UiO Department of Chemistry
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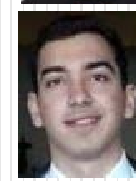
Structural and electrochemical properties of hydrated mixed conductor

$Ba_{1-x}Gd_{0.8}La_{0.2+x}Co_2O_{6-\delta}$ (BGLC)



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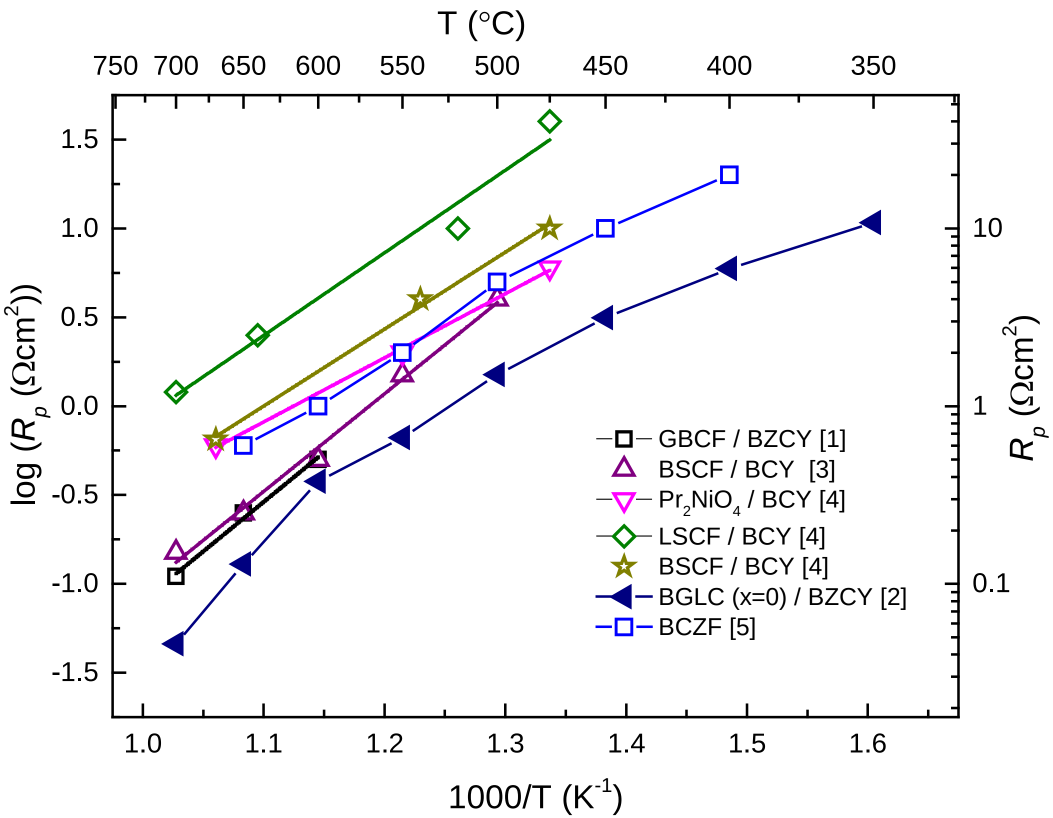
$BaGd_{0.8}La_{0.2}Co_2O_{6-\delta}$



1: H. Ding et al., International Journal of Hydrogen Energy (2010).

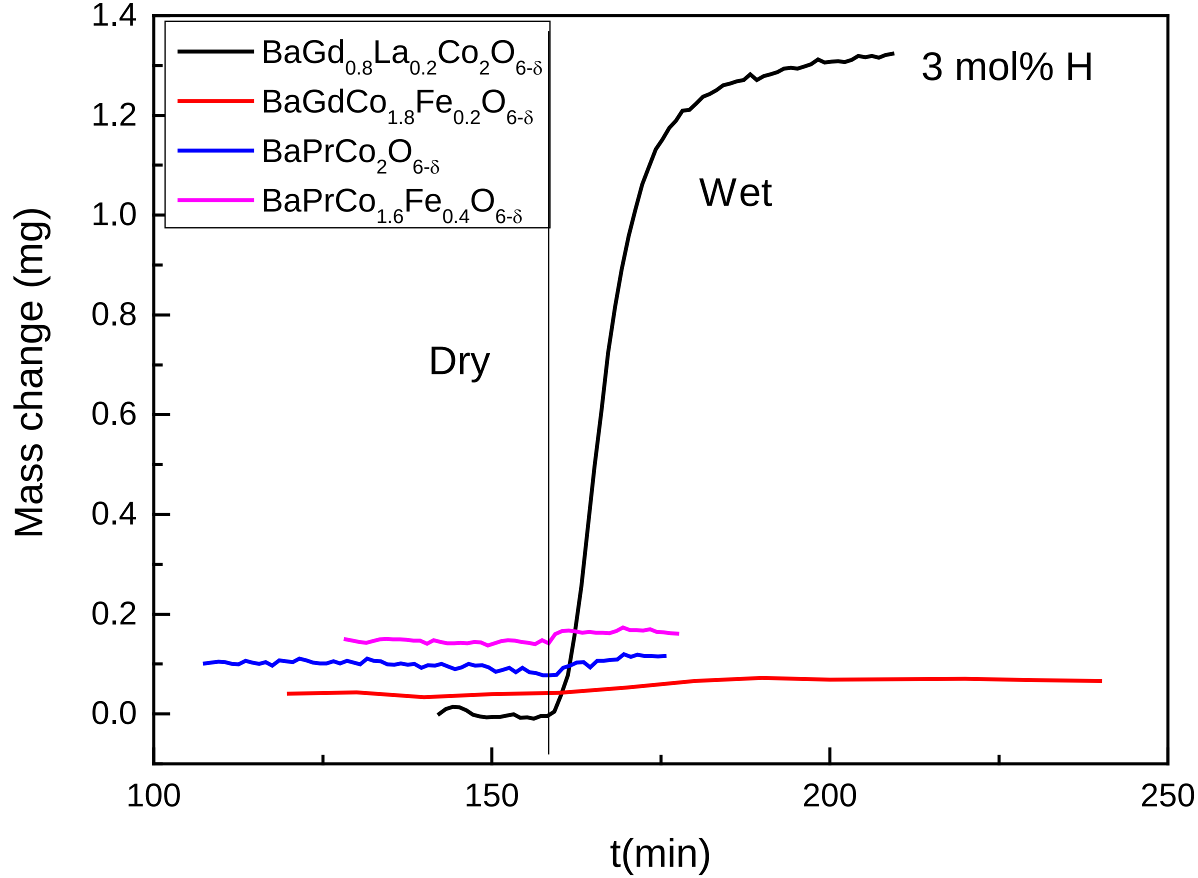
2: R. Strandbakke et al., Solid State Ionics (2015).

3: Y. Lin et al., Journal of Power Sources (2008).

4: J. Dailly et al., Electrochimica Acta (2010).

5: M. Shang et al., RSC Advances, (2013)

Hydration



$400°C, pO_2 = 4 \cdot 10^{-4}$ atm

R. Strandbakke et al. / Solid State Ionics 278 (2015) 120–132

$Ba_{1-x}Gd_{0.8}La_{0.2+x}Co_2O_{6-\delta}$

Stability

High steam pressures

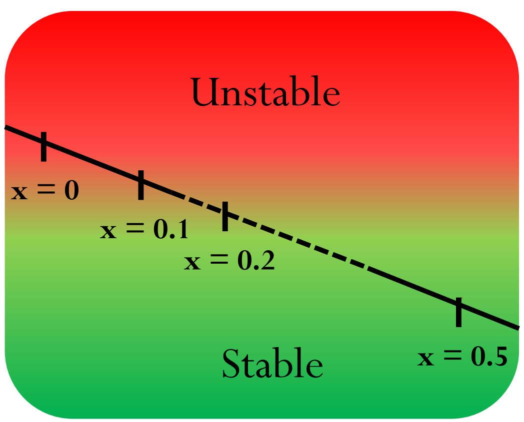
- $BaGd_{0.8}La_{0.2}Co_2O_{6-\delta}$ stable in wet air - decomposes in $pH_2O > 0.5$ bar at 700°C.

Substitute La for Ba

- La less basic
- Effect on hydration?
- Effect on O vacancy ordering?

Stability tests

- Increasing stability with increasing x

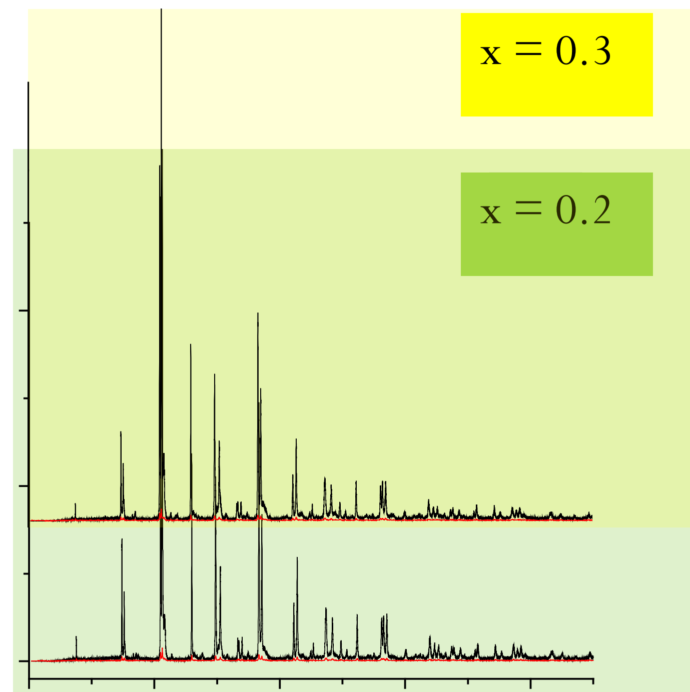


T: 700°C, pH_2O: 1.5 bar

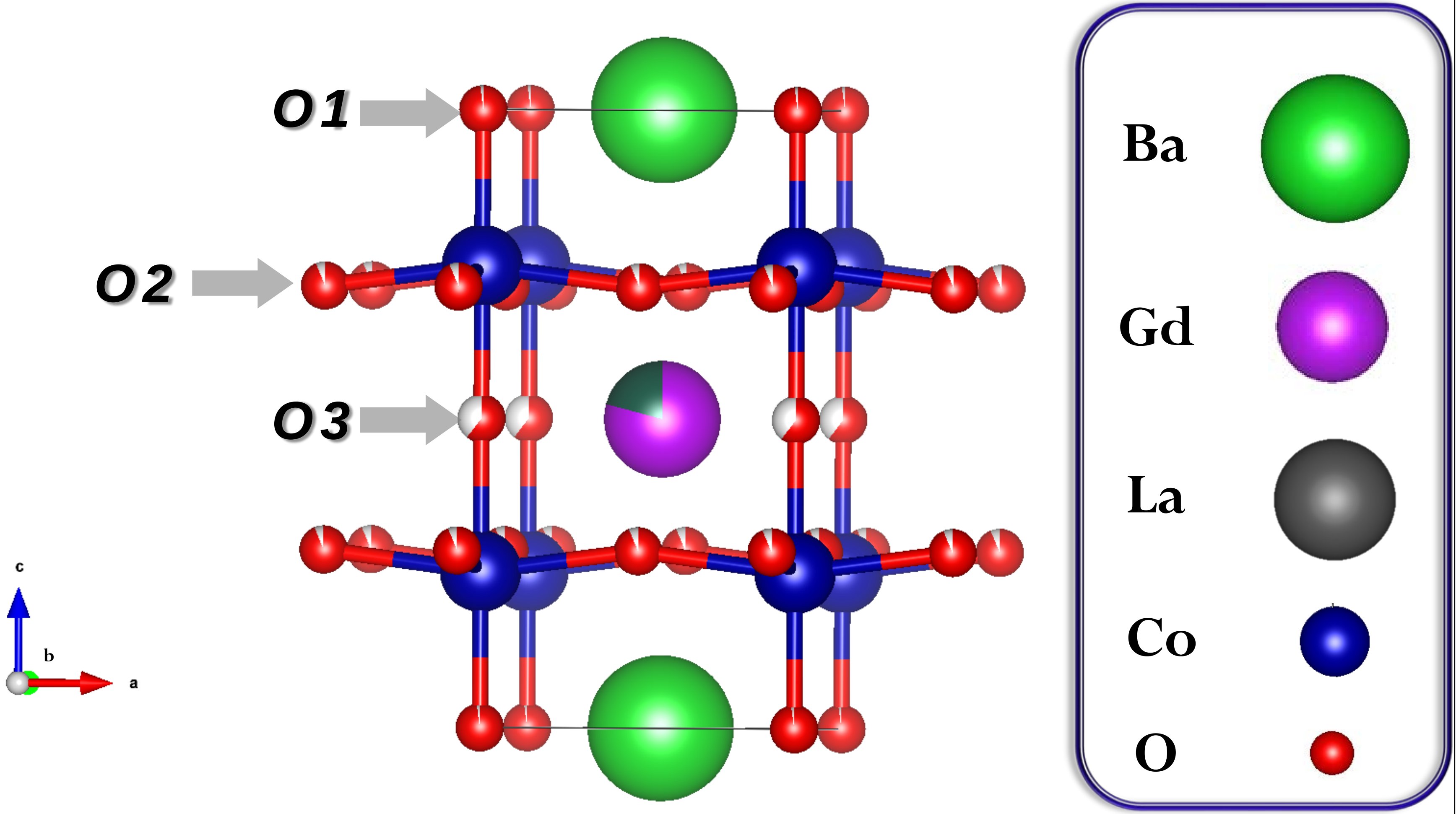
$Ba_{1-x}Gd_{0.8}La_{0.2+x}Co_2O_{6-\delta}$

Structure

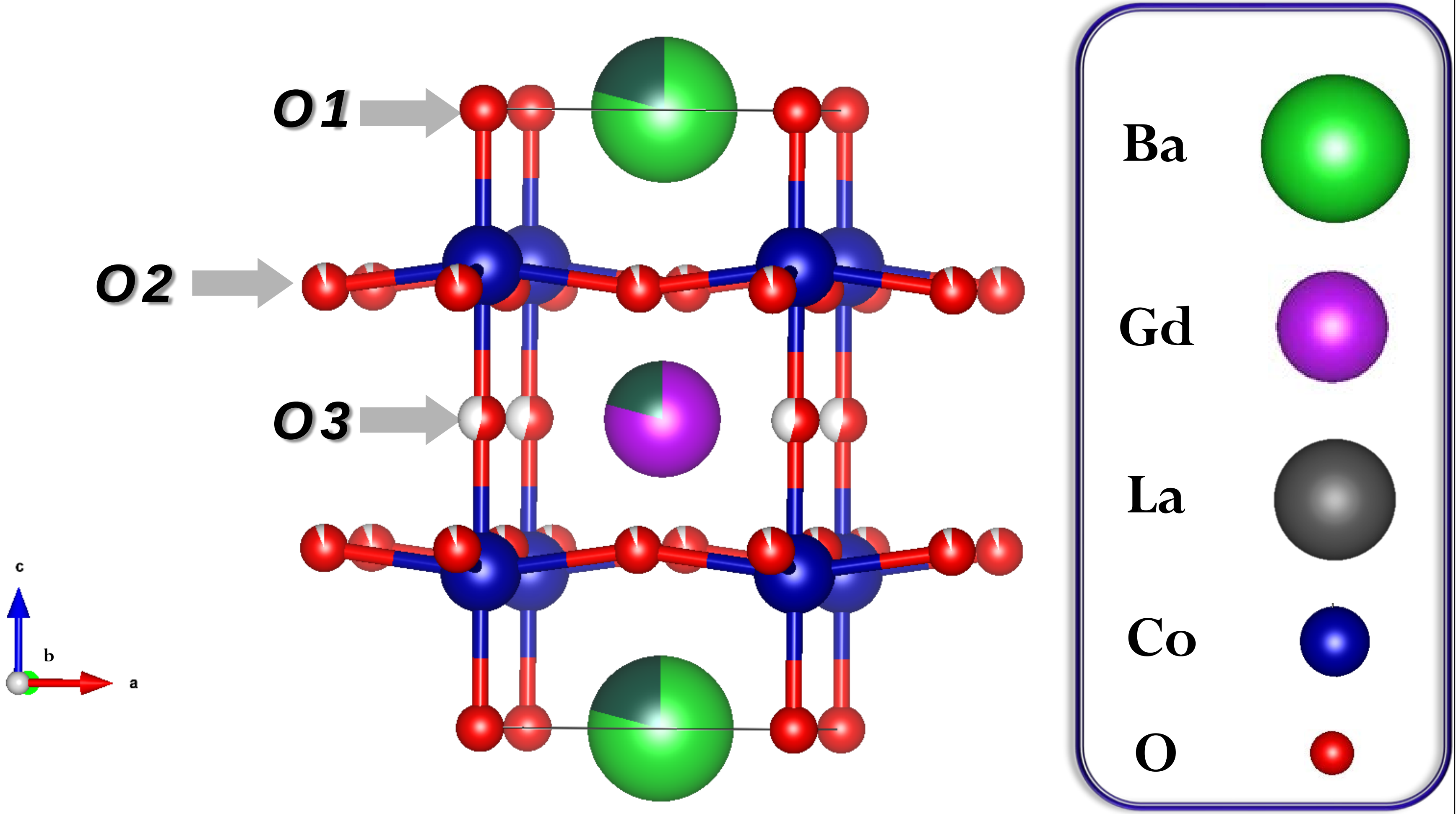
- Synchrotron powder XRD
  - BGLC (x = 0, 0.2, 0.3)
  - High quality structural refinements
    - Cell parameters
    - Symmetry
    - Site occupancies
    - Bond angles



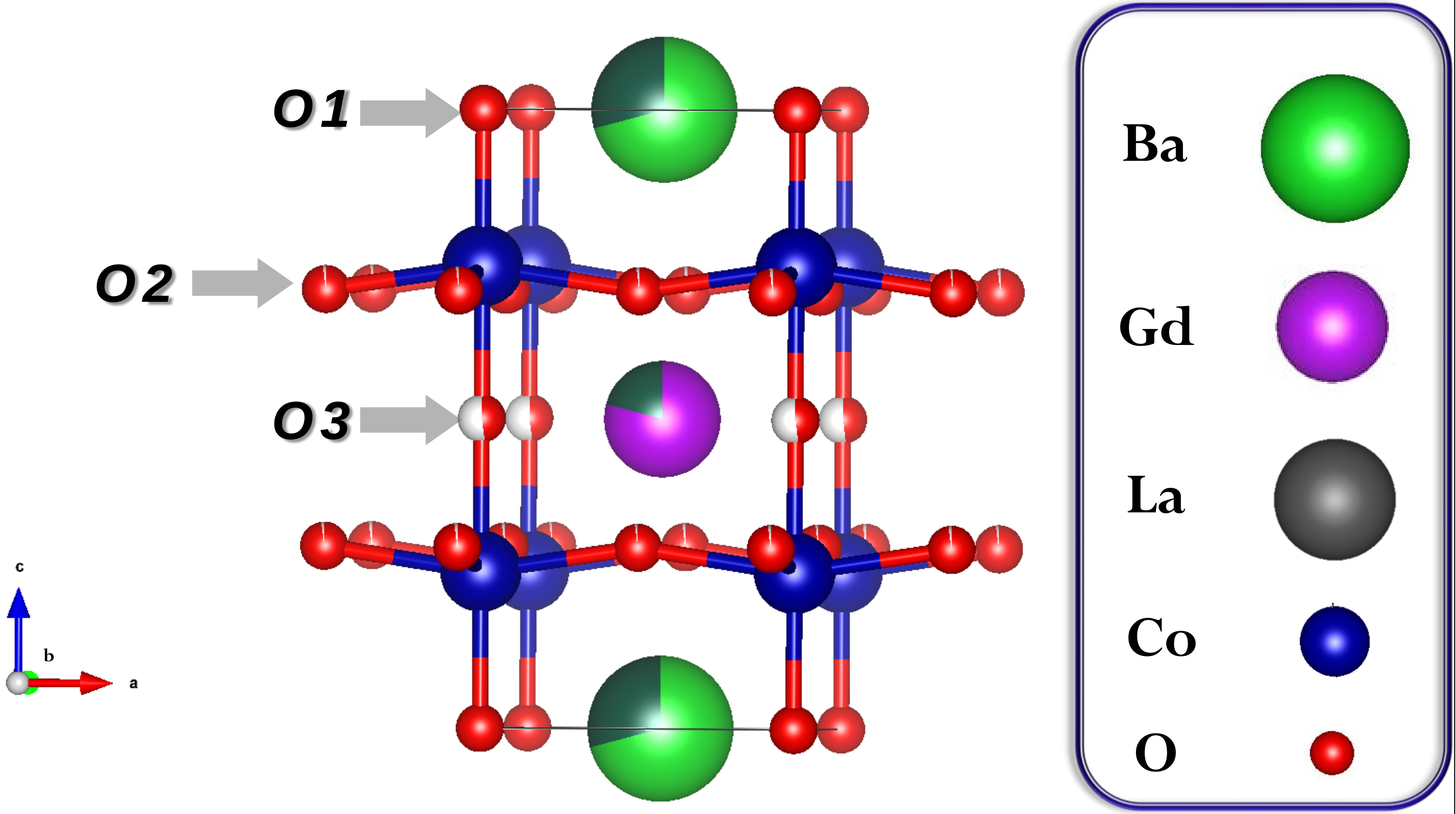
$Ba_{1-x}Gd_{0.8}La_{0.2+x}Co_2O_{6-\delta}$ (x = 0)



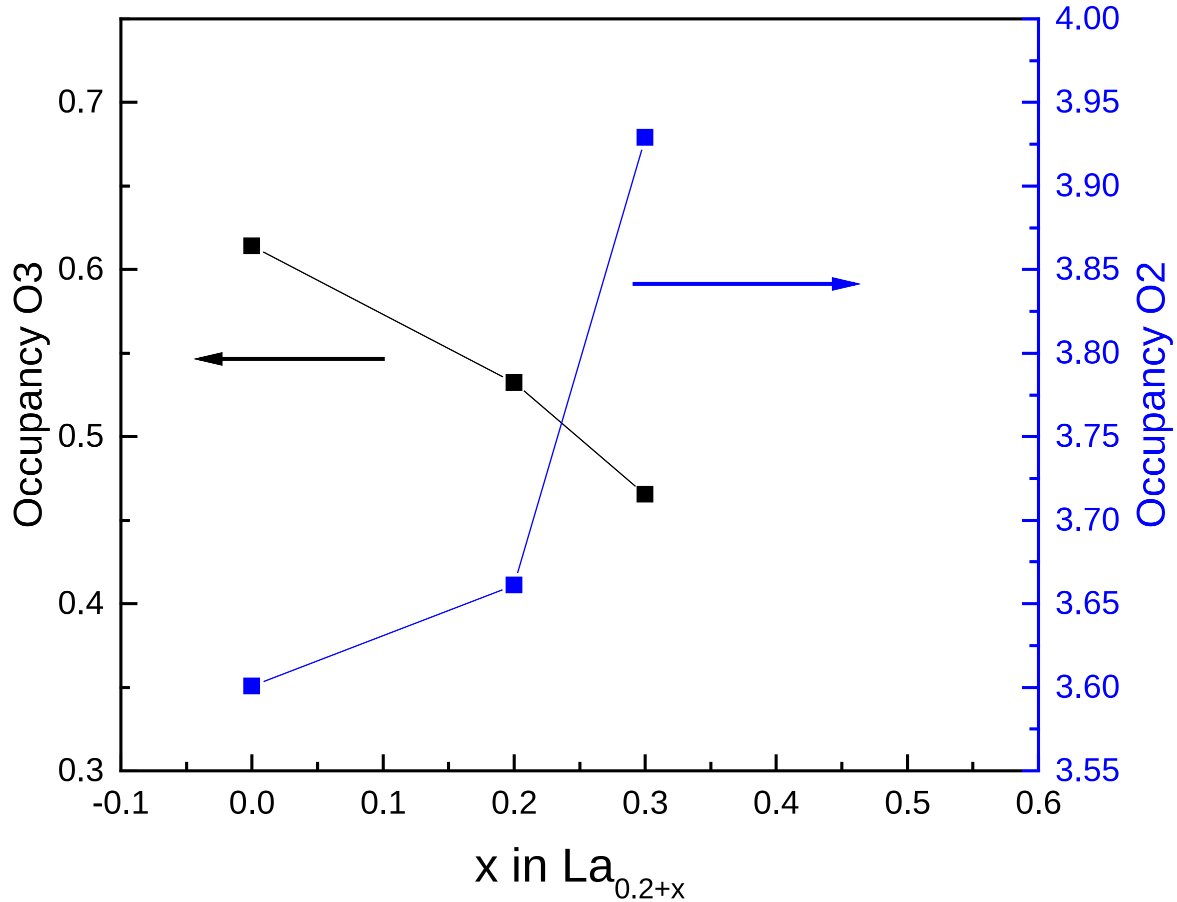
$Ba_{1-x}Gd_{0.8}La_{0.2+x}Co_2O_{6-\delta}$ (x = 0.2)



$Ba_{1-x}Gd_{0.8}La_{0.2+x}Co_2O_{6-\delta}$ (x = 0.3)



Oxygen vacancies on O2 and O3

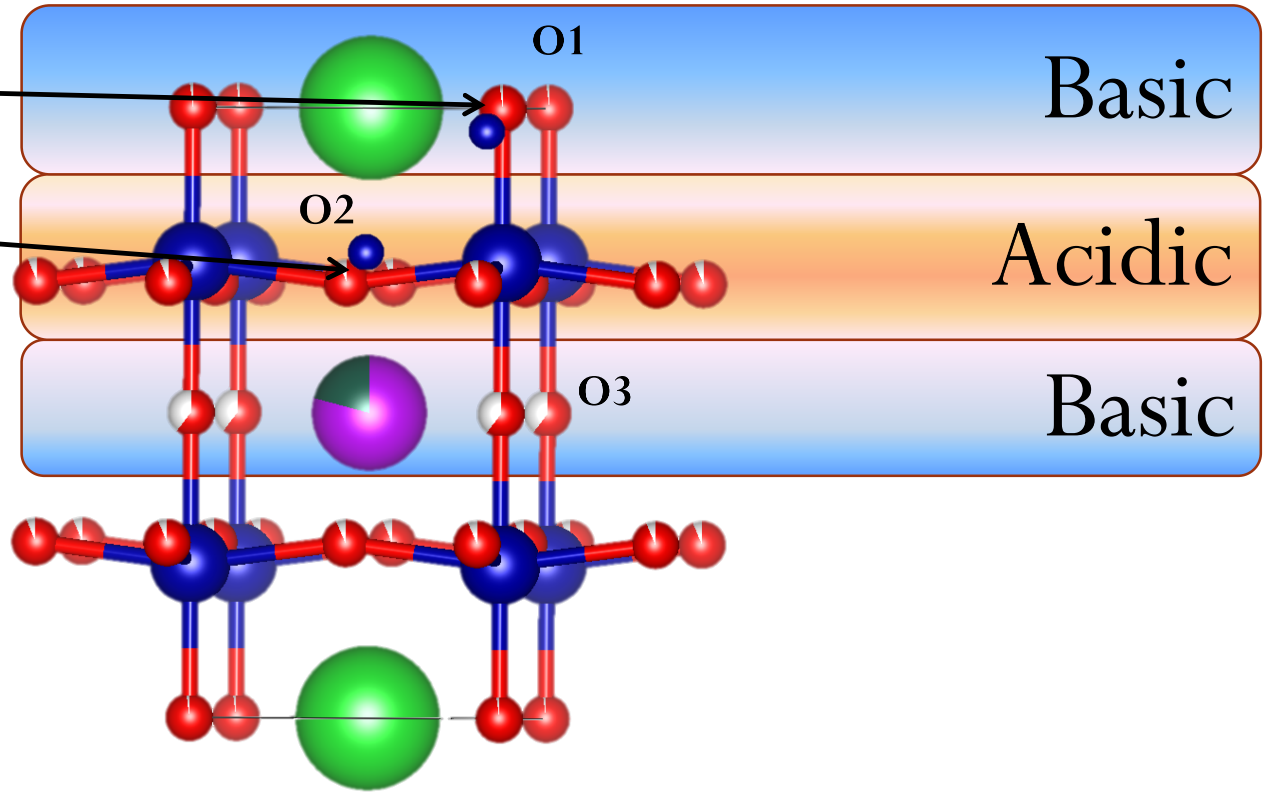


Hydration

Acidic vacancies in the Co-O-Co layer with basic BaO neighbours

Protonated oxide ion

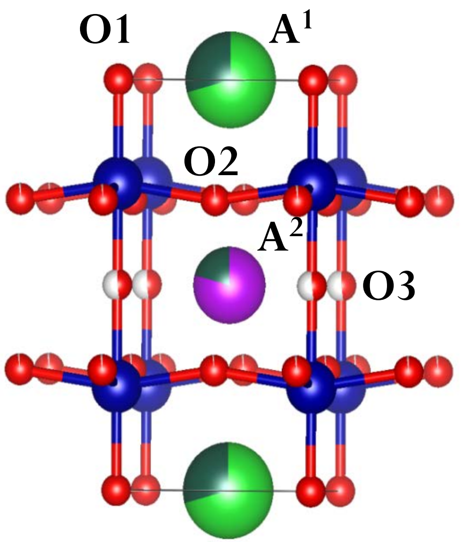
Hydroxylated oxygen vacancy



$$H_2O(g) + O_{O1}^{x} + v_{O2}^{\bullet\bullet} \leftrightarrow OH_{O1}^{\bullet} + OH_{O2}^{\bullet}$$

Defect chemistry

- Reference states
  - Oxidation state: $Co^{3.5+}$
  - Available O sites: 6 (1+4+1)



Electrons / electron holes

$$Co^{4+}: Co_{Co}^{\frac{1}{2}\bullet}$$

$$Co^{3+}: Co_{Co}^{\frac{1}{2}'}$$

$$Co^{2+}: Co_{Co}^{\frac{3}{2}'}$$

$$OH_{O1/O2}^{\bullet}$$

Ionic defects

$$O_{O2}^{x} \leftrightarrow v_{O2}^{\bullet\bullet}$$

$$O_{O3}^{x} \leftrightarrow v_{O3}^{\bullet\bullet}$$

$$La_{Ba}^{\bullet}$$

Defect chemistry

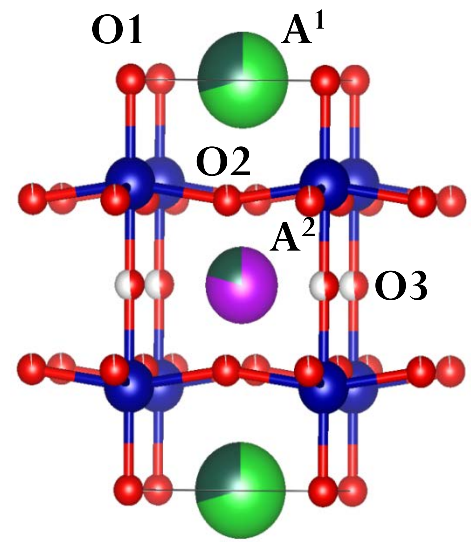
Site balance

$$\delta = [\,v_{O2}^{\bullet\bullet}] + [\,v_{O3}^{\bullet\bullet}]$$

$$[O_{O2}^{x}] + [v_{O2}^{\bullet\bullet}] = 4$$

$$[O_{O3}^{x}] + [v_{O3}^{\bullet\bullet}] = 1$$

$$\left[Co_{Co}^{\frac{1}{2}\bullet}\right] + \left[Co_{Co}^{\frac{1}{2}\prime}\right] + \left[Co_{Co}^{\frac{3}{2}\prime}\right] = 2$$



Electroneutrality

$$\frac{3}{2}\left[Co_{Co}^{\frac{3}{2}\prime}\right] + \frac{1}{2}\left[Co_{Co}^{\frac{1}{2}\prime}\right] = \frac{1}{2}\left[Co_{Co}^{\frac{1}{2}\bullet}\right] + [La_{Ba}^{\bullet}] + 2\delta + [OH_{O}^{\bullet}]$$

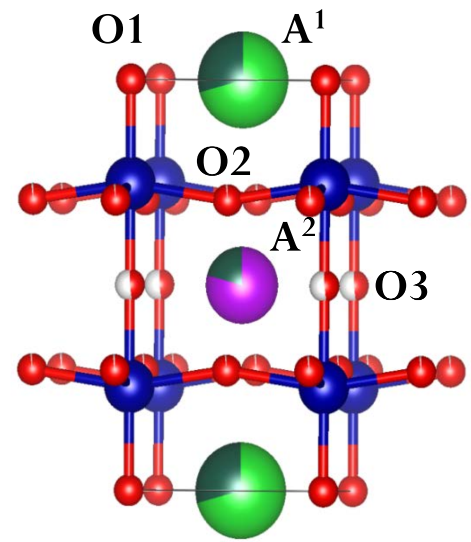
$$[La_{Ba}^{\bullet}]$$ ↑

$$[OH_{O}^{\bullet}]\ [v_{O}^{\bullet\bullet}]$$ ↓

Hydration

$$H_2O(g) + O_{O1}^{x} + v_{O2}^{\bullet\bullet} = OH_{O1}^{\bullet} + OH_{O2}^{\bullet}$$

$$K_{\mathrm{Hydr}} = \frac{\left[OH^{\bullet}_{O1/O2}\right]^2}{[v^{\bullet}_{O2}][O^{x}_{O1}]pH_2O} = K^0_{\mathrm{Hydr}}exp\left(-\frac{\Delta H^0_{\mathrm{Hydr}}}{RT}\right)$$



<u>Oxygen interaction:</u> $O^{x}_{O2} + v^{\bullet\bullet}_{O3} = v^{\bullet\bullet}_{O2} + O^{x}_{O3}$

$$K_{Oint} = \frac{[v^{\bullet\bullet}_{O2}][O^{x}_{O3}]}{[v^{\bullet\bullet}_{O3}][O^{x}_{O2}]}$$

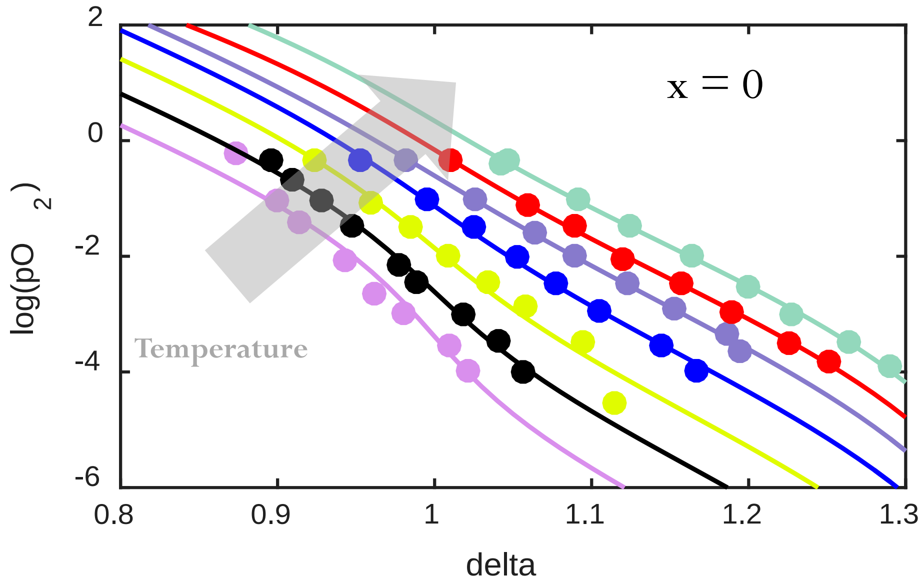
<u>Reduction reaction:</u> $O^{x}_{O3} + 2Co^{\frac{1}{2}\prime}_{Co} = \frac{1}{2}O_2(g) + v^{\bullet\bullet}_{O3} + 2Co^{\frac{3}{2}\prime}_{Co}$

$$K_{red} = \frac{[v^{\bullet\bullet}_{O3}]\left[Co^{\frac{3}{2}\prime}_{Co}\right]^2}{[O^{x}_{O3}]\left[Co^{\frac{1}{2}\prime}_{Co}\right]^2}p_{O_2}^{1/2}$$

<u>Co disproportionation:</u> $2Co^{\frac{1}{2}\prime}_{Co} = Co^{\frac{1}{2}\bullet}_{Co} + Co^{\frac{3}{2}\prime}_{Co}$

$$K_{disp} = \frac{\left[Co^{\frac{1}{2}\bullet}_{Co}\right]\left[Co^{\frac{3}{2}\prime}_{Co}\right]}{\left[Co^{\frac{1}{2}\prime}_{Co}\right]^2}$$

Defect modelling of oxygen nonstoichiometry



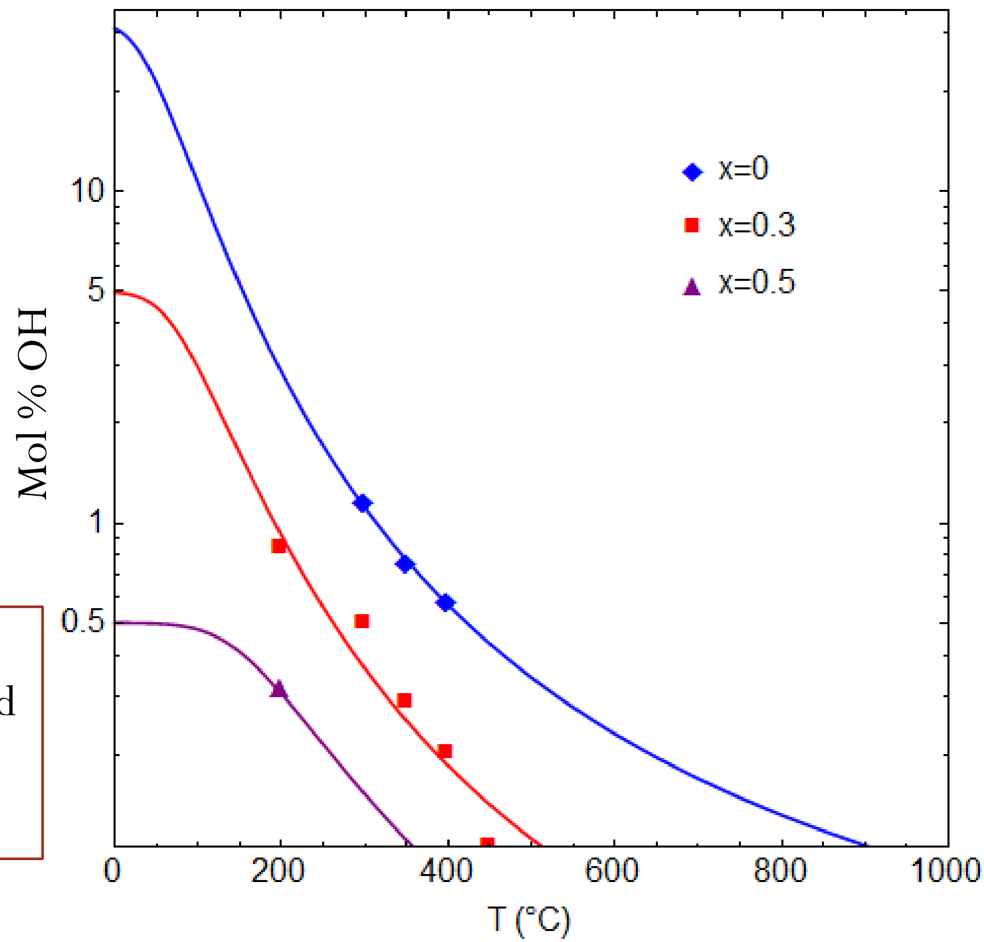
δ in $Ba_{1-x}Gd_{0.8}La_{0.2+x}Co_2O_{6-\delta}$ (x = 0)

x = 0	ΔH (kJ/mol)	ΔS (J/molK)
Reduction reaction	33 ± 3	59 ± 2
Co disproportionation	44(fixed)	0(fixed)
Oxygen interaction	55 ± 2	6 ± 1

Hydration

$$H_2O(g) + O_{O1}^{x} + v_{O2}^{\bullet\bullet} \leftrightarrow OH_{O1}^{\bullet} + OH_{O2}^{\bullet}$$

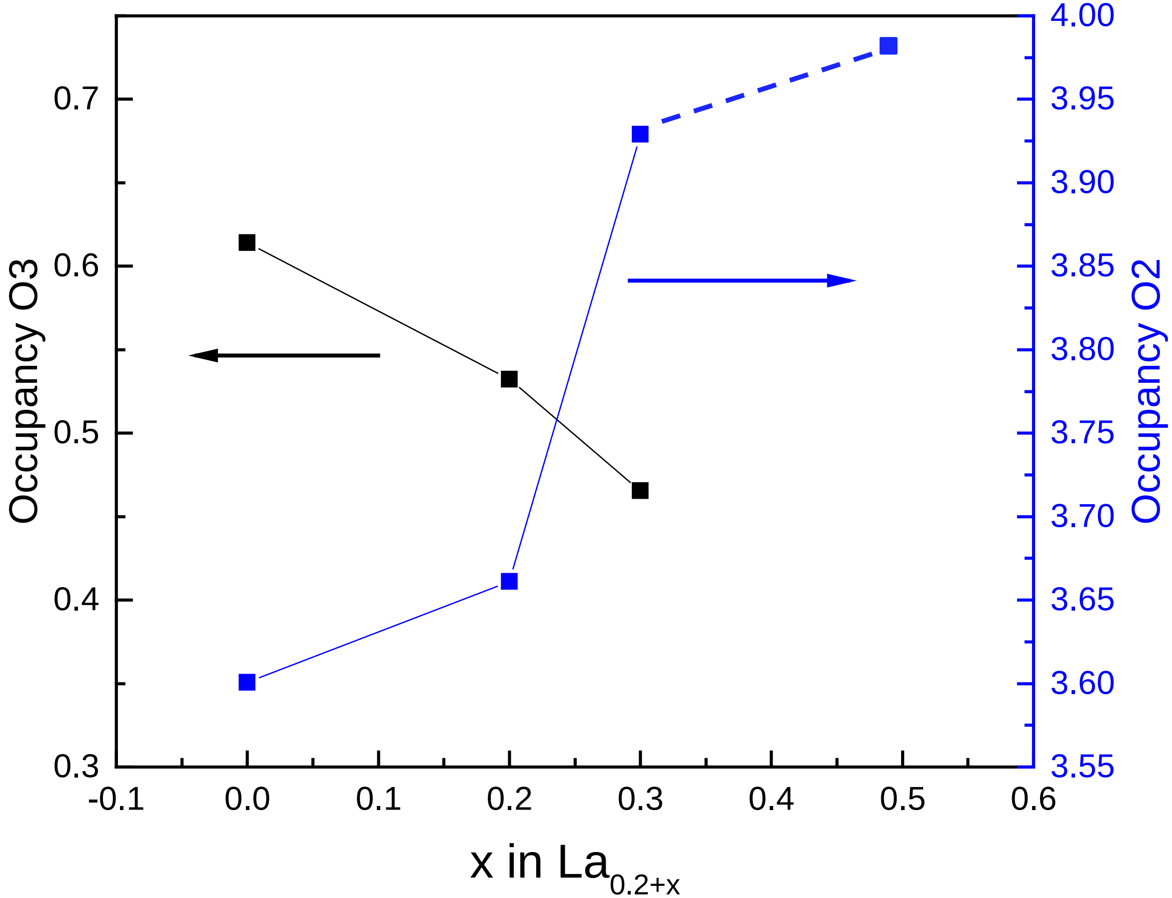
ΔH: -44 kJ/mol
ΔS: 120 J/mol·K



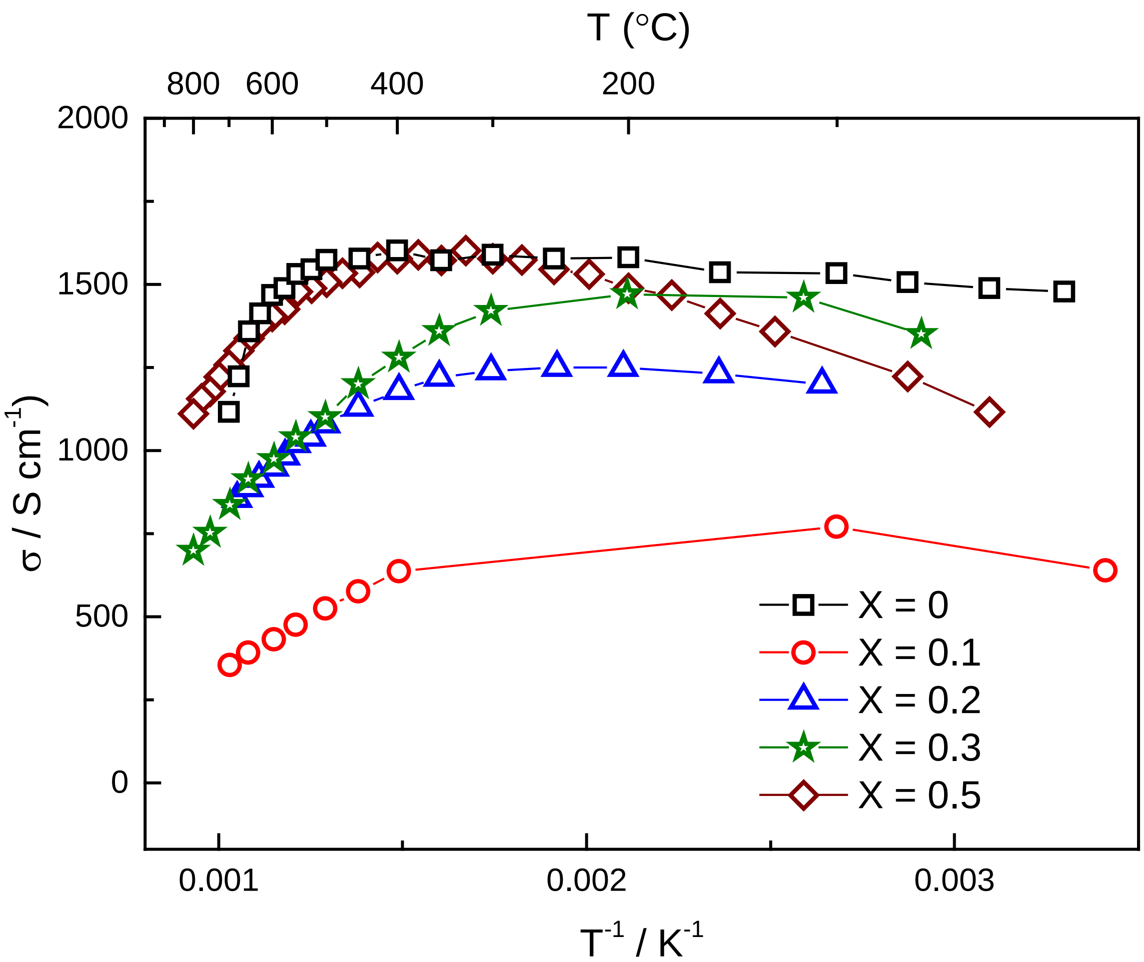
$[v_{O2}^{\bullet\bullet}]$ is fixed to room temperature values from synchrotron measurements for $x = 0$ and 0.3.

Thermodynamic parameters fixed and used to find $[v_{O2}^{\bullet\bullet}]$ for $x = 0.5$.

Occupancy on O2 and O3

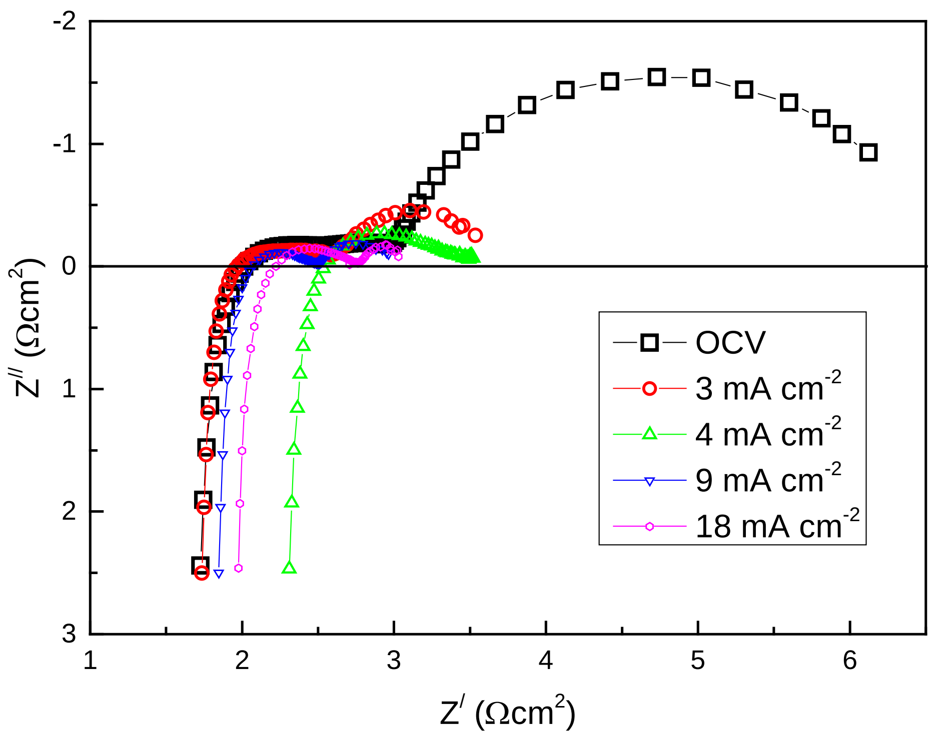


Conductivity



$pO_2 = 0.2$ atm

Electrochemical performance of $Ba_{0.5}Gd_{0.8}La_{0.7}Co_2O_{6-\delta}$ / $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-\delta}$ composite electrode on a tubular PCE.



T: 700°C, pH_2O: 1.5 bar

Conclusions

- BGLC hydrates in an exothermic hydration reaction with $\Delta H = -44$ kJ/mol
- The concentraion of protons scales with the concentration of oxygen vacancies at the O2 site in the O-Co-O layer
- The concentration of O2 site vacancies scales inversely with La donors
- Hydration requires an acidic oxygen vacancy with a basic neighbouring oxygen
- 50 % substitution of La for Ba (still) gives good electrochemical performance for a PCE anode.

Acknowledgements

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