# Defect Thermodynamics and Transport Properties of Proton Conducting Oxide $BaZr_{1-x}Y_xO_{3-\delta}$ (x≤0.1) Evaluated Based on Density Functional Theory Modeling

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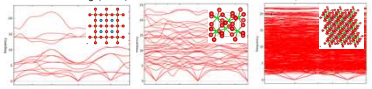
## First Principles-Based Modeling of Defect and Transport Properties for Proton Conducting Oxides

A first principles-based model was developed to describe defect chemistry and transport properties of the proton conducting oxide $BaZr_{1-x}Y_xO_{3-\delta}$ (x≤0.1) for solid oxide cell and other energy applications.[1]

### *Ab Initio* Thermodynamics [1-3]

cubic $BaZrO_3$ (PBE) monoclinic-$ZrO_2$ (LDA) $Y_4Zr_3O_{12}$ (PBEsol)



**Gas thermodynamics:**

$$\mu^{O/H}(T,p(gas)) = \frac{1}{2}\left[\begin{matrix} E_{DFT}(gas) \\ +(h^{gas}(T,p(gas)^0) - h^{gas}(T^0,p(gas)^0) - T\cdot s^{gas}(T,p(gas)^0)) \\ +k\cdot T\cdot ln\frac{p(gas)}{p(gas)^0}\end{matrix}\right]$$

**Metal chemical potentials :**

$$\begin{cases} \mu_{Ba} = E_{DFT}(BaZrO_3) + G^{vib}(BaZrO_3)(T) - \mu_{Zr} - 3\mu_O\ (T,\ P(gas)) \\ \mu_{Zr} = E_{DFT}(ZrO_2) + G^{vib}(ZrO_2)(T) - 2\mu_O\ (T,\ P(gas)) \\ \mu_Y = \frac{1}{4}[E_{DFT}(Y_4Zr_3O_{12}) + G^{vib}(Y_4Zr_3O_{12})(T) - 3\mu_{Zr} - 12\mu_O\ (T,\ P(gas)] \end{cases}$$

### First principles-based defect model formalism [1,3]

**Site balance:** $\Sigma c(X_A^q) + c(Ba_A^x) = 1, (A-site);\ \ \Sigma c(X_B^q) + c(Zr_B^x) = 1, (B-site);\ \ 3\cdot\left(\Sigma c(X_O^q) + c(O_O^x)\right) = 3, (O-site)$

**Defect formation:** $\Delta G^{form}(X^q) = E_{defect}^{DFT}(X^q) + G_{defect}^{vib}(X^q) - E_{bulk}^{DFT}(X^q) + G_{bulk}^{vib} + +\Sigma n_i\mu_i + q\mu_e + E_{corr};\ \Rightarrow\ c(X^q) = \frac{\exp(-\frac{\Delta G^{form}(X^q)}{k_bT})}{\exp\left(-\frac{\Delta G^{form}(X^q)}{k_bT}\right)+1}$

**Free electron concentration:** $c(e') = N_C\ exp\left(-\frac{E_{gap}-E_{Fermi}}{k_bT}\right),\ N_C = 2\left(\frac{2\pi\cdot m_e^* k_bT}{h^2}\right)^{3/2}$

**Free hole concentration:** $c(h^\bullet) = N_V\ exp\left(-\frac{E_{Fermi}}{k_bT}\right),\ N_V = 2\left(\frac{2\pi\cdot m_h^* k_bT}{h^2}\right)^{3/2}$

**Acceptor-bound hole concentration**[4]:

$$\varepsilon_A = \varepsilon_F - k_bTln[\frac{r_A\cdot(x-c(h_{A'}^\bullet))}{c(h_{A'}^\bullet)}]$$

**Equilibrium constants of key chemical reactions:**

- ***Oxidation Reaction:*** $\frac{1}{2}O_2(g) + V_O^{\bullet\bullet} \leftrightarrow 2h_{A'}^\bullet + O_O^x$

$$K_{Oxidation} = \exp\left(\frac{-\Delta E_{oxidation} + T\Delta S_{oxidation}}{k_bT}\right) = \frac{O_O^x\cdot {h_{A'}^\bullet}^2}{[V_O^{\bullet\bullet}]\cdot P(O_2)^{0.5}}$$

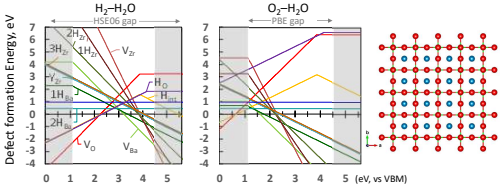
- ***Hydration Reaction:*** $H_2O(g) + V_O^{\bullet\bullet} + O_O^x \leftrightarrow 2OH_O^\bullet$

$$K_{Hydratoin} = \exp\left(\frac{-\Delta E_{Hydration} + T\Delta S_{Hydration}}{k_bT}\right) = \frac{[OH_O^\bullet]^2}{P(H_2O)\cdot[V_O^{\bullet\bullet}]\cdot[O_O^x]}$$

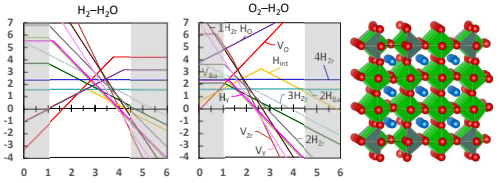
**Charge neutrality:** $\sum_{X^q} n_L\cdot c(X^q)\cdot q + c(h^\bullet) - c(e') + c(h_{A'}^\bullet) + c(A') = 0$

Model formalism coded with Octave based on the Density Functional Theory (DFT) results as inputs

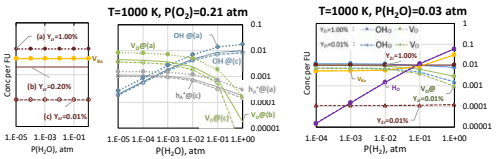
### $BaZrO_3$ First Principles Charged Defect Analysis



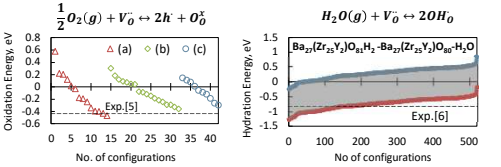

### $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ First Principles Charged Defect Analysis




### $BaZrO_3$ Brower Diagram with Varying $Y_{Zr}$ Conc. (≤1%)

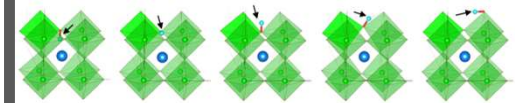



### Configurational Dependence of Chemical Reaction Energies

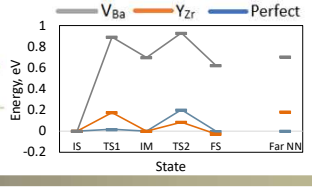



## H trapping effect of $V_{Ba}$ vs. $Y_{Zr}$ in $BaZrO_3$

$Y_{Zr}$ defects located at the light green octahedral site

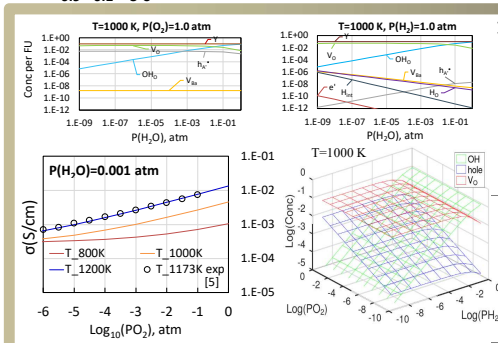



$V_{Ba}$ defect located at the blue sphere (A-site)




- The defect equilibria suggests increased $OH^\bullet_O$ concentration with increased A-site cation deficiency/$V_{Ba}$
- However, strong $H^+$ trapping @$V_{Ba}$ may impede $H^+$ transport

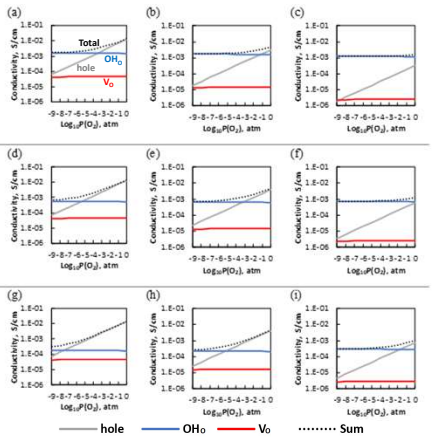
## $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ Brower Diagrams, Conductivities, Transport Numbers vs. $P(O_2)/P(H_2)$ and $P(H_2O)$



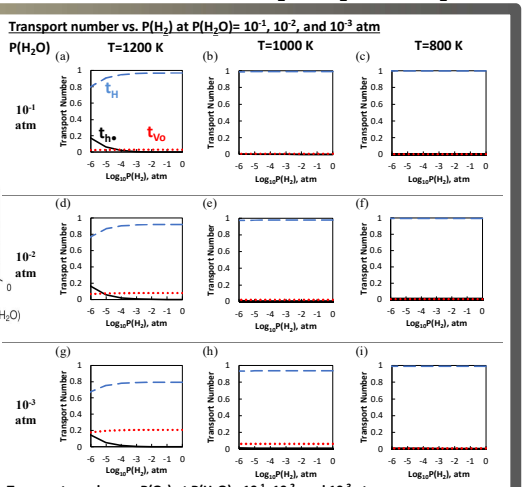

**Activation energies and pre-factors in the transport modeling**

| | Hole (acceptor-bound hole) | Proton | Oxygen vacancy |
|---|---|---|---|
| Pre-exponential factors, cm/s | $3\times10^3$ | 1.1 | $2\times10^{-2}$ |
| Hopping barriers, eV | 0.7 | 0.3 | 0.6 |

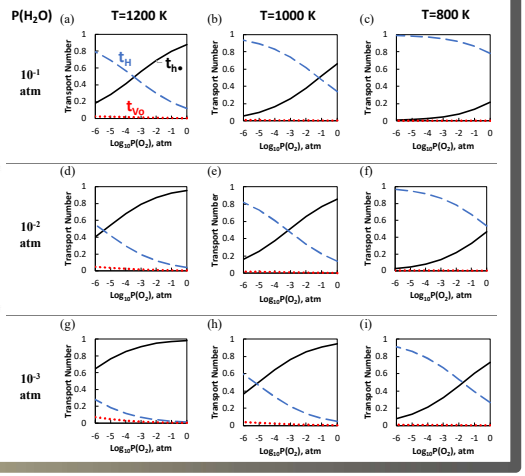
**Total conductivity vs. $P(O_2)$ at $P(H_2O)$= $10^{-1}$, $10^{-2}$, and $10^{-3}$ atm**




**Transport number vs. $P(H_2)$ at $P(H_2O)$= $10^{-1}$, $10^{-2}$, and $10^{-3}$ atm**




**Transport number vs. $P(O_2)$ at $P(H_2O)$= $10^{-1}$, $10^{-2}$, and $10^{-3}$ atm**




## Conclusions

- DFT-based thermodynamic modeling was performed to determine the effect of humidity and $H_2/O_2$ gas pressure on the defect chemistry and transport properties of proton conducting oxide $BaZr_{1-x}Y_xO_{3-\delta}$ (x≤0.1) in the temperature range of 800–1200 K for solid oxide cell and other energy applications.
- The first-principles charge defect analysis was carried out to obtain the defect energetic ensembles as a function of Fermi level, as well as the dependence of the hydration and oxidation reaction energies on complex defect-dopant configurations.
- Oxygen vacancies introduced to compensate for the extra Ba vacancies may cause a slight increase in the concentration of hydroxyl and proton species upon hydration of Ba deficient $BaZr_{1-x}Y_xO_{3-\delta}$, while the overall proton diffusivity is predicted to decrease with increased proton hopping barriers upon trapping near the Ba vacancies.
- The developed defect model can describe the bulk defect chemistry and transport properties of $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ while providing configurational, energetic, and electronic characteristics as a complementary tool to experimental measurements for testing various mechanistic pathways or to provide essential mechanistic data.

## References

1. Y.-L. Lee, Y. Duan, et al, *Defect Thermodynamics and Transport Properties of Proton Conducting Oxide $BaZr_{1-x}Y_xO_{3-\delta}$ (x≤0.1) Guided by Density Functional Theory Modeling*; Accepted in **JOM** special issue (2022)
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4. V.I. Tsidilkovski and L.P. Putilov, *J. Solid State Electrochem.*, 20, 629-643 (2016).
5. D.S. Tsvetkov, et al, **J. Electrochem. Soc.**, 166, F232-F238 (2019)(j)
6. K.D. Kreuer, et al, ***Solid State Ionics***, 145, 295-306 (2001). (b) M.D. Gonçalves, ***The Journal of Physical Chemistry C***, 124, 11308-11316 (2020).

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