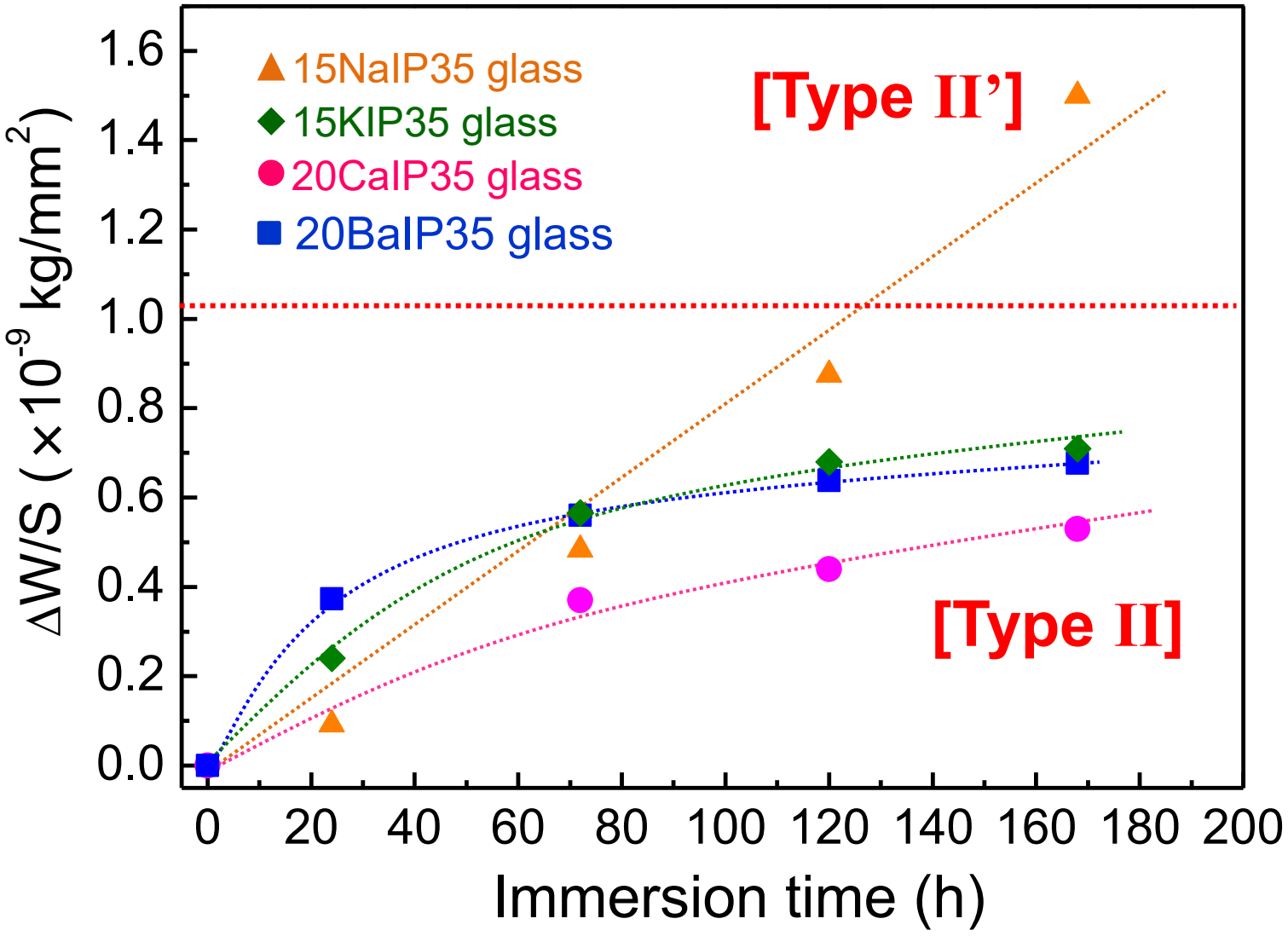
- 15NaIP35 glass



Cracks Here and there

R_2O, R'O addition

ΔW/S vs immersion time



Summary 3

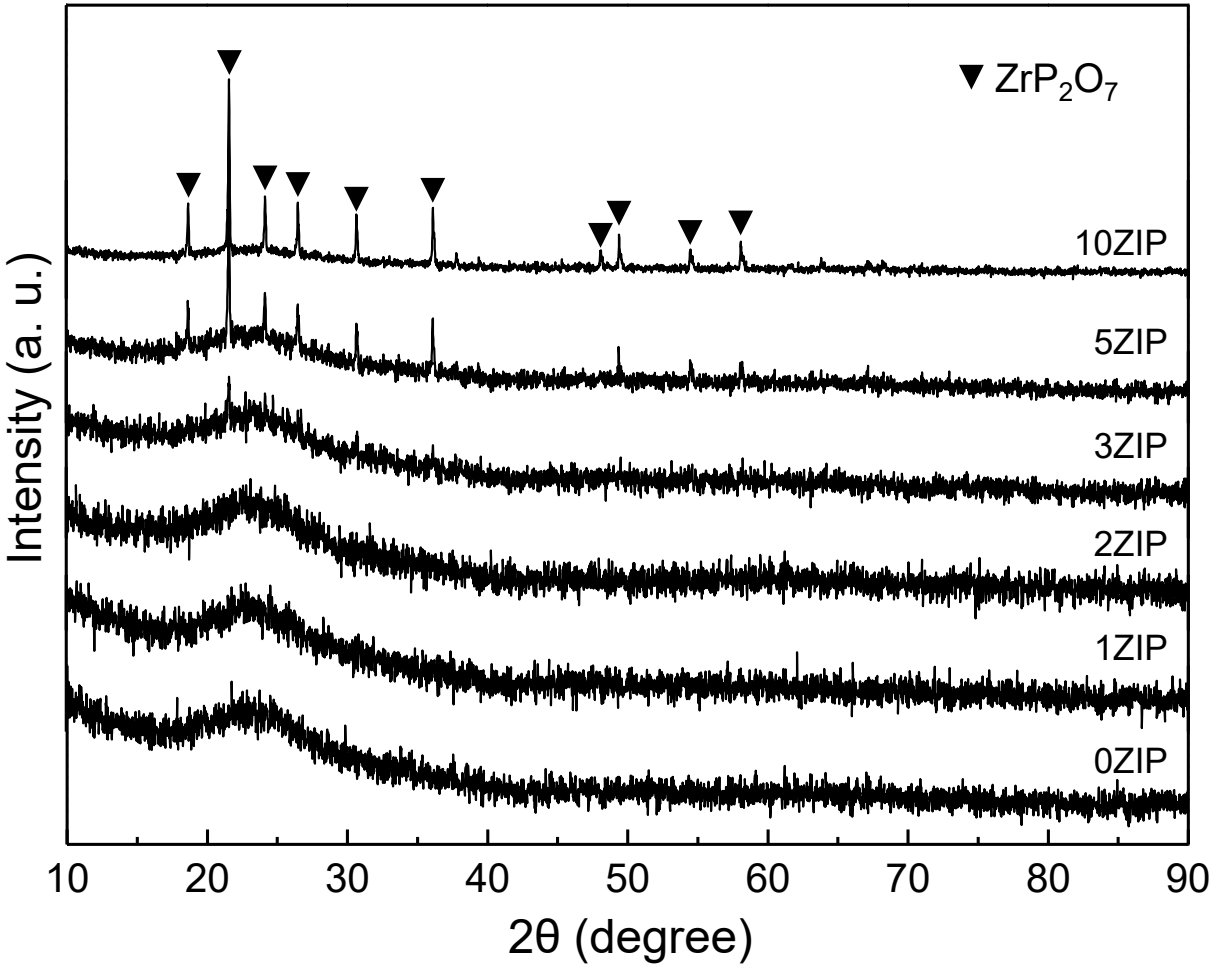
- CaO, K_2O-IP glasses show a similar behavior of BaO-IP glasses with excellent water durability due to the in-situ protective layer on sample surface.
- Na_2O-IP glasses have relatively-poor water durability due to the formation of many cracks in the protective layer after immersion tests.
- The behavior of Na_2O-IP glasses may be related to the heterogeneity of glass structure. Further study is need in terms of structural heterogeneity.

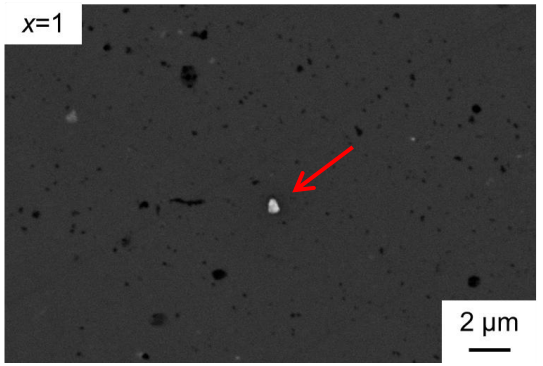
4. ZrO_2-doped iron phosphate glasses

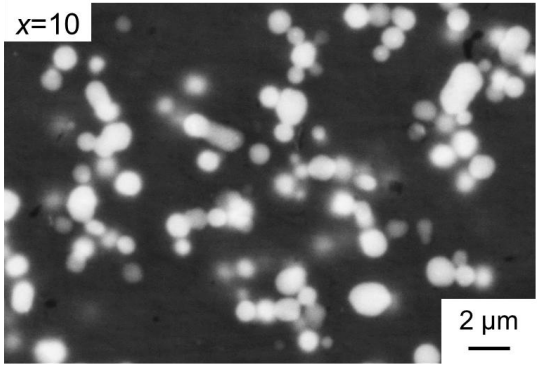
Glass composition

	Sample	Nominal composition (mol%)
ZIP	0ZIP	$30Fe_2O_3–70P_2O_5$
	1ZIP	$1ZrO_2–99(0.3Fe_2O_3–0.7P_2O_5)$
	2ZIP	$2ZrO_2–98(0.3Fe_2O_3–0.7P_2O_5)$
	3ZIP	$3ZrO_2–97(0.3Fe_2O_3–0.7P_2O_5)$
	5ZIP	$5ZrO_2–95(0.3Fe_2O_3–0.7P_2O_5)$
	10ZIP	$10ZrO_2–90(0.3Fe_2O_3–0.7P_2O_5)$
BZIP	10B5Z	$10BaO–5ZrO_2–85(0.3Fe_2O_3–0.7P_2O_5)$
	10B10Z	$10BaO–10ZrO_2–80(0.3Fe_2O_3–0.7P_2O_5)$

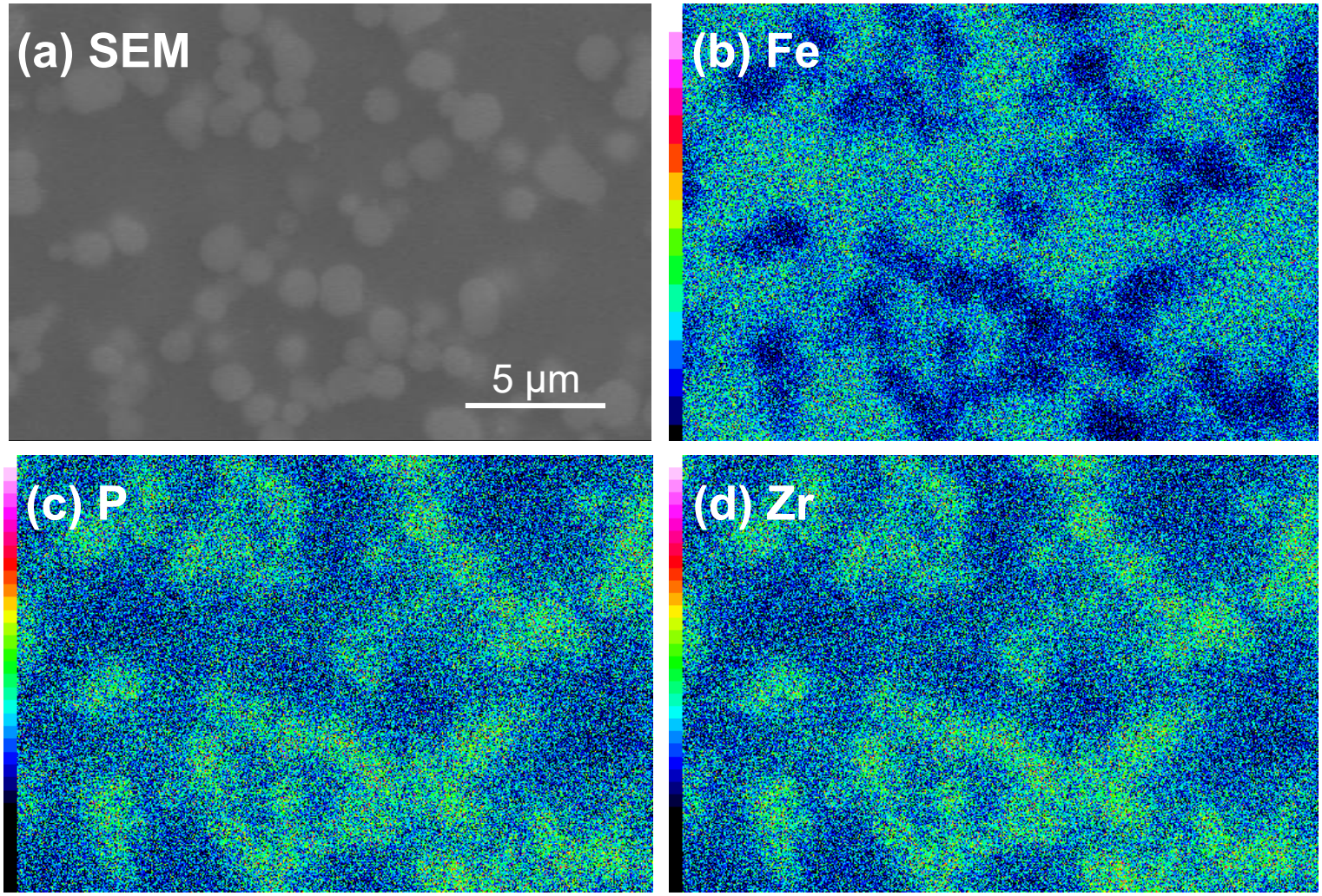
XRD spectra


▼ ZrP_2O_7
10ZIP
5ZIP
3ZIP
2ZIP
1ZIP
0ZIP
Intensity (a. u.)
10
20
30
40
50
60
70
80
90
2θ (degree)


x=1
2 μm


x=10
2 μm

Elemental mapping



Composition of precipitate by SEM-EDS

Composition	Molar ratio
P_2O_5	58 (±10)
Fe_2O_3	16 (±7)
ZrO_2	26 (±17)

The point analysis by SEM-EDS shows a similar ratio of Zr/P (=0.45) at the precipitate, compared to that of ZrP_2O_7 (=0.5). The Fe-O content may be due to the detection limit of SEM-EDS (Contribution from the matrix of IP glass.)

Appearance

After @120 ºC for 72 h by MCC-2 static leaching method

[Type I']

- 5ZIP30



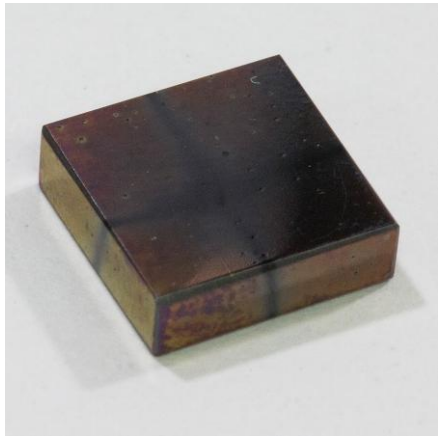
ZIP

[Type II]

- 10BaO−5ZIP30



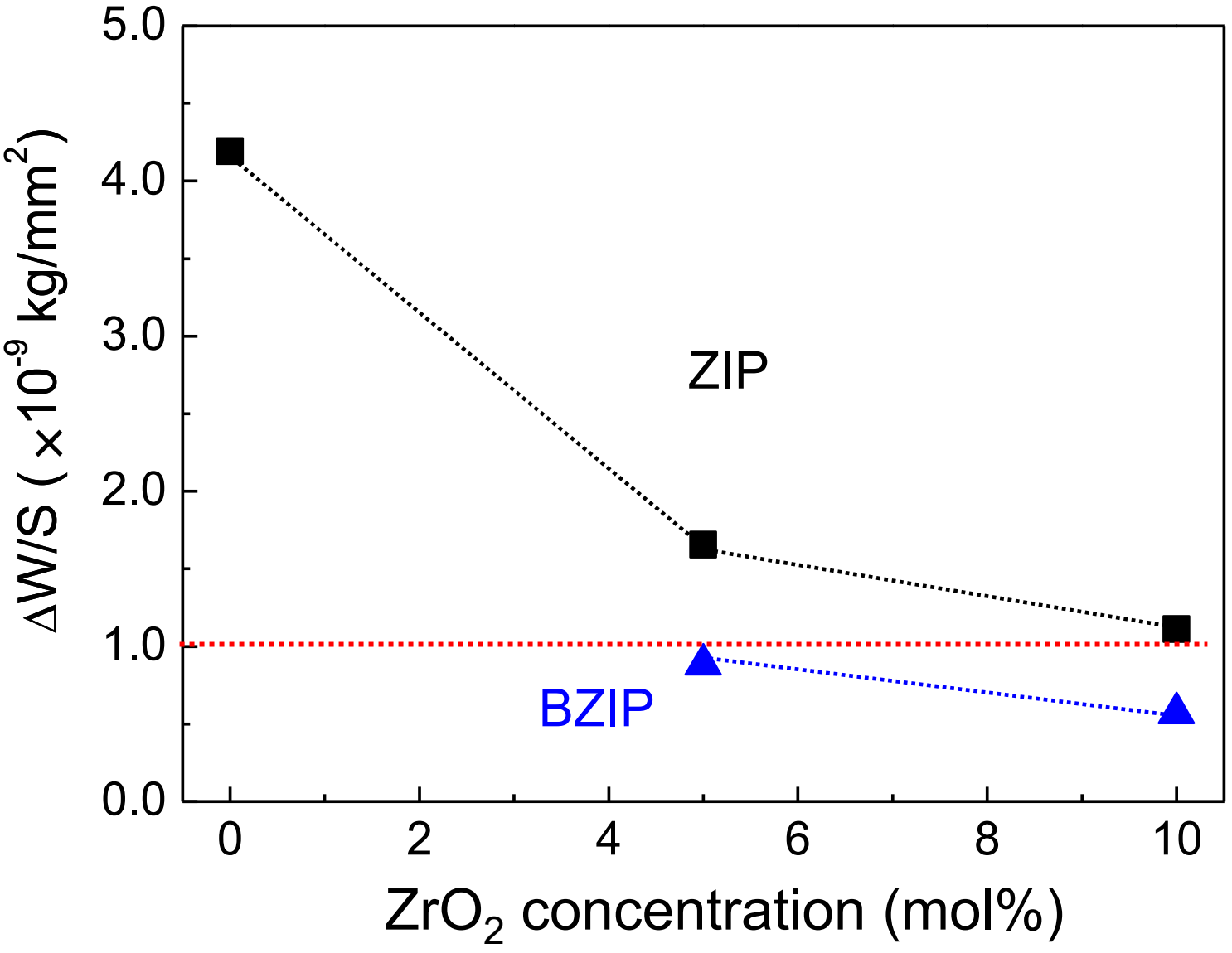
- 10BaO−10ZIP30



BZIP

Weight loss per specific area

After @120 ºC for 72 h by MCC-2 static leaching method



PCT-B test method

According to PCT-B test method

Immersion condition: 90ºC, 168 hours

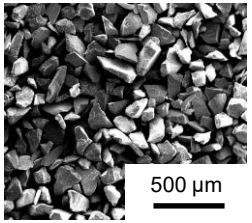
Evaluation methods: Normalized leaching rate (NLi)

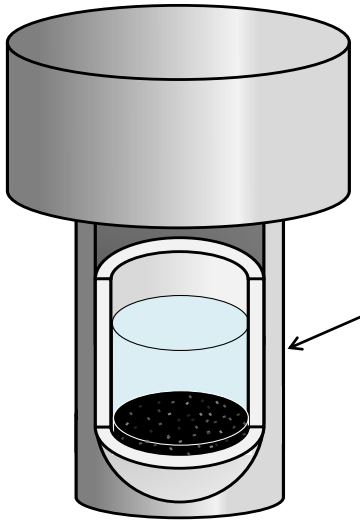
$$NL_i = \frac{C_i}{f_i \cdot (S/V/d)}$$

C_i: measured concentration by ICP-MS (ppm)
f_i: mass fraction (wt.%)
S: surface area (mm^2)
V: leachate volume (L)
d: Immersion time (day)

Ultrapure water
(18.2 MΩ･cm)

Sample powder
(5g, 75−150 μm)

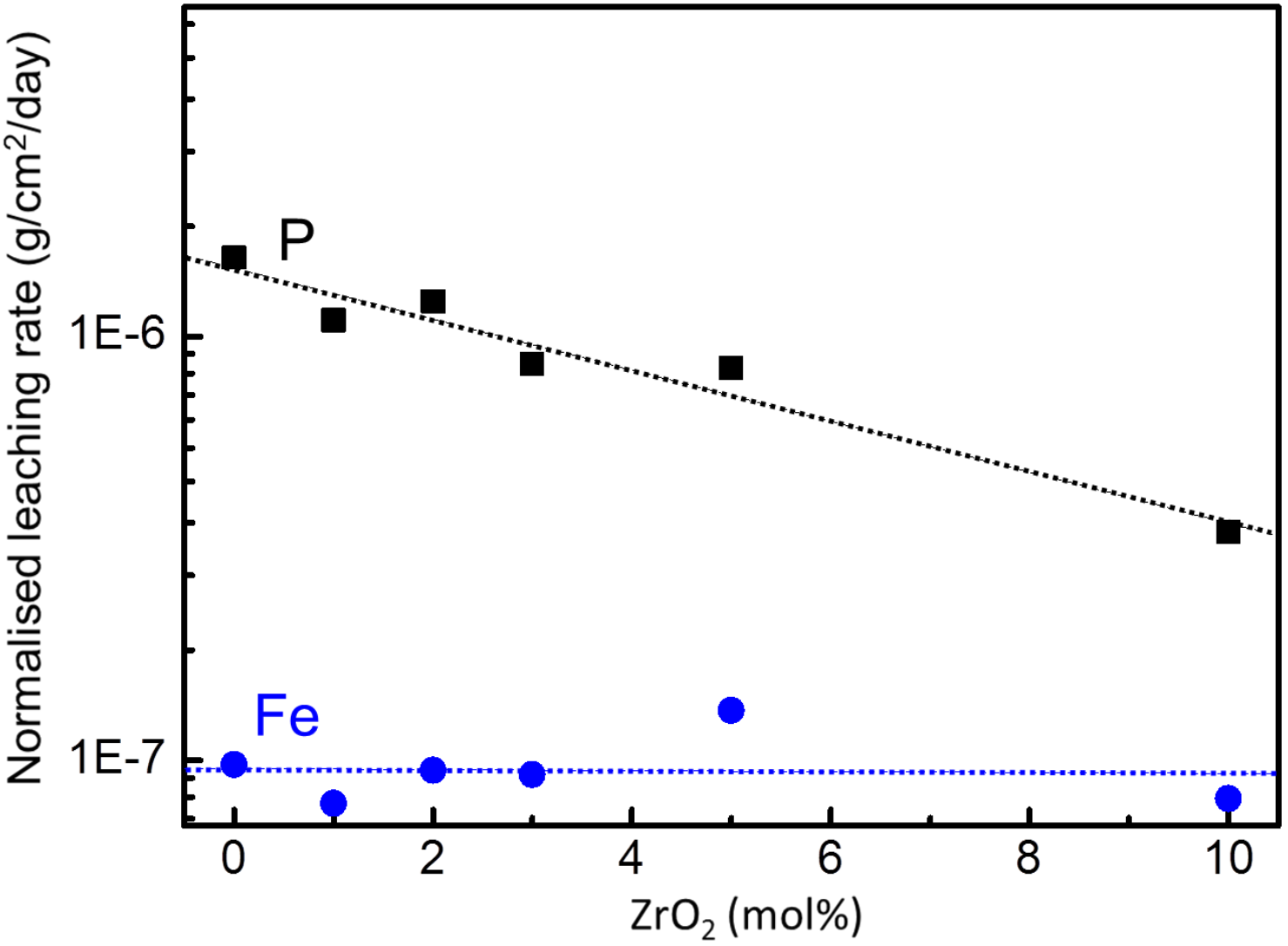




Stainless steel container

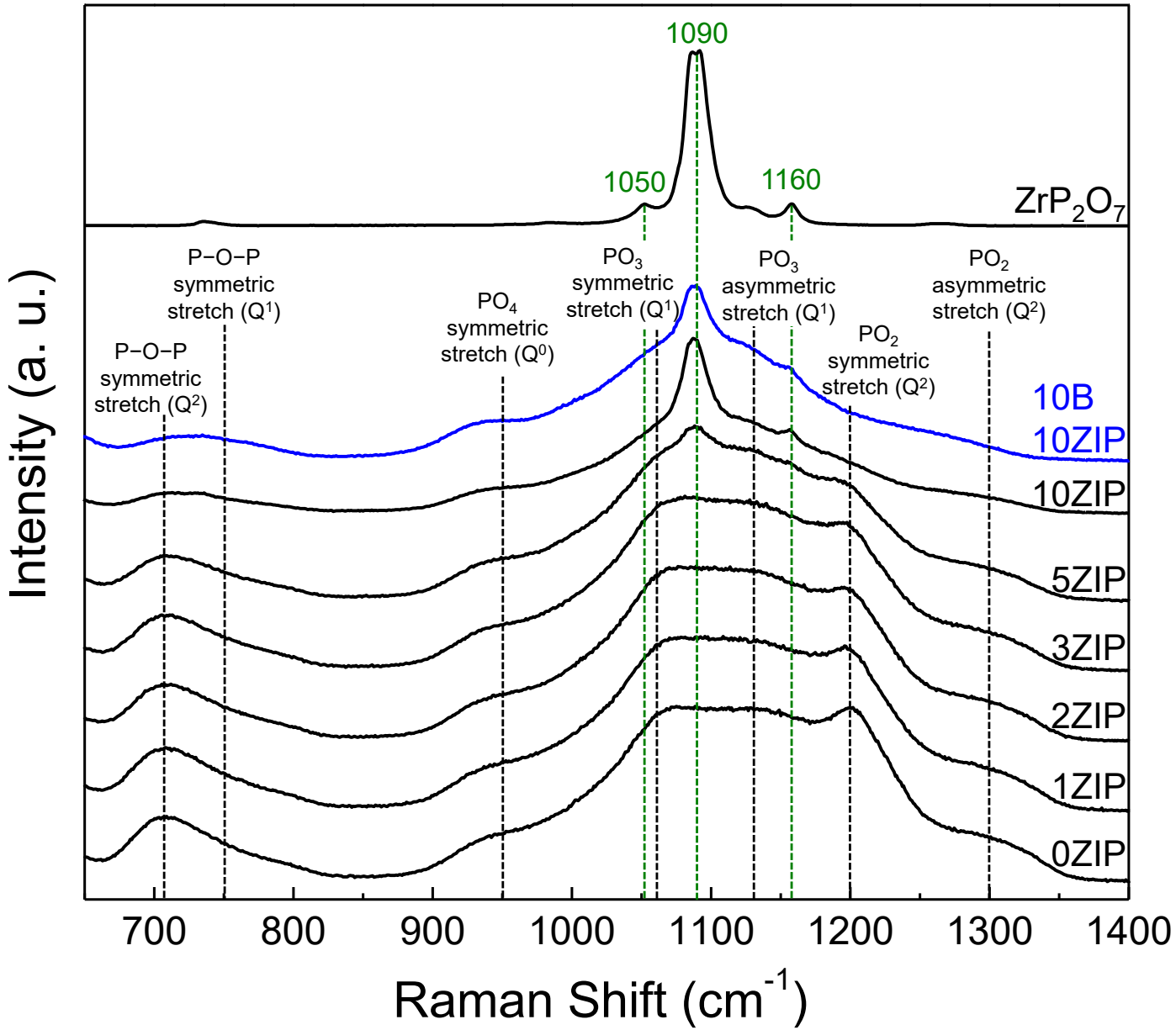
Teflon vessel

Leaching rate of Fe and P



No Zr was detected after immersion tests.

Raman spectra



Summary 4

- ZrP_2O_7 precipitates form by ZrO_2 addition.
- The compensation of P_2O_5 content due to the ZrP_2O_7 precipitation results in the shift in composition of IP glass matrix toward FeO-richer one.
- The FeO-richer composition of glass matrix is related to the decreases of $\Delta W/S$ and of P leaching rate.
- The fracture of ZrO_2-IP bulk samples after immersion tests (Type I) probably concerns with the selective dissolution remaining PO_4 Q^2 species (Heterogeneity of glass structure).

Summary – What's next?

Type A / Type B [by O/P ratio]

Degradable	Un-degradable
Type of modifier	Especially, iron phosphate glass
Classification	Modified by mono- and di-valent ions [BaO, CaO, Na_2O, K_2O etc.]
	Formation of ferri-hydrate layer for self (in-situ) protection
☐ Biomedical application ● Control of ion releasing ● Apatite formation etc.	*Similar components?, e.g, Al_2O_3, Ga_2O_3 etc.
	Homogeneity/heterogeneity of glass structure?