Functional Inorganic Materials
Fall 2021

Tuesdays: 14.15 - 16.00
Thursdays: 12.15 - 14.00
Remote Zoom lectures

#	Date	Who	Topic
1	Tue 02.11.	Maarit	Introduction + Materials design
2	Thu 04.11.	Antti	Computational materials design
3	Tue 09.11.	Maarit	Superconductivity: High-T_c superconducting Cu oxides
4	**Thu 11.11.**	**Maarit**	**Ionic conductivity (Oxygen): SOFC and Oxygen storage**
5	Tue 16.11.	Maarit	Ionic conductivity (Lithium): Li-ion battery
6	Thu 18.11.	Antti	Thermal conductivity
7	Tue 23.11.	Antti	Thermoelectricity
8	Thu 25.11.	Maarit	Hybrid materials
9	Tue 30.11.	Maarit	Luminescence and optically active materials
10	Thu 02.12.	Antti	Piezoelectricity
11	Tue 07.12.	Antti	Pyroelectricity and ferroelectricity
12	Thu 09.12.	Antti	Magnetic and multiferroic oxides

LECTURE 4: Ionic conductivity: Oxygen

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

LECTURE EXERCISE 4

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. You can use Zr, Ce or Y oxides or their mixed compounds. How would you (HYPOTHETICALLY) construct your material if you like to make (HINT: think of the oxidation states); each time, explain WHY:

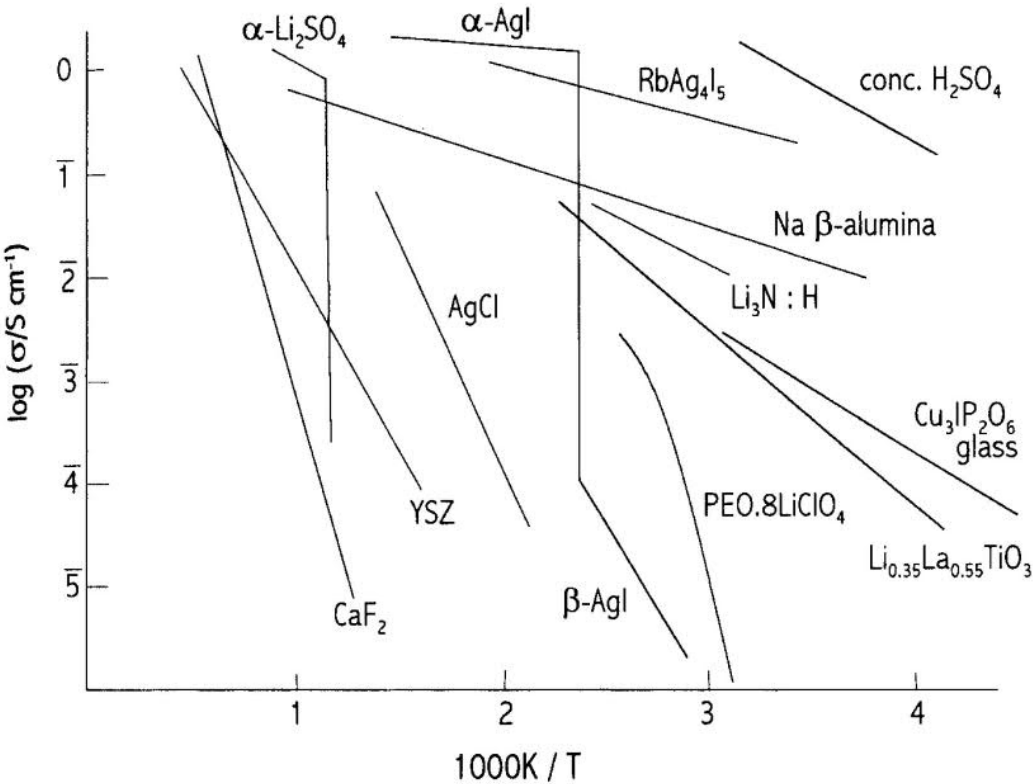
   (a) good electrical conductor but bad ionic conductor
   (b) good ionic conductor but bad electrical conductor
   (c) good electrical and good ionic conductor

4. What are the requirements (qualitatively) in terms of electrical conductivity and ionic conductivity for SOFC (i) cathode, (ii) anode, and (iii) electrolyte ?

5. You have four (HYPOTHETICAL) perovskite compounds, $La(Ga,Mg)O_{3-\delta}$, $(La,Y)GaO_{3-\delta}$, $(La,Sr)GaO_{3-\delta}$ and $(La,Sr)CrO_{3-\delta}$. Explain and justify (for all the four materials separately) whether the material could show some promise as a SOFC cathode or electrolyte material (HINT: think of the oxidation states).

IONIC CONDUCTIVITY

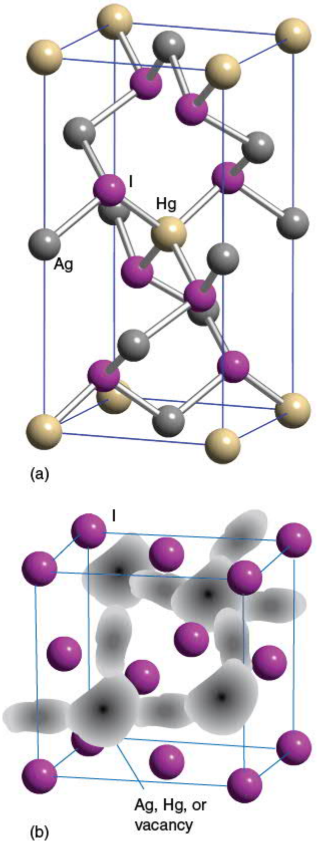
- Movement of ions in **solid** (or liquid): “non-perfect” (defective/disordered) crystals, glasses, polymers, gels, nanocomposites
- Ion conductivity increases with increasing temperature
- Faraday 1839: laws of electrolysis apply to ionic solids: e.g. PbF_2 & Ag_2S
- Prototype superionic conductor: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



Ag_2HgI_4

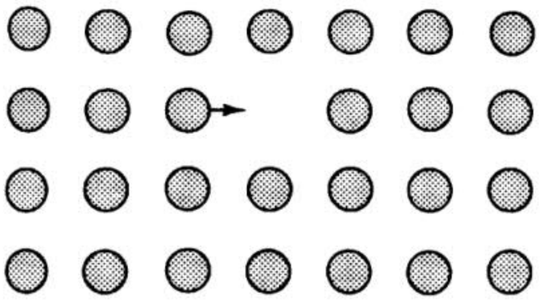
(a) Low-T: ordered structure, Ag^+ and Hg^{2+} at tetrahedral sites

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

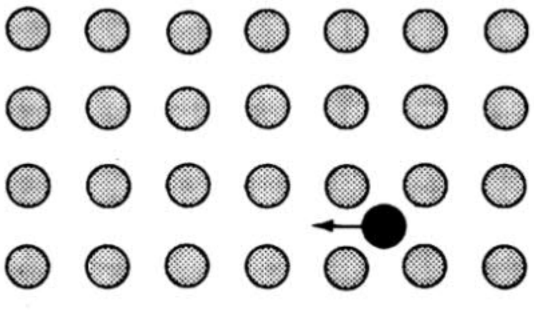


IONIC CONDUCTOR (solid)

- 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)
- Energy applications: O^{2-}, Li^{+}, H^{+} ion conductivity important
- **APPLICATIONS:**
  batteries, fuel cells (e.g. **SOFC**), supercapacitors, chemical sensors, separation membranes, gas (e.g. **oxygen) storage**



mobile vacancy

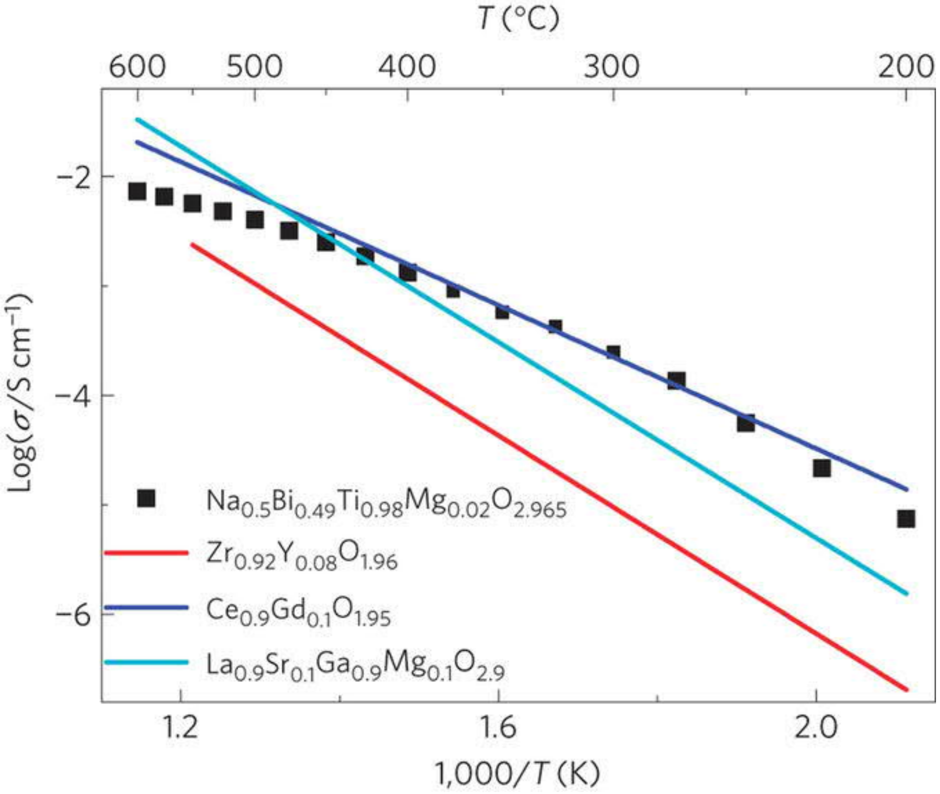


mobile interstitial

EFFECTIVE IONIC RADII

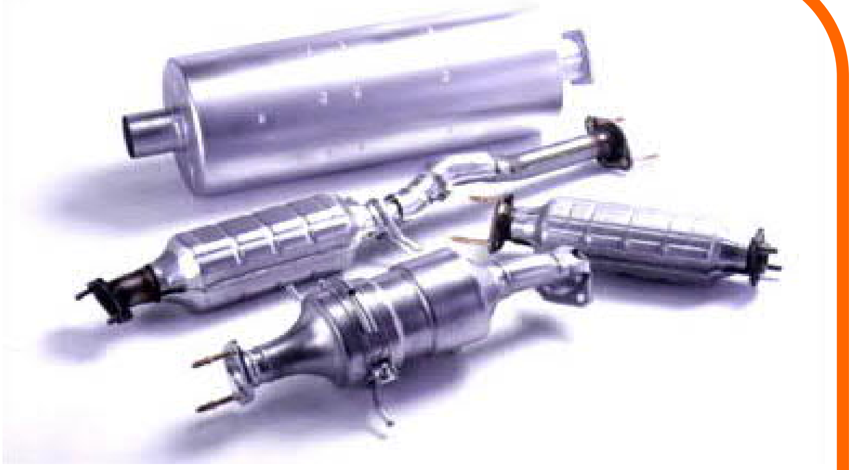
O^{2-}	**140 pm**
OH^{-}	**137 pm**
Li^{+}	**60 pm**
H^{+}	**very small**

	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}

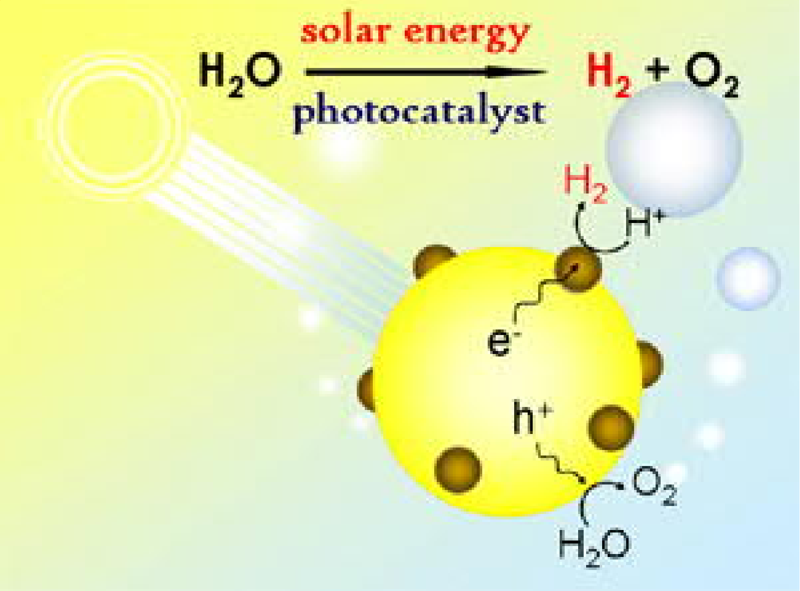


Examples of APPLICATIONS

Solid oxide fuel cell (SOFC)
oxide-ion conducting materials
NISSAN Motor Co. Ltd.



Redox exhaust gas catalyst
TOKYO ROKI Co. Ltd.



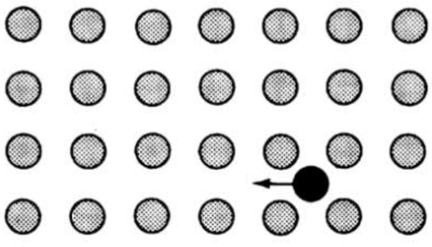
H_2/O_2 separation
in photocatalytic water splitting
Domen Lab. (Univ. of Tokyo)

- Separation
- Purification
- Sensors

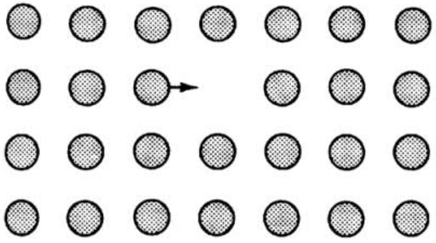
OXIDE-ION CONDUCTIVITY & OXYGEN-STORAGE

MATERIAL DESIGN CONSIDERATIONS

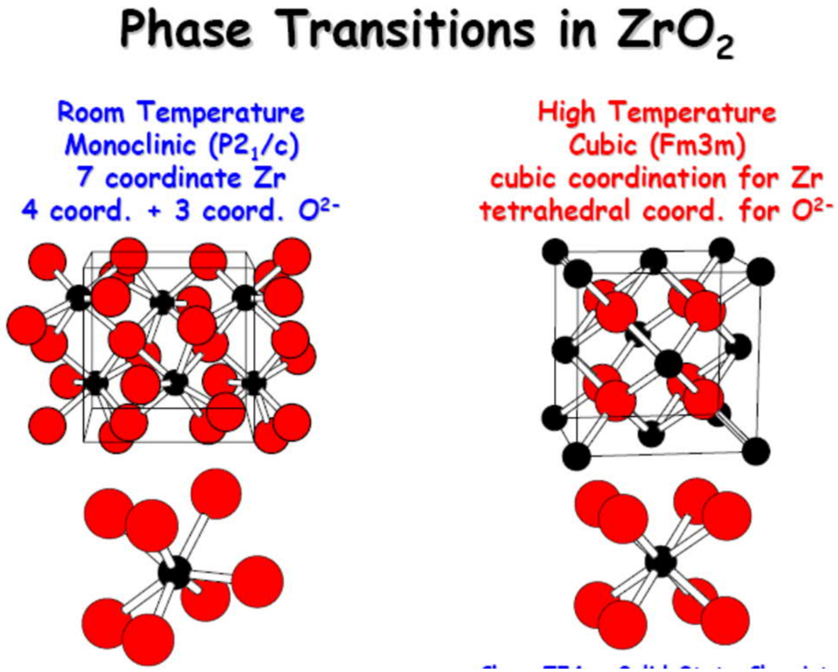
- **Open structure**: space for O^{2-} ion diffusion
- **Oxygen vacancies**: efficient O^{2-}-ion hopping
- **High crystal symmetry**: all oxygen sites equivalent (e.g. cubic ZrO_2 desired)
- **Redox-ative cations**: oxygen-content variation → OXYGEN STORAGE
- For sensor and separation applications →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



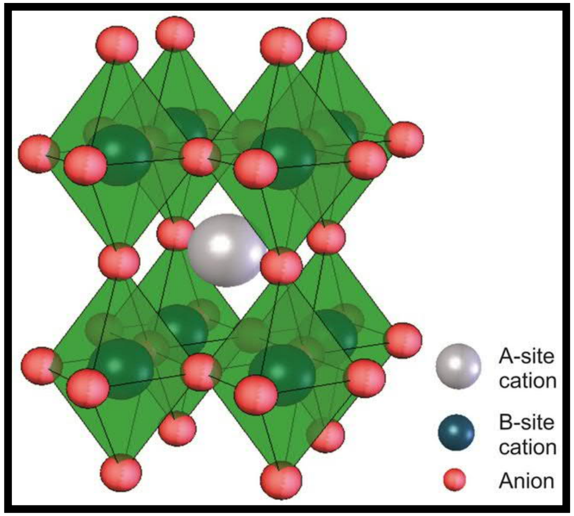
mobile interstitial



mobile vacancy



Phase Transitions in ZrO_2

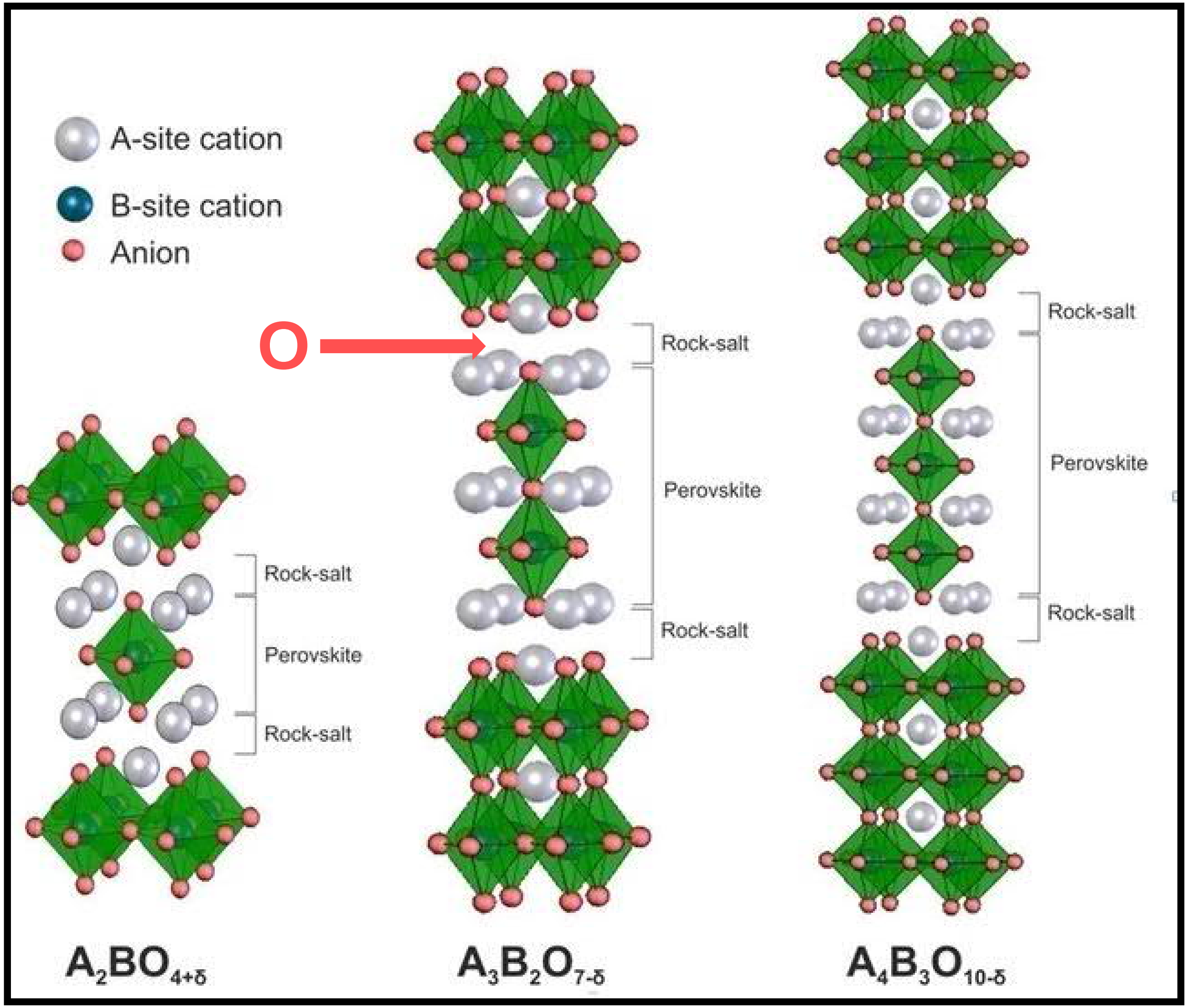


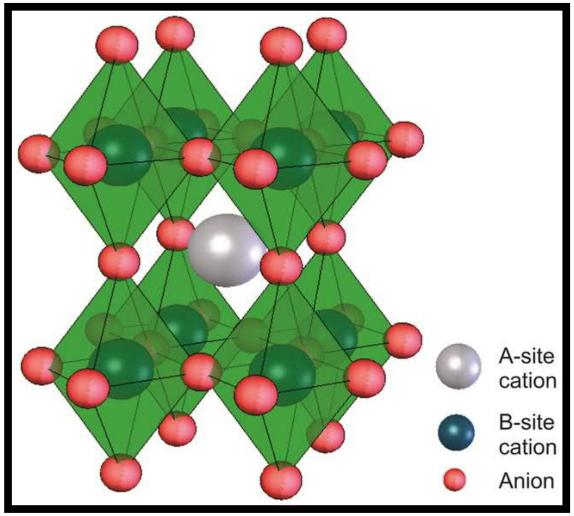
Perovskite ABO_3

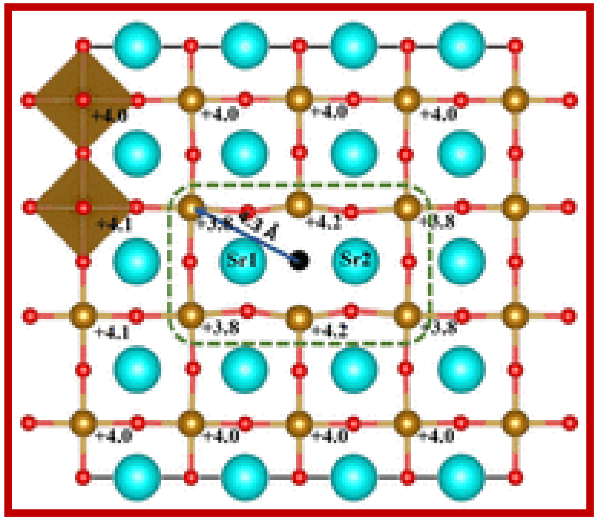
- No space for interstitial oxygen

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

- Enough space for interstitial oxygen





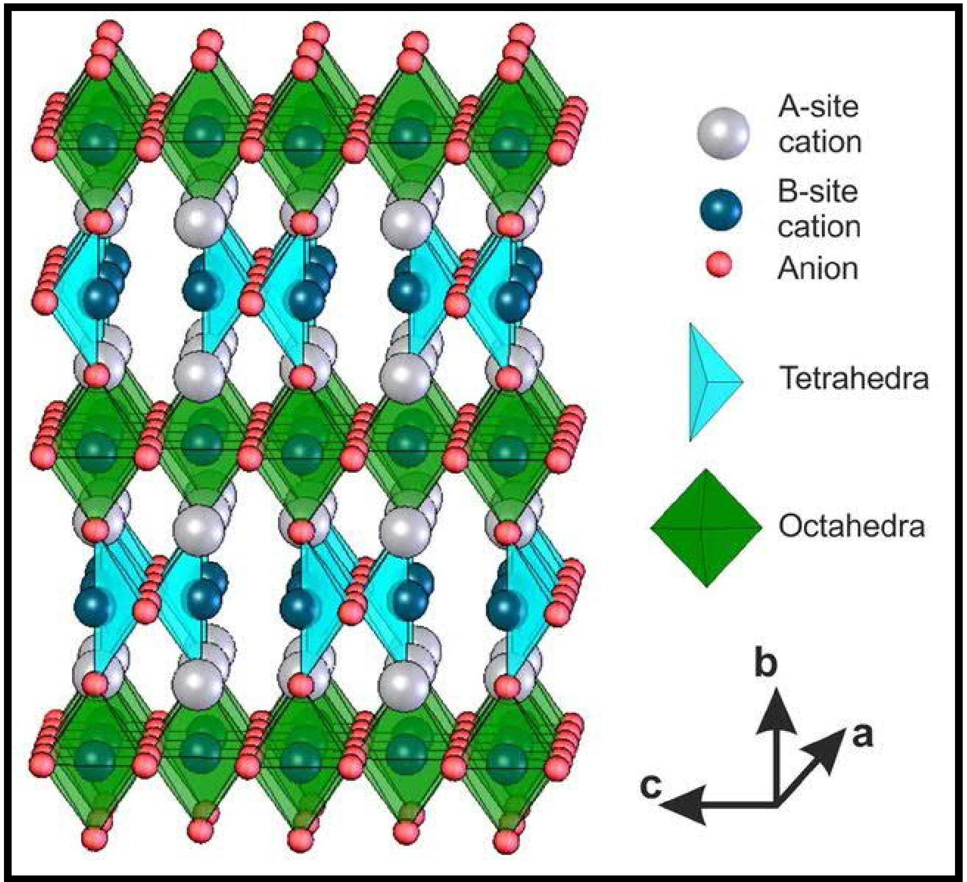


Perovskite $ABO_{3-\delta}$

- Prone for oxygen vacancies

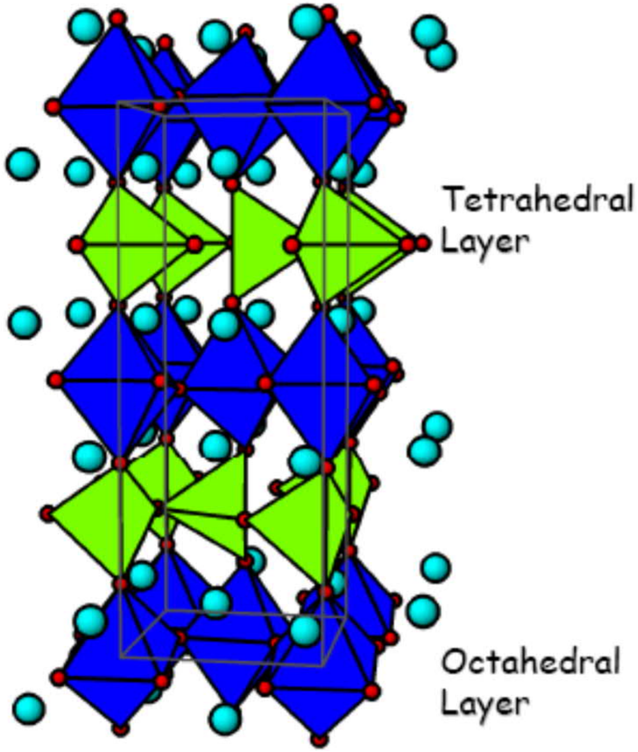
Oxygen-vacancies ordered:

- Brownmillerite $ABO_{2.5}$

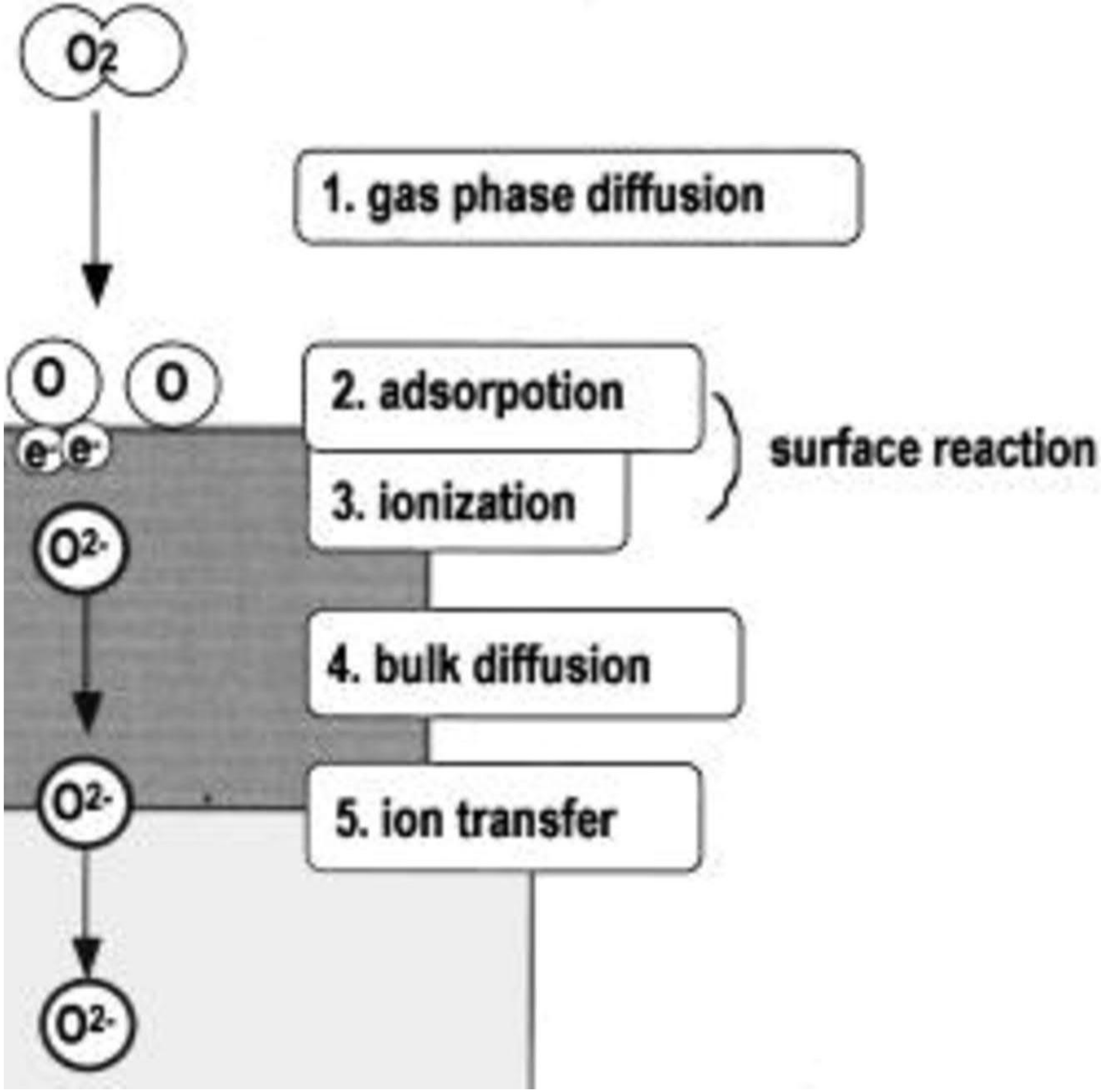


$Ba_2In_2O_5$ ($BaInO_{2.5}$)

- **Brownmillerite structure** derived from the **perovskite structure** (oxygen vacancies ordered into layers)
- **At 800 °C oxygen vacancies disorder and the ionic conductivity jumps from 10^{-3} S/cm to 10^{-1} S/cm**



WHAT KIND(S) of OXYGEN SPECIES ?

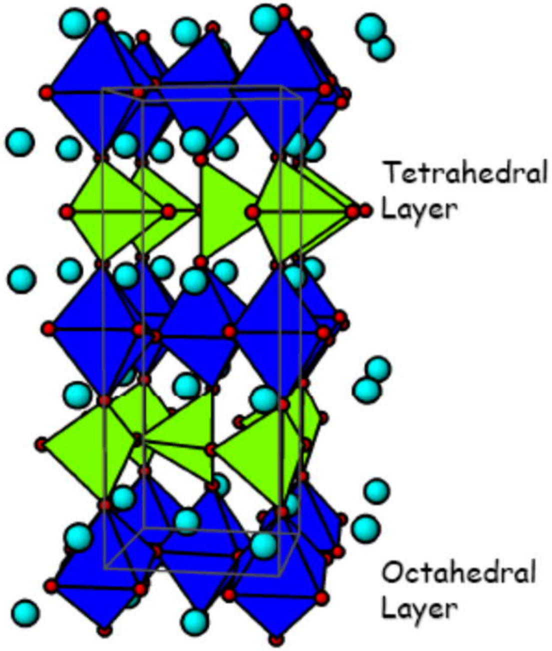


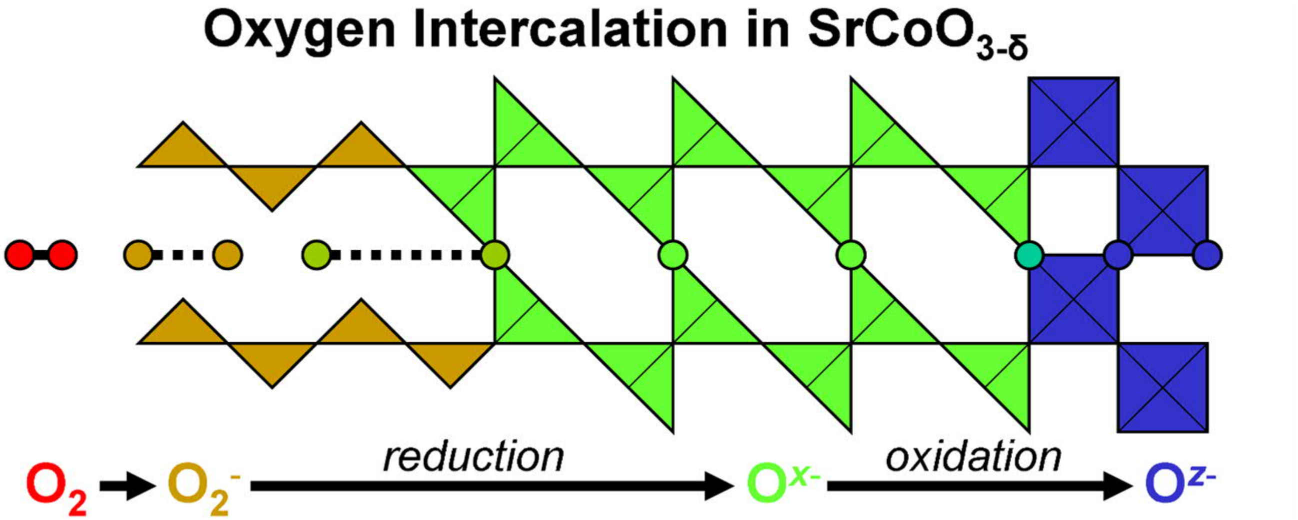
O-*K* and Co-*L* XANES spectroscopy

(in surface and bulk sensitive modes)

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

- **O_2 is first absorbed on the surface as O_2^-**
- **then reductively split into O^{x-}**
- **finally in the bulk reoxidized to O^{z-} ($0 < z < x$)**



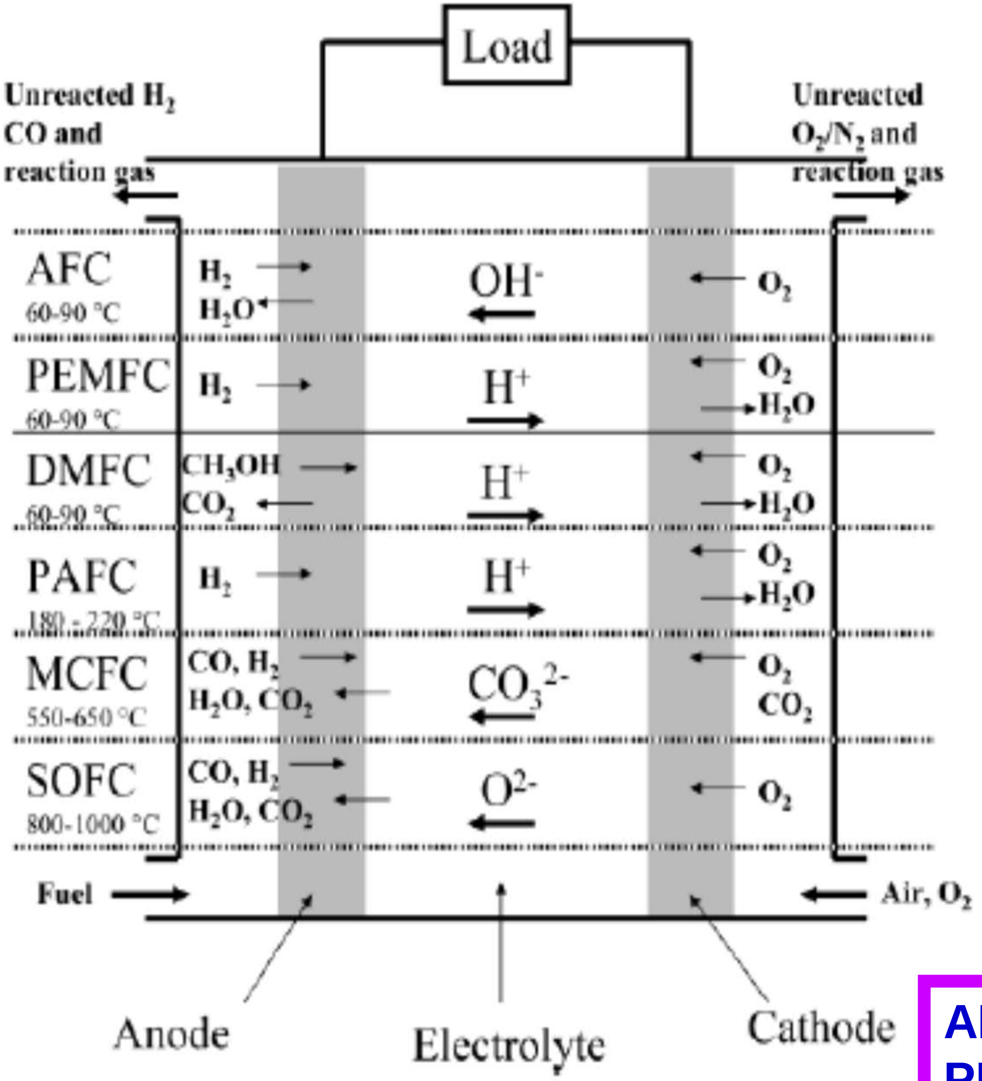


L. Karvonen, M. Valkeapää, R.S. Liu, J.M. Chen, H. Yamauchi & M. Karppinen,
O-*K* and Co-*L* XANES study on oxygen intercalation in perovskite $SrCoO_{3-\delta}$, *Chemistry of Materials* **22**, 70 (2010).

FUEL CELLS

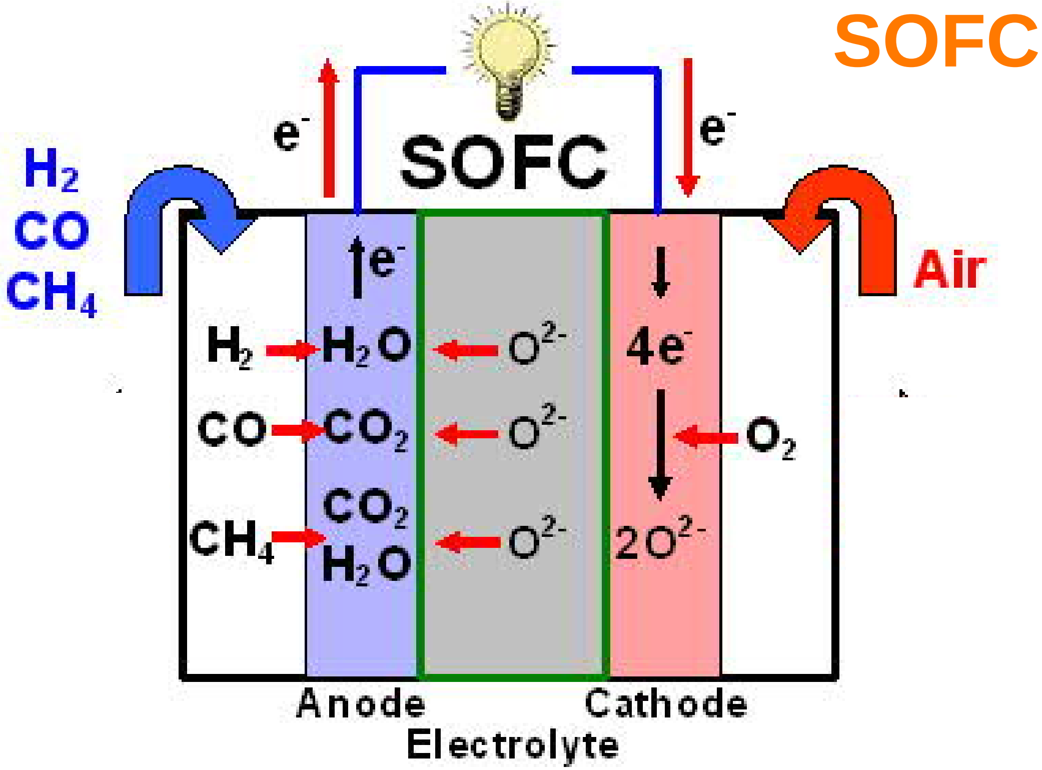
- **ELECTROCHEMICAL DEVICE:** converts the chemical energy from **continuously fed fuel** into electricity through a chemical **reaction with oxygen** or another oxidizing agent
- **POSSIBLE FUELS:** H_2, NH_3, carbon, CO, CH_4, CH_3CH_2OH, propane, butane, natural gas, diesel, Al, Mg, Zn
- Principle 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:** no need for a catalyst, but the thermodynamic efficiency decreases with increasing temperature

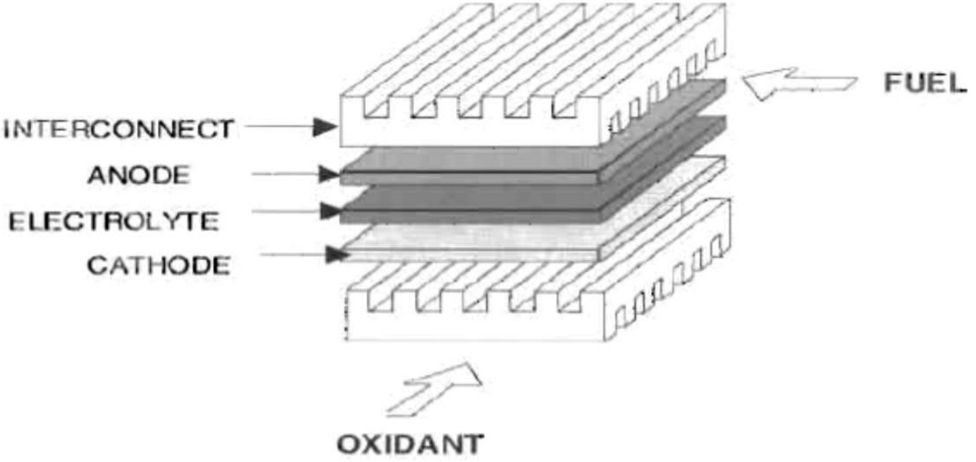
FUEL CELLS

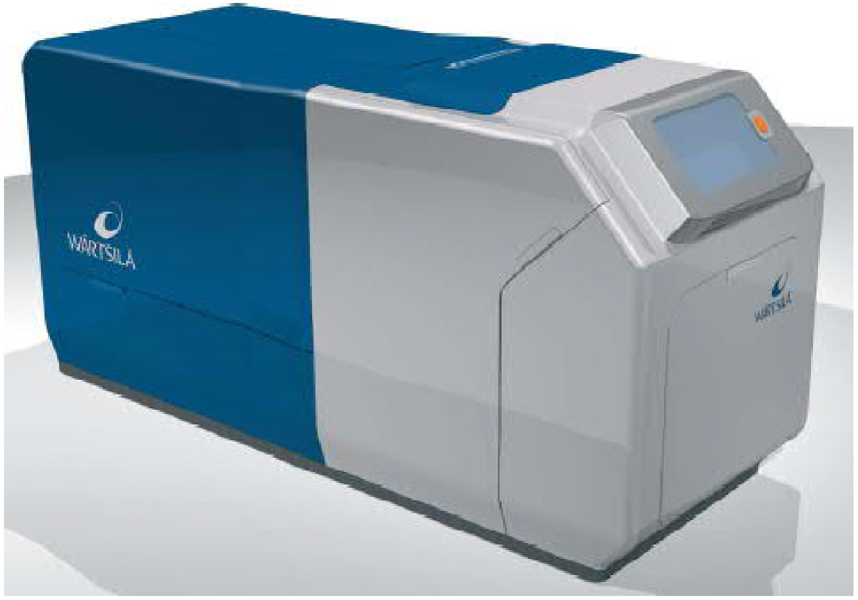


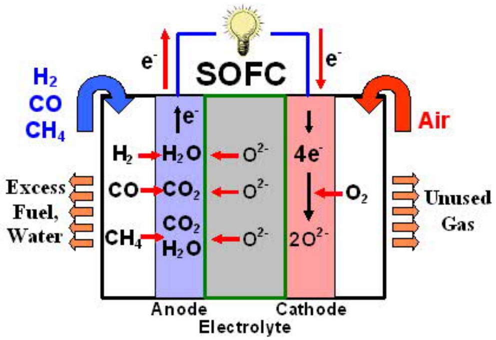
AFC	Alkaline fuel cell
PEMFC	Proton exchange membrane
DMFC	Methol direct oxidize fuel cell
PAFC	Phosphate fuel cell
MCFC	Molten carbonate fuel cell
SOFC	Solid-oxide fuel cell

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**
- **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**
- 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: (La,Sr)MnO$_3$

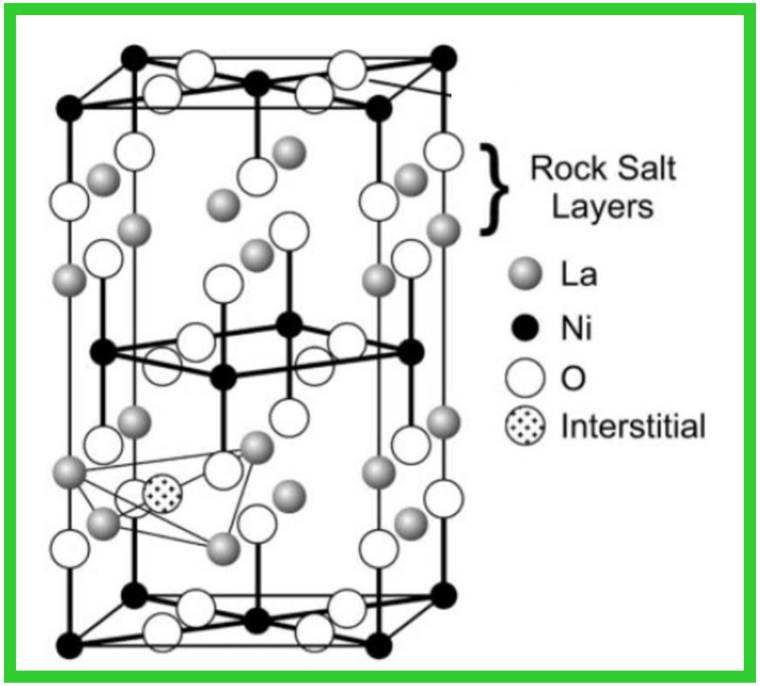
- Perovskite structure
- Sr^{2+}-for-La^{3+} substitution: **Mn^{3+} → Mn^{4+}**
  → **Good electronic conductivity** (σ = 500 S/cm @ 800 °C)
- Stable under highly oxidizing conditions & Low price
- **PROBLEM: too low ionic conductivity**
  → mixing with electrolyte for a composite

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

- Perovskite structure
- (La,Sr)**Co**O$_{3-\delta}$
  - Sr^{2+}-for-La^{3+} substitution: **Co^{3+} → Co^{4+} & Oxygen vacancies**
  - **Very good MIEC**
  - **PROBLEM: Co is expensive**
- (La,Sr)**Fe**O$_{3-\delta}$
  - Fe much cheaper than Co
  - Better thermal expansion characteristics
  - But lower electrical conductivity

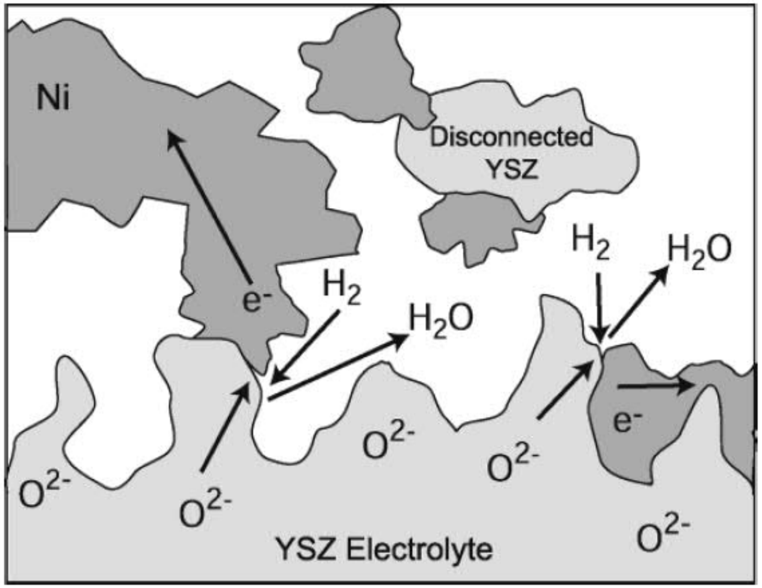
NEW CATHODE CANDIDATE: La_2NiO_4

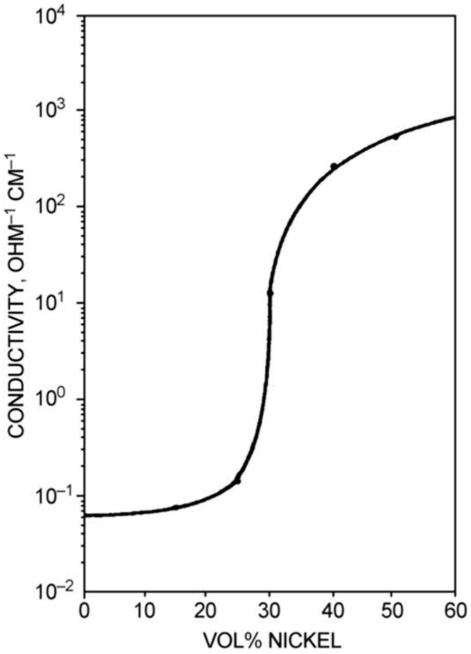
- Ruddlesden-Popper (RP) structure
- Excellent electrical conductivity: semiconductor-metal transition around 400°C
- Very good ionic conductivity: **interstitial oxygen !**
- Reacts with YSZ; long term stability ?



PRESENT ANODE: NICKEL

- Reducing conditions → metals → Ni best
- High electronic conductivity (~10^5 S/cm)
- Low price
- **No oxide-ion conductivity** → **mixing with electrolyte for a composite (cermet)**
- Works perfectly with H_2 as a fuel
- **Poisoning when the fuel contains C or S**





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

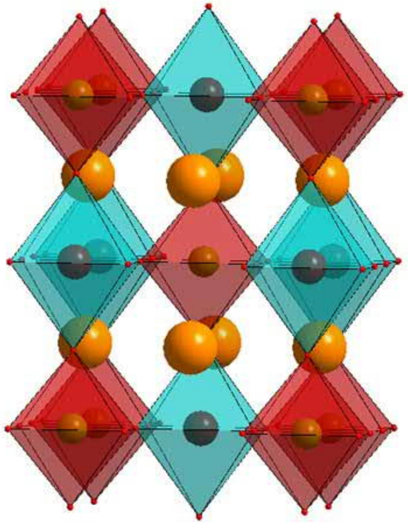
- $LaCrO_3$: too low conductivity
- Sr^{2+}-for-La^{3+}: $Cr^{3+} \rightarrow Cr^{4+}$, **increased electrical conductivity** (but *p*-type, **not good!)**
- Decent sulfur tolerance

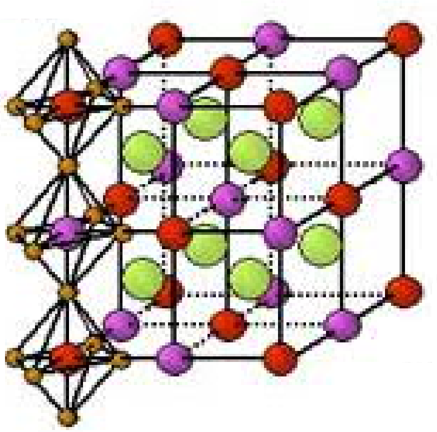
NEW ANODE CANDIDATE: Sr_2MgMoO_6

- *B*-site ordered double perovskite, **n-type**
- Decent electronic conductivity ($Mo^{6+} \rightarrow Mo^{5+}$; σ = 1-10 S/cm)
- Stable in both reducing and oxidizing conditions
- **Stable with C and S containing fuels**
- Substitution: $La^{3+} \rightarrow Sr^{2+}$
  - $Mo^{6+} \rightarrow Mo^{5+}$
  - Works perfectly with hydrocarbons
- **VERY PROMISING !**

Y.H. Huang, **J.B. Goodenough**, *et al*., *Science* **312**, 254 (2006).

$A_2B'B''O_6$



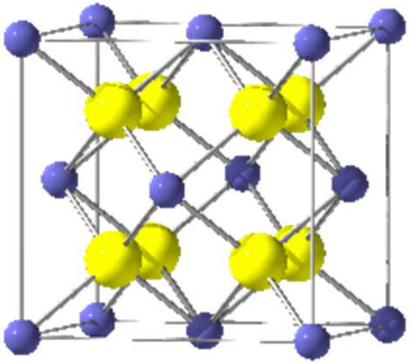


Sr_2FeMoO_{6-w}

Sr_2MgMoO_{6-w}

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]

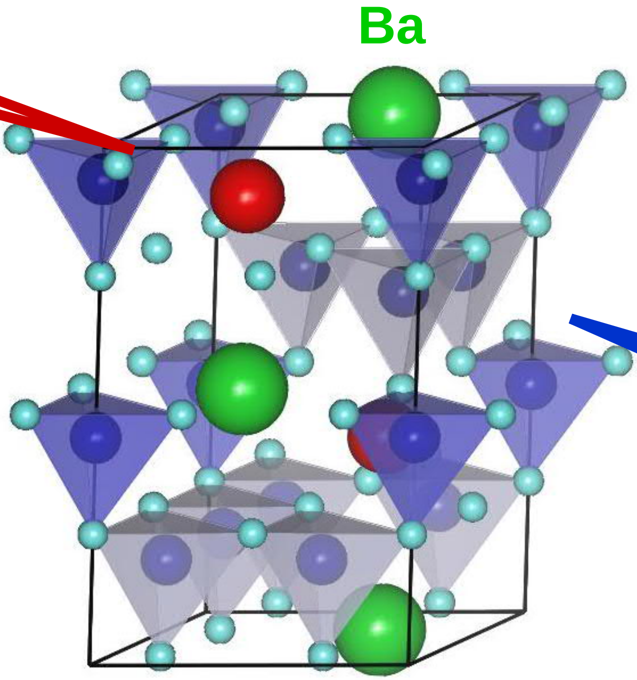
OSC (oxygen-storage capacity): μmol O/g

YBaCo$_4$O$_7$

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

OXYGEN ???

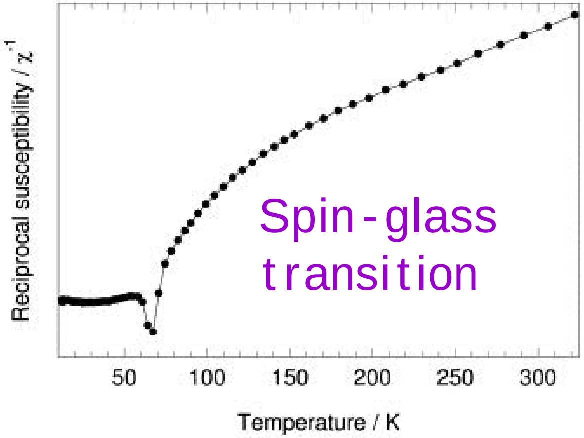
Y: Dy ~ Lu, Ca, In



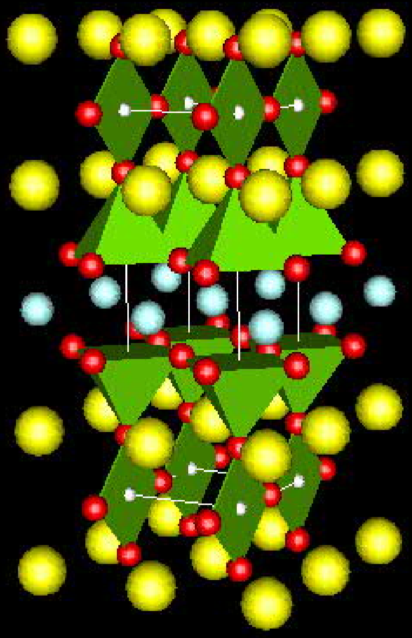
Triangular Layer (Co^{III})

Kagomé Layer (Co^{II})

Co: Al, Zn, Fe

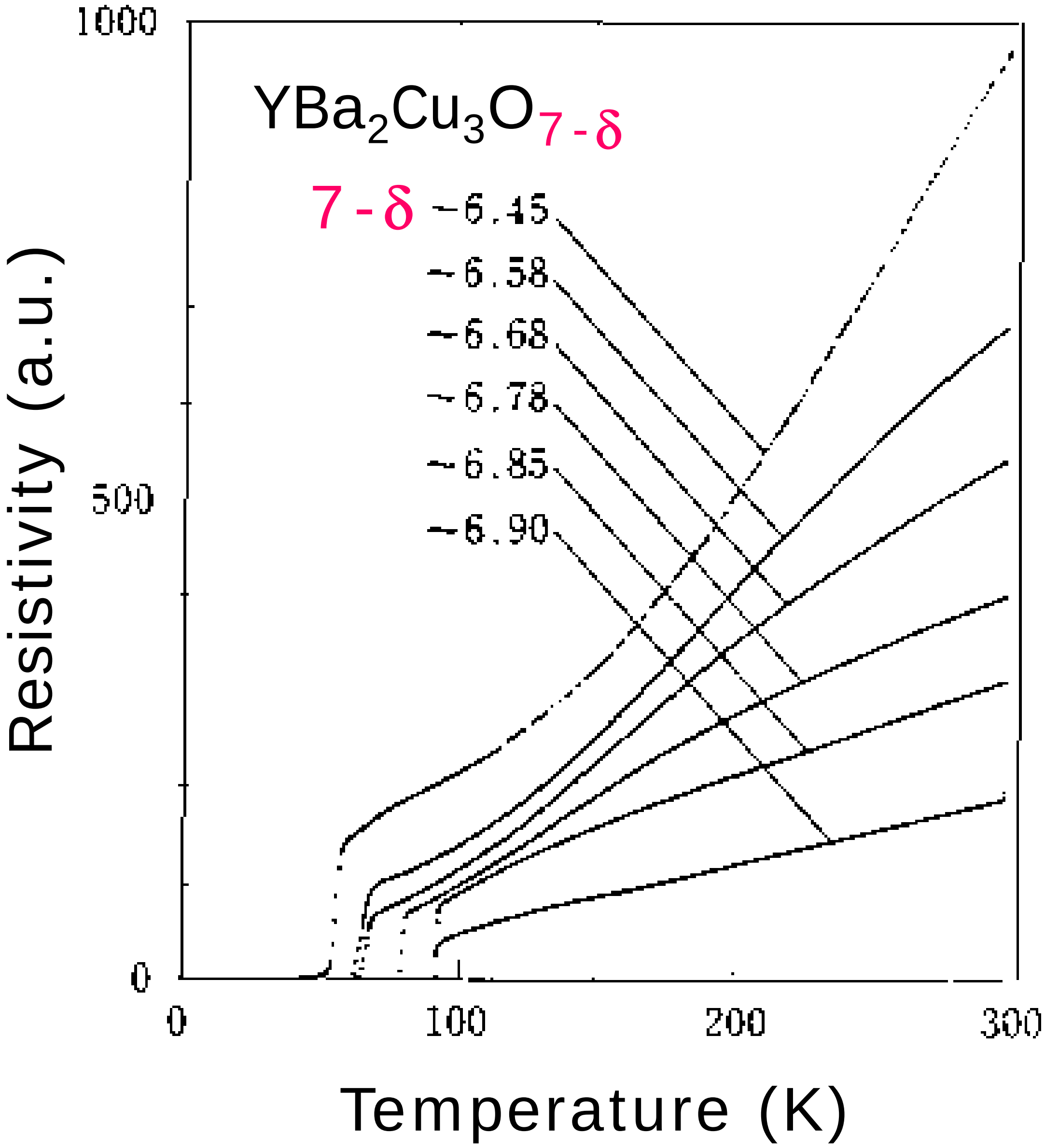


SUPERCONDUCTIVITY depends on OXYGEN CONTENT

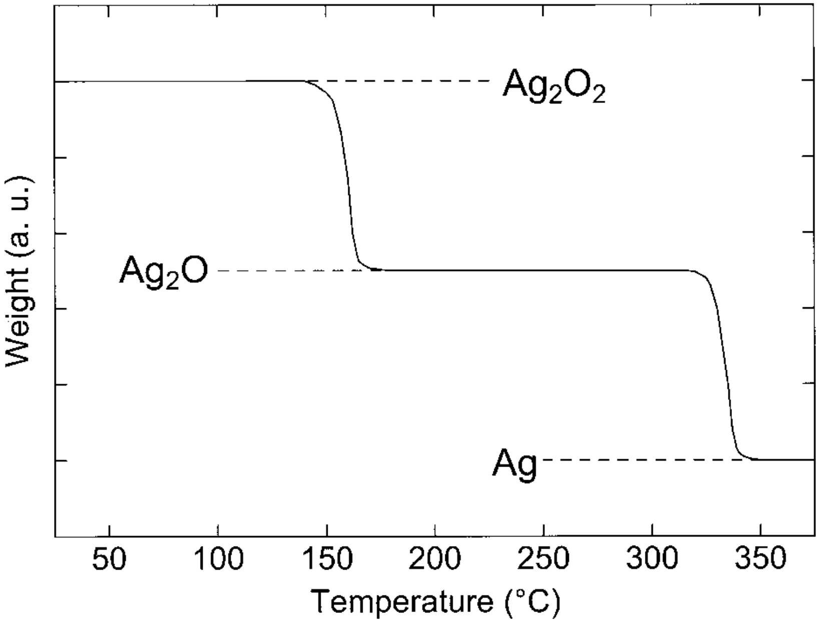


$CuBa_2YCu_2O_{7-\delta}$

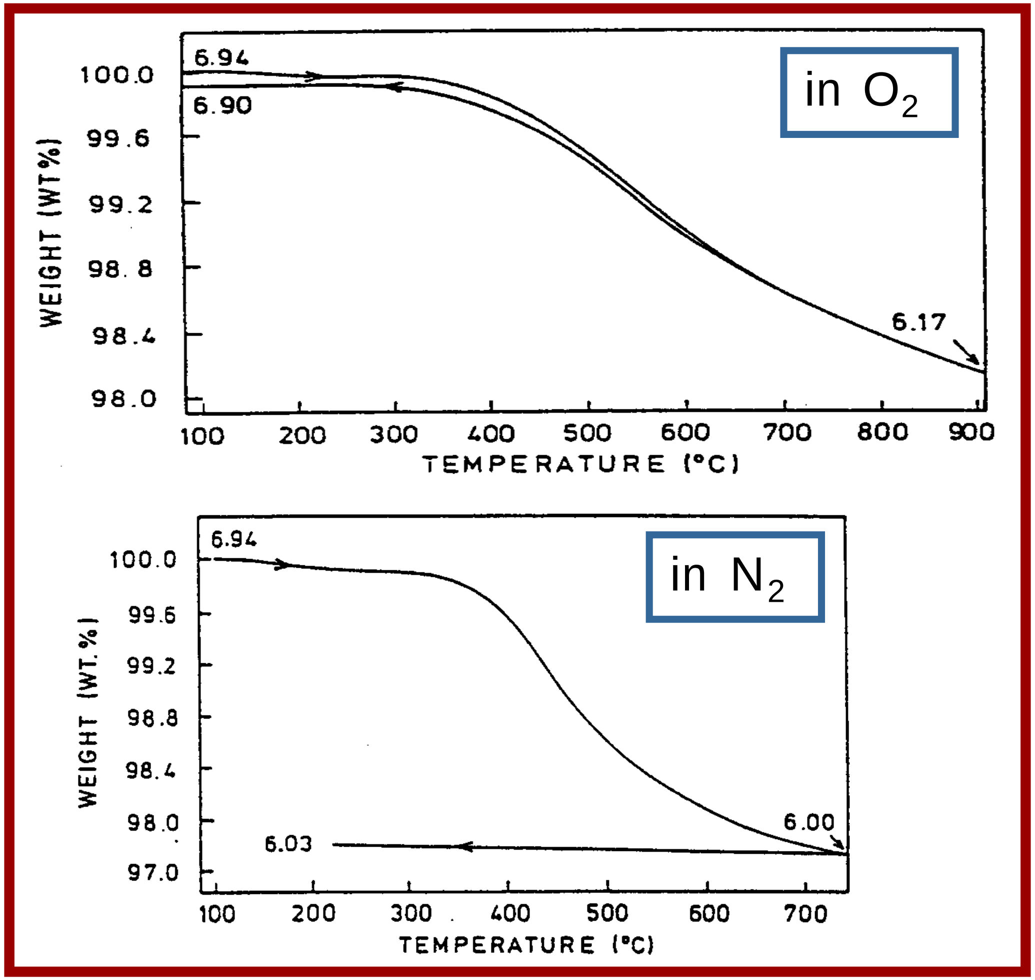
High-T_c
Superconductivity

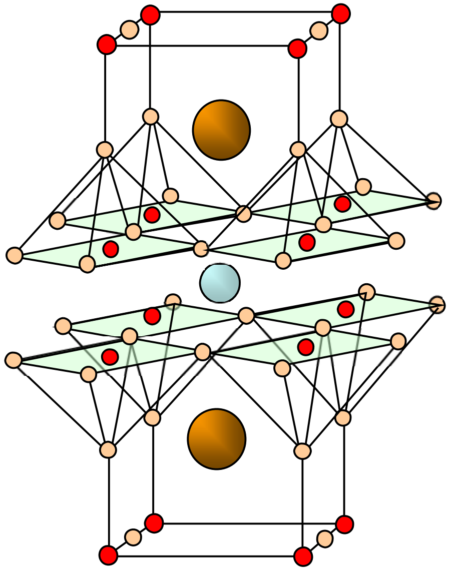


Thermogravinetry (TG): **AgO in air**

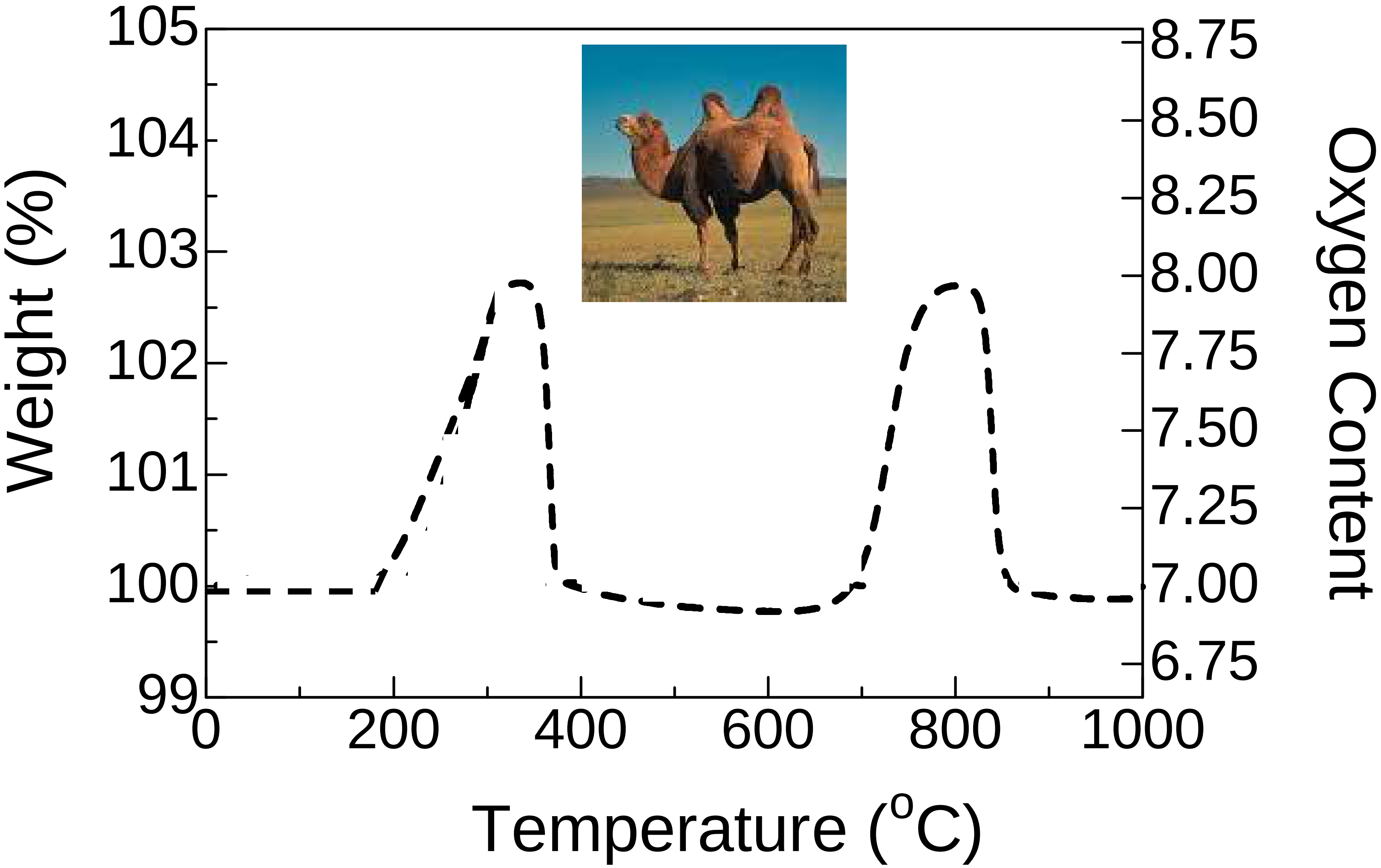


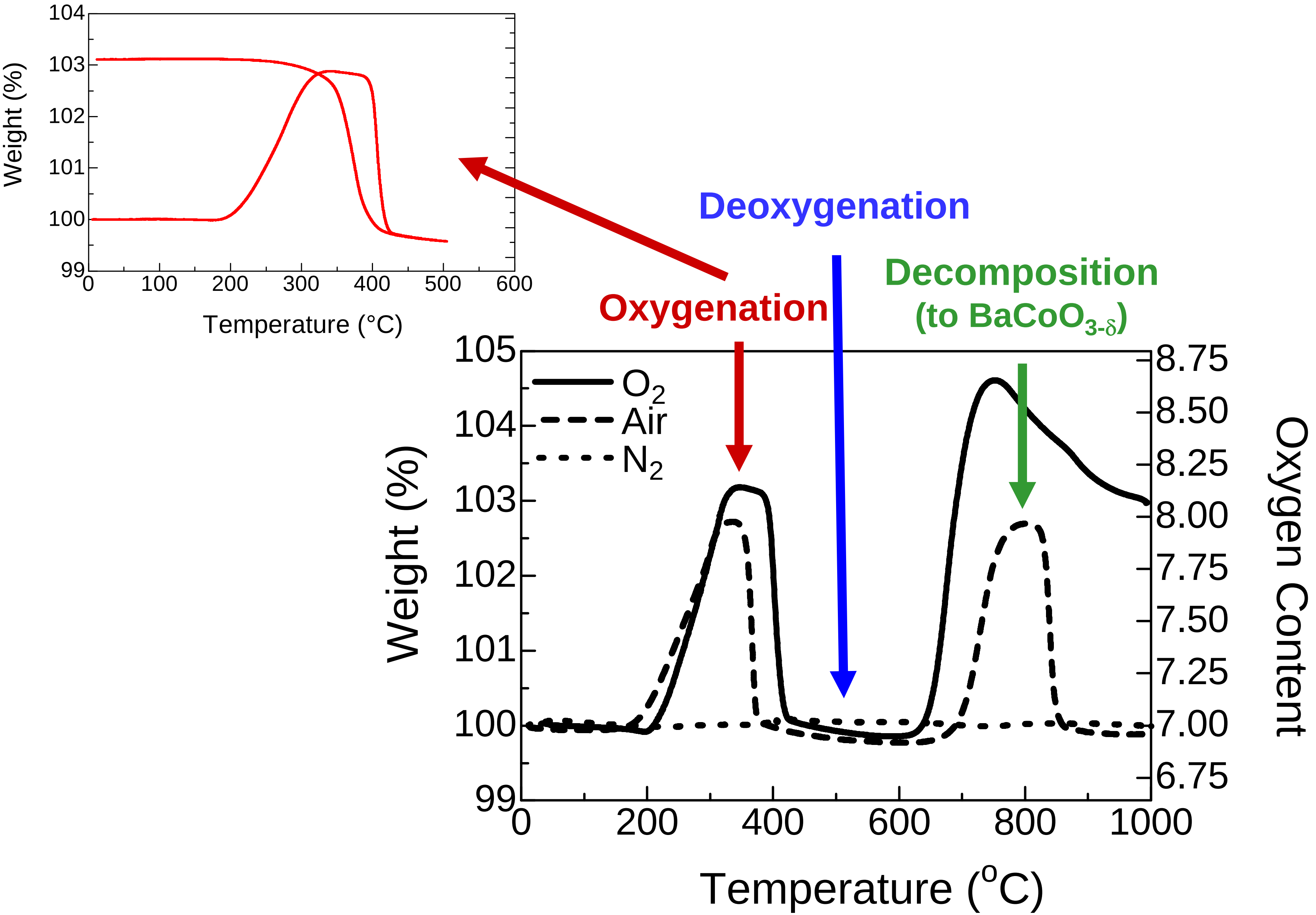
$YBa_2Cu_3O_{7-\delta}$





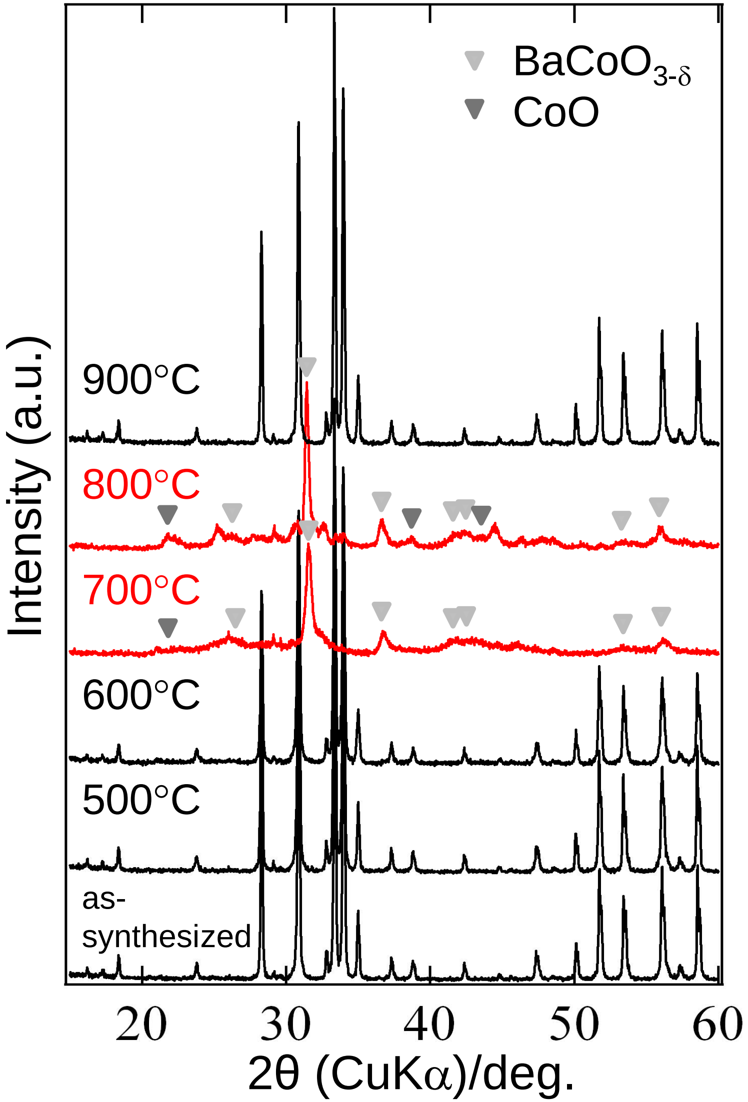
YBaCo$_4$O$_7$: heating in air in a thermobalance

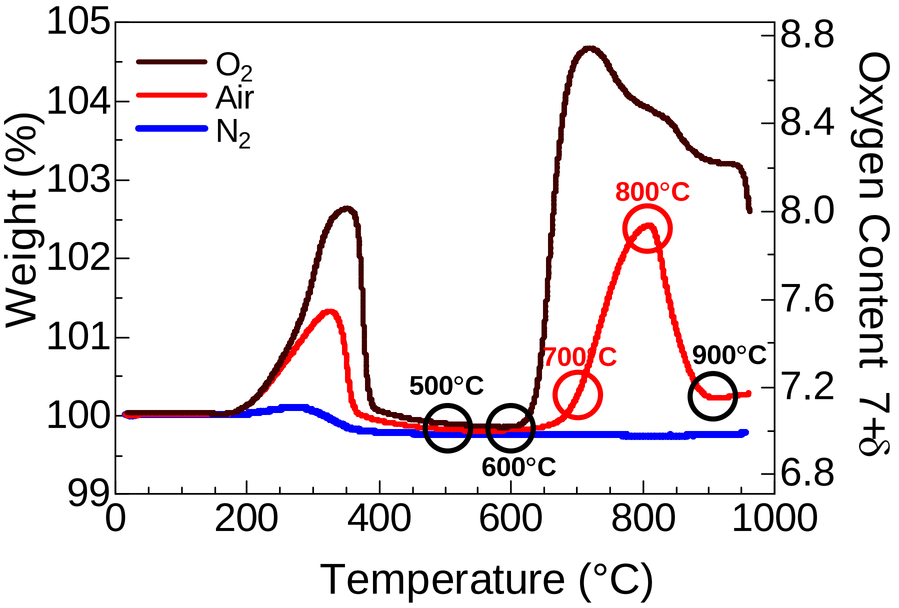




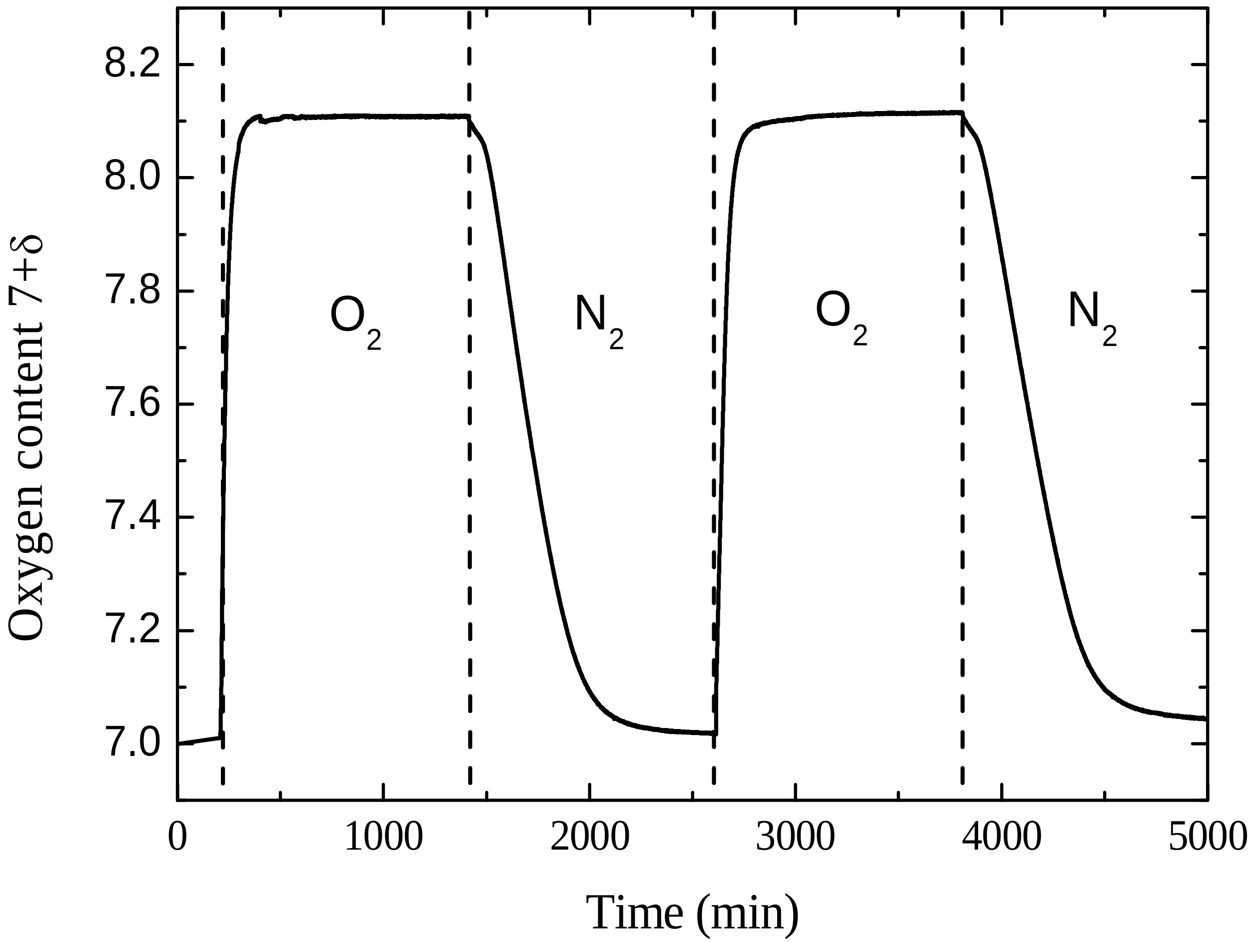
M. Karppinen, H. Yamauchi, S. Otani, T. Fujita, T. Motohashi, Y.-H. Huang, M. Valkeapää & H. Fjellvåg, *Chem. Mater*. **18**, 490 (2006).

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



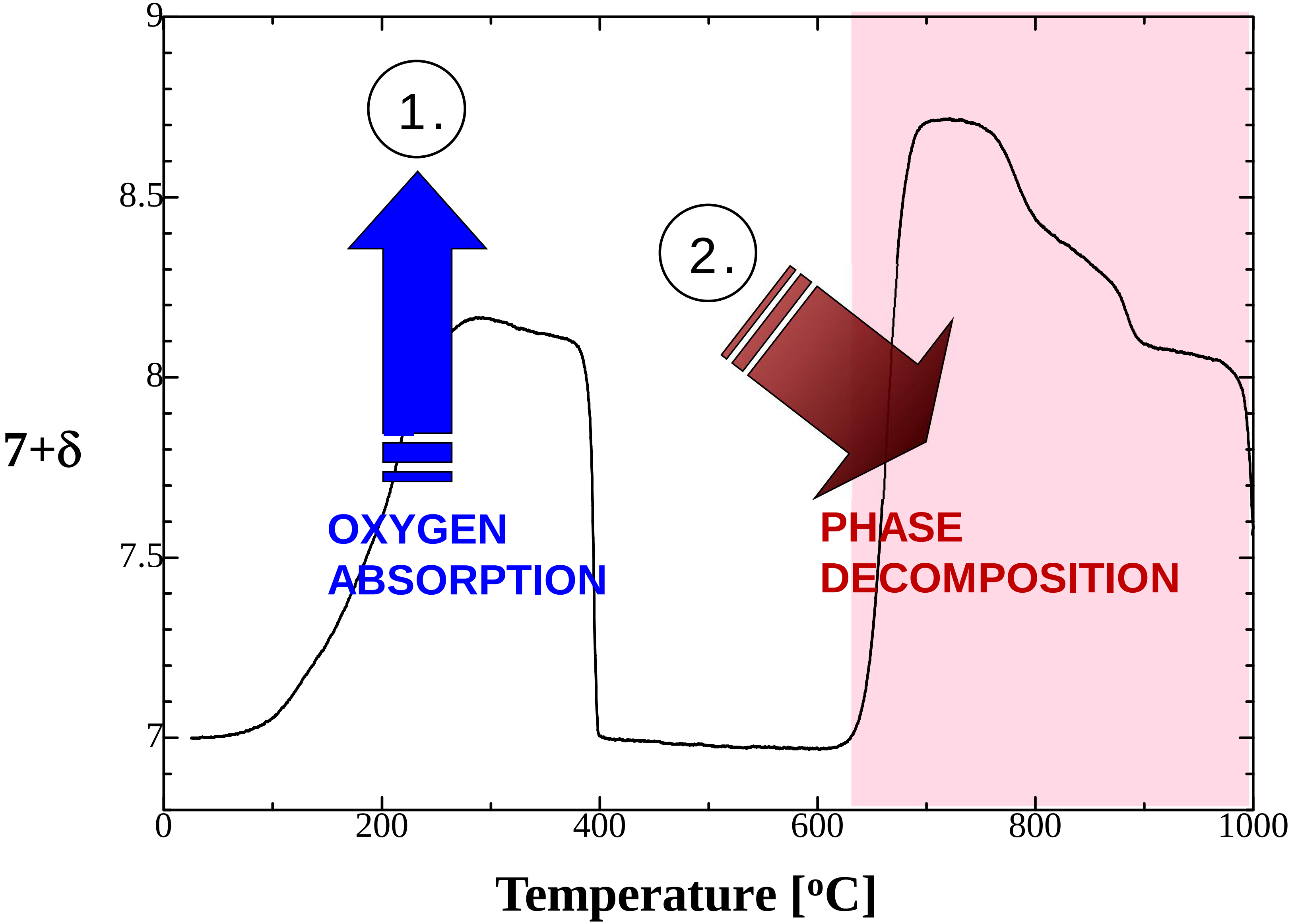


Temperature: 300 °C



Further Improvements

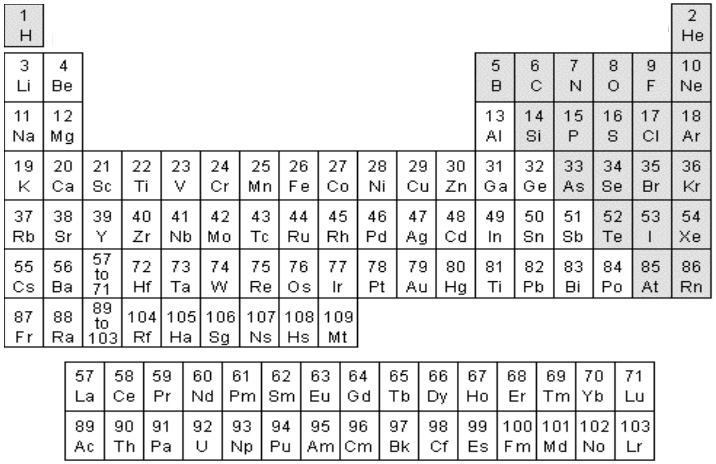
$YBaCo_4O_{7+\delta}$



$RBaCo_4O_{7+\delta}$

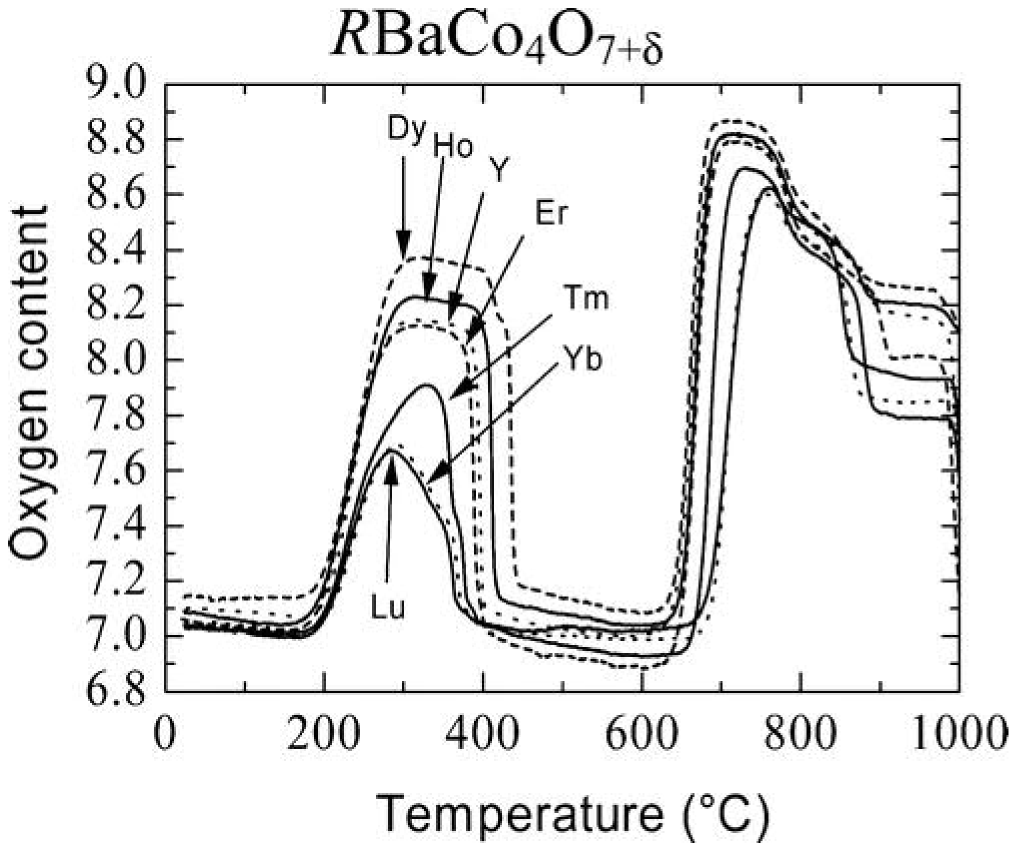
$r(R^{III})$ ionic radiys decreases

→ decomposition temperature increases (but OSC decreases)



1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 to 71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 to 103	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt									

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

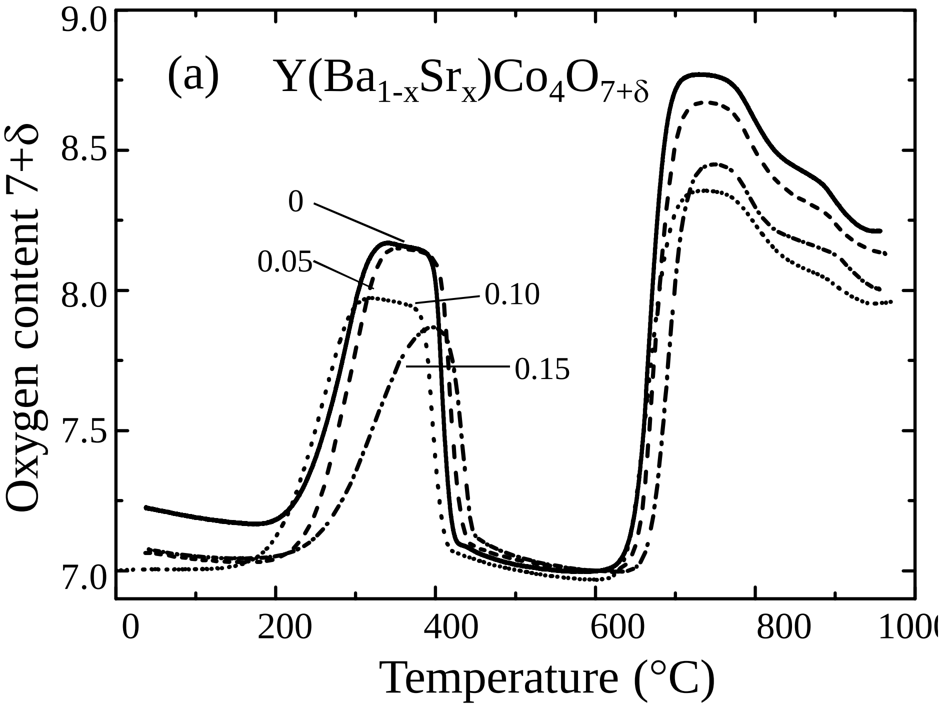


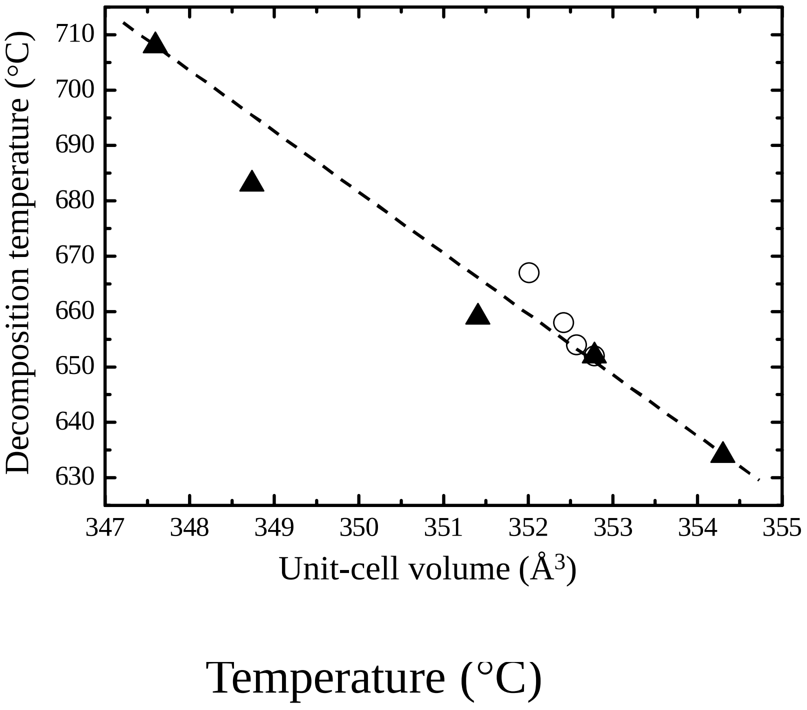
S. Kadota, M. Karppinen, T. Motohashi & H. Yamauchi,
Chem. Mater. **20**, 6378 (2008).

$Y(Ba_{1-x}Sr_x)Co_4O_{7+\delta}$

***r*(Ba,Sr) ionic radius decreases**

→ decomposition temperature increases (but OSC decreases)

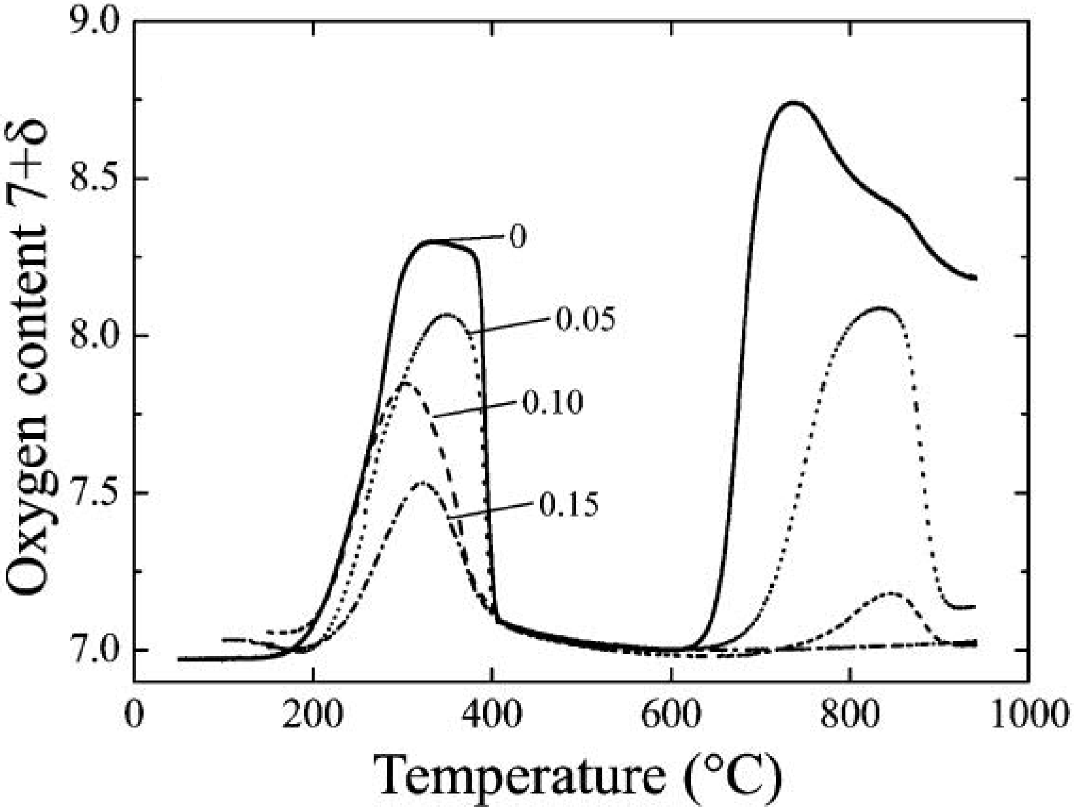




O. Parkkima, H. Yamauchi & M. Karppinen, *Chem. Mater.* **25**, 599 (2013).

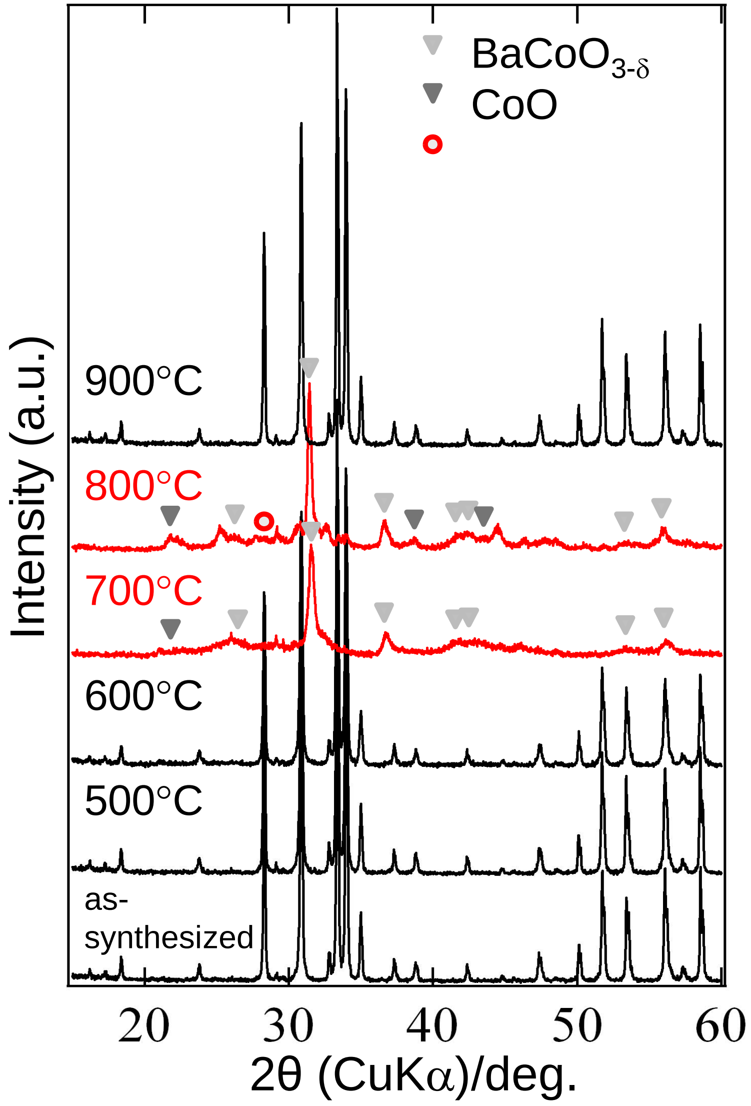
$YBa(Co_{1-x}Al_{x/2}Ga_{x/2})_4O_{7+\delta}$

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

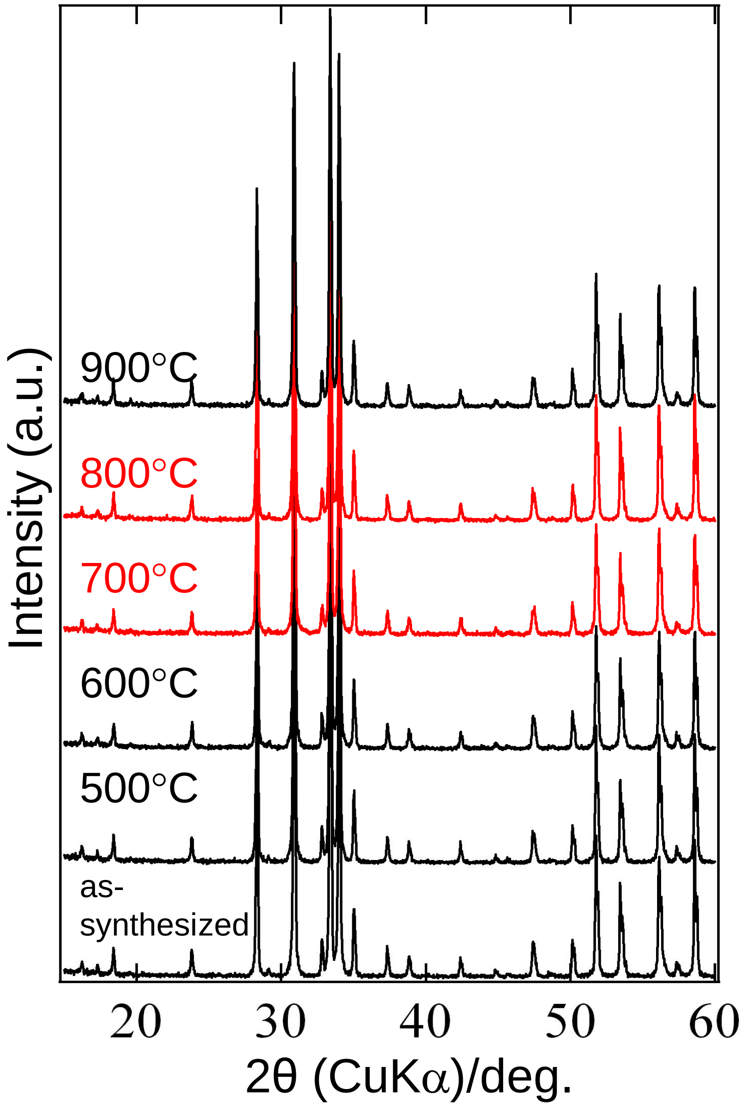


O. Parkkima, H. Yamauchi & M. Karppinen,
Chem. Mater. **25**, 599 (2013).

x = 0



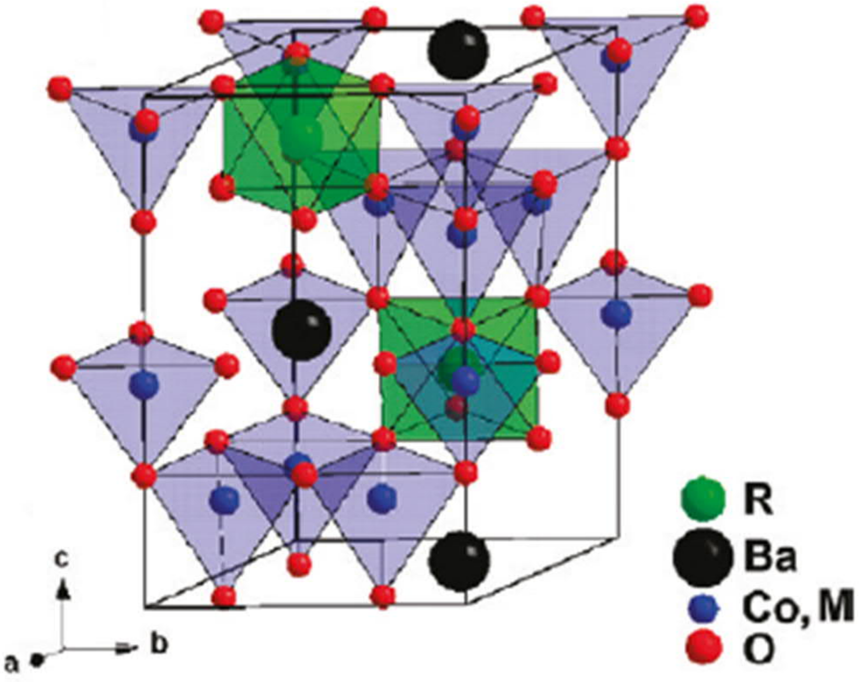
x = 0.15



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

YBaCo$_4$O$_7$: NEW TYPE OF ELECTROLYTE ?

- Excellent oxide-ion conductivity (σ_i > 30 S/cm)
- Stability issues: Co → Zn, Al, Ga etc.
- Reactivity with other SOFC materials ???



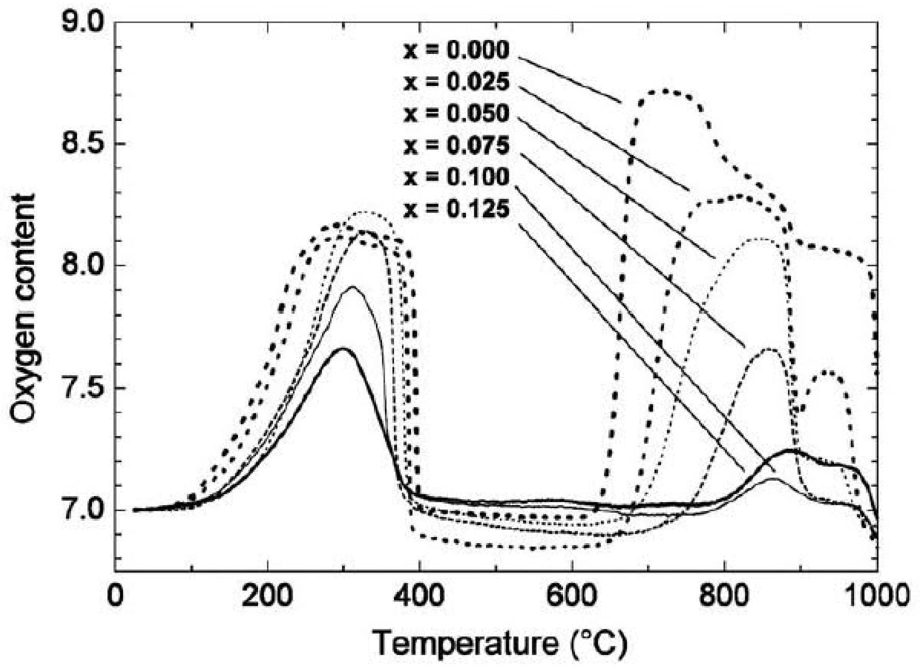


Fig. 3. TG curves for the YBa(Co$_{1-x}$Al$_x$)$_4$O$_{7+\delta}$ samples ($0.00 \le x \le 0.125$; $\delta \approx 0$) recorded upon heating the sample material in an O$_2$ gas flow.

$YBaCo_4O_{7+\delta}$ has already been investigated 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)]