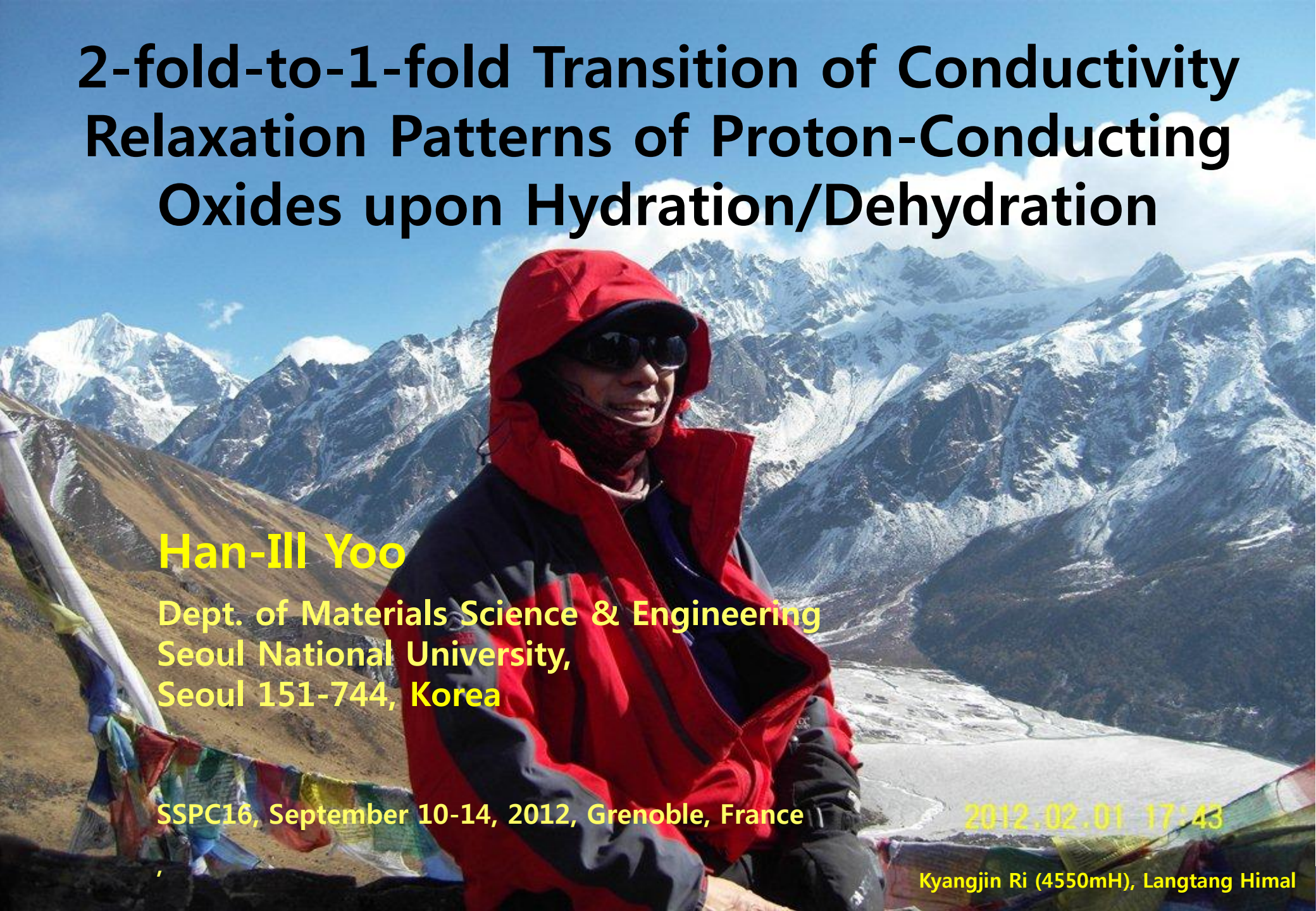
2-fold-to-1-fold Transition of Conductivity Relaxation Patterns of Proton-Conducting Oxides upon Hydration/Dehydration



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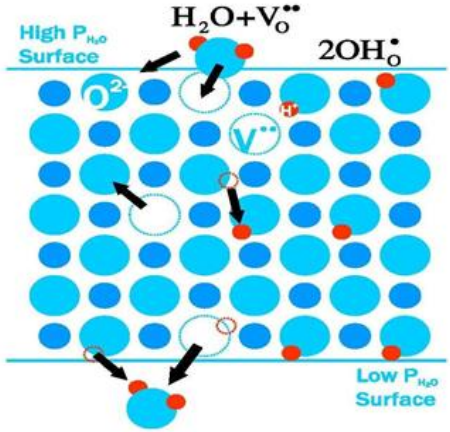
Conventional Interpretation

- **Thermodynamics**

$$H_2O(g) + V_O^{\bullet\bullet} + O_O^{X} \rightleftarrows 2OH_O^{\bullet} : \quad K_W = \frac{[OH_O^{\bullet}]^2}{a_{H_2O}[V_O^{\bullet\bullet}][O_O^{X}]}$$

$$\left(H_2O(g) + V_O^{\bullet\bullet} \rightleftarrows O_O^{X} + 2H_i^{\bullet} \quad : K_W' = \frac{[O_O^{X}][H_i^{\bullet}]^2}{a_{H_2O}[V_O^{\bullet\bullet}]} \right)$$



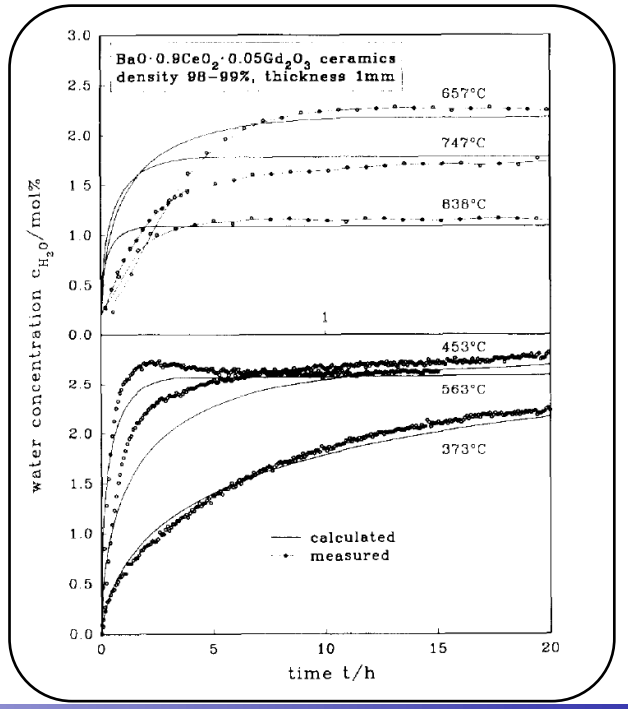
- **Kinetics**

Chemical diffusion of H_2O;

Ambipolar diffusion of $2H^+ + O^{2-}$ (or $2H_i^{\bullet} + V_O^{\bullet\bullet}$)

$$J_{H_2O} = -\tilde{D}_{H_2O}\nabla C_{H_2O} = J_O = \frac{1}{2}J_H$$

Humidified Ar (TGA[1])

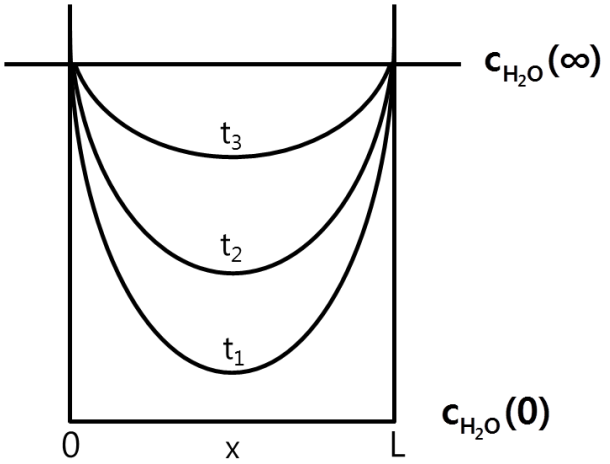


[1] *K. D. Kreuer et al., Solid State Ionics , 70/71 (1994) 278.*

Conventional Interpretation

- Equilibrium H_2O solubility via TGA

$$\frac{\partial c_{H_2O}}{\partial t} = \nabla(\tilde{D}_{H_2O}\nabla c_{H_2O}) \approx \tilde{D}_{H_2O}\nabla^2 c_{H_2O}$$



$$\frac{\Delta m(t)}{\Delta m(\infty)} = \frac{\bar{c}_{H_2O}(t) - c_{H_2O}(0)}{c_{H_2O}(\infty) - c_{H_2O}(0)} = 1 - f(\tau_{H_2O})\ ;$$

$$f(\tau_{H_2O}) = \frac{8}{\pi^2}\sum_{j=0}\frac{1}{(2j+1)^2}\exp\left[\frac{-(2j+1)^2 t}{\tau_{H_2O}}\right]\ ;\quad \tau_{H_2O} = \frac{L^2}{\pi^2 \tilde{D}_{H_2O}}$$

$$c_{H_2O}^{(sat)} = \frac{m_0 + \Delta m(\infty)}{M_{H_2O} V_0}$$

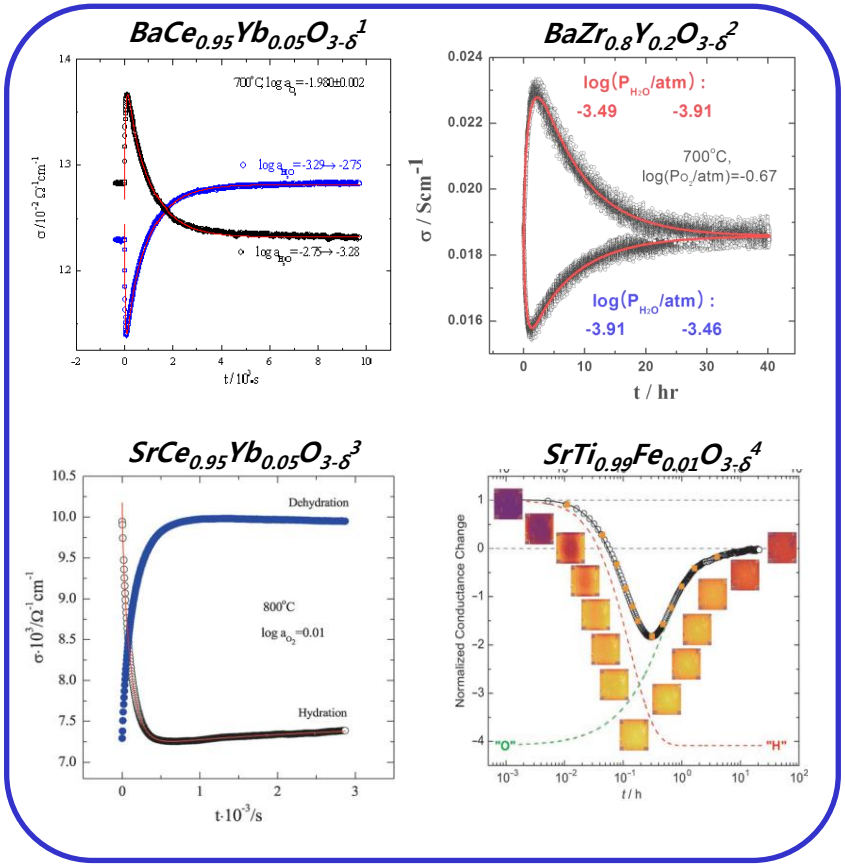
(M_{H_2O} = molar weight of H_2O (18 g/mol)
V_0 = Sample volume
m_0 = Initial water content (=0))

$$\Rightarrow\ K_W = \exp\left(-\frac{\Delta G^o_{Hyd}}{RT}\right)\ ;\quad \Delta H^o_{Hyd} = \left[\frac{\partial(\Delta G^o_{Hyd}/T)}{\partial(1/T)}\right]_{C^{(sat)}_{H_2O}}\ ;\quad \Delta S^o_{Hyd} = -\left[\frac{\partial \Delta G^o_{Hyd}}{\partial T}\right]_{C^{(sat)}_{H_2O}}$$

Conflicting Observations

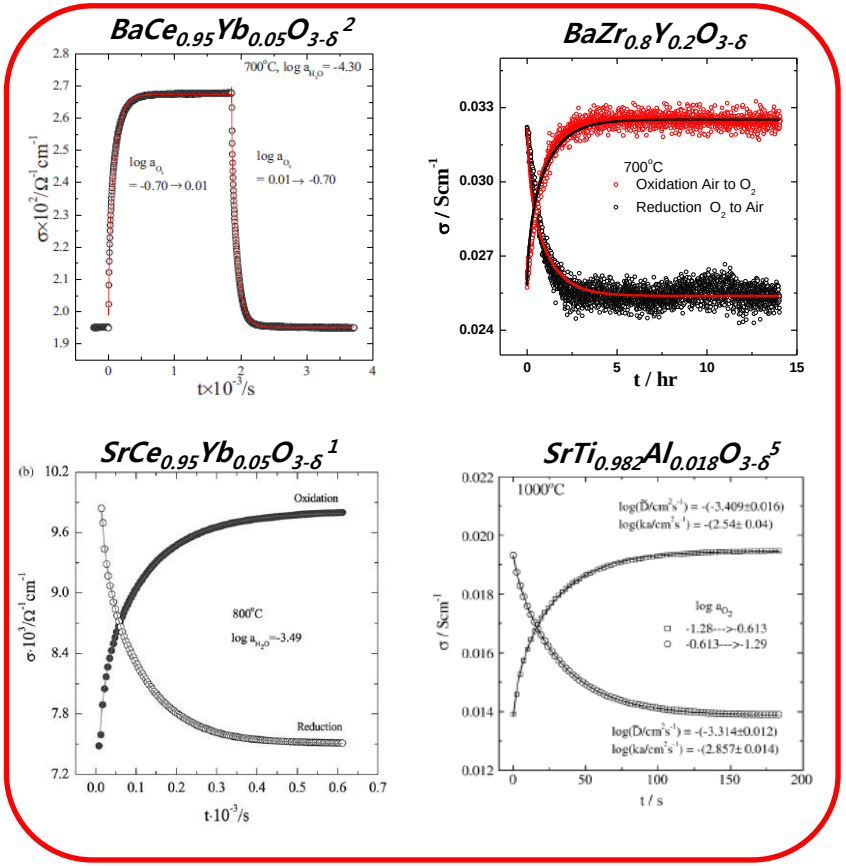
Conductivity relaxation

• Hydration/dehydration ($\nabla\mu_{H_2O}\neq0$, $\nabla\mu_O=0$)



2-fold non-monotonic

• Oxidation/reduction ($\nabla\mu_{H_2O}=0$, $\nabla\mu_O\neq0$)



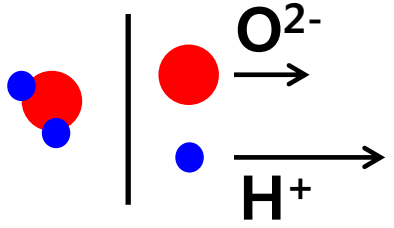
1-fold monotonic

[1]H.-I. Yoo, J.-K. Kim, and C.-E. Lee, J. Electrochem. Soc., 156 (2009) B66-B73. [2]J. I. Yeon , H. -I. Yoo*, Solid State Ionics, 181(2010) 1323.
[3]H.-I. Yoo, J.-Y. Yoon, J.-S. Ha, and C.-E. Lee, Phys. Chem. Chem. Phys., 10 (2008) 974-982.
[4]J. H. Yu, J.-S. Lee, J .Maier, Angew. Chem. Int. Ed. 46 (2007) 1. [5]C.-J. Shin, H.-I. Yoo*, Solid state Ionics, 178(2007) 1089.

New Interpretation

- **2-fold relaxation** due to the decoupled 2-fold chem. diff. of H and O

$$H_2O \begin{cases} H + h^{\bullet} \rightleftarrows H_i^{\bullet} & \{H^+, h^+\} \\ O + V_O^{\bullet\bullet} \rightleftarrows O_O^{X} + 2h^{\bullet} & \{O^{2-}, 2h^+\} \end{cases}$$



- **Quantification**

-Fundamental equation of motion: $J = LX$

$$\begin{pmatrix} J_{O^{2-}} \\ J_{H^+} \\ J_{h^+} \end{pmatrix} = - \begin{pmatrix} \frac{\sigma_{O^{2-}}}{4F^2} & 0 & 0 \\ 0 & \frac{\sigma_{H^+}}{F^2} & 0 \\ 0 & 0 & \frac{\sigma_{h^+}}{F^2} \end{pmatrix} \begin{pmatrix} \nabla\eta_{O^{2-}} \\ \nabla\eta_{H^+} \\ \nabla\eta_{h^+} \end{pmatrix}$$

Note: $L_{ij} = L_{ij}\delta_{ij}$ *(no Onsagerian cross effect)*

If Onsagerian, 6 independent L_{ij}

-Transform of forces: $X' = \alpha X$

$$\begin{pmatrix} \nabla\mu_O \\ \nabla\mu_{H_2O} \\ \nabla\eta_{h^+} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 2 \\ 1 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \nabla\eta_{O^{2-}} \\ \nabla\eta_{H^+} \\ \nabla\eta_{h^+} \end{pmatrix}$$

-Transform of fluxes: $J' = \tilde{\alpha}^{-1}J = \tilde{\alpha}^{-1}L\alpha^{-1}X' = L'X'$

$$\begin{pmatrix} J'_{O^{2-}} \\ J'_{H^+} \\ J'_{h^+} \end{pmatrix} = \begin{pmatrix} 1 & -1/2 & 0 \\ 0 & 1/2 & 0 \\ -2 & 1 & 1 \end{pmatrix} \begin{pmatrix} J_{O^{2-}} \\ J_{H^+} \\ J_{h^+} \end{pmatrix} = \begin{pmatrix} J_O \\ J_{H_2O} \\ I/F \end{pmatrix}$$

New Interpretation

-Ad hoc condition: Open-circuit condition

$$I/F=\Sigma z_i J_i=0 \Rightarrow \nabla\eta_{h^+} = -t_{H^+}\nabla\mu_H+\frac{t_{O^{2-}}}{2}\nabla\mu_O = -\frac{t_{H^+}}{2}\nabla\mu_{H_2O}+\frac{t_{O^{2-}}+t_{H^+}}{2}\nabla\mu_O$$

-Chemical diffusion fluxes

$$-J_v = J_O = -\frac{\sigma_{O^{2-}} t_{h^+}}{4F^2}\nabla\mu_O - \frac{\sigma_{O^{2-}} t_{H^+}}{4F^2}\nabla\mu_{H_2O}$$

$$J_i = J_H = \frac{\sigma_{H^+} t_{h^+}}{2F^2}\nabla\mu_O - \frac{\sigma_{H^+}(1-t_{H^+})}{2F^2}\nabla\mu_{H_2O}$$

-4 D_{kK}'s ($\tilde{k}$=i,v K=O,H)

$$\tilde{D}_{vO}=\frac{\sigma_{O^{2-}} t_{h^+}}{4F^2}\left|\frac{\partial\mu_O}{\partial c_v}\right|_{\nabla\mu_{H_2O}=0} ; \quad \tilde{D}_{vH}=\frac{\sigma_{O^{2-}} t_{H^+}}{4F^2}\left|\frac{\partial\mu_{H_2O}}{\partial c_v}\right|_{\nabla\mu_O=0}$$

$$\tilde{D}_{iO}=\frac{\sigma_{H^+} t_{h^+}}{2F^2}\left|\frac{\partial\mu_O}{\partial c_i}\right|_{\nabla\mu_{H_2O}=0} ; \quad \tilde{D}_{iH}=\frac{\sigma_{H^+}(1-t_{H^+})}{2F^2}\left|\frac{\partial\mu_{H_2O}}{\partial c_i}\right|_{\nabla\mu_O=0}$$

-Hydration Kinetics ($\nabla\mu_O = 0; \nabla\mu_{H_2O} \neq 0$)

$$\frac{\partial c_v}{\partial t} = -\nabla J_v \simeq \tilde{D}_{vH}\nabla^2 c_v$$

$$\frac{\partial c_i}{\partial t} = -\nabla J_i \simeq \tilde{D}_{iH}\nabla^2 c_i$$

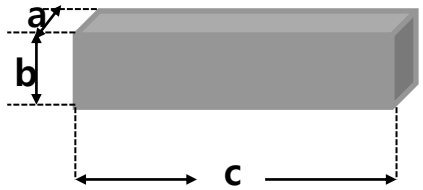
-Oxidation Kinetics ($\nabla\mu_O \neq 0; \nabla\mu_{H_2O} = 0$)

$$\frac{\partial c_v}{\partial t} = -\nabla J_v \simeq \tilde{D}_{vO}\nabla^2 c_v$$

$$\frac{\partial c_i}{\partial t} = -\nabla J_i \simeq \tilde{D}_{iO}\nabla^2 c_i \approx 0 \ (\because \partial\mu_O / \partial c_i = 0)$$

New Interpretation

-Closed-form solution



$$\bar{c}_k - c_{k,0} = (c_{k,\infty} - c_{k,0})[1 - f(\tau_k)] \qquad (k = i, v)$$

$$f(\tau_k) = \prod_{\chi=a,b,c} \left(\sum_{l=1}^{\infty} \frac{2L^2 \exp\left(-\frac{\beta_l^2 D_{kH} t}{\chi^2} \right)}{\beta_l^2 (\beta_l^2 + L^2 + L)} \right)$$

-Conductivity relaxation upon hydration

Carriers: $2[V_O^{\cdot\cdot}] + [H_i^{\cdot}] + [h^{\cdot}] = [A_c']$

or $2c_v + c_i + p = m_A$

Conducitivty: $\bar{\sigma} = \bar{\sigma}_v + \bar{\sigma}_i + \bar{\sigma}_h$

$= 2\bar{\sigma}_v eu_v + \bar{c}_i eu_i + \bar{p} eu_h$

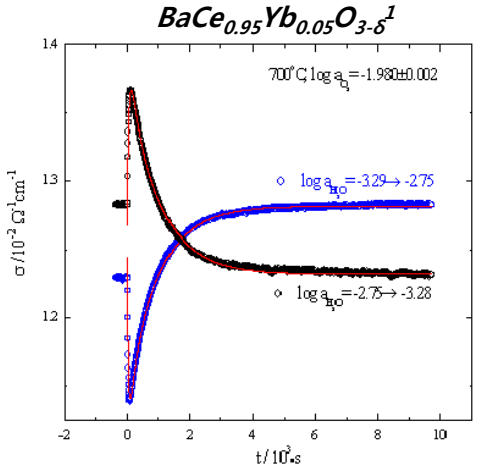
$= m_A eu_h - 2e(u_h - u_v)\bar{c}_v - e(u_h - u_i)\bar{c}_i$

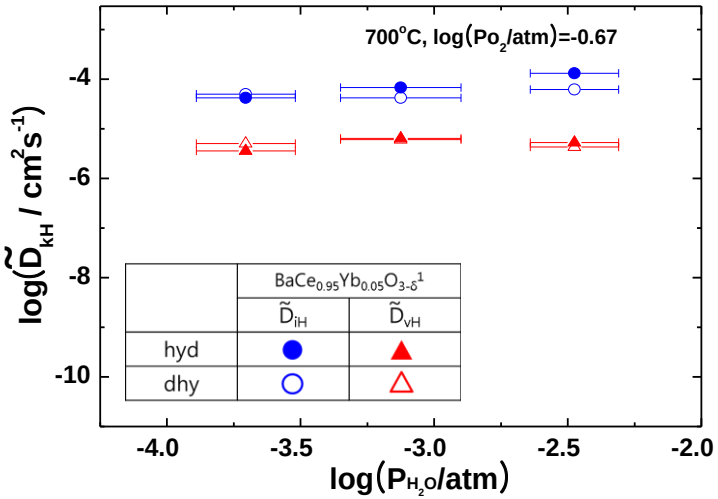
$$\bar{\sigma}(t) - \sigma_0 = -\lambda_{h,i}(\bar{c}_i - c_{i,0}) - \lambda_{h,v}(\bar{c}_v - c_{v,0})$$

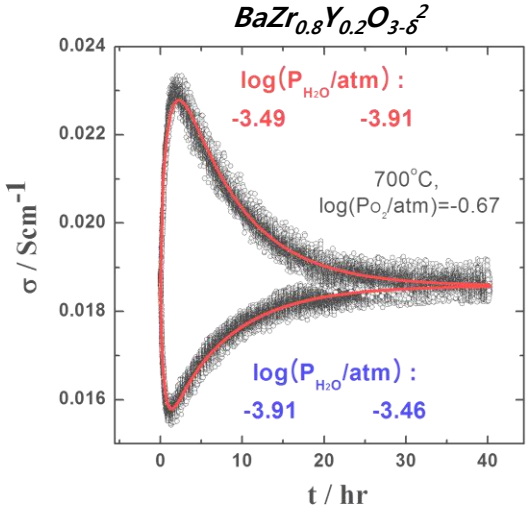
$$\lambda_{h,i} = e_0(u_h - u_i) \; ; \; \lambda_{h,v} = 2e_0(u_h - u_v)$$

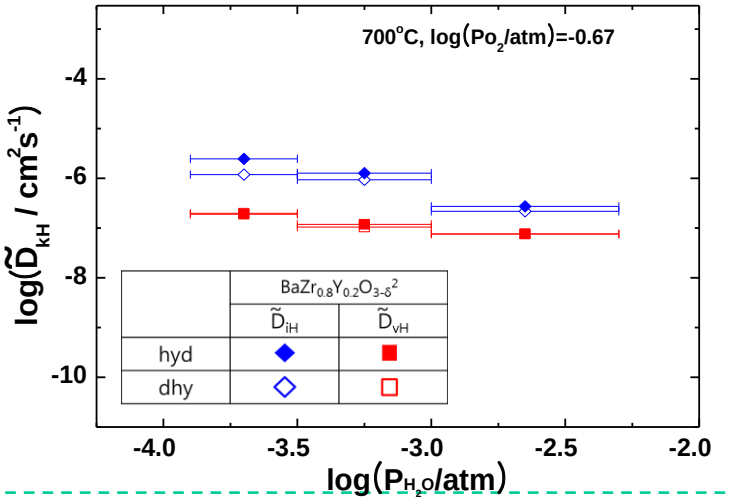
New Interpretation

- **In reality**









[1]H.-I. Yoo, J.-K. Kim, and C.-E. Lee, J. Electrochem. Soc., 156 (2009) B66-B73. [2]J. I. Yeon , H. -I. Yoo*, Solid State Ionics, 181(2010) 1323.

New Interpretation

- **Mass-relaxation**

$$\frac{m(t)-m_0}{V_0} = \omega_i(\bar{c}_i - c_{i,0}) - \omega_v(\bar{c}_v - c_{v,0})$$

where ω_i=1 g/mol ; ω_v=16 g/mol

- **Uncomfortable truth**

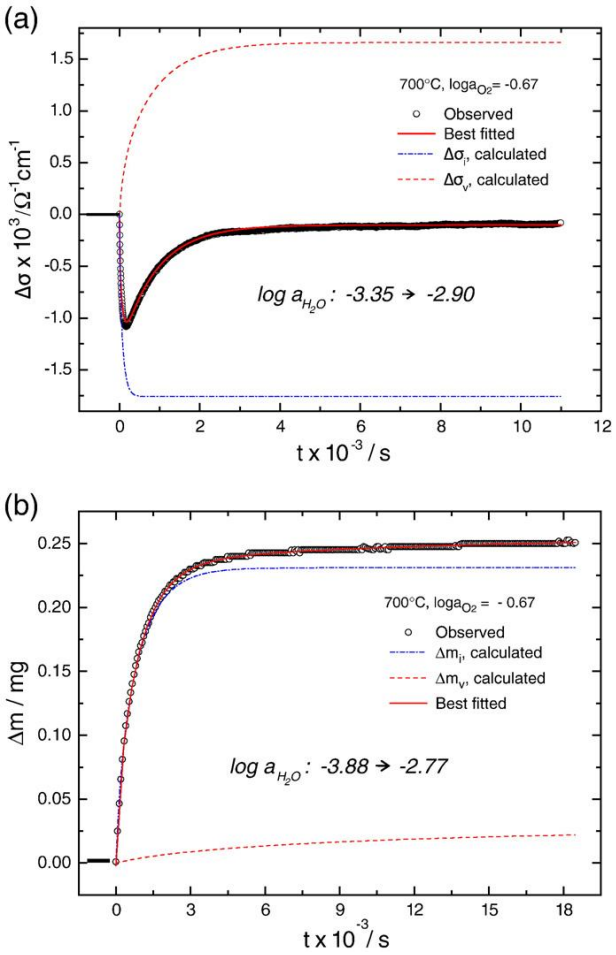
$$\text{If } (c_{i,\infty}-c_{i,0}) = 2(c_{v,\infty}-c_{v,0}) = 2\left(c_{H_2O,\infty}^{sat}-c_{H_2O,0}^{sat}\right),$$

$$\text{then } R_m = \frac{\omega_i(\bar{c}_{i,\infty}-c_{i,0})}{-\omega_v(\bar{c}_{v,\infty}-c_{v,0})} = \frac{2\omega_i}{\omega_v} \equiv \frac{1}{8}.$$

$$\text{But } R_m = \begin{cases} 9 & @\ 700°C \\ 11 & @\ 800°C \end{cases}$$

More H gets in!!

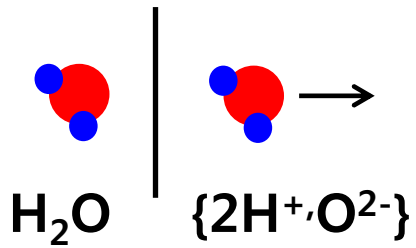
- **Reality[1]**



[1] *H.-I. Yoo, J.-I. Yeon, J.-K. Kim, Solid State Ionics, 180 (2009) 1443.*

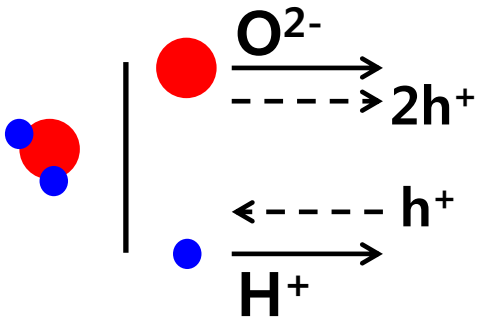
Unified Interpretation

- **Apparent conflict so far**



Conventional view:

Chem. Diffusion of H_2O



New view:

Decoupled Chem. Diff. of H and O

- **Two extreme representations of the same phenomenon?**

Unified Interpretation

- Eqns of motion under $\nabla\mu_O=0$; $\nabla\mu_{H_2O}\neq 0$

$$J_O = -J_v = -\frac{\sigma_{O^{2-}} t_{H^+}}{4F^2}\nabla\mu_{H_2O} \quad ; \quad \tilde{D}_{vH} = \frac{\sigma_{O^{2-}} t_{H^+}}{4F^2}\left|\frac{\partial\mu_{H_2O}}{\partial c_v}\right|_{\nabla\mu_O=0}$$

$$J_H = J_i = -\frac{\sigma_{H^+}(1-t_{H^+})}{2F^2}\nabla\mu_{H_2O} \quad ; \quad \tilde{D}_{iH} = \frac{\sigma_{H^+}(1-t_{H^+})}{2F^2}\left|\frac{\partial\mu_{H_2O}}{\partial c_i}\right|_{\nabla\mu_O=0}$$

✓ Note:

$1 - t_{H^+} = t_{O^{2-}} + t_{h^+}$;

ΘΔic factors

- As $t_{h^+}\rightarrow 0$ (with decreasing μ_O)

$$J_H = -\frac{\sigma_{H^+} t_{O^{2-}}}{2F^2}\nabla\mu_{H_2O} = 2J_O$$

Ambipolar diffusion of $2H^+$ and O^{2-}

$$\therefore J_{H_2O} = -\frac{\sigma_{O^{2-}} t_{H^+}}{4F^2}\nabla\mu_{H_2O} = -\frac{\sigma_{O^{2-}} t_{H^+}}{4F^2}\left|\frac{\partial\mu_{H_2O}}{\partial c_{H_2O}}\right|\nabla c_{H_2O} = -\tilde{D}_{H_2O}\nabla c_{H_2O}$$

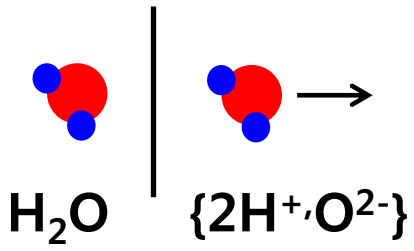
- As $p\rightarrow 0$

$2\delta c_v + \delta c_i = 0$ for charge neutrality

$$\tilde{D}_{vH} = \tilde{D}_{iH} = \frac{\sigma_{O^{2-}} t_{H^+}}{4F^2}\left|\frac{\partial\mu_{H_2O}}{\partial c_v}\right| = \frac{\sigma_{O^{2-}} t_{H^+}}{4F^2}\left|\frac{\partial\mu_{H_2O}}{\partial c_{H_2O}}\right| = \tilde{D}_{H_2O}$$

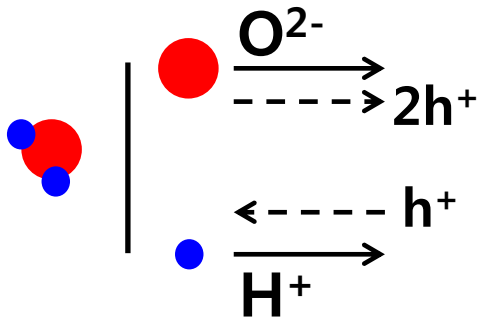
Unified Interpretation

- **Apparent conflict**



Conventional view:

Chem. Diffusion of H_2O



New view:

Decoupled Chem. Diff. of H and O

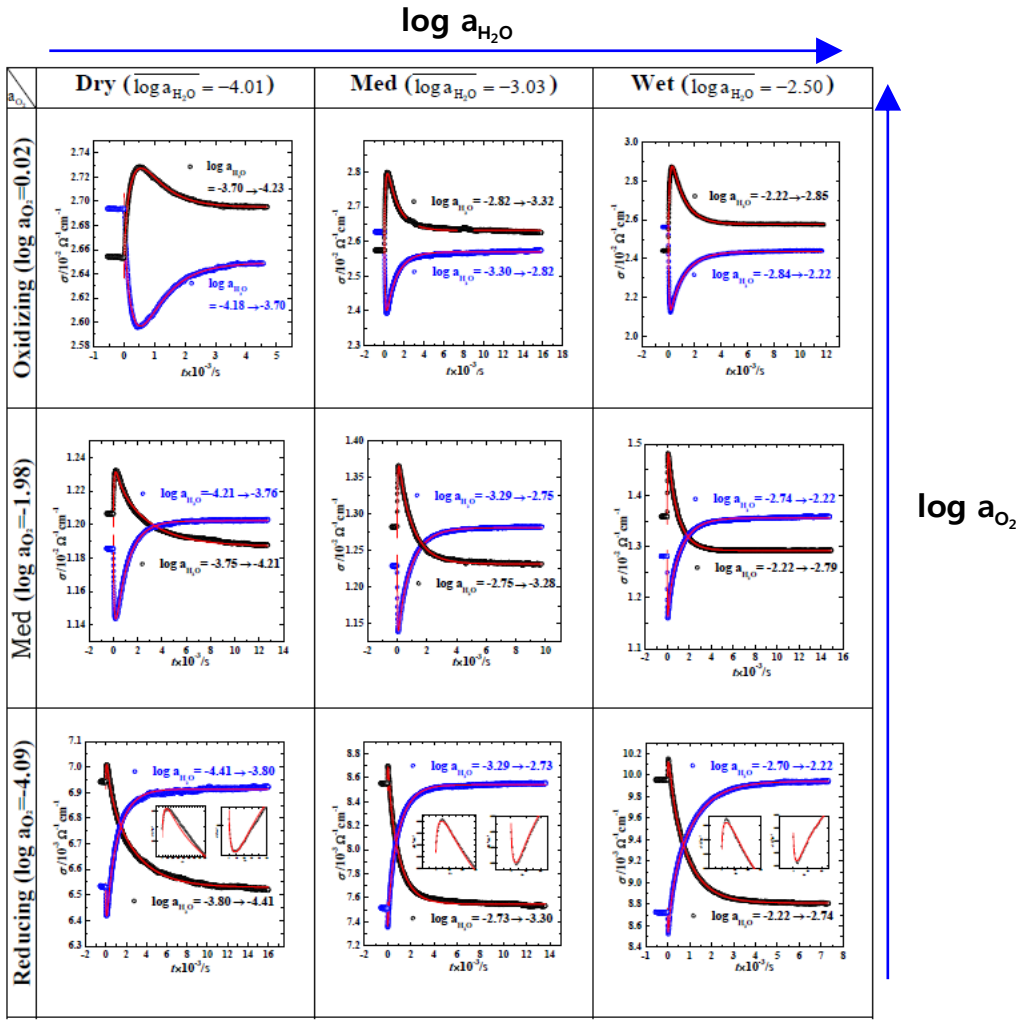
- **Gradual transition from 2-fold ($\tilde{D}_{vH} \neq \tilde{D}_{iH}$) to 1-fold ($\tilde{D}_{vH} = \tilde{D}_{iH} = \tilde{D}_{H_2O}$) as $t_{h^+} \rightarrow 0$**

$$\{ \tau_{H_2O} \} \leftarrow \{ \tau_{iH}, \tau_{vH} \}$$

$$t_{h^+}, \mu_O$$

Experimental Demonstration

- Earlier hint from $BaCe_{0.95}Yb_{0.05}O_{3-\delta}$[1]



-> The more reducing, the less 2-fold characteristic!

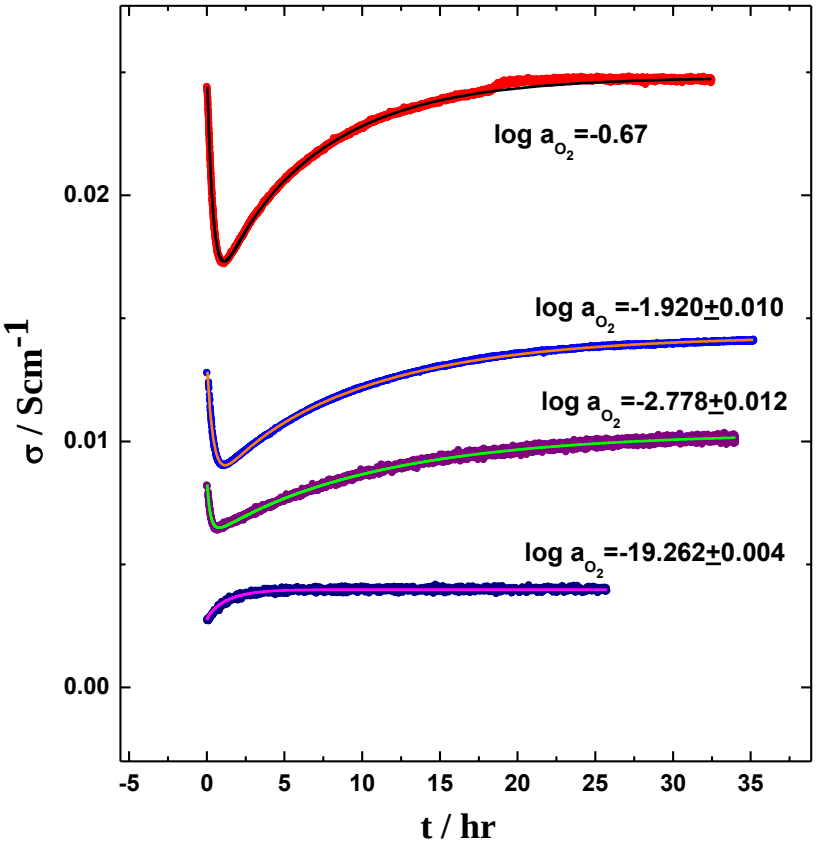
[1] *H.-I. Yoo, J.-K. Kim, and C.-E. Lee, J. Electrochem. Soc., 156 (2009) B66-B73.*

Experimental Demonstration

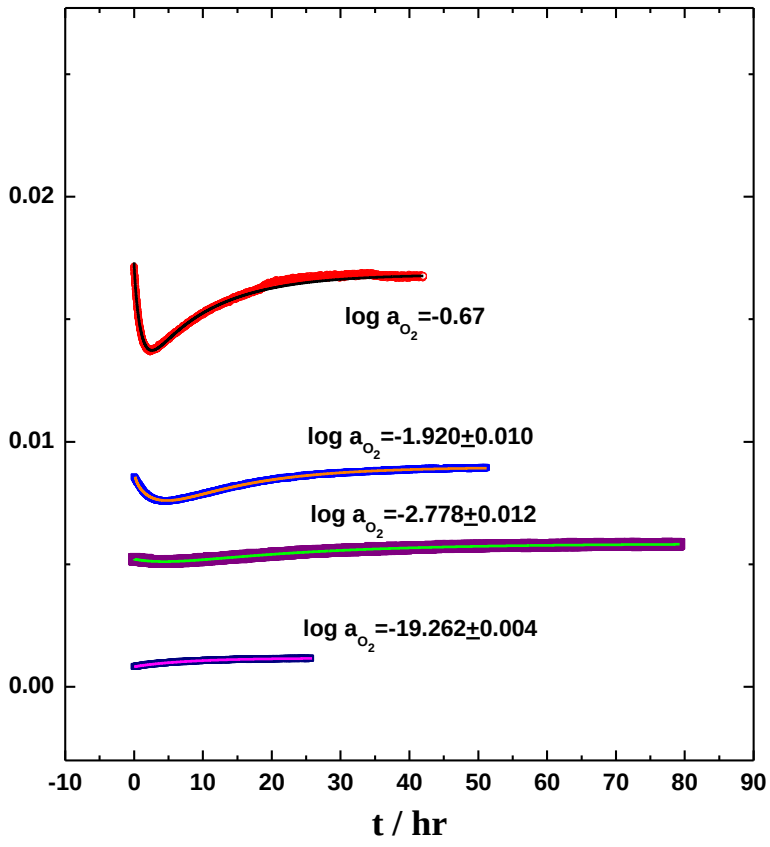
- **Unambiguous demonstration with $BaZr_{0.8}Y_{0.2}O_{3-\delta}$**

-Overview @ 700°C, $\log a_{H_2O} = -(2.80 \pm 0.10) \rightarrow -(2.30 \pm 0.18)$

BZY20+0 w/o NiO



BZY20+1 w/o NiO

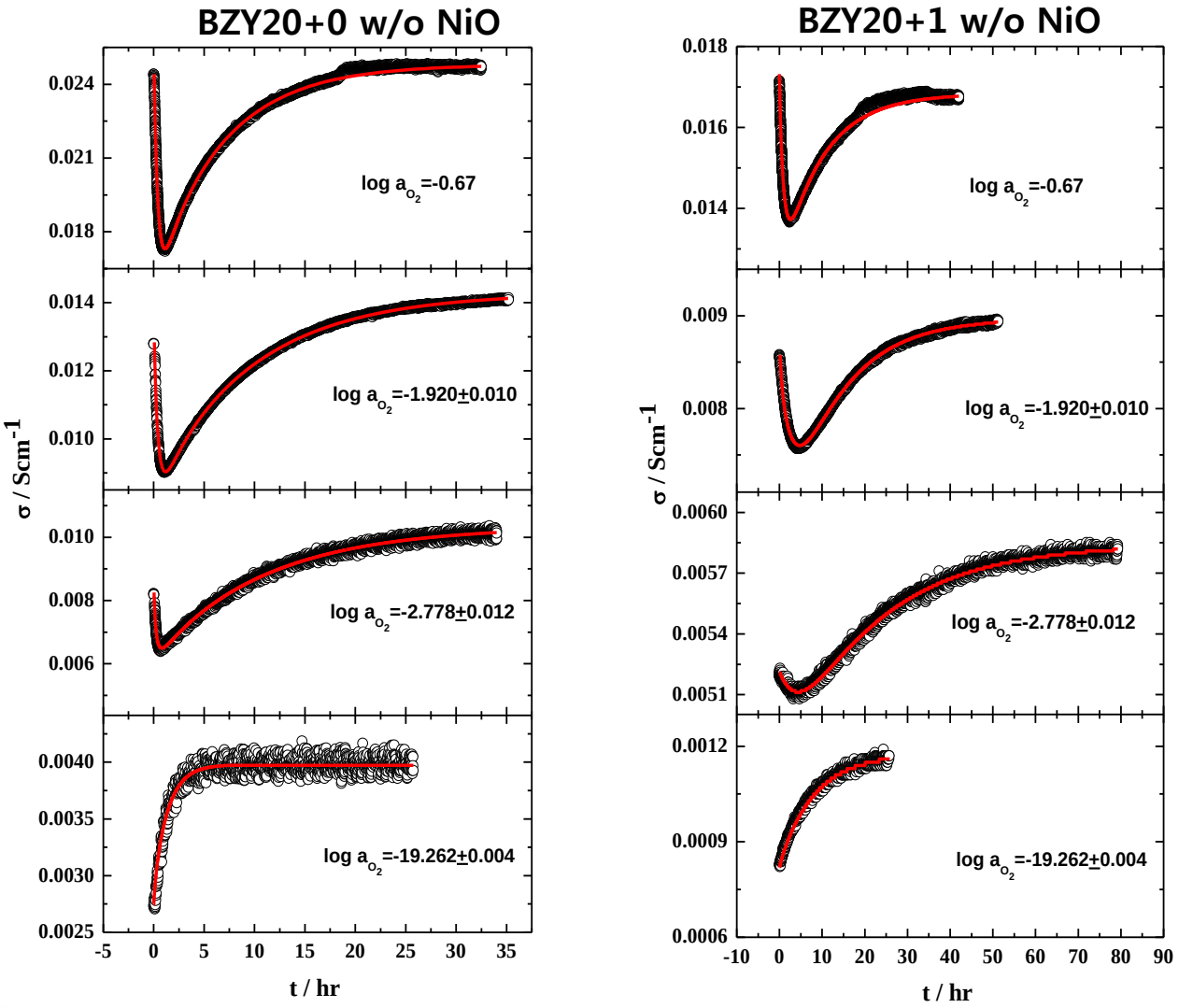


➢ *Effect of sintering aid*

➢ *Gradual transition from 2-fold to 1-fold as μ_O decreases !*

Experimental Demonstration

-Exploded view @ 700°C, $\log a_{H_2O}$ = -(2.80±0.10) → -(2.30±0.18)

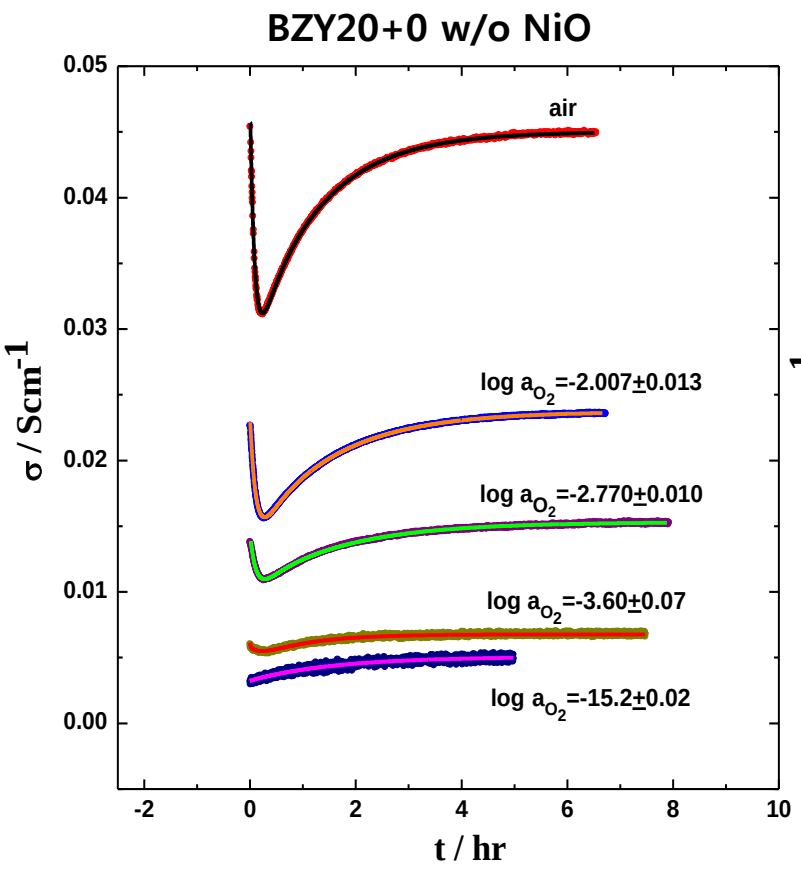


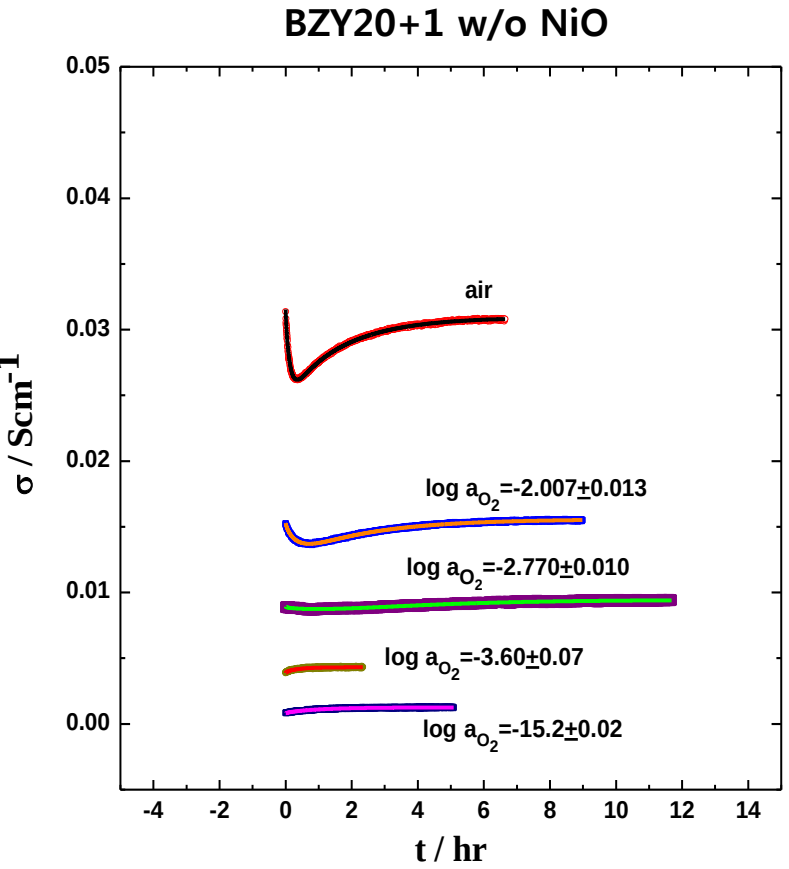
- Solid lines as calculated.

Experimental Demonstration

- **Unambiguous demonstration @ another temperature**

-Overview @ 800°C, $\log a_{H_2O} = -(2.88 \pm 0.02) \rightarrow -(2.22 \pm 0.02)$



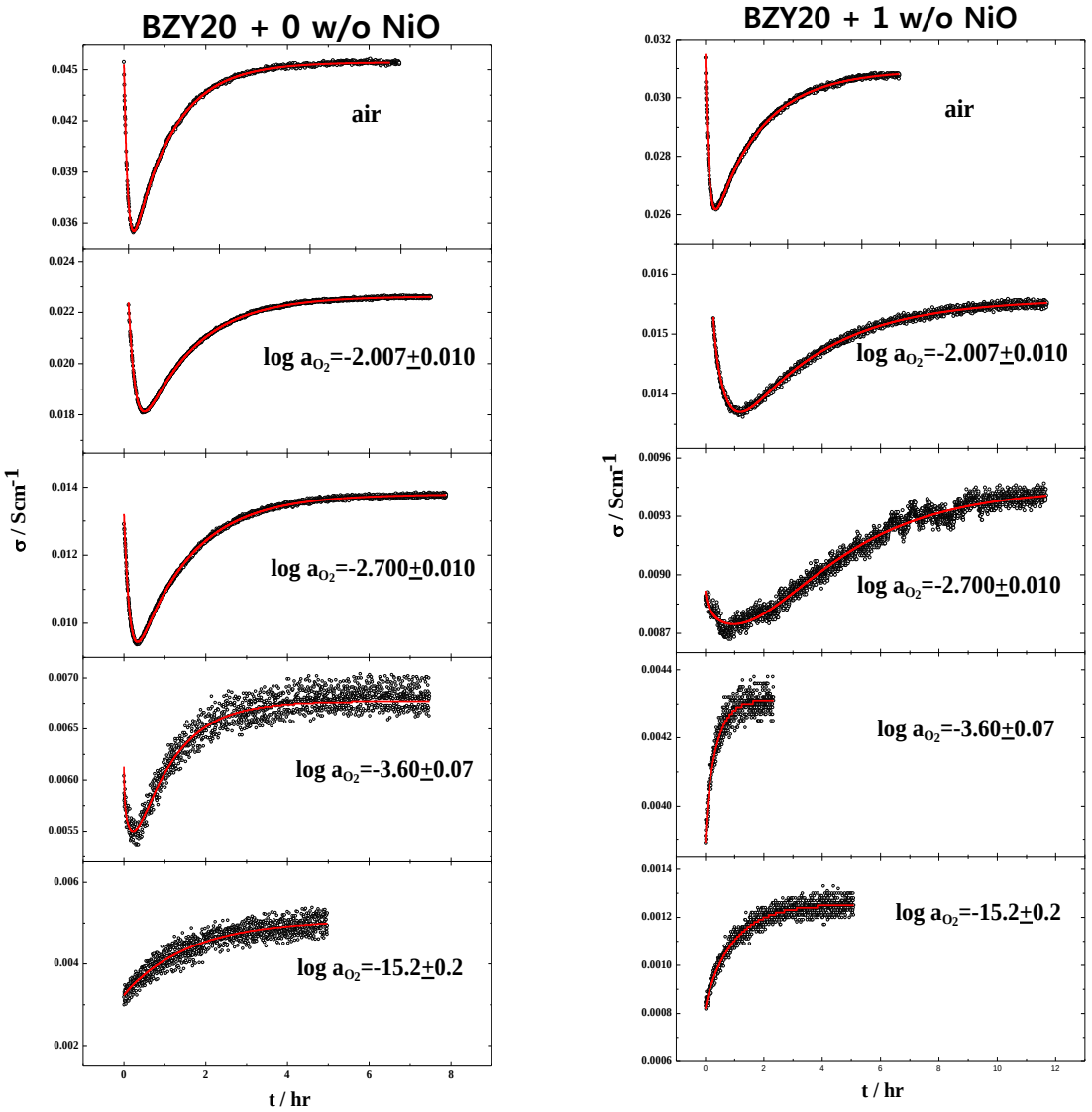


➢ *Effect of sintering aid*

➢ *Gradual transition from 2-fold to 1-fold as μ_O decreases !*

Experimental Demonstration

-Exploded view @ 800°C, $\log a_{H_2O}$ = -(2.88±0.02) → -(2.22±0.02)



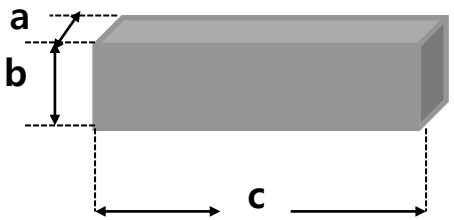
- **Solid lines as calculated.**

Quantitative Analysis

- **1-fold solution**

$$J_{H_2O} = -\tilde{D}_{H_2O}\nabla c_{H_2O} \; ; \; \tilde{D}_{H_2O} = \frac{\sigma_{O^{2-}} t_{H^+}}{4F^2}\left|\frac{\partial \mu_{H_2O}}{\partial c_{H_2O}}\right|$$

$$\frac{\partial c_{H_2O}}{\partial t} \simeq \tilde{D}_{H_2O}\nabla^2 c_{H_2O}$$



Bar-shaped specimen ,

a x b x c

- **σ-relaxation**

$$\sigma = 2eu_v c_v + eu_i c_i \quad (\because t_{h+}=0)$$
$$= 2e(u_v+u_i)c_v \quad (\because c_i = 2c_v)$$

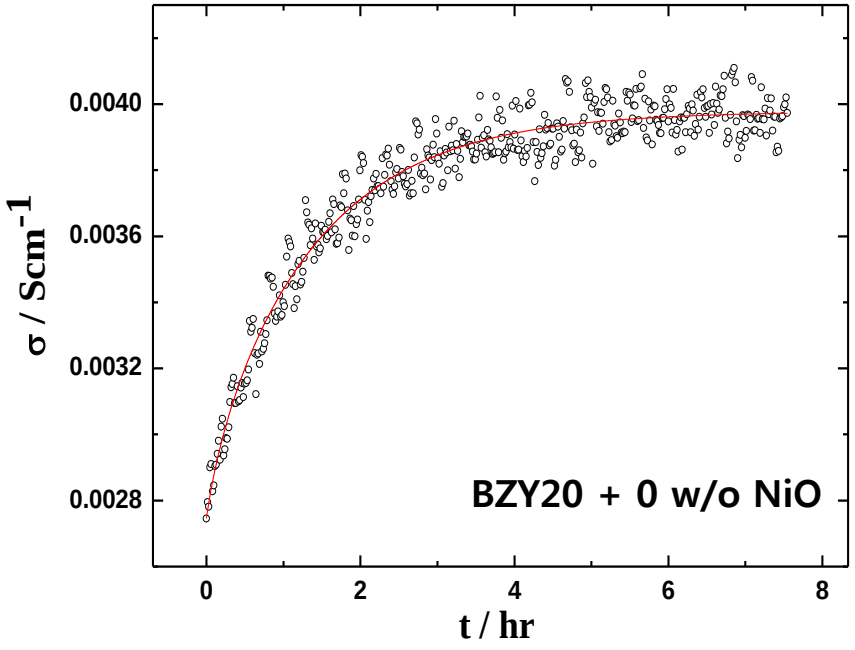
$$\bar{\sigma}(t) = 2e(u_v+u_i)\bar{c}_v(t)$$
$$= 2e(u_v+u_i)\bar{c}_{H_2O}(t)$$

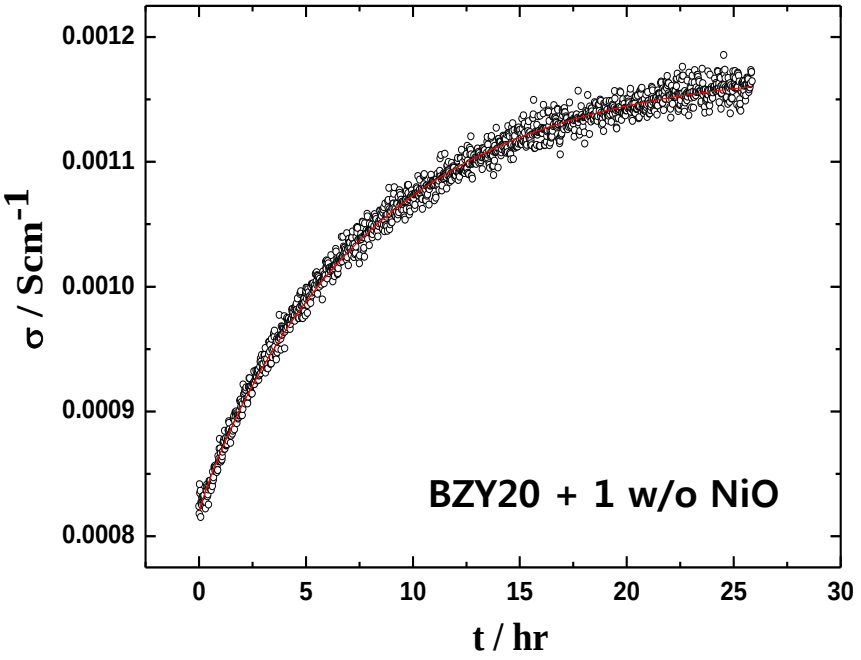
$$\bar{c}_{H_2O} - c_{H_2O,0} = (c_{H_2O,\infty} - c_{H_2O,0})[1 - f(\tau_{H_2O})] \; ; \; f(\tau_{H_2O}) = \prod_{\chi=a,b,c}\left(\sum_{l=1}^{\infty}\frac{2L^2\exp\left(-\frac{\beta_l^2 D_{H_2O} t}{\chi^2}\right)}{\beta_l^2(\beta_l^2+L^2+L)}\right)$$

Quantitative Analysis

- Analysis of 1-fold $\bar{\sigma}(t)$: $\Delta\bar{\sigma}(t)=\Delta\sigma_{\infty,0}[1-f(\tau_{H_2O})]$

@ 700°C, log a_{O_2} =(-19.262±0.004) , log a_{H_2O}= (-2.80±0.10) → (-2.30±0.18)



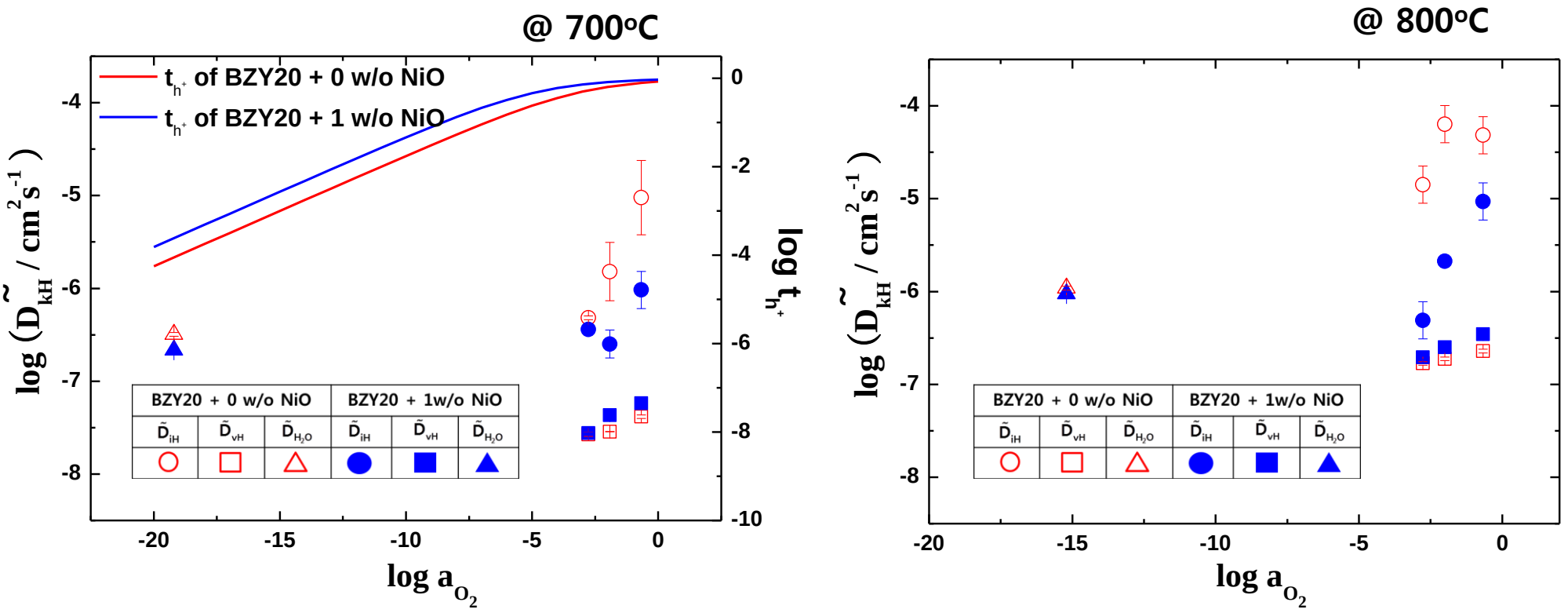


	BZY20 + 0 w/o NiO
$\tilde{D}_{H_2O}$	(3.2±0.2)x10^{-7}cm^2/s

	BZY20 + 1 w/o NiO
$\tilde{D}_{H_2O}$	(2.16±0.08)x10^{-7}cm^2/s

Quantitative Analysis

- H_2O Chemical Diffusivity

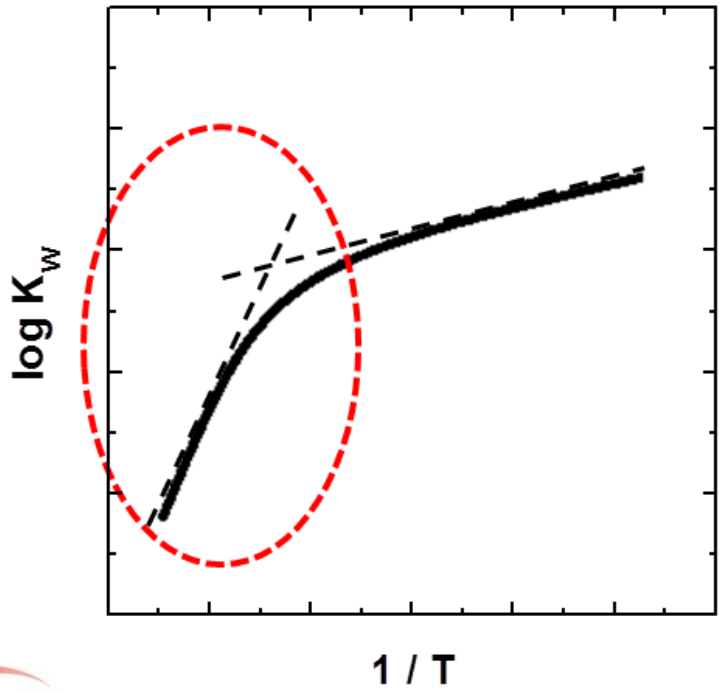


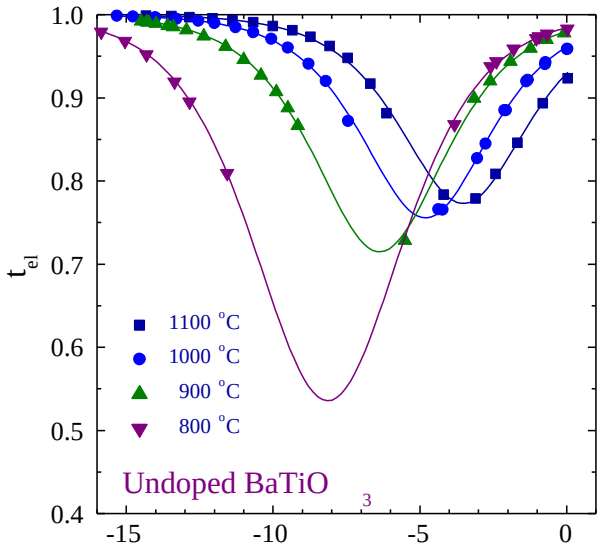
As $t_{h+} \rightarrow 0$,

$\tilde{D}_{iH} \neq \tilde{D}_{vH} \rightarrow \tilde{D}_{iH} = \tilde{D}_{vH} = \tilde{D}_{H_2O}$

Implications

- $\Delta m(\infty)$ at $t_{h^+} > 0 \neq \Delta m_{H_2O}$; $\Delta m(\infty)$ at $t_{h^+} \rightarrow 0 = \Delta m_{H_2O}$
- Saturation water solubility only at $t_{h^+} \rightarrow 0$
- High T slope or low T slope?: Where t_{h^+} smaller





∵ t_h tends to get smaller as T increases.

Conclusion

- **Hydration/Dehydration Kinetics ($\nabla\mu_O=0$; $\nabla\mu_{H_2O}\neq0$)**

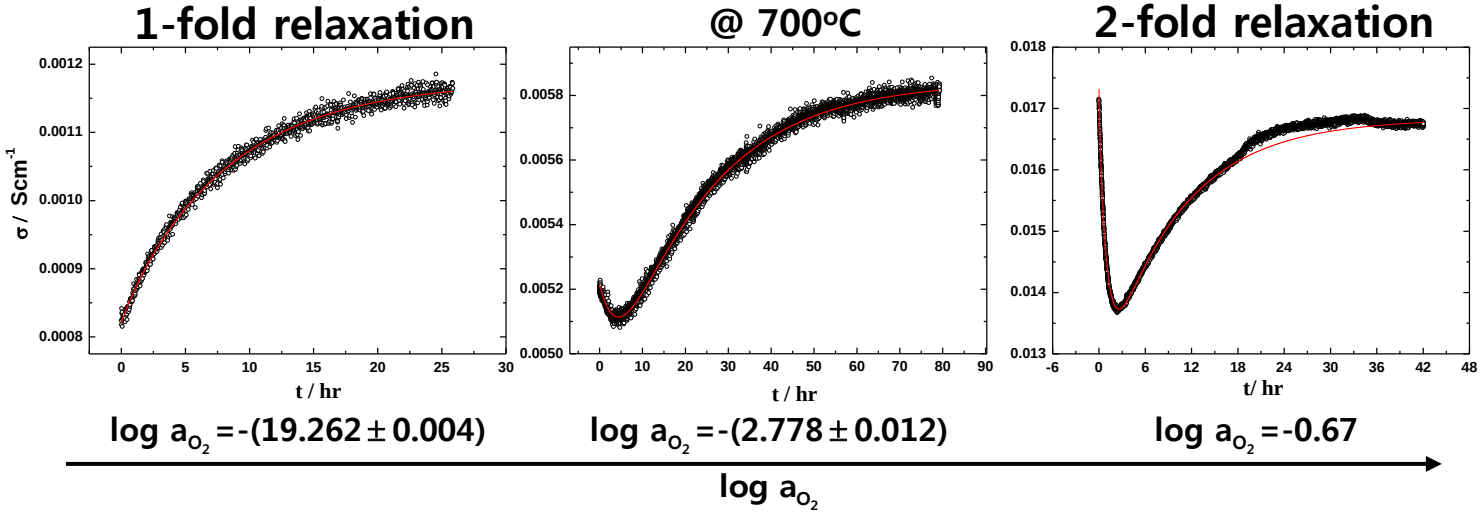
Chem. Diff. of H_2O:

$$\tilde{D}_{iH} = \tilde{D}_{vH} \ (=\tilde{D}_{H_2O})$$

as $t_{h+}\rightarrow 0$

Decoupled Chem. Diff. of H and O:

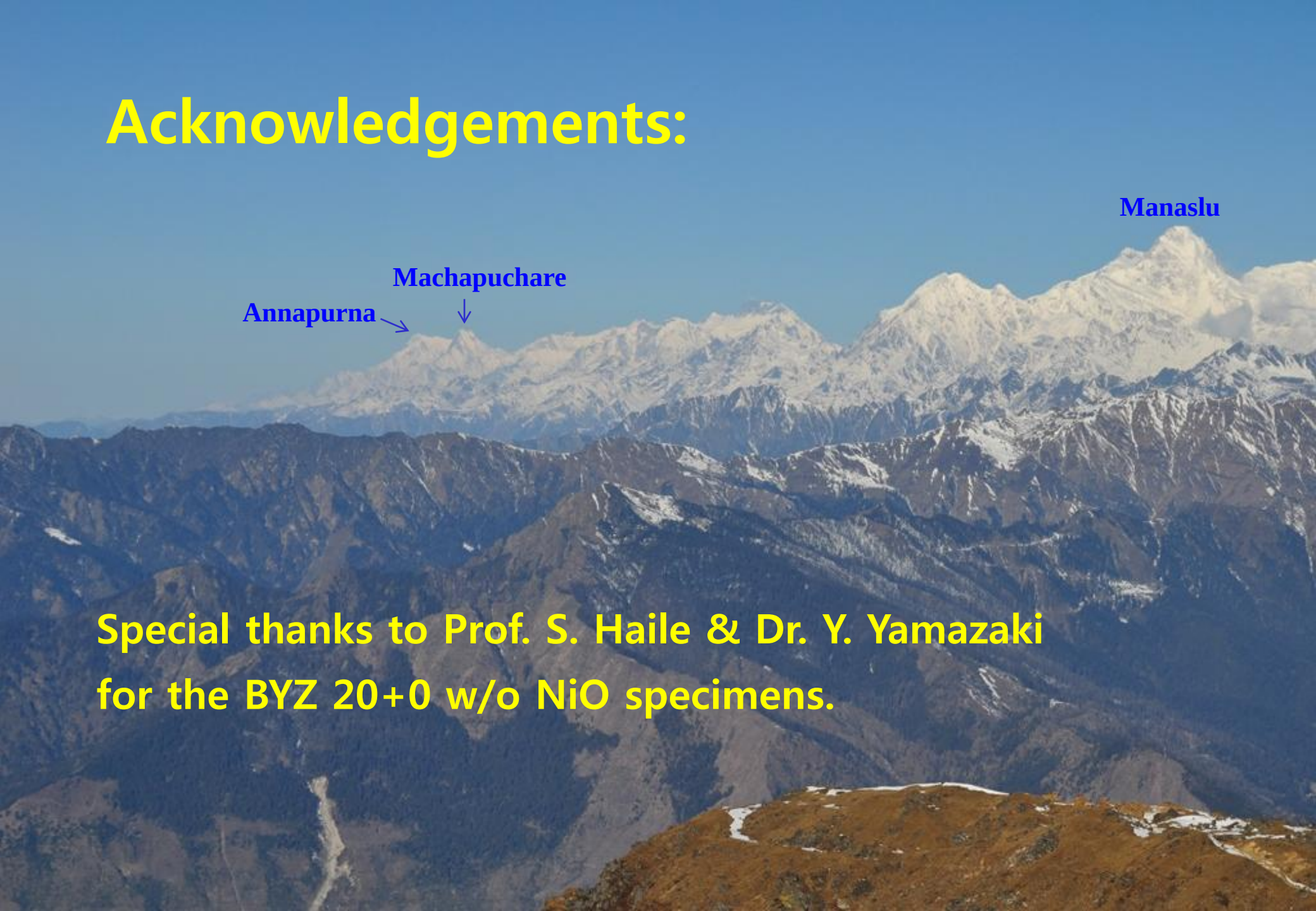
$$\tilde{D}_{iH} \neq \tilde{D}_{vH}$$



- **Saturation water solubility**

$$\Delta m(\infty) = M_{H_2O}c_{H_2O}^{(sat)} \ \text{ as } \ t_{h^+}\rightarrow 0 \ ; \ \Delta m(\infty) \neq M_{H_2O}c_{H_2O}^{(sat)} \ \text{ as } \ t_{h^+}>0$$

Acknowledgements:



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