Functional Inorganic Materials
Fall 2023

Mondays: 10.15 - 12.00
Thursdays: 10.15 - 12.00

Lecture hall locations: U7 in Otakaari 1 / U-wing
Ke1 in Kemistintie 1 (CHEM building)

You can use https://usefulaaltomap.fi/ to see the exact location of U7.

#	Date	Place	Who	Topic
1	Mon 4.9.	U7 (U135a)	Maarit	Introduction + Materials design
2	Thu 7.9.	Ke1 (A305)	Antti	Introduction + Computational materials design
3	Mon 11.9.	U7 (U135a)	Maarit	Superconductivity: High-T_c superconducting Cu oxides
4	Thu 14.9.	Ke1 (A305)	Maarit	Magnetic oxides
5	**Mon 18.9.**	**U7 (U135a)**	**Maarit**	**Ionic conductivity (Oxygen): Oxygen storage and SOFC**
6	Thu 21.9.	Ke1 (A305)	Maarit	Ionic conductivity (Lithium + Proton): Li-ion battery
7	Mon 25.9.	U7 (U135a)	Antti	Thermal conductivity
8	Thu 28.9.	Ke1 (A305)	Antti	Thermoelectricity
9	Mon 2.10.	U7 (U135a)	Antti	Piezoelectricity
10	Thu 5.10.	Ke1 (A305)	Antti	Pyroelectricity and ferroelectricity
11	Mon 9.10.	U7 (U135a)	Antti	Luminescent and optically active materials
12	Thu 12.10.	Ke1 (A305)	Maarit	Hybrid materials

Learning Diary

- **Purpose of the learning diary**
  - Deepen **your understanding** of the subject (from passive to active)
  - Urge you to develop **your learning process**
  - Help the teachers to improve the course
- **Structure of diary (for each individual lecture)**
  - State clearly whether you attended or not the lecture
  - Short summary of the lecture topic (with your own words)
  - Summarize shortly what did you know about the topic beforehand
  - What was the **most important new knowledge/understanding** you gained from the lecture
  - Did something remain unclear / Did you try to **clarify** afterwards (or **ask** during the lecture)
  - What kind of **additional information related to the topic** you got inspired to find (particularly important when you: (i) aim at the highest grade, (ii) did not attend the lecture)
- **Practicalities**
  - The whole diary in a single file & return it weekly in MyCourses
  - For each lecture 2-3 pages (some figures may be included); In total 20-30 pages
  - Write a last short summary chapter, where you reflect on the whole course (4 points):
    - * Did your interest in the course subjects change during the course
    - * Did your learning process change during the course
    - * What grade would you give for yourself
- **Important to remember:** your learning diary is the most important part of your course evaluation!

SOME COMMENTS on your Lecture DIARY writings so far

- If you miss the lecture: it is not enough to just write a short abstract of the lecture topic based on the lecture slides. To learn more/earn higher points you should study the topic by yourself beyond the lecture slides. You should also describe how you did this individual study. A good starting point is to look at the key words found from the lecture slides. Unfortunately, it is often difficult to find comprehensive review papers which would cover the entire lecture topic.
- In the diary, the only focus should not be in reporting the lecture content in detail; if you like for your own learning to write a very extensive summary of the lecture, that is perfectly fine, but you could include this longer summary for example as a “separate info box” in the diary.
- Answering the given questions (What did you know beforehand; What was the most important new knowledge; What remained unclear) in a cursory way is NOT enough.
- The emphasis should be on the new understanding; Did the lecture topic create new questions or ideas in your mind; Did it motivate you to study the topic further or deeper; Did the latest lecture add some further understanding on the topics discussed in previous lectures?
- You should also mention: Did you ask questions during the lecture? Or after the lecture? Did these clarify your understanding? Did you discuss with your fellow students?

LECTURE 5: Ionic conductivity: Oxygen

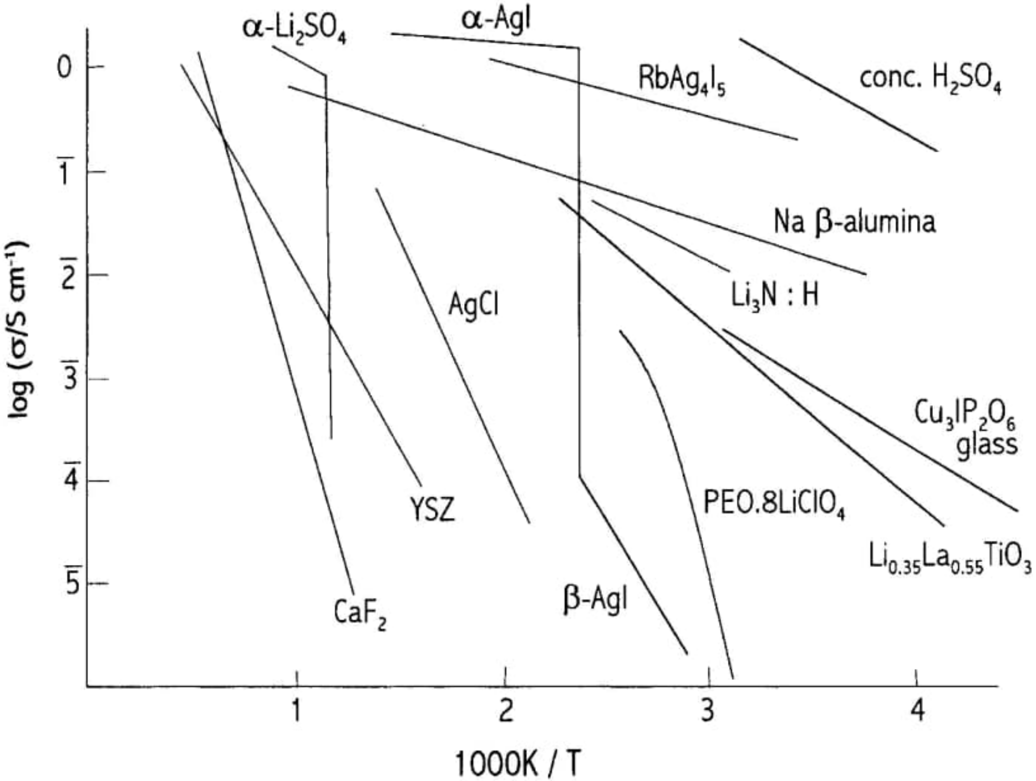
- SOFC (Solid Oxide Fuel Cell) & Oxygen storage
- Oxide ion conductivity & Electrical conductivity & MIEC
- Oxygen vacancies
- Redox-active cations & Mixed valency
- Cation substitutions (isovalent/aliovalent)
- Crystal symmetry (e.g. defected perovskite)

LECTURE EXERCISE 5

1. **(a) Are all oxide-ion conductors good oxygen-storage materials ? Justify !**
   (b) Are all oxygen-storage materials good oxide-ion conductors ? Justify !
2. **Explain the differences of the two compounds,** $YBa_2Cu_3O_{7-\delta}$ **and** $YBaCo_4O_{7+\delta}$**, regarding the oxygen non-stoichiometry, i.e. how they absorb/desorb oxygen upon heating.**
3. **Consider the following perovskite compounds,** $La(Ga,Mg)O_{3-\delta}$**,** $(La,Y)GaO_{3-\delta}$**,** $(La,Sr)GaO_{3-\delta}$ **and** $(La,Sr)CrO_{3-\delta}$**, as possible SOFC cathode or electrolyte materials. Some of these may be just hypothetical compounds not investigated before, while some of them are well-known compounds and may have been investigated for SOFC application. However, you need/should not check these previous studies/reports. Just by looking at the periodic table and considering the chemistry, e.g. oxidation state(s), please predict (and justify your prediction!!!) whether you consider the compound in question as a good candidate for the aforementioned SOFC components.**

IONIC CONDUCTIVITY

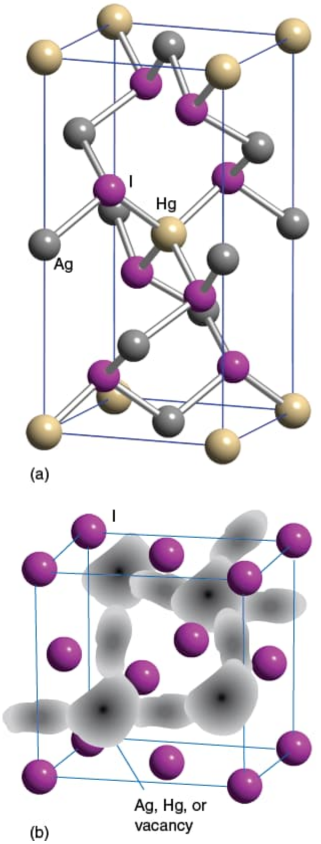
- Movement of ions in **solid** (or liquid)
- Seen in **defective/disordered (non-perfect) crystals**, glasses, polymers, gels, etc.
- Ion conductivity **increases with increasing temperature (ref. semiconductors)**
- Faraday 1839: laws of electrolysis apply to ionic solids: e.g. PbF_2 & Ag_2S
- Prototype “superionic conductor”: AgI (disordered >147 °C)
- Ford Motor Co.: BASE (β-alumina solid electrolyte): Na-Al_2O_3 → Na-S battery
- Other conventional examples: Ag_2HgI_4 (Ag^+ ion), LaF_3 (F^- ion)



Ag_2HgI_4

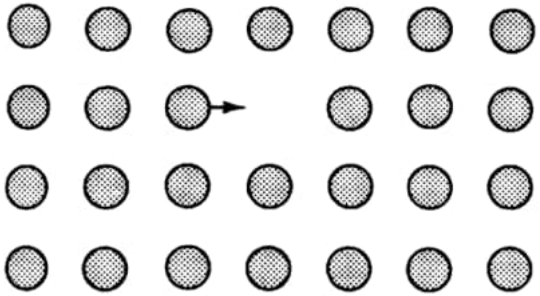
(a) Low-T: ordered structure, Ag^+ and Hg^{2+} at tetrahedral sites

(b) High-T: disordered structure and more sites than there are ions → conductivity increases

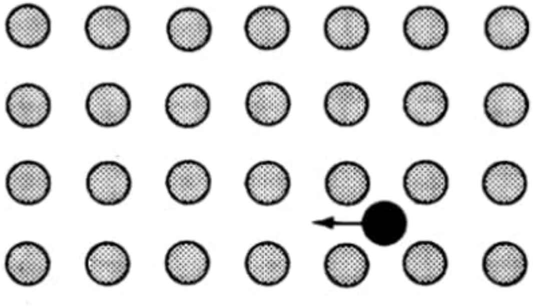


IONIC CONDUCTOR (solid)

- Other terminologies:
  Fast ion conductor, Superionic conductor, Solid electrolyte, Solid state ionics
- Highly mobile ions move/hop through an otherwise rigid crystal structure
- Measurement of ionic conductivity: electrochemical impedance spectroscopy (EIS)
- Important in energy applications: O^{2-}, Li^+, H^+
- **APPLICATIONS:**
  batteries, fuel cells (e.g. **SOFC**), supercapacitors, chemical sensors, separation membranes, gas (e.g. **oxygen) storage**



mobile vacancy

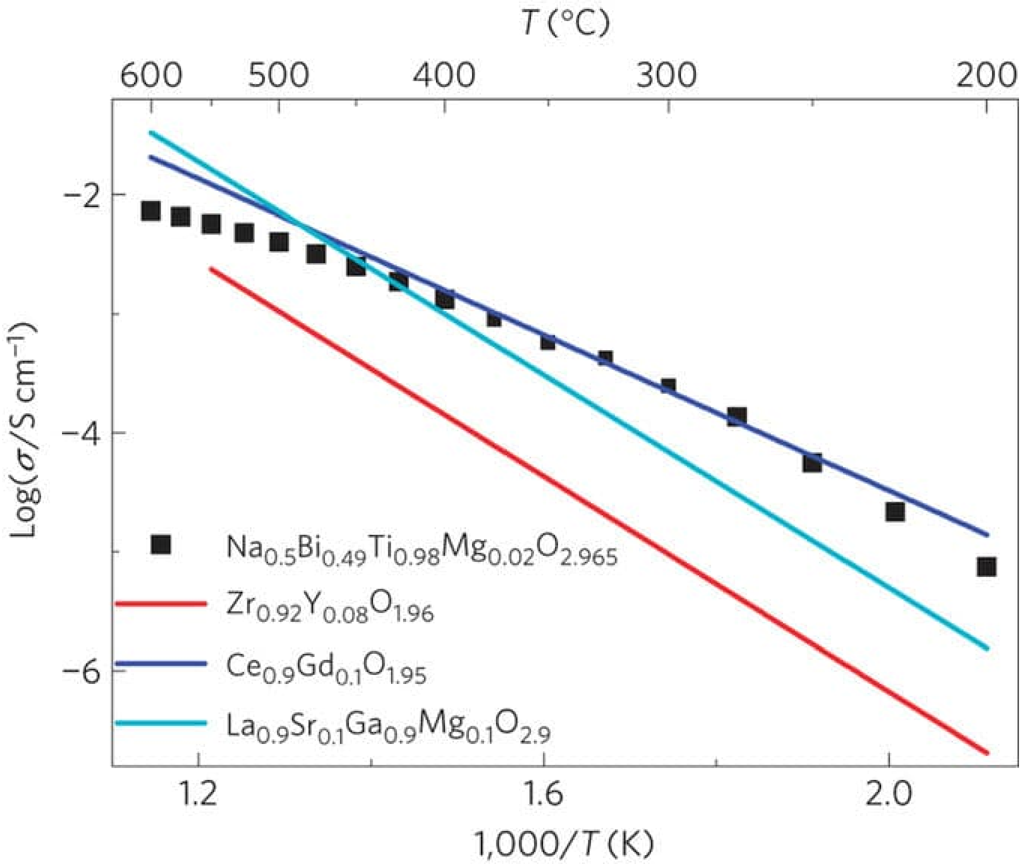


mobile interstitial

EFFECTIVE IONIC RADII

O^{2-}	**140 pm**
OH^-	**137 pm**
Li^+	**60 pm**
H^+	**very small**

	Material	**Conductivity (S m^{-1})**
Ionic conductors	Ionic crystals	$< 10^{-16} – 10^{-2}$
	Solid Electrolytes	10^{-1}-10^{3}
	Liquid electrolytes	10^{-1}-10^{3}
Electronic conductors	Metals	10^{3}-10^{7}
	Semiconductors	10^{-3}-10^{4}
	Insulators	$< 10^{-10}$

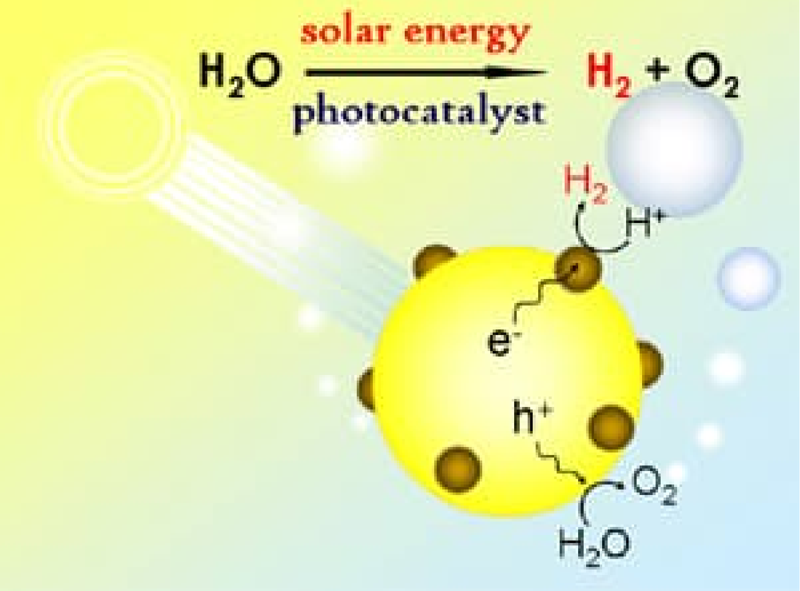


Examples of APPLICATIONS

- Storage
- Separation
- Purification
- Sensors

Redox exhaust gas catalyst

TOKYO ROKI Co. Ltd.



H_2/O_2 separation in photocatalytic water splitting

Domen Lab. (Univ. of Tokyo)

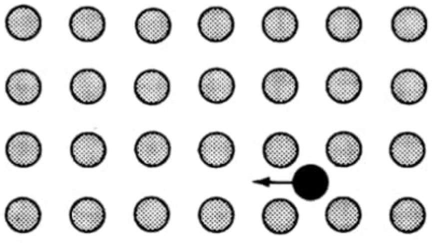
Solid oxide fuel cell (SOFC)
oxide-ion conducting materials

NISSAN Motor Co. Ltd.

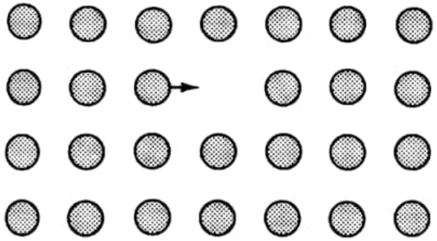
OXIDE-ION CONDUCTIVITY & OXYGEN-STORAGE

MATERIAL DESIGN CONSIDERATIONS

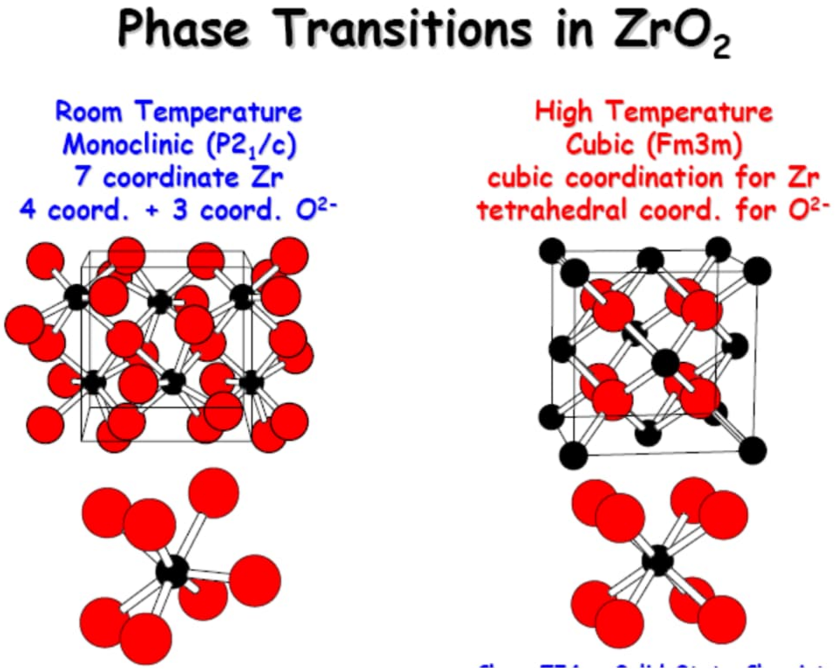
- **Open structure**: space for O^{2-} ion diffusion
- **Oxygen vacancies**: efficient O^{2-}-ion hopping
- **[High crystal symmetry**: all oxygen sites equivalent (e.g. cubic ZrO_2 desired)]
- **Redox-ative cations**: oxygen-content variation → **OXYGEN STORAGE**
- **For sensor and separation applications → thin films**
- **Other important factors: chemical/thermal stability, thermal expansion, …**

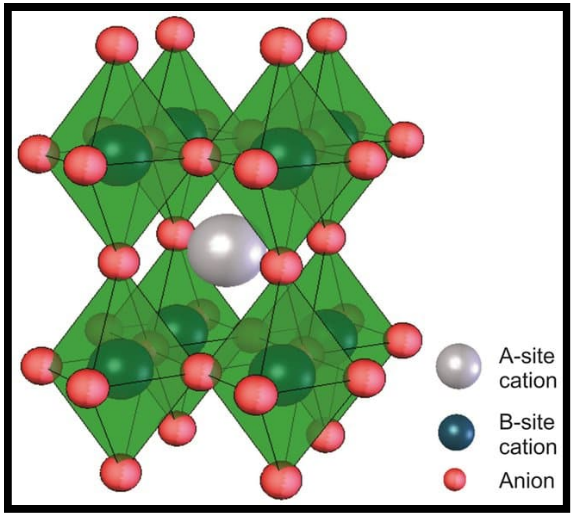


mobile interstitial



mobile vacancy



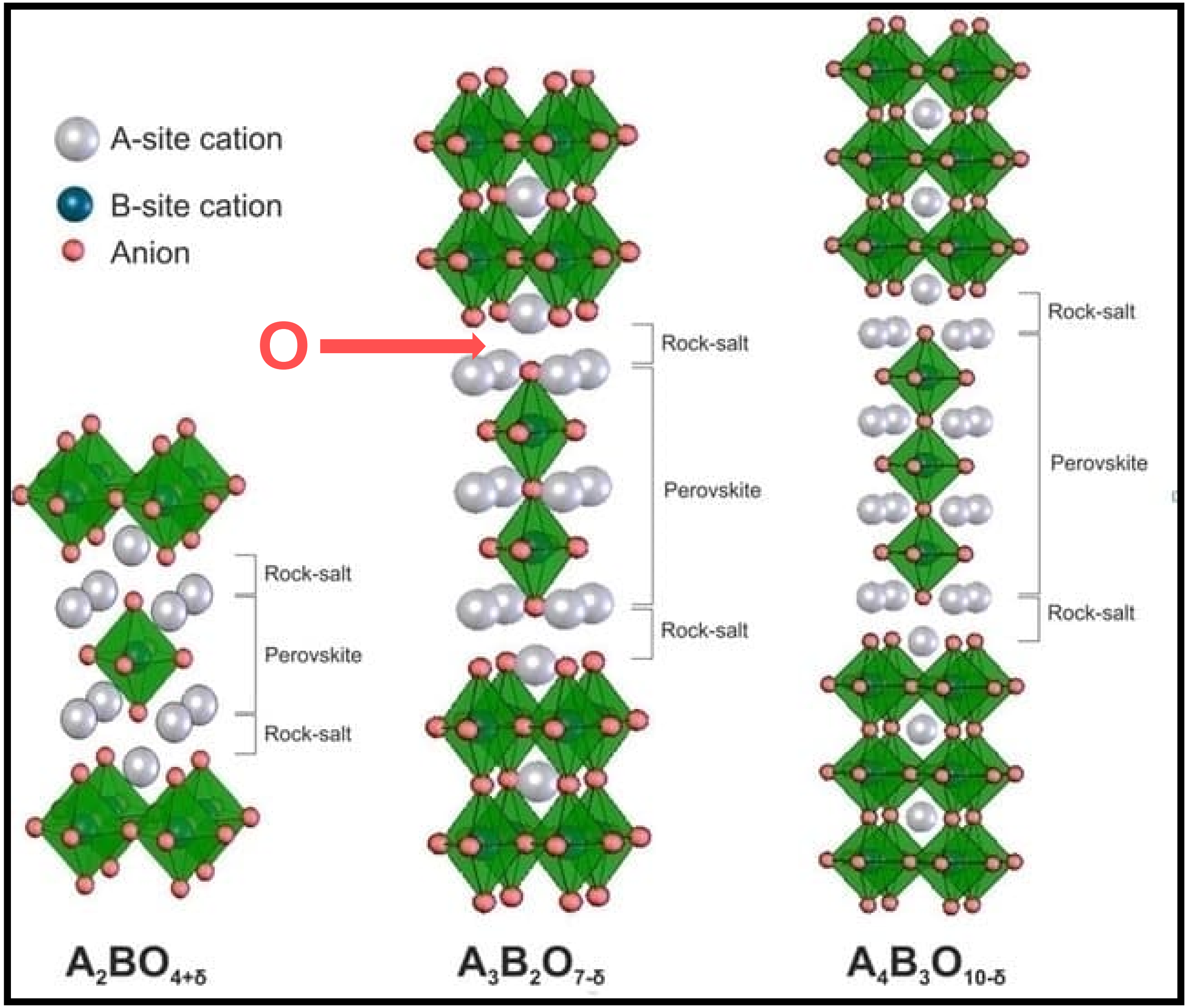


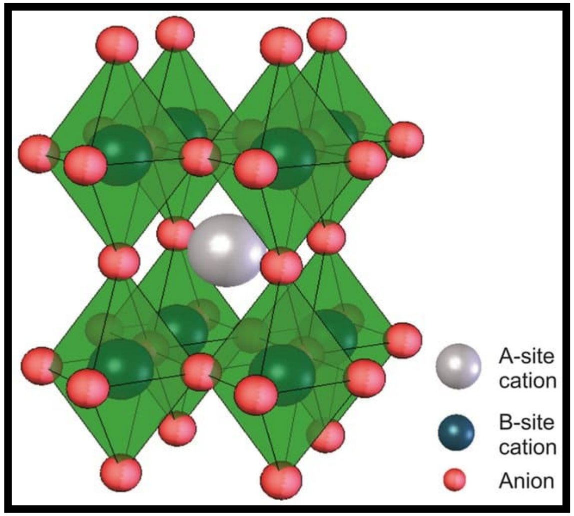
Perovskite ABO_3

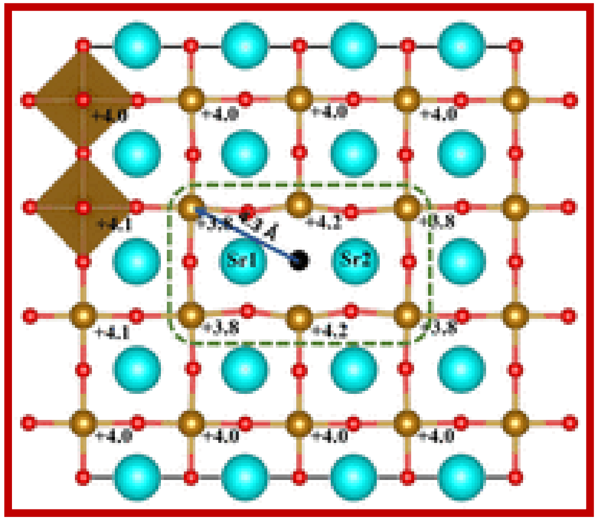
- No space for interstitial oxygen

Ruddlesden-Popper $A_{n+1}B_nO_{1+3n}$

- Enough space for interstitial oxygen



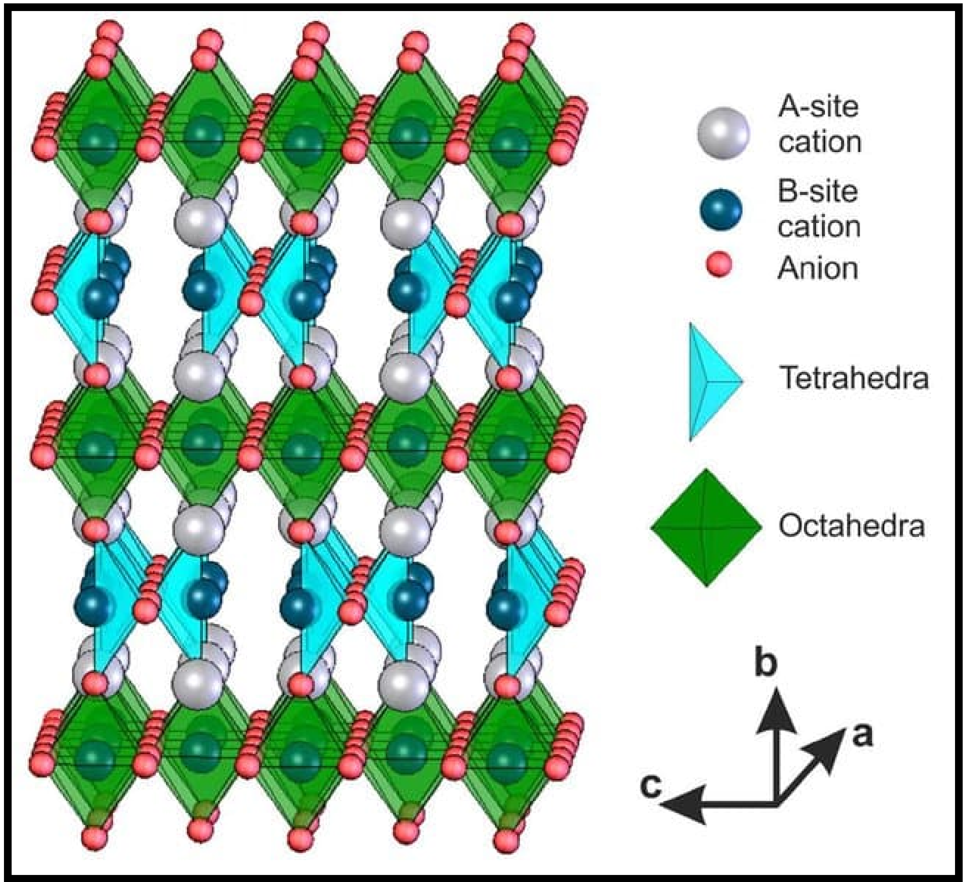




Perovskite $ABO_{3-\delta}$

- (random) oxygen vacancies

ABOUT THE SITE SYMMETRY?

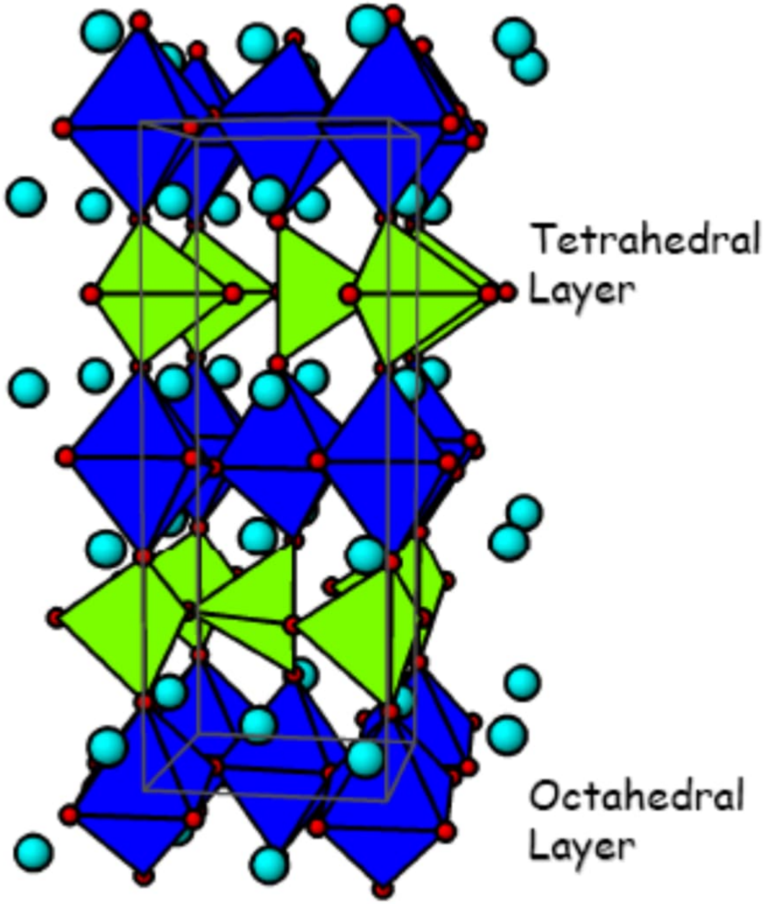


Brownmillerite $ABO_{2.5}$

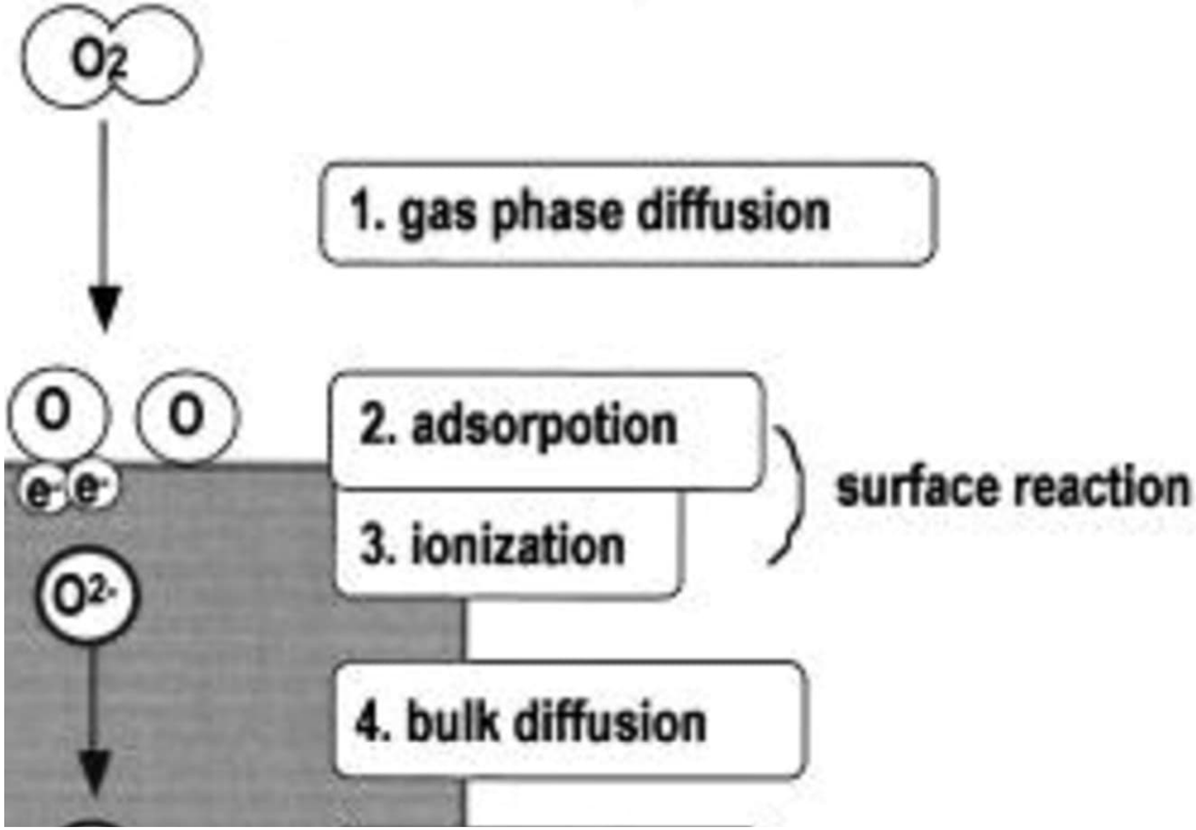
- Oxygen-vacancy ordered

$Ba_2In_2O_5$ ($BaInO_{2.5}$)

- **Brownmillerite structure**
  derived from the perovskite structure
  (oxygen vacancies ordered into layers)
- **With increasing temperature, the ordering of the oxygen vacancies disappears around 800 °C above which the oxygen vacancies exist randomly in the lattice; simultaneously the oxide ion conductivity jumps**
  from 10^{-3} S/cm to 10^{-1} S/cm

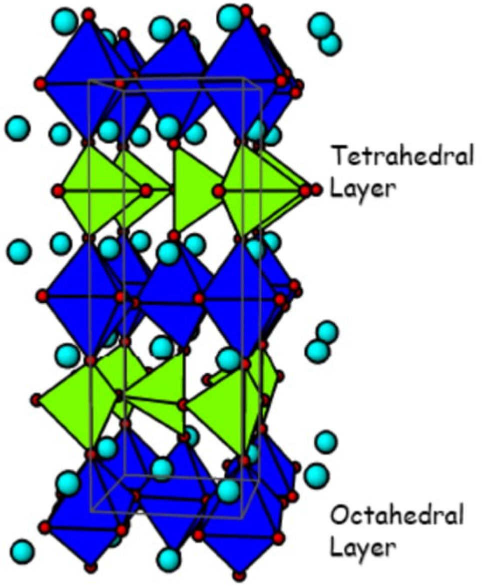


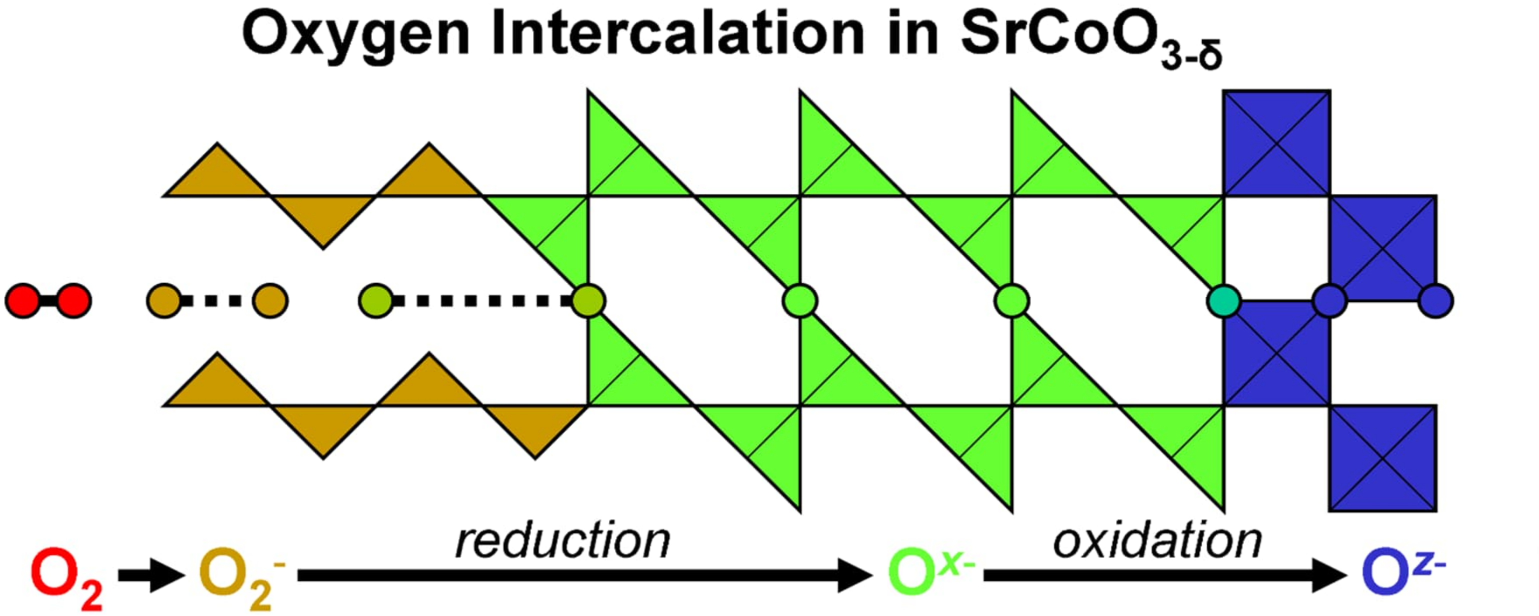
WHAT KIND(S) of OXYGEN SPECIES ?



Perovskite (brownmillerite) $SrCoO_{3-\delta}$ upon increasing oxygen content from 2.5 to 2.8

- O *K-edge* and Co *L-edge* XANES spectroscopy in both surface and bulk sensitive modes →
- first: O_2 is first absorbed on the surface as O_2^-
- then: O_2^- is split into O^{x-} in a reductive manner
- finally: O^{x-} is oxidized to O^{z-} in the bulk ($0 < z < x$)



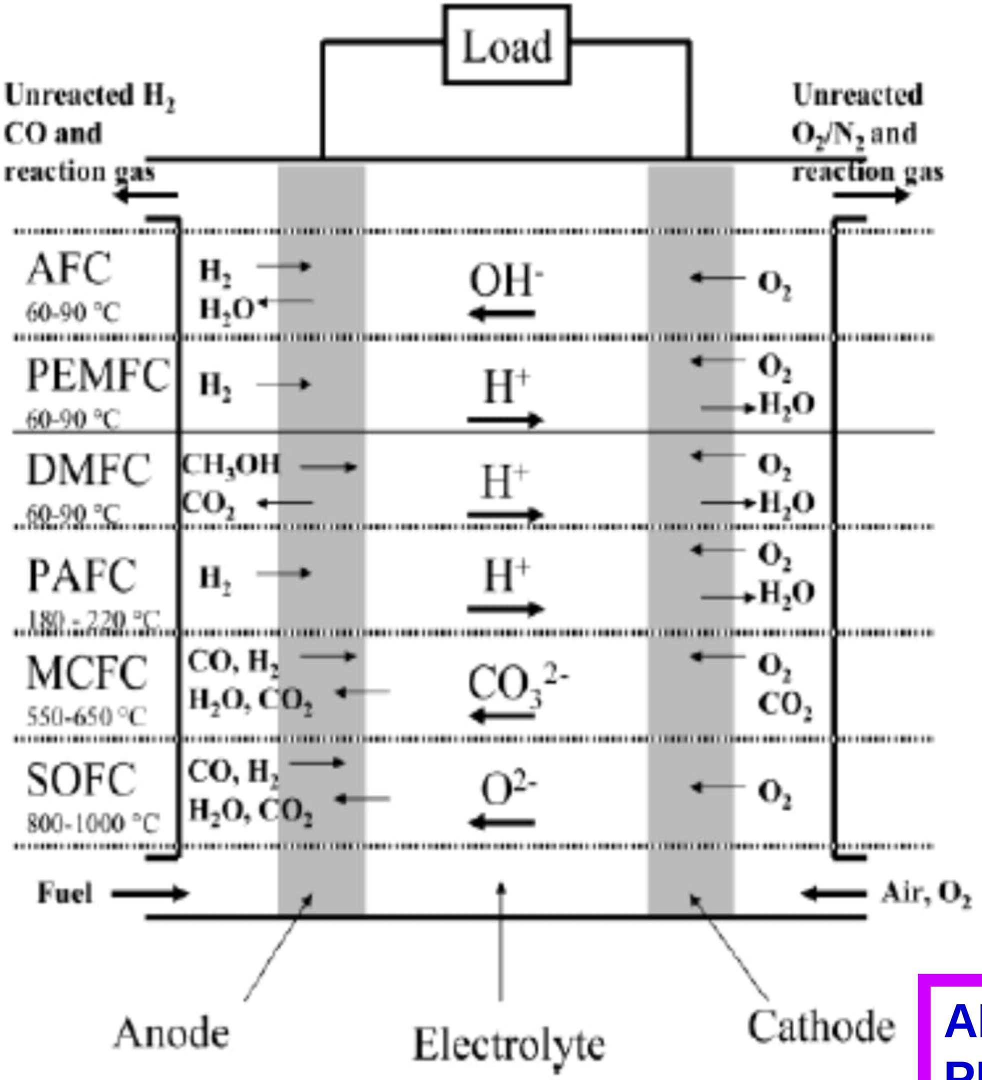


L. Karvonen, M. Valkeapää, R.S. Liu, J.M. Chen, H. Yamauchi & M. Karppinen,
O-*K* and Co-*L* XANES study on oxygen intercalation in perovskite $SrCoO_{3-\delta}$, *Chemistry of Materials* **22**, 70 (2010).

FUEL CELLS

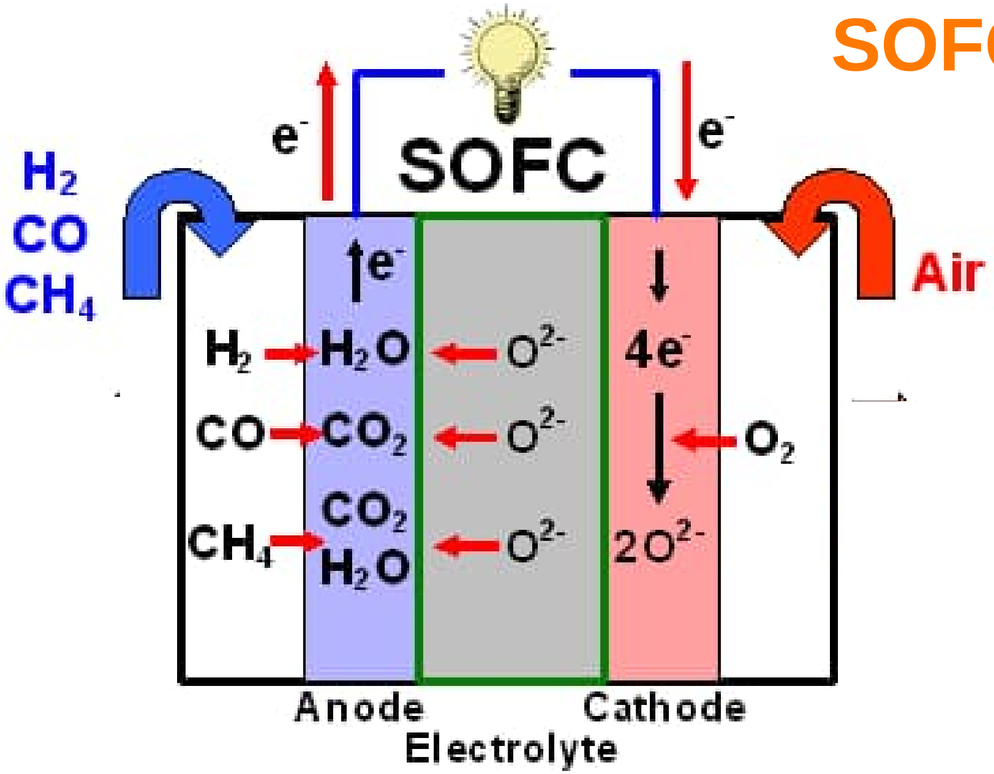
- **ELECTROCHEMICAL DEVICE:** converts the chemical energy from **continuously fed fuel** into electricity through a **chemical reaction with oxygen** or another oxidizing agent
- **POSSIBLE FUELS:** H_2, NH_3, carbon, CO, CH_4, CH_3CH_2OH, propane, butane, natural gas, diesel, Al, Mg, Zn
- Principle of fuel cell: Schönbein 1838
- First practical fuel cell: Bacon 1959
- First applications: Apollo space crafts by NASA in 1970s
- Potential (future) applications: mobile devices, cars, ships, combined heat and electricity production for buildings, …
- **LOW-TEMPERATURE FUEL CELLS:** the main problem is the slowness of oxidation reactions → Pt catalyst → nanostructuring to increase the active Pt surface
- **HIGH-TEMPERATURE FUEL CELLS:** catalyst not needed, but thermodynamic conversion efficiency decreases with increasing temperature

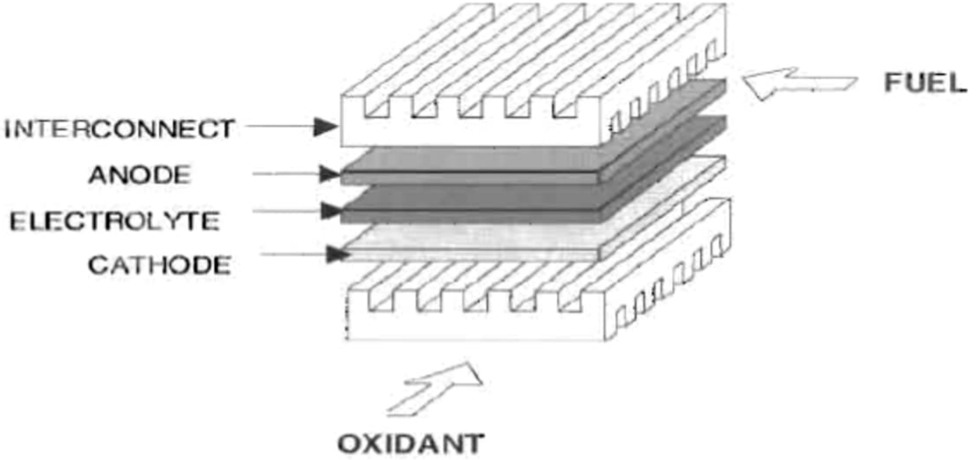
FUEL CELLS

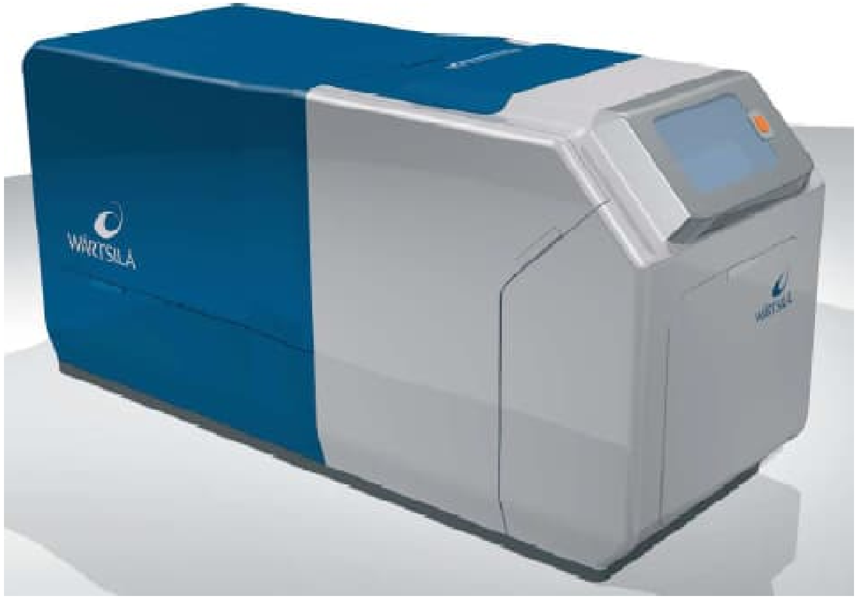


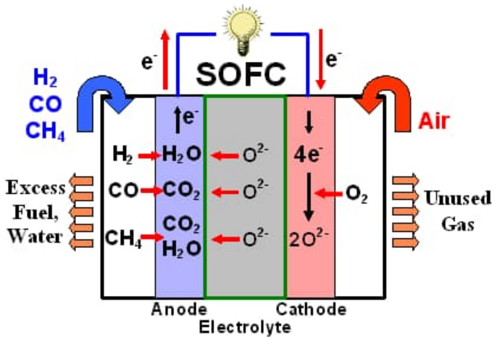
AFC	**Alkaline fuel cell**
PEMFC	**Proton exchange membrane**
DMFC	**Methol direct oxidize fuel cell**
PAFC	**Phosphate fuel cell**
MCFC	**Molten carbonate fuel cell**
SOFC	**Solid-oxide fuel cell**

SOFC: Solid Oxide Fuel Cell









SOFC Material Requirements

ANODE & CATHODE

- MIEC: **Mixed Ionic and Electronic (1–100 S/cm) Conductor**
- Chemical & mechanical stability (at 600-900 °C) under oxidizing conditions for cathode (oxides), under highly reducing conditions for anode (metals); **no coking or sulfur poisoning for anode**
- **PREFERABLY: cathode p-type, anode n-type !!!**
- Thermal expansion coefficients to match with the electrolyte
- **Sufficient porosity** to facilitate transport of O_2 gas

ELECTROLYTE

- **High oxide ion conductivity but very low electronic conductivity**
- Stable in both reducing and oxidicing conditions (pO_2: 10^{-20}–1 atm)
- **Free of porosity**

INTERCONNECT (between anode and cathode): **stainless steel or (La,Sr)CrO_3**

- High electronic conductivity and negligible ionic conductivity
- **Free of porosity**
- Stable in both oxidizing and reducing conditions
- Chemical and thermal **compatibility** with other components

ELECTROLYTE

- oxide-ion conductor & electrical insulator
- $(Zr,Y)O_2$ (= YSZ; cubic structure & oxygen vacancies)
  (works well only at high operation temperatures)
- $(La_{0.2}Sr_{0.8})(Ga_{0.3}Mg_{0.7})O_{3-\delta}$ (Ga is expensive)
- $YBaCo_4O_{7+\delta}$ [M. Karppinen, et al., *Chem. Mater*. 18, 490 (2006)]

ANODE

- MIEC (mixed ionic & electronic conductor)
- Ni/YSZ composite
  (works with H_2, but not for C- and S-containing fuels)
- $(La,Sr)_{0.9}(Cr_{0.5}Mn_{0.5})O_{3-\delta}$ [S.W. Tao & J.T.S. Irvine, *Nature Mater.* 2, 320 (2003)]
- $Sr_2(Mg,Mn)MoO_{6-\delta}$ [Y.H. Huang, J.B. Goodenough, *et al*., *Science* 312, 254 (2006)]

CATHODE

- MIEC (mixed ionic & electronic conductor)
- $(La,Sr)MnO_{3-\delta}$ (reacts with the electrolyte)
- $(Sr,Ba)(Co,Fe)O_{3-\delta}$ [Z.P. Shao & S.Haile, *Nature* 431, 170 (2004)]

PRESENT ELECTROLYTE: Y-STABILIZED ZIRKONIA (YSZ)

- $(Zr,Y)O_2$: cubic fluorite structure
- Y^{3+}-for-Zr^{4+} (8%) substitution creates oxygen vacancies
- **Electronic conductivity low enough (no mixed valency)**
- Good mechanical properties & relatively low price
- **PROBLEM: oxide-ion conductivity somewhat low**
  (could be improved by *e.g*. replacing Y with Sc, but Sc very rare/expensive)

NEW ELECTROLYTE CANDIDATE: $(La,Sr)(Ga,Mg)O_{3-\delta}$

- Perovskite structure
- Sr^{2+}-for-La^{3+} & Mg^{2+}-for-Ga^{3+} → **oxygen vacancies → oxide-ion conductivity**
- **Electronic conductivity low enough**
- **PROBLEMS:**
  - Decomposes at high temperatures & reducing conditions → operation < 800 °C
  - Mechanical properties not as good as for YSZ
  - Reacts with some electrode materials → buffer layers ?
  - Ga is expensive → Al-for-Ga substitution ?

PRESENT CATHODE: Perovskite (La,Sr)MnO_3

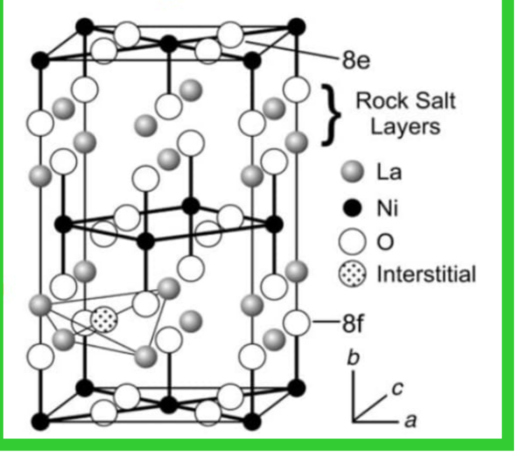
- Sr^{2+}-for-La^{3+} substitution: **$Mn^{3+} \rightarrow Mn^{4+}$** → **Good electronic cond.** (500 S/cm @ 800°C)
- Stable under highly oxidizing conditions & Low price
- **PROBLEM: too low ionic conductivity** → mixing with electrolyte for a composite

NEW CATHODE CANDIDATE: Perovskite (La,Sr)$(Co,Fe)O_{3-\delta}$

- (La,Sr)$CoO_{3-\delta}$
  - Sr^{2+}-for-La^{3+} substitution: **$Co^{3+} \rightarrow Co^{4+}$ & O-vacancies → MIEC**
  - **PROBLEM: Co is expensive**
- (La,Sr)$FeO_{3-\delta}$
  - Better thermal expansion characteristics
  - But lower electrical conductivity

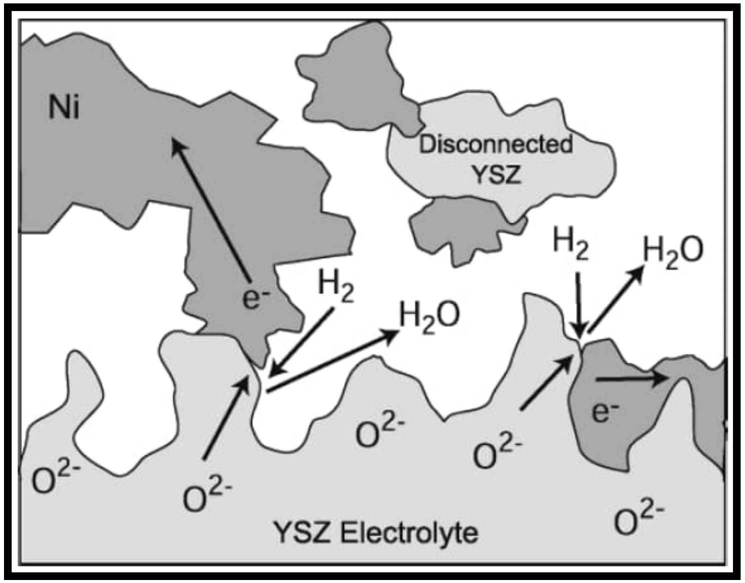
NEW CATHODE CANDIDATE: Ruddlesden-Popper La_2NiO_4

- Very good ionic conductivity: **interstitial oxygen !**
- Excellent electrical conductivity:
  semiconductor-metal transition around 400°C
- Reacts with YSZ; long term stability ?



PRESENT ANODE: NICKEL

- Reducing conditions → metals → Ni best (cheap)
- High electronic conductivity (~10^5 S/cm)
- **No oxide-ion conductivity** → **mixing with electrolyte (composite ”cermet”)**
- Works perfectly with H_2, but **poisoning when the fuel contains C or S**



NEW ANODE CANDIDATE: Perovskite $(La,Sr)CrO_3$

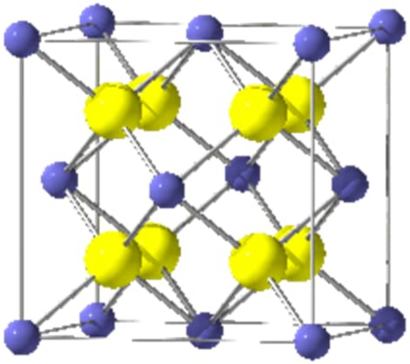
- $LaCrO_3$: too low conductivity
- Sr^{2+}-for-La^{3+}: $Cr^{3+} \rightarrow Cr^{4+}$, **increased electrical conductivity** (but *p*-type, **not good!)**
- Decent sulfur tolerance

NEW ANODE CANDIDATE: Double Perovskite Sr_2MgMoO_{6-w}

- **n-type; d**ecent electronic conductivity (intrinsic $Mo^{6+} \rightarrow Mo^{5+}$; σ = 1-10 S/cm)
- Stable in both reducing and oxidizing conditions, and with C and S containing fuels

Y.H. Huang, R.I. Dass, Z.L. Xing & J.B. Goodenough, Double perovskites as anode materials for solid-oxide fuel cells, *Science* **312**, 254 (2006).

OXYGEN STORAGE



COMMERCIAL CeO_2

- $CeO_{2-\delta}$: $Ce^{III/IV}$
- $(Ce,M)O_{2-\delta}$: M = Zr, Ti, Y, Bi, etc. (commercial)
- OSC ≈ 1500 μmol-O / g_{cat} (500 °C)

  [Y. Nagai *et al.*, *Catalysis Today* 74, 225 (2002)]
- good oxide-ion conductivity when T >500 °C
  → exhaust catalyst, SOFC electrolyte

NEW OXYGEN-STORAGE MATERIAL !!

- $YBaCo_4O_{7+\delta}$: $Co^{II/III}$ $(0 < \delta < 1.5)$
- OSC ≈ 2700 μmol-O / g_{cat} (200 ~ 350 °C)

  [M. Karppinen *et al*., *Chem. Mater*. **18**, 490 (2006);
  Int. Patent Appl. PCT/JP2006313436, filed June 6, 2006]

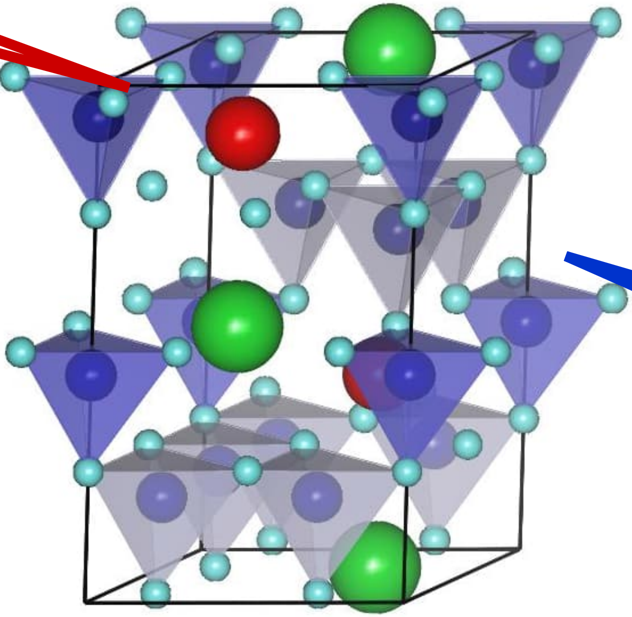
OSC (oxygen-storage capacity): μmol O/g

$YBaCo_4O_7$

- **Compound discovered in 2002 in Sweden**
  [M. Valldor & M. Andersson, *Solid State Sci.* 4, 923 (2002).]
- **Investigated for: - magnetic properties (frustrated Kagome-lattice)**
  - thermoelectric properties (layered Co oxide)

OXYGEN
???

Y: Dy ~ Lu, Ca, In

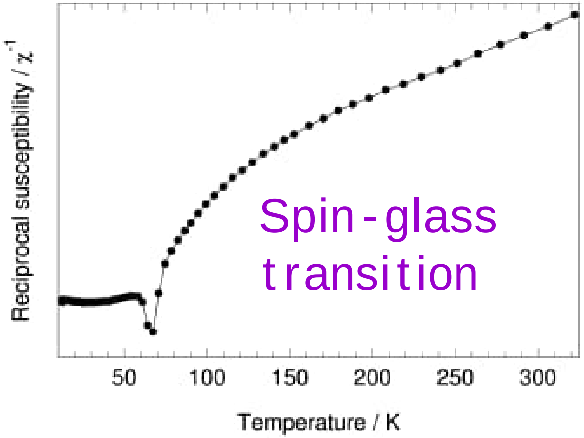


Ba

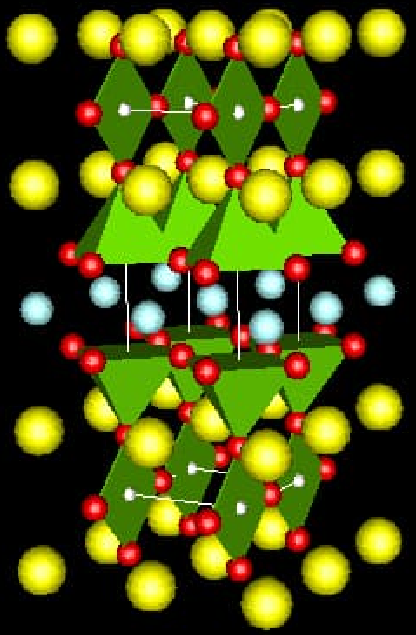
Triangular Layer (Co^{III})

Kagomé Layer (Co^{II})

Co: Al, Zn, Fe

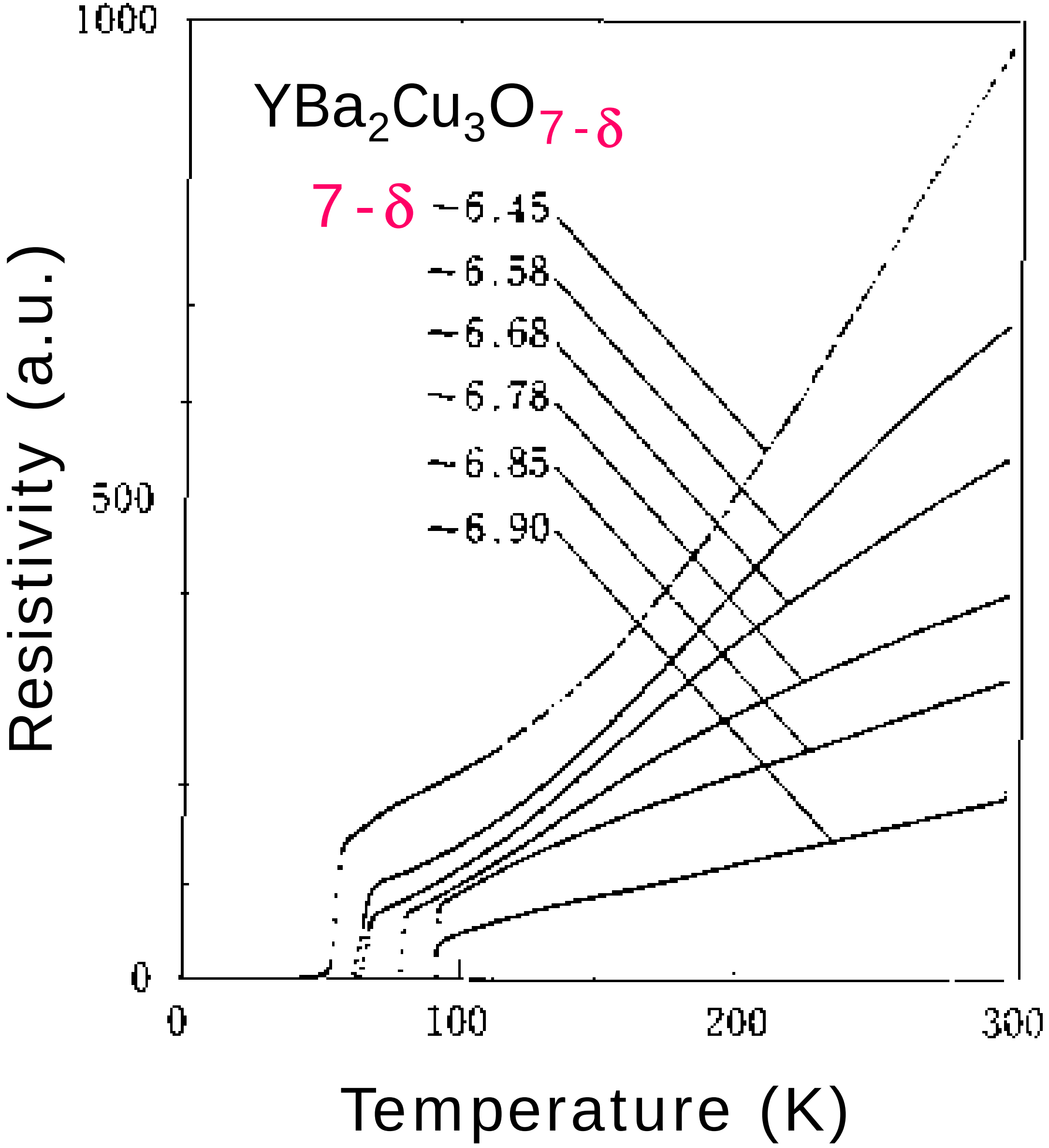


SUPERCONDUCTIVITY depends on OXYGEN CONTENT

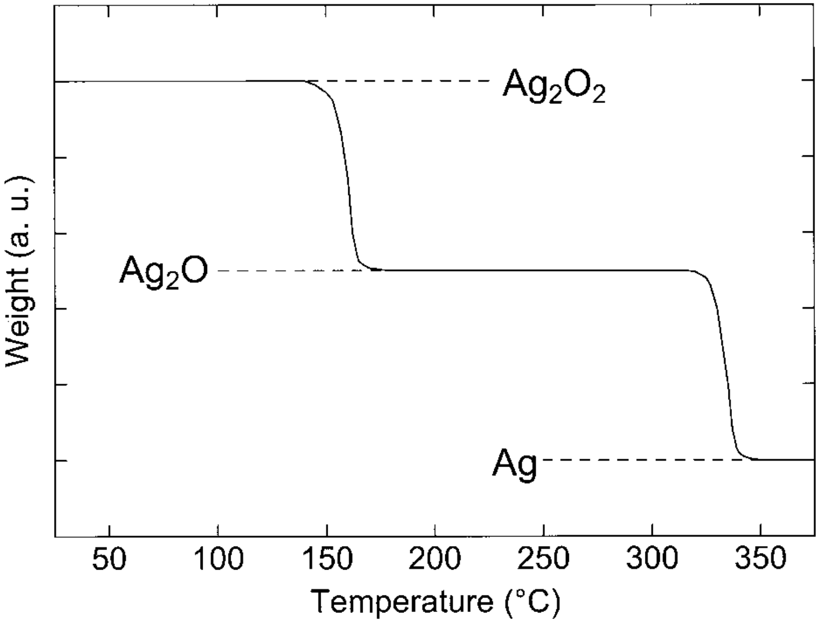


$CuBa_2YCu_2O_{7-\delta}$

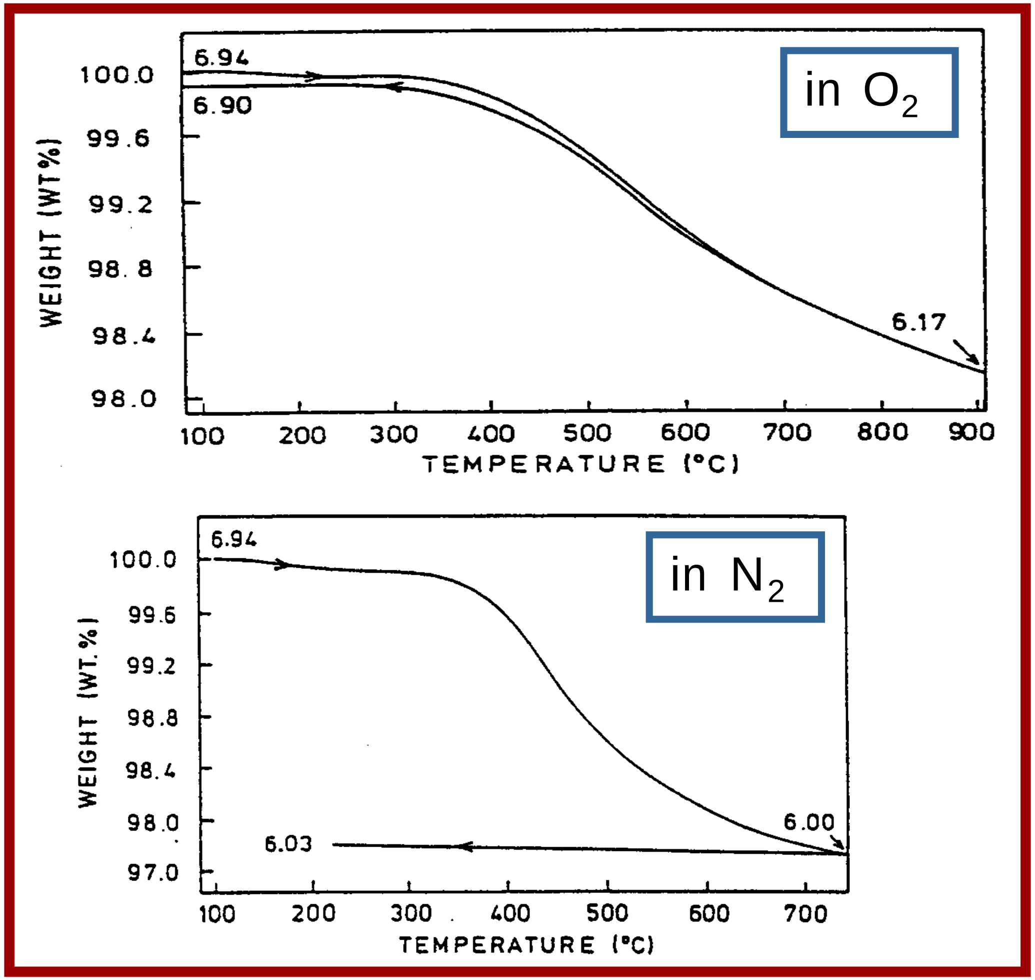
High-T_c Superconductivity

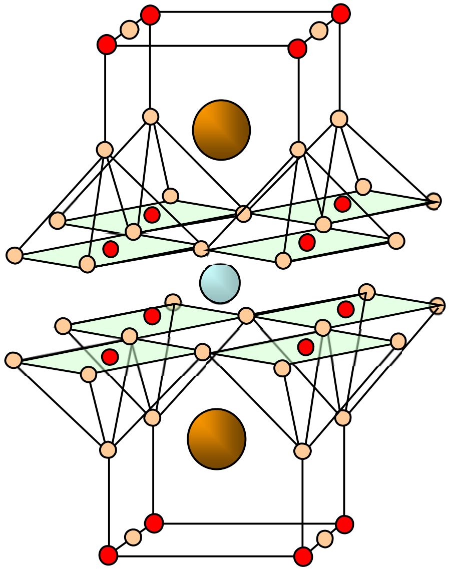


Thermogravinetry (TG): AgO in air

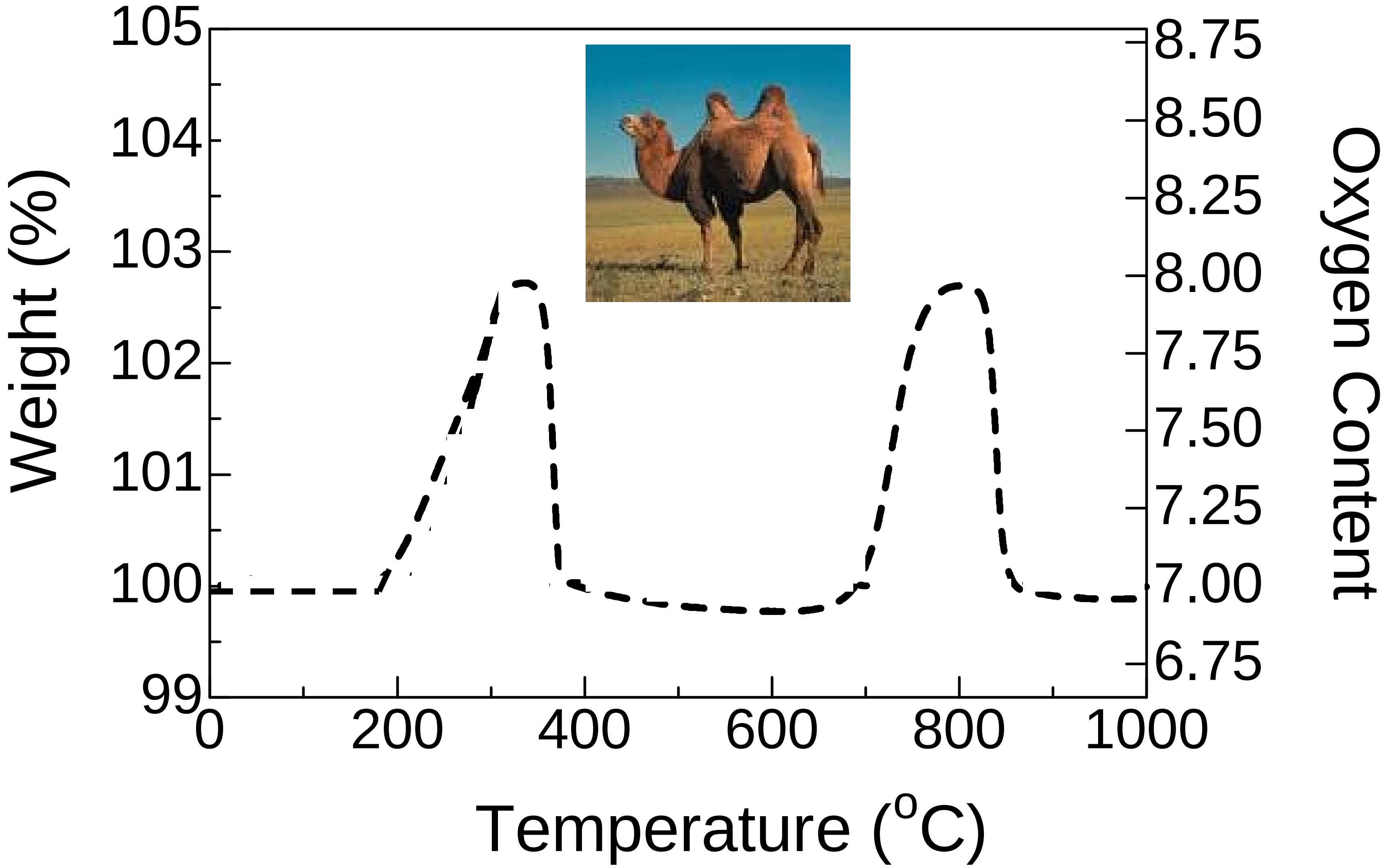


$YBa_2Cu_3O_{7-\delta}$

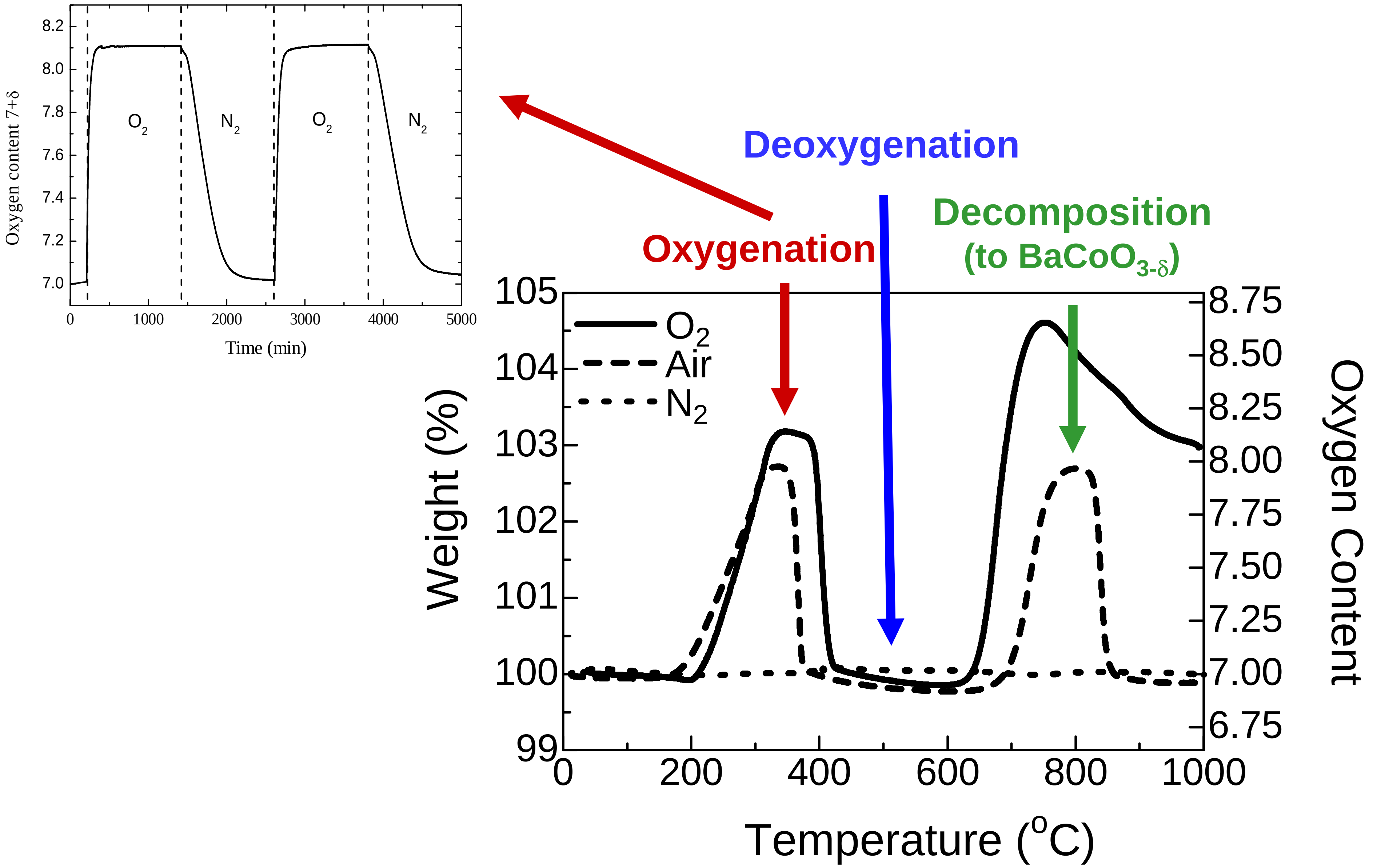




$YBaCo_4O_7$: heating in air in a thermobalance



Temperature: 300 °C



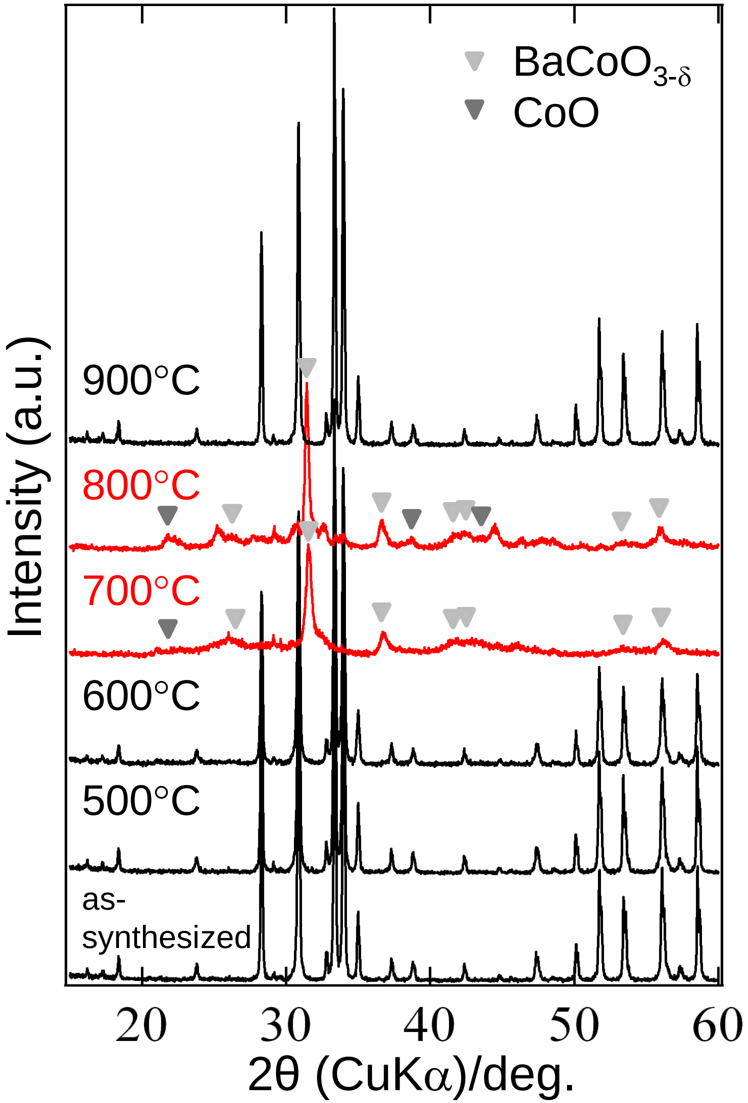
Oxygenation

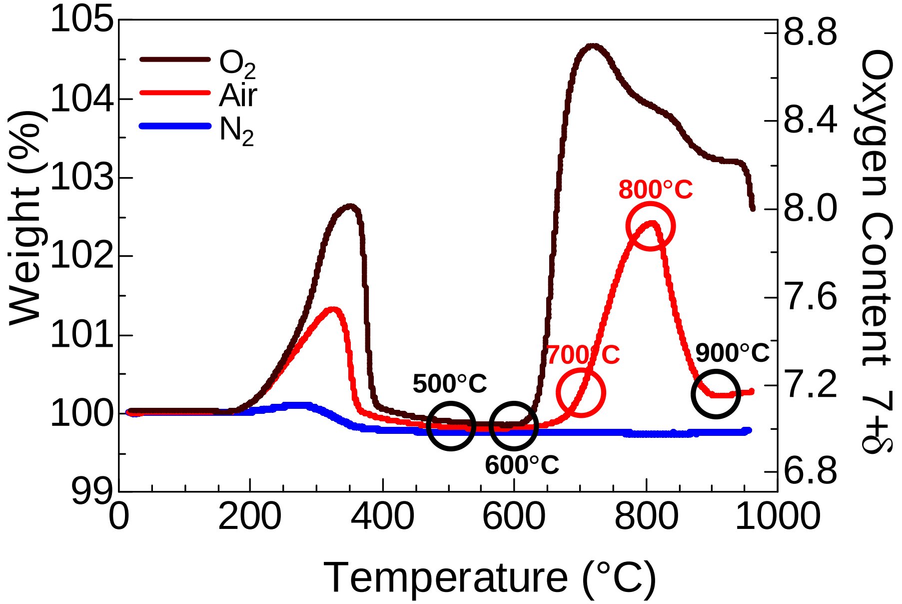
Deoxygenation

Decomposition **(to $BaCoO_{3-\delta}$)**

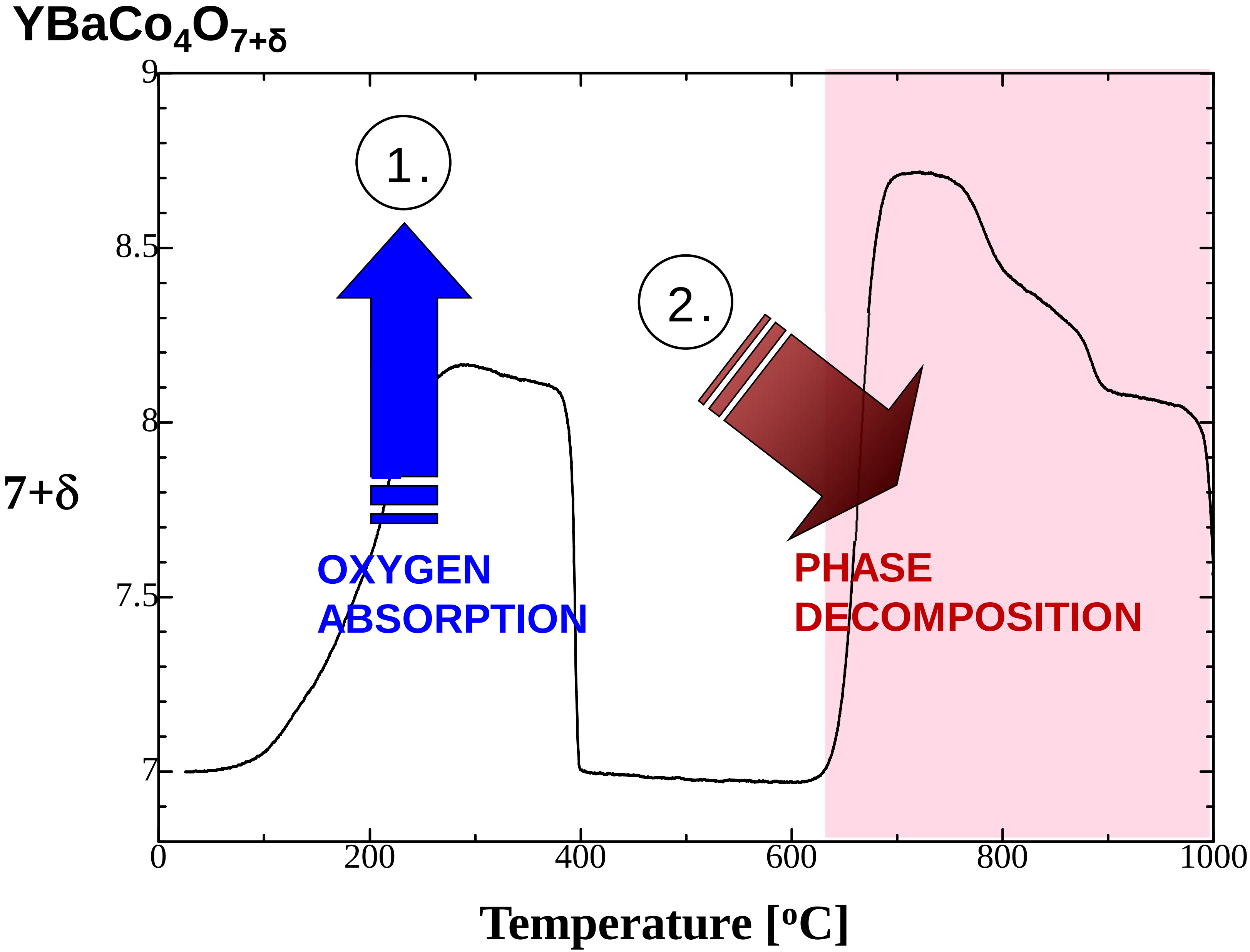
M. Karppinen, H. Yamauchi, S. Otani, T. Fujita, T. Motohashi, Y.-H. Huang, M. Valkeapää & H. Fjellvåg, *Chem. Mater*. **18**, 490 (2006).

Decomposition of $YBaCo_4O_{7+\delta}$ at high temperatures



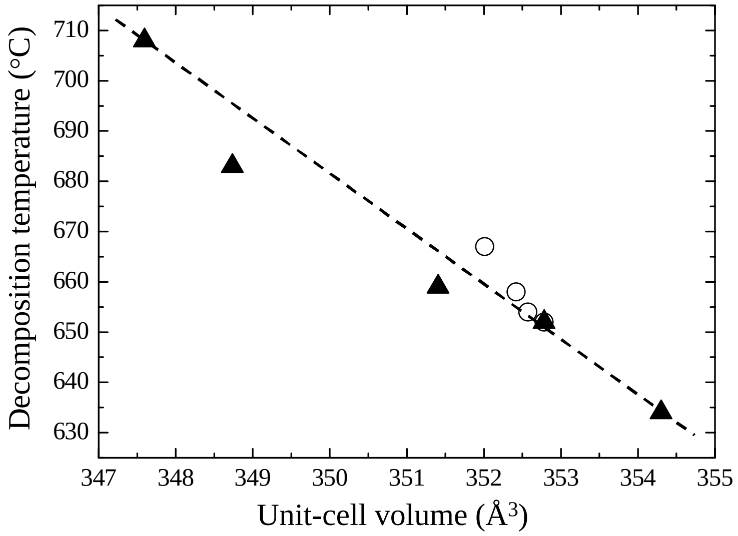


Further Improvements



ISOVALENT SUBSTITUTIONS

(= Chemical Pressure on $YBaCo_4O_{7+\delta}$)

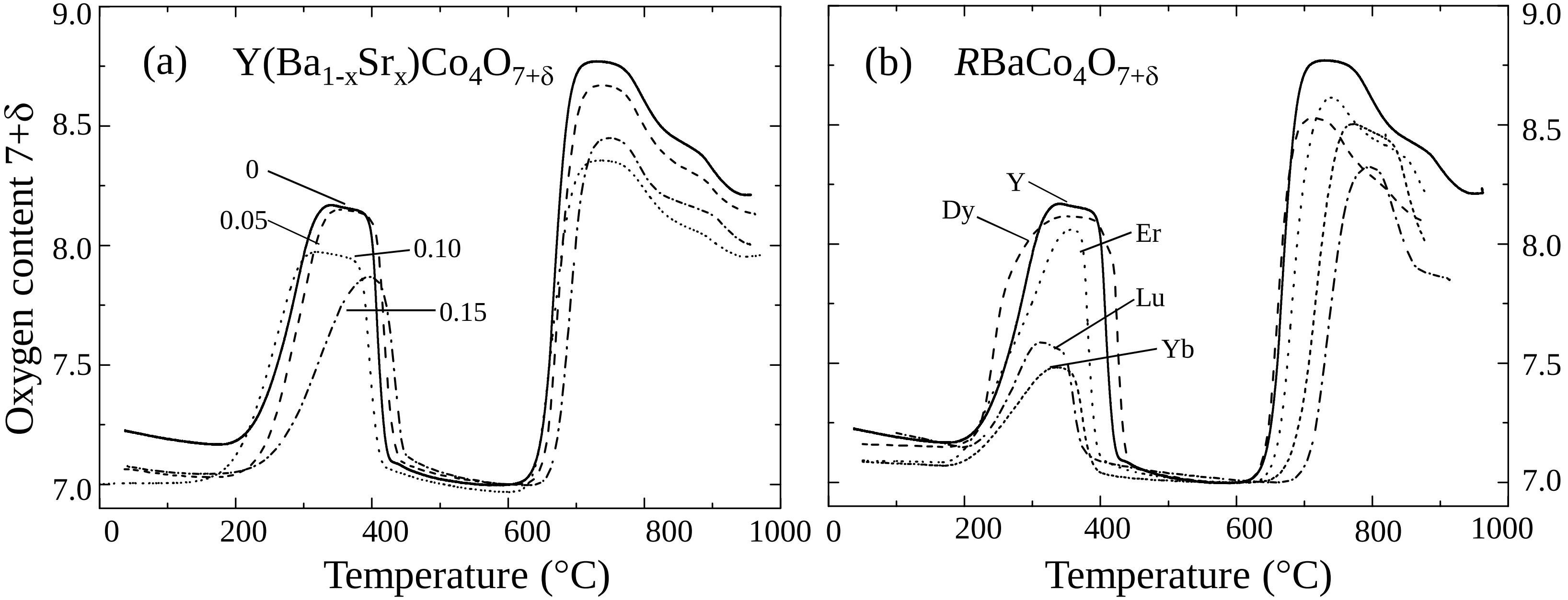


$Y\textit{A}Co_4O_{7+\delta}$

A^{II} ionic radius decreases → decomp. temp. increases but OSC decreases

$\textit{R}BaCo_4O_{7+\delta}$

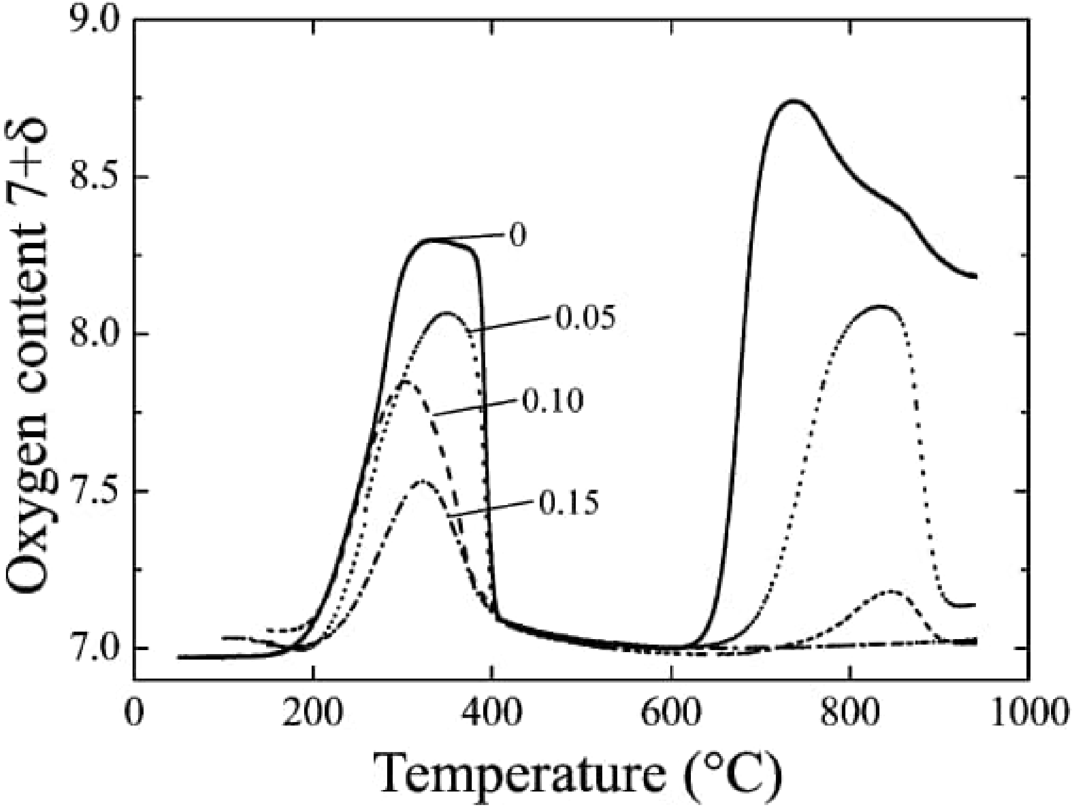
R^{III} ionic radius decreases → decomp. temp increases but OSC decreases



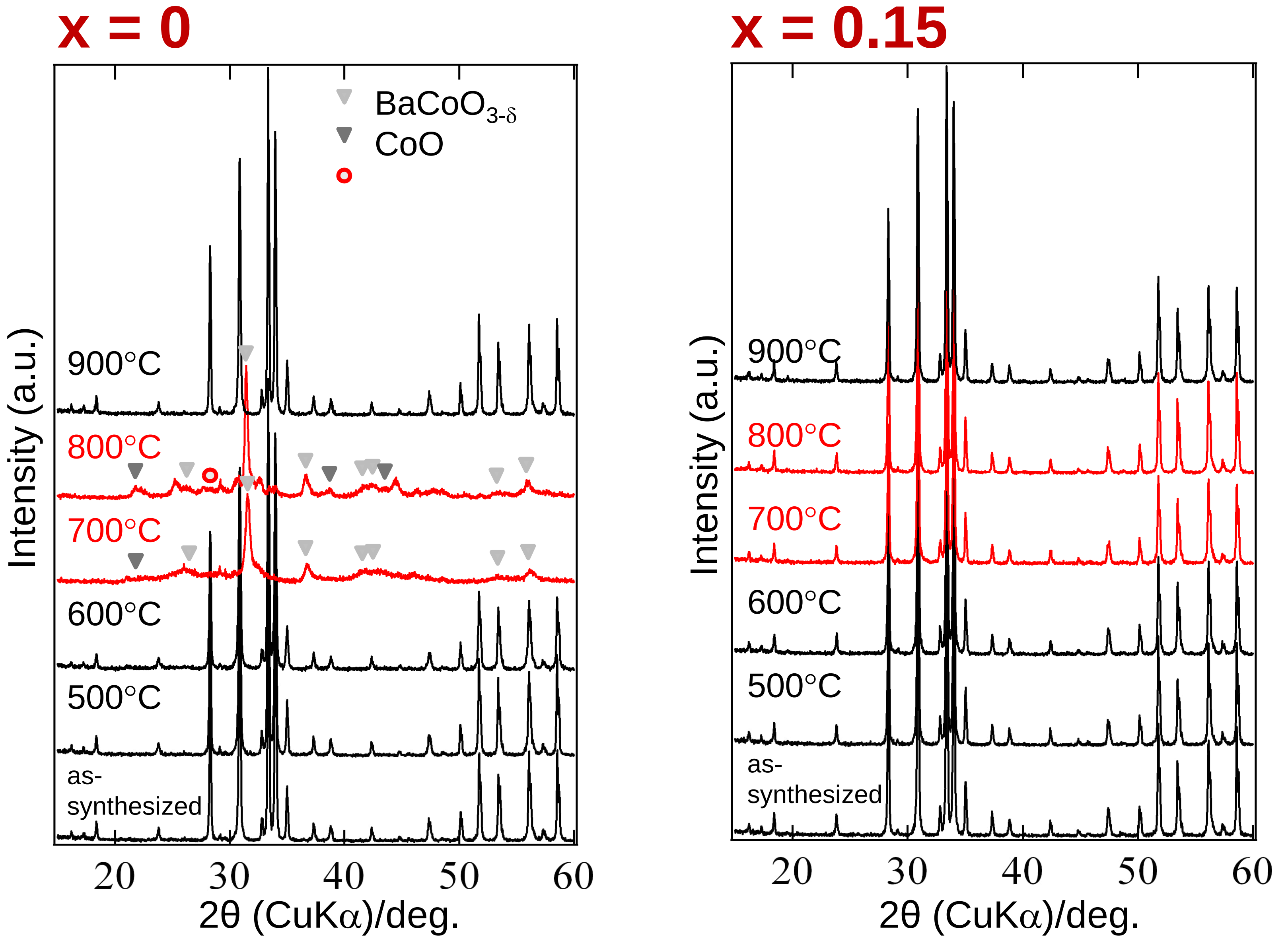
- S. Kadota, M. Karppinen, T. Motohashi & H. Yamauchi, *Chem. Mater*. **20**, 6378 (2008)
- O. Parkkima, H. Yamauchi & M. Karppinen, *Chem. Mater.* **25**, 599 (2013).

$YBa(Co_{1-x}Al_{x/2}Ga_{x/2})_4O_{7+\delta}$

Al-substitution: $x < 0.10$
Ga-substitution: $x < 0.25$



O. Parkkima, H. Yamauchi & M. Karppinen,
Chem. Mater. **25**, 599 (2013).



$YBa(Co_{1-x}Al_{x/2}Ga_{x/2})_4O_{7+\delta}$

$YBaCo_4O_{7+\delta}$ has been investigated for example for:

- **H_2/O_2 separation after photocatalytic water splitting (Mitsubishi Chemical Corp.)**
- sorbent material for oxygen-enriched CO_2 stream production
- oxygen-separating membrane material
- cathode material for solid oxide fuel cell
- catalyst in epoxidation reaction requiring active oxygen species

[O. Parkkima, A. Silvestre-Albero, J. Silvestre-Albero & M. Karppinen, Superior performance of oxygen-nonstoichiometric $YBaCo_4O_{7+\delta}$ as a catalyst in H_2O_2 oxidation of cyclohexene, *Catal. Lett.* ***145***, 576 (2015)]