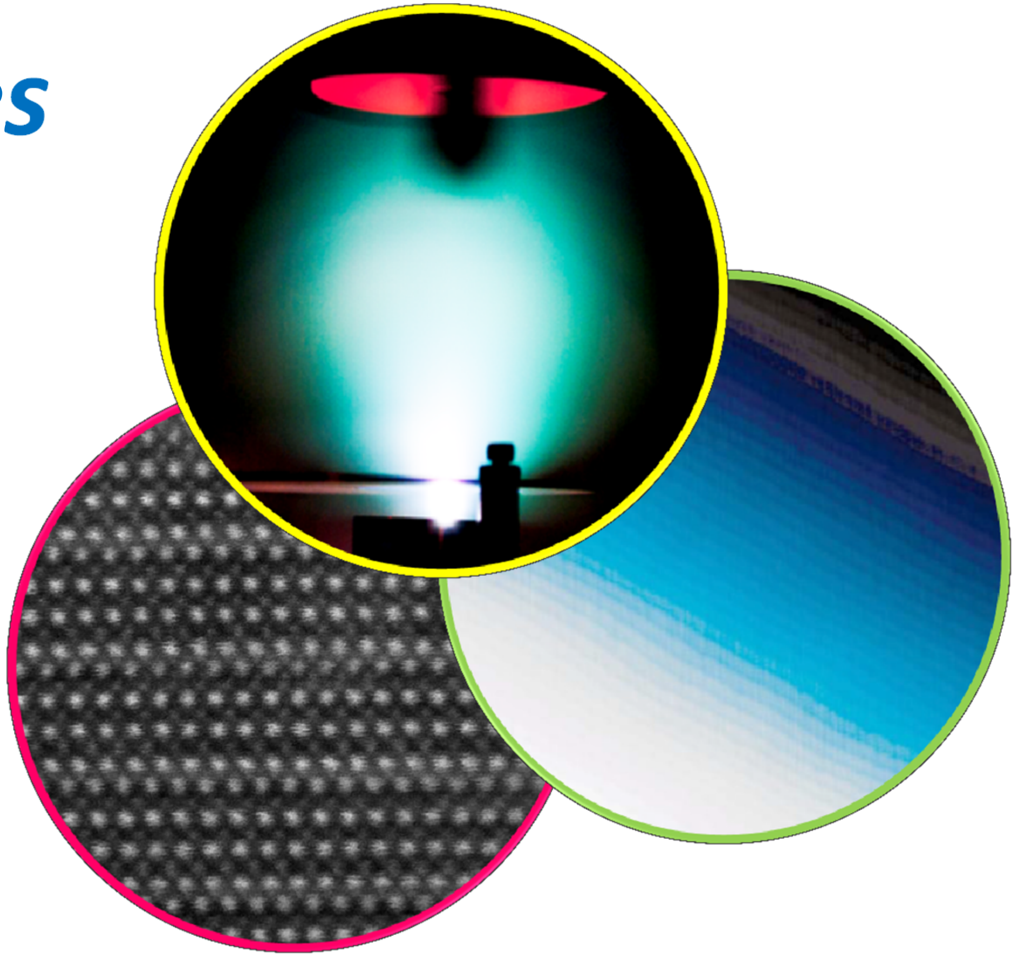
Reversible electronic & magnetic structures in epitaxial strontium cobaltites



Woo Seok Choi

Department of Physics,
Sungkyunkwan University
Materials Science & Technology Division,
Oak Ridge National Laboratory

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SUNG KYUN KWAN UNIVERSITY
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Dr. D. W. Shin (*Oak Ridge Nat'l Lab.*)	**Thermodynamic modeling**
Dr. J. H. Lee (*Princeton Univ.*)	**First principles calculations**
Prof. S. S. A. Seo (*Univ. Kentucky*)	**Optical measurements**
Dr. J. W. Freeland (*Argonne Nat'l Lab.*)	**X-ray absorption spectroscopy**
Dr. M. F. Chisholm (*Oak Ridge Nat'l Lab.*)	**Scanning Transmission Electron Microscopy**
Prof. H. Ohta (*Hokkaido Univ.*)	**Transport measurement**

and **many others…**

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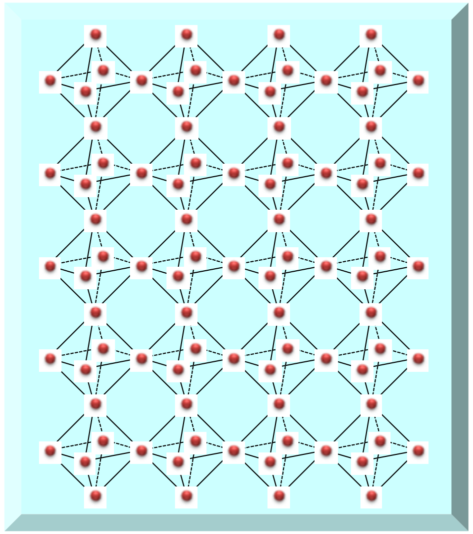
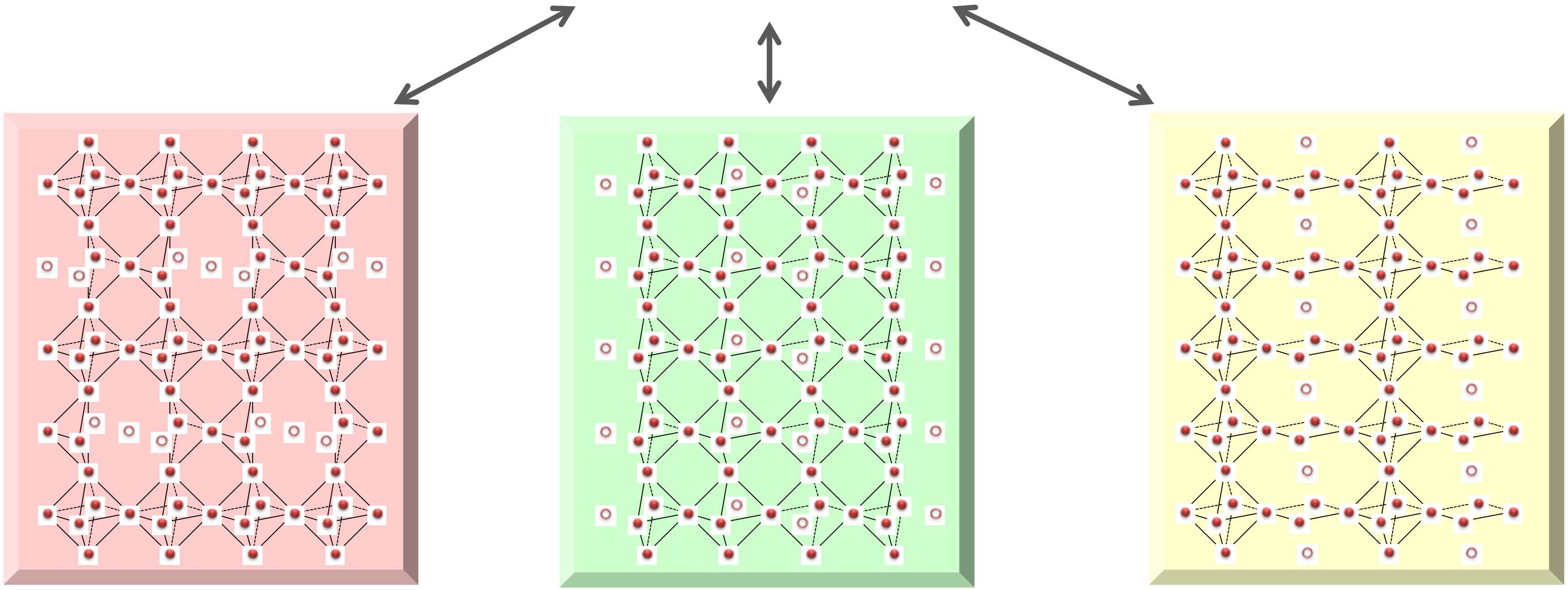
Topotactic phase transformation

A structural transformation within a crystal lattice, which may include loss or gain of material, so that the final phase has one or more crystallographically equivalent orientational relationships to the lattice of the parent phase.



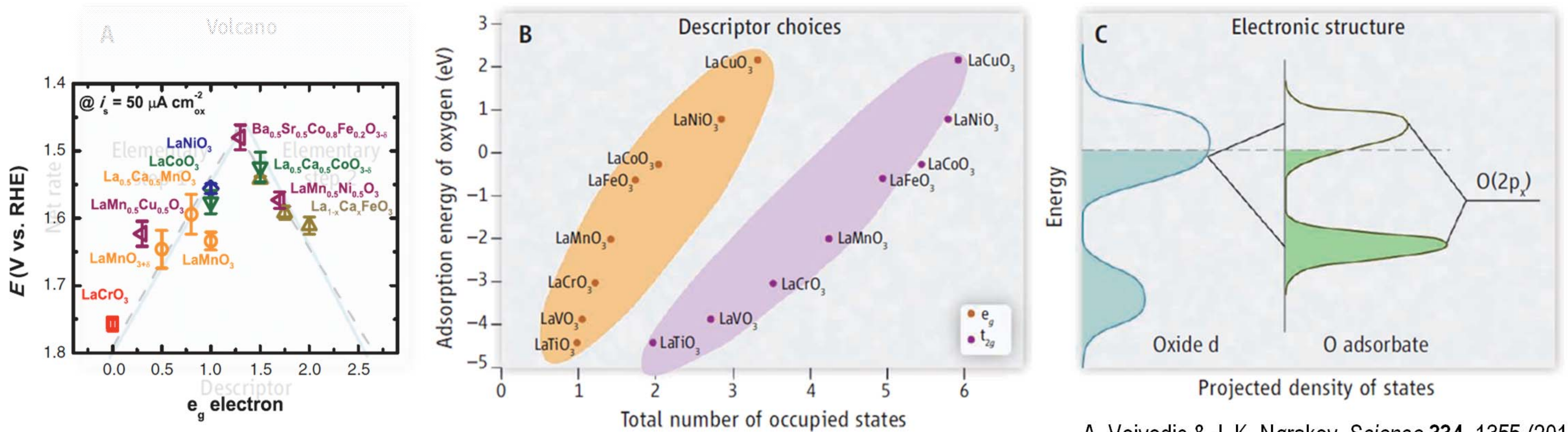
Advantages

- Systematic tailoring of new (meta-)stable compounds
- Controlled modification of physical properties
- Many technological applications e.g.) oxide electronics, ionic conductors, cathodes in SOFCs, catalytic converters.



K. Vidyasagar *et al.*, *J. Chem. Soc. Chem. Comm.* 1, 7-8 (1985)

In search for catalytic descriptors



A. Vojvodic & J. K. Nørskov, *Science* **334**, 1355 (2011)
J. Suntivich *et al.*, *Science* 334, 1383 (2011)

Fundamental physical properties

- Structural property
  - Crystal field
- Stoichiometry
  - Valence state or Oxidation state
- Electronic structure
- Electronic and magnetic property

Topotactic phase reversal

Electrochemical reaction

- Catalytic activity
- Gas conversion
- Cathodes for SOFCs and batteries
- Redox of the host material

Ionic transport

A perfect model system for studying the correlation between fundamental physical properties and electrochemical activities!
i.e., physical signatures for electrochemical processes.

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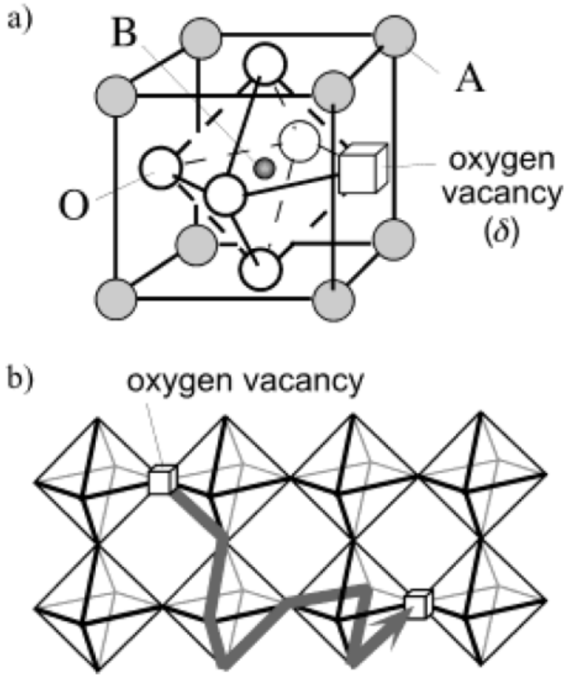
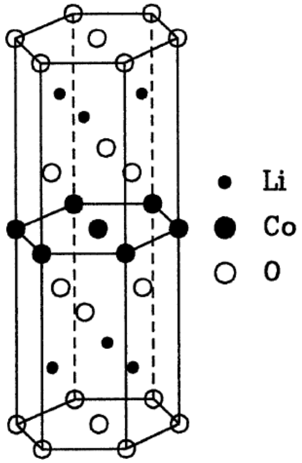
Oxygen (ion) movement in oxides – Energy materials

- Oxygen ion conduction
- Cathode for solid oxide fuel cells and rechargeable batteries
- Catalytic gas sensors
- Oxygen separation membranes

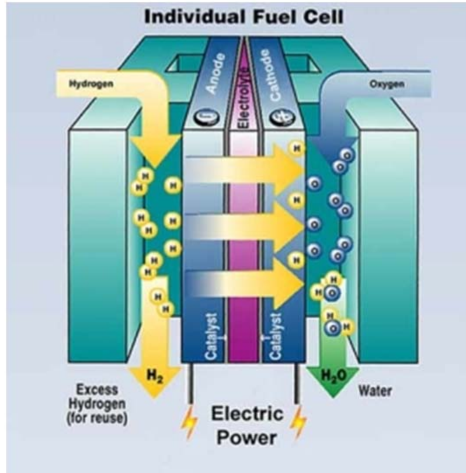
→ ***Multivalency***
in transition metal oxides

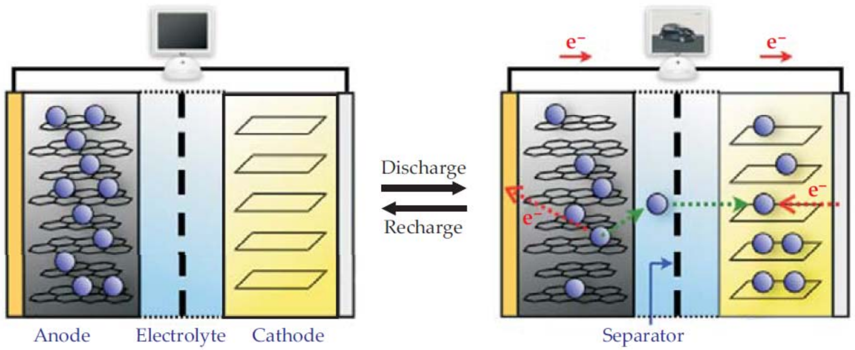


S. B. Adler, *Chem. Rev.* 104, 4791 (2004).



J. N. Reimers & J. R. Dahn, *J. Electrochem. Soc.* 139, 2091 (1992).

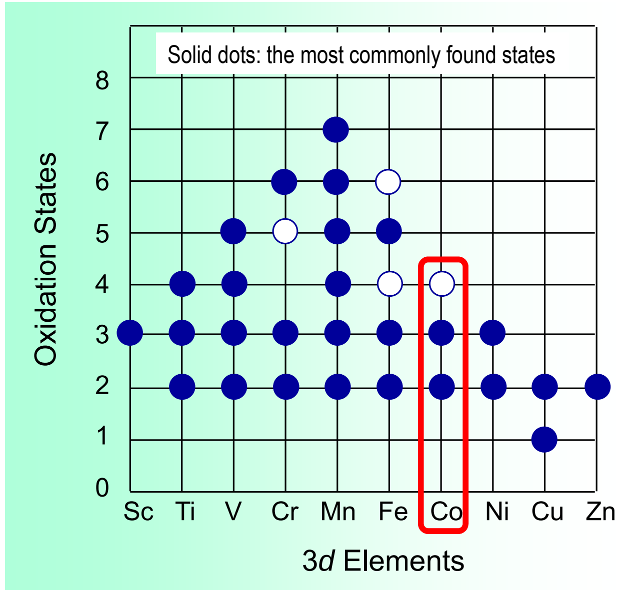




Multivalent Cobalt in transition metal oxides

27
Co
$3d^7 4s^2$

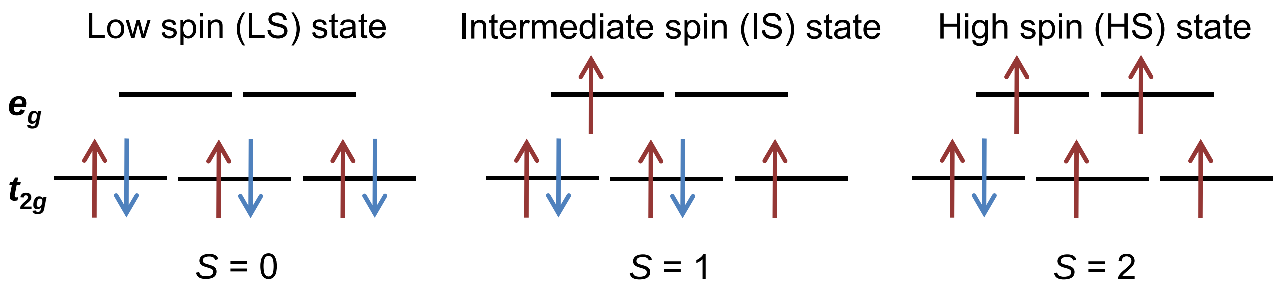
- Multivalent transition metal
- Common oxidation states: 2+ & 3+
- Less common: 4+

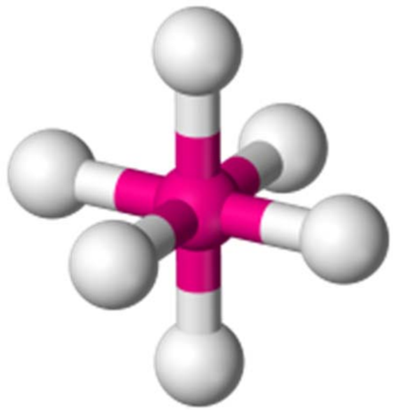


d^6: $La^{3+}Co^{3+}O_3$
d^5: $Sr^{2+}Co^{4+}O_3$
d^6: $Sr^{2+}Co^{3+}O_{2.5}$

Multiple sources to control
the valence & spin state: A-site ion & oxygen

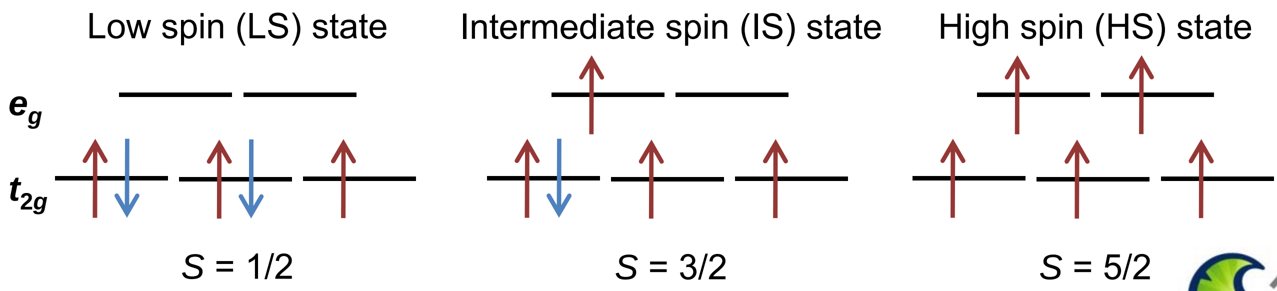
Co^{3+} ($3d^6$)





octahedral crystal field

Co^{4+} ($3d^5$)



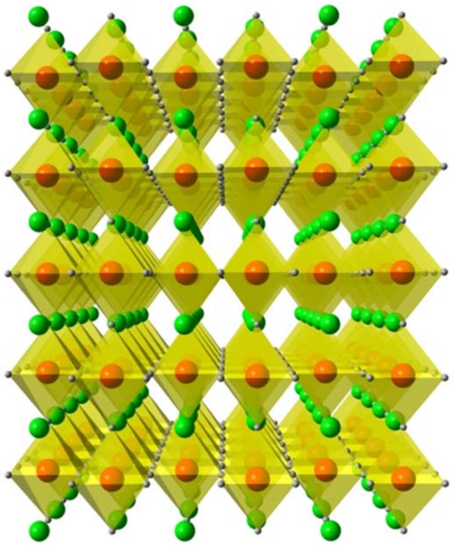
$SrCoO_x$ (SCO)

27
Co
$3d^7 4s^2$

- Multivalent transition metal
- Common oxidation states: 2+ & 3+
- Less common: 4+

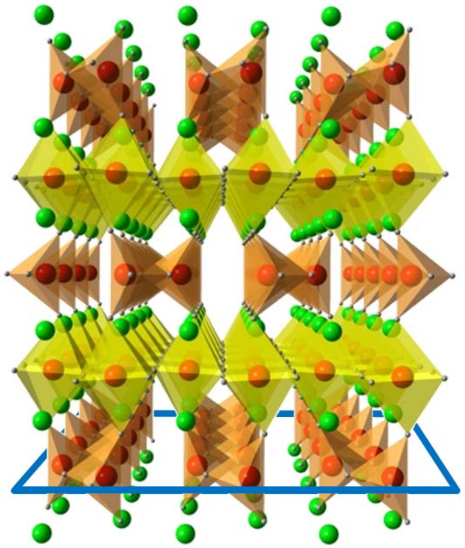
Perovskite	Brownmillerite
Cubic	Orthorhombic
FM-M	AFI-I
a_c = 3.829 Å	a = 5.545 Å,
	b = 15.738 Å,
	c = 5.448 Å

d^5: $Sr^{2+}Co^{4+}O_3$

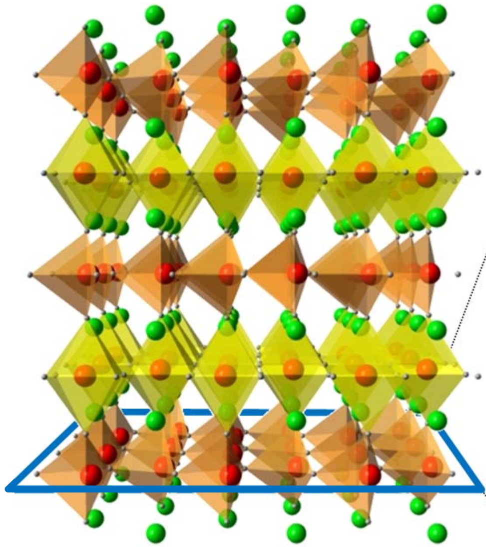


Perovskite (PV) (110)

d^6: $Sr^{2+}Co^{3+}O_{2.5}$

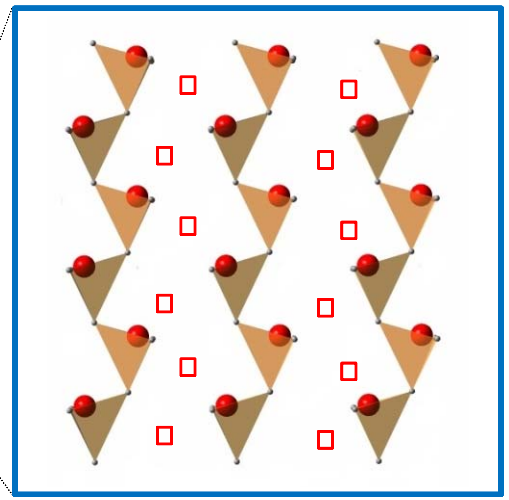


Brownmillerite (BM) (110)

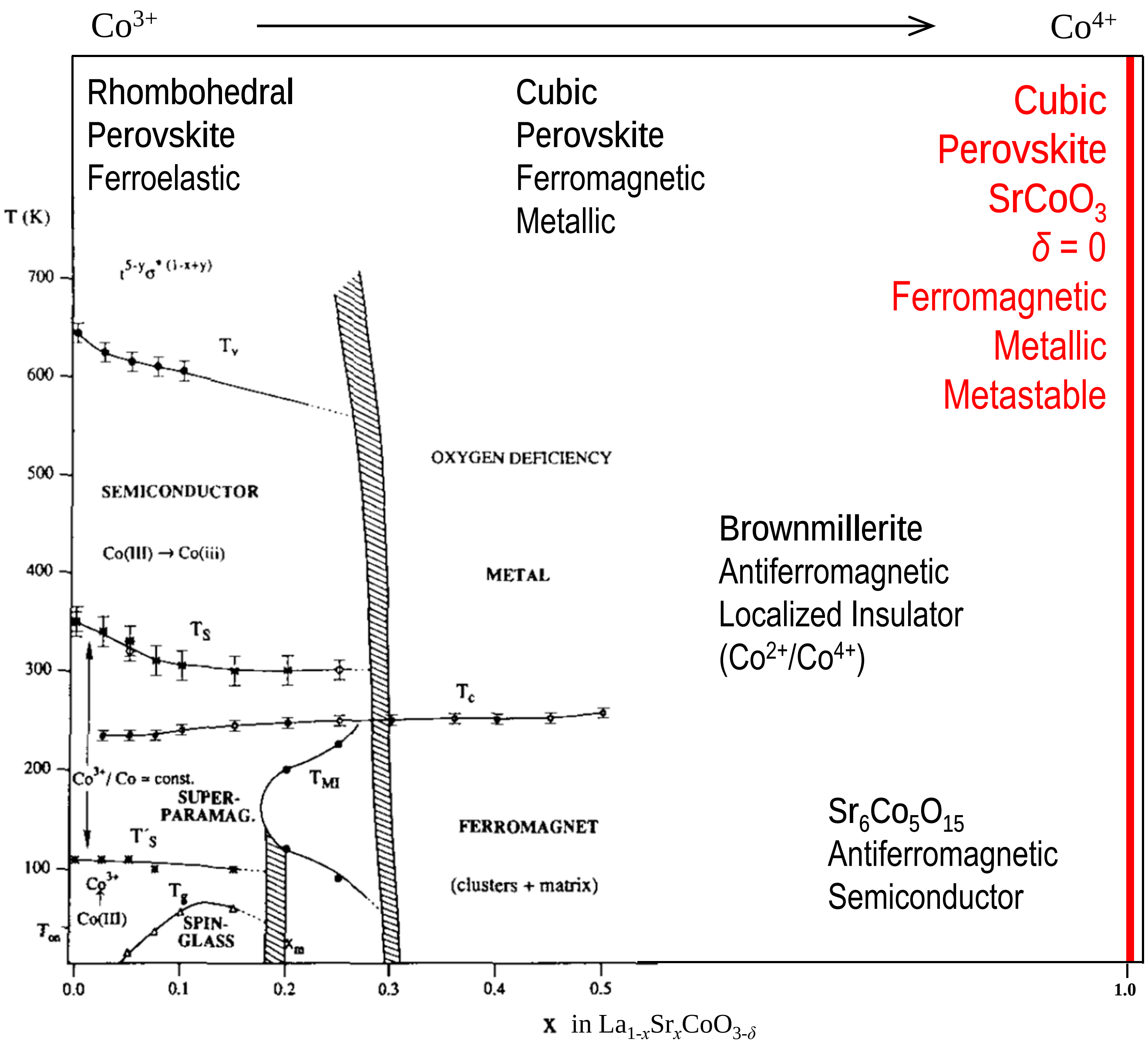


Brownmillerite (BM) (1-10)

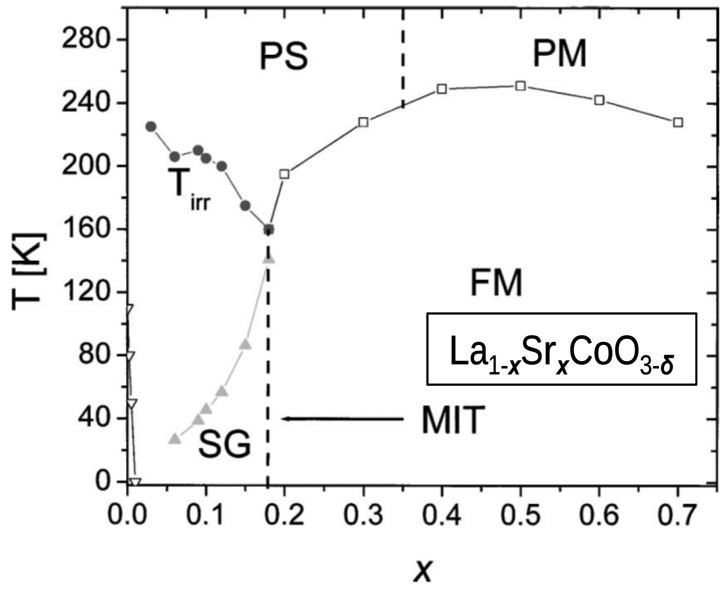
1D vacancy channel



Phase diagram of $La_{1-x}Sr_xCoO_{3-\delta}$



M. A. Senaris-Rodriguez & J. B. Goodenough, *J. Solid State Chem.* 118, 323 (1995).



J. Wu & C. Leighton. *Phys. Rev. B* 67, 174408 (2003).

- Promising cathode for SOFC
- Mixed ionic and electronic conductor
- Good catalytic activities
- Magnetic material

Difficult to achieve Co^{4+}
(or, Perovskite $SrCoO_3$)

Attempts to stabilize Co^{4+}

- Quenching
  : Yakel, *Acta. Cryst.*, 8, 394 (1955) (Co^{4+} = 3.8 %)
  : Takeda & Watanabe, *J. Phys. Soc. Jpn.* 33, 973 (1972) (x = 2.5)

- Electrochemical approach
  : Bezdicka et al., *Z. anorg. Allg. Chem.* 619, 7 (1993) (x = 2.5 → 3.0)
  : Le Toquin et al., *J. Am. Chem. Soc.* 128, 13161 (2006)

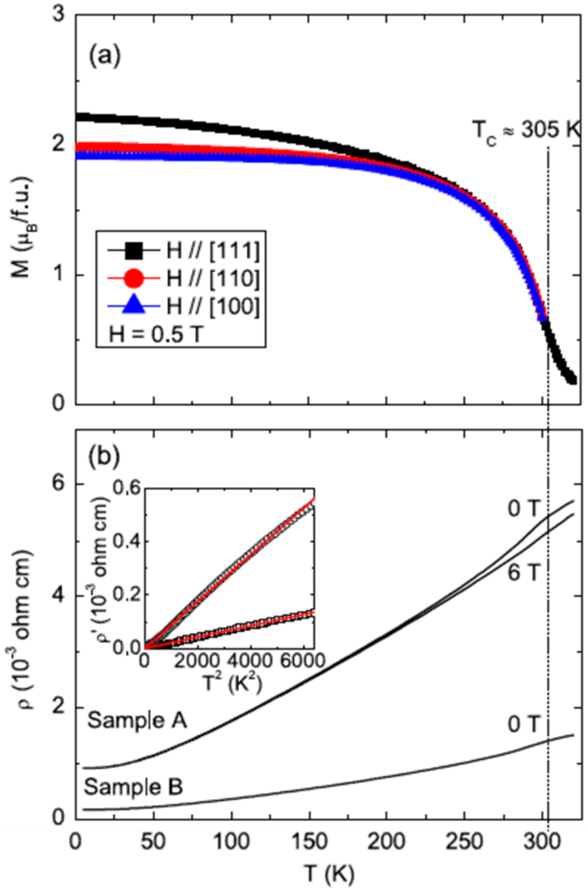
- High pressure/high temperature approach
  : Takeda & Watanabe, *J. Phys. Soc. Jpn.* 33, 973 (1972) (x = 2.75 ~ 2.95)

- Hybrid method (high pressure/high temperature + oxidant)
  : Long & Tokura et al., *J. Phys.: Condens. Matter* 23, 245601 (2011)

IOP Publishing — Journal of Physics: Condensed Matter
J. Phys.: Condens. Matter **23** (2011) 245601 (6pp) — doi:10.1088/0953-8984/23/24/245601

Synthesis of cubic $SrCoO_3$ single crystal and its anisotropic magnetic and transport properties

Youwen Long[1,4], Yoshio Kaneko[1], Shintaro Ishiwata[2,3], Yasujiro Taguchi[2] and Yoshinori Tokura[1,2,3]



→ ***First Single Crystal!***

However, all of these **bulk** synthesis methods require post treatments such as **high temperature**, **high pressure**, and **long time annealing**, or **chemical treatments**.

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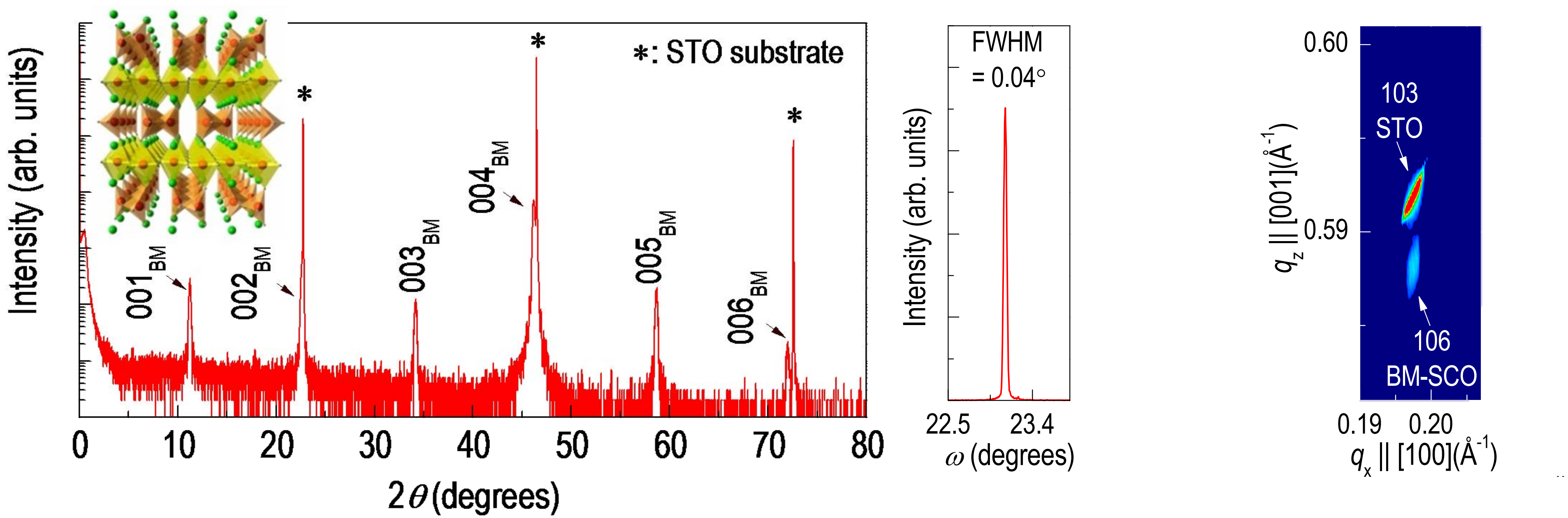
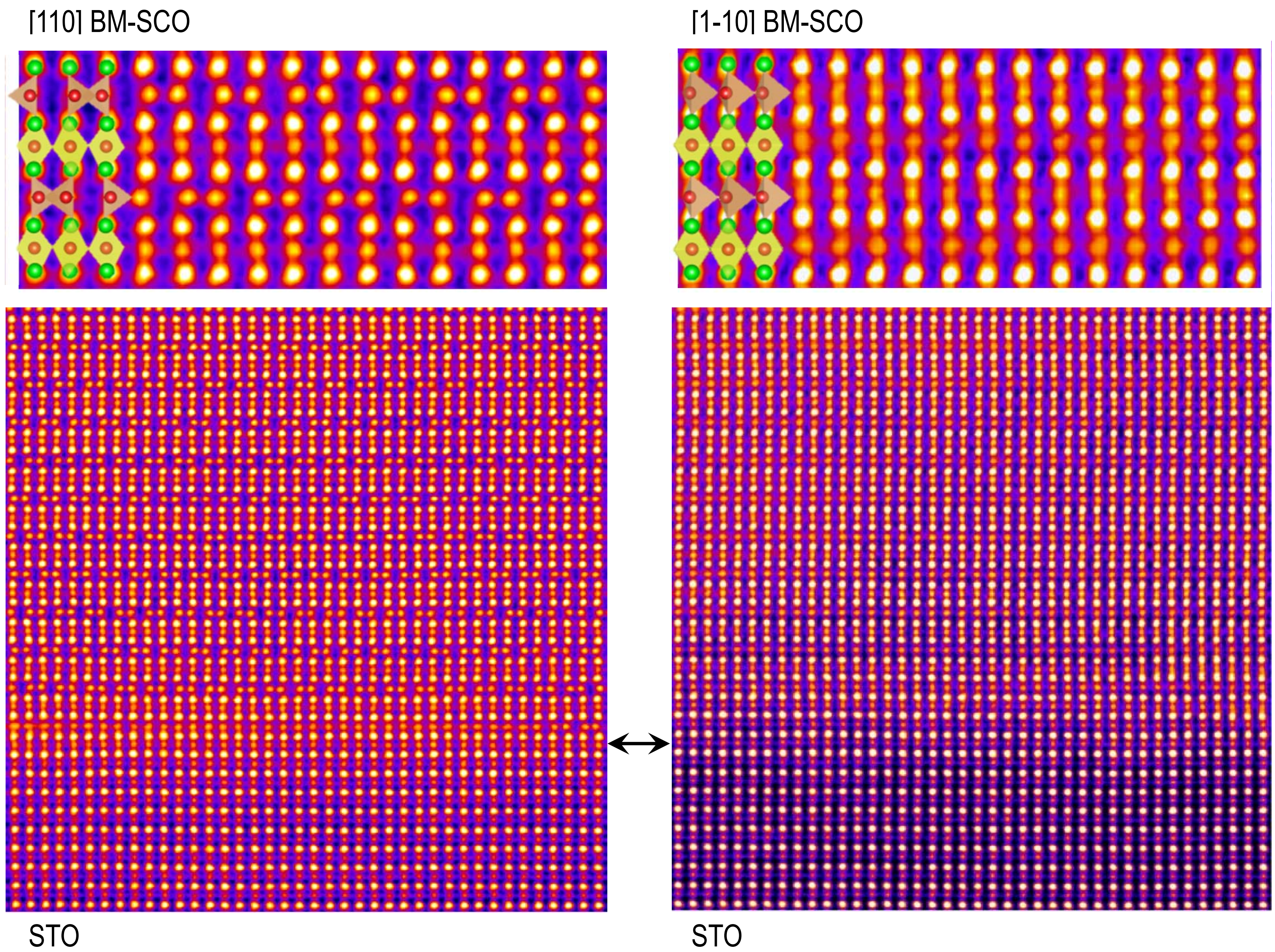
$SrCoO_{2.5}$ epitaxial thin film

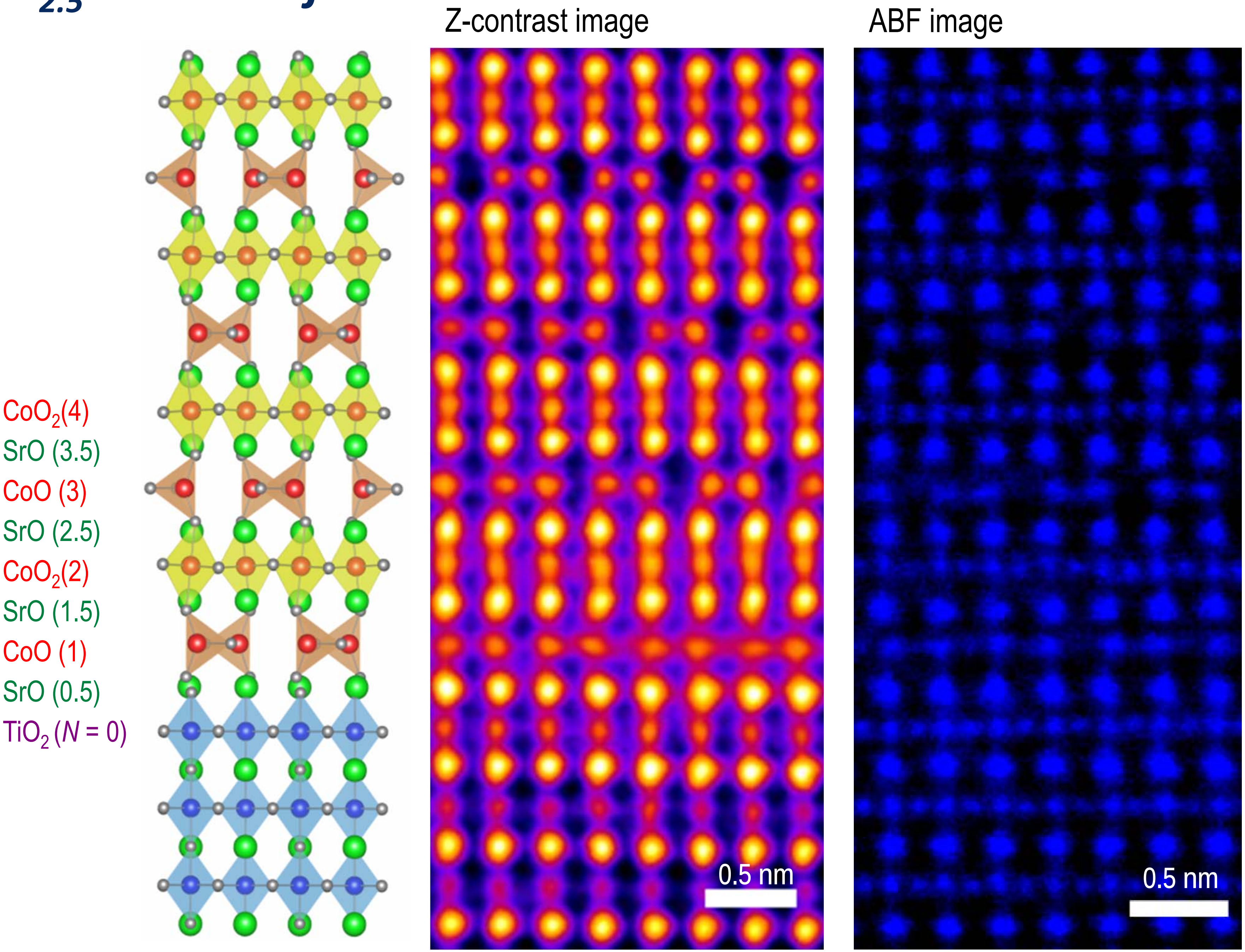


- Stable $SrCoO_{2.5}$ phase readily formed.

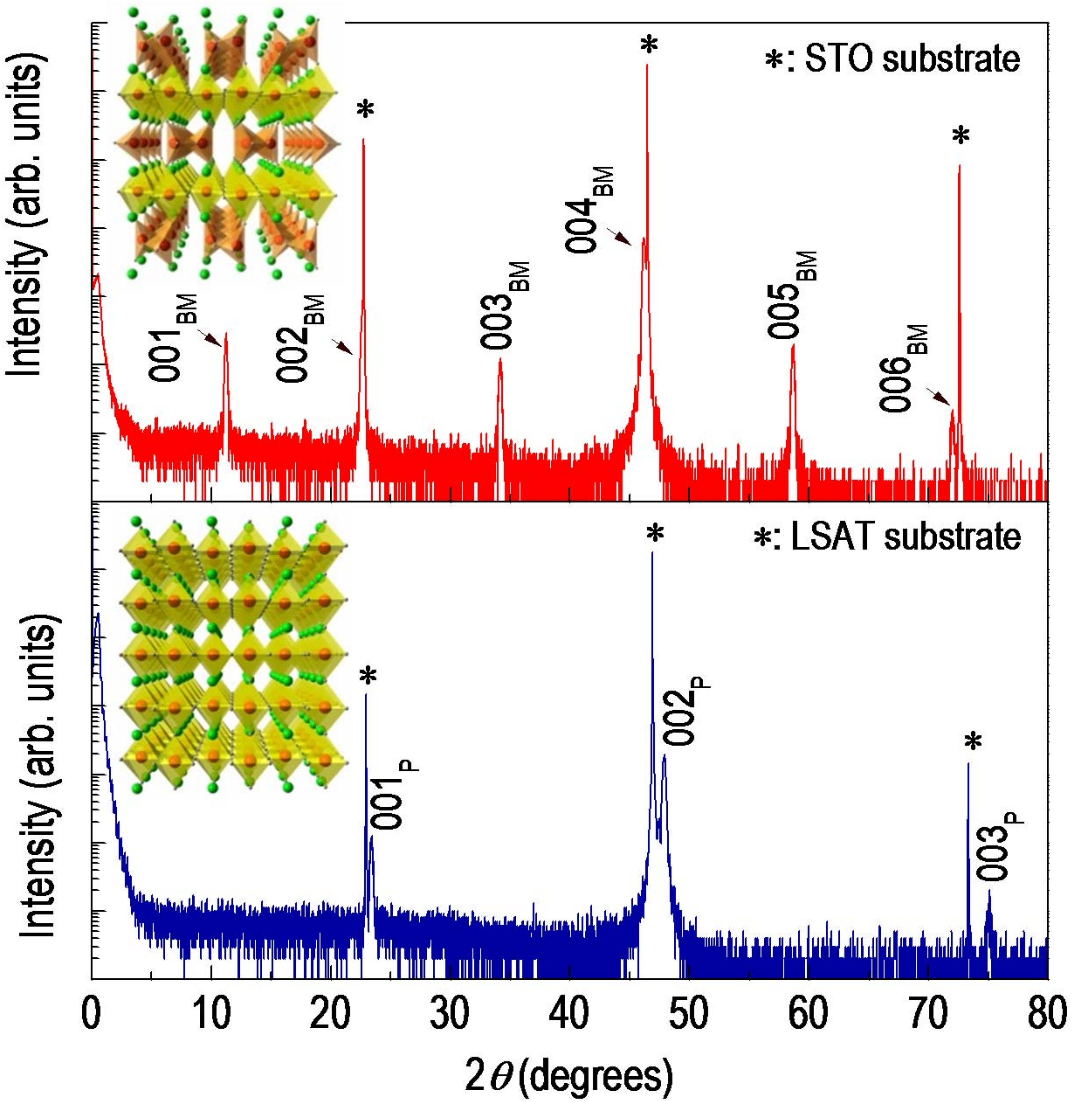
Defect-free brownmillerite $SrCoO_{2.5}$ thin film

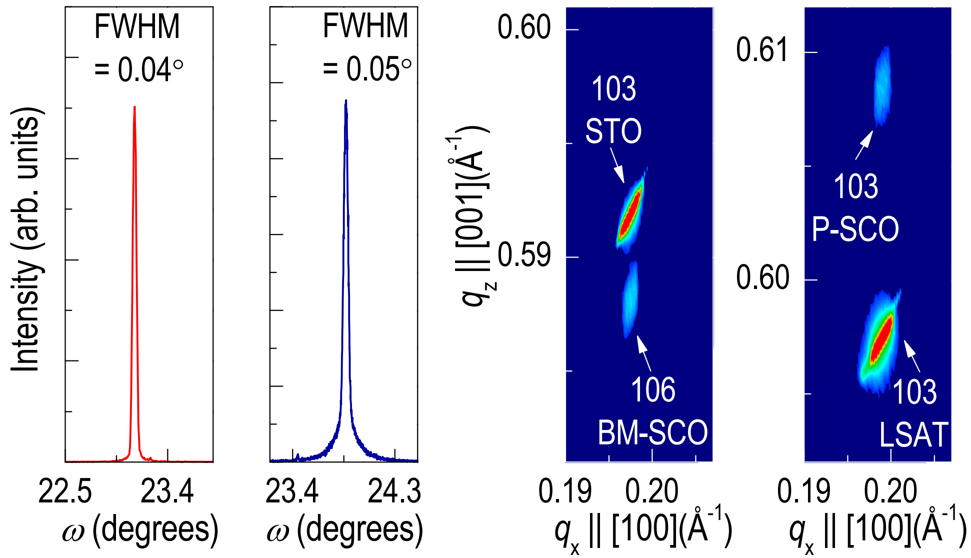


$SrCoO_{2.5}$ near interface



First $SrCoO_3$ epitaxial thin film, structural properties



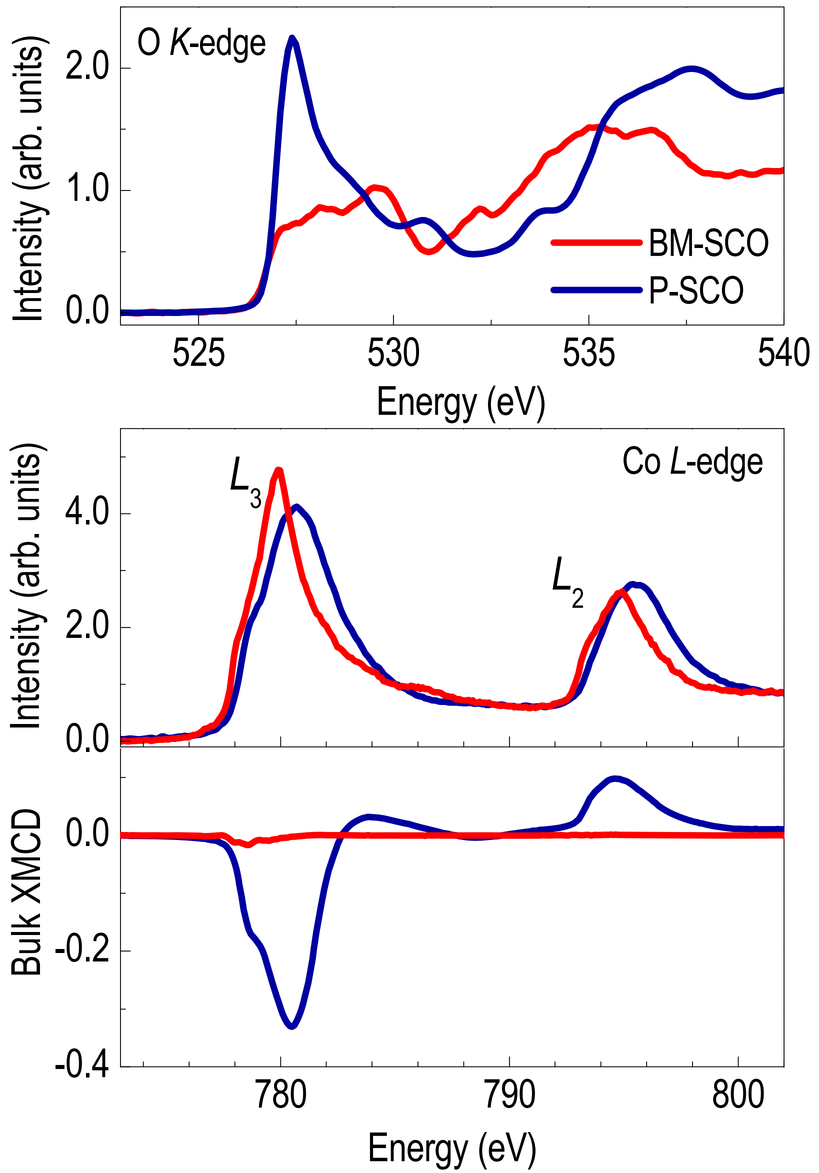


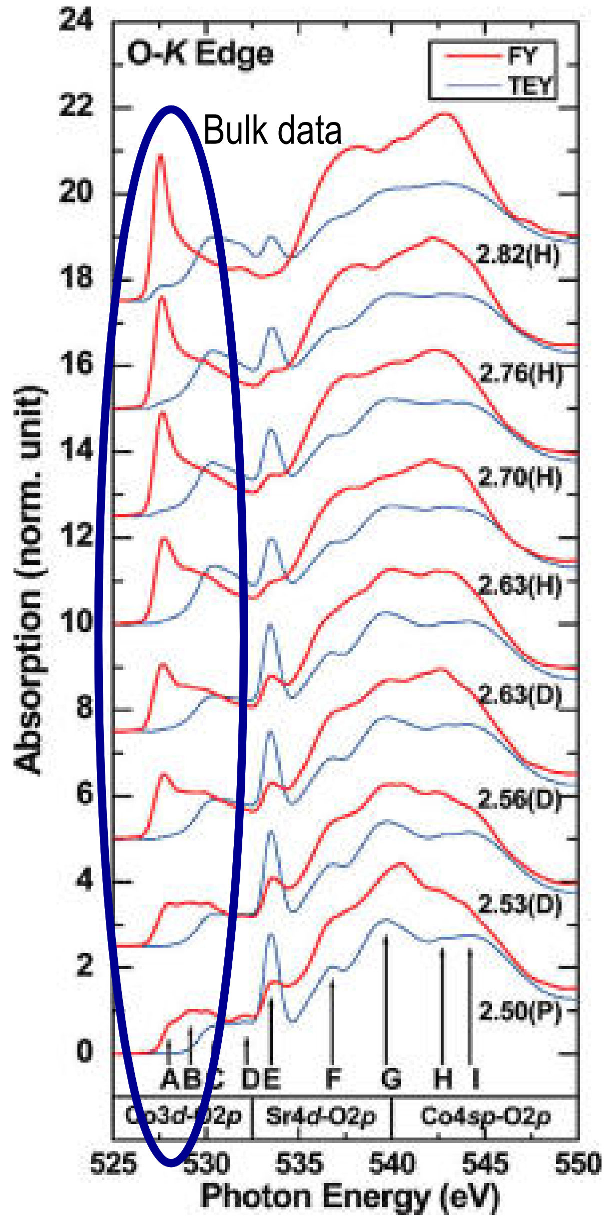
- Stable $SrCoO_{2.5}$ phase readily formed.
- Direct synthesis of oxidized perovskite $SrCoO_3$ phase by ozonized growth.

→ ***First Epitaxial Perovskite Thin Film!***

Determination of oxidation state: XAS

Distinct contrast in physical properties





Karvonen *et al.*, *Chem. Mater*. 22, 70, (2010)

- Significant change in the pre-peak spectral shape with the increase of the oxidation state (Co 3*d* - O 2*p* hybridization).
- Shift of *L*-edge toward high energy upon introduction of Co^{4+}.

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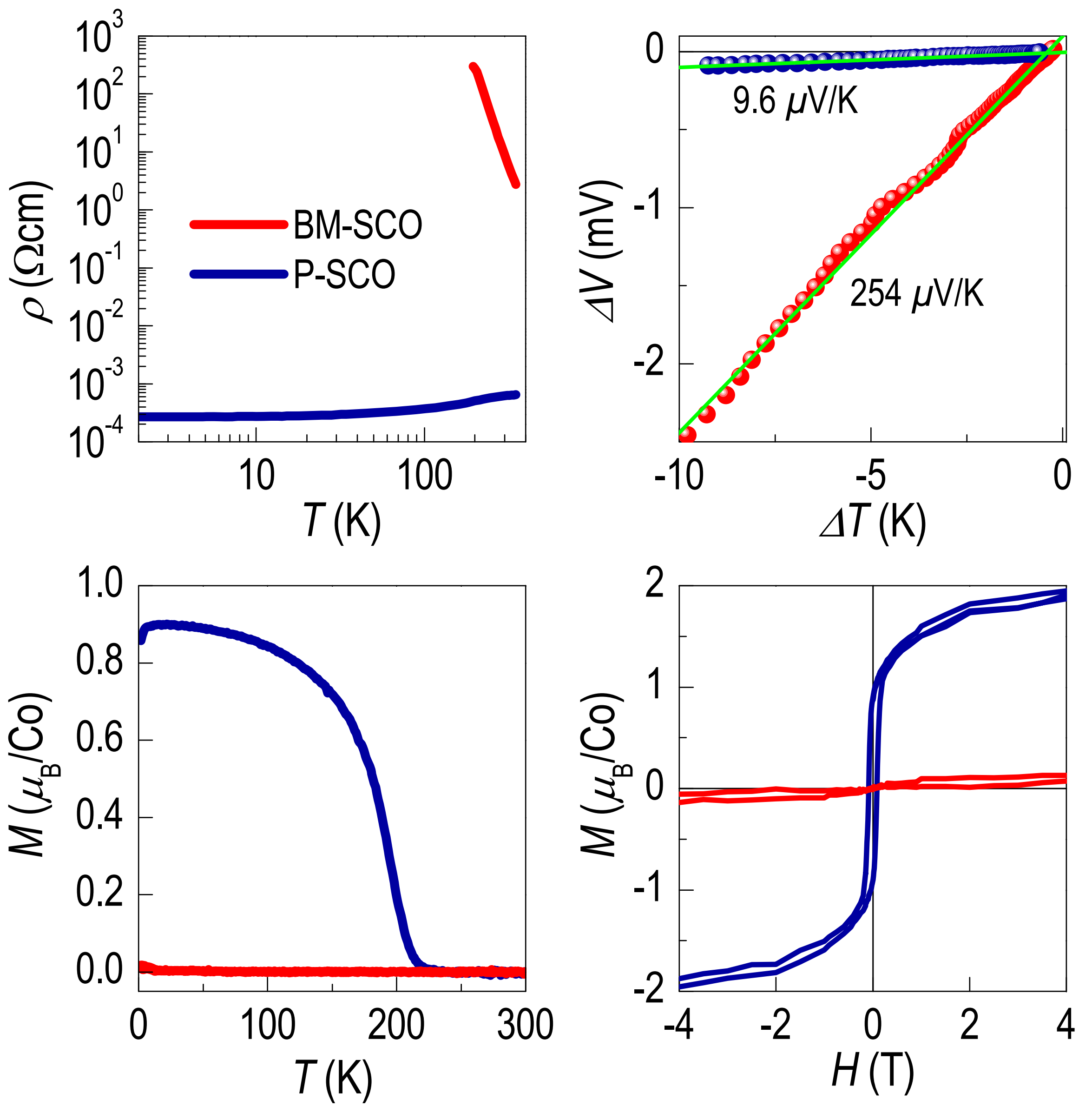
Electronic and magnetic phase transition in $SrCoO_x$

Distinct contrast in physical properties



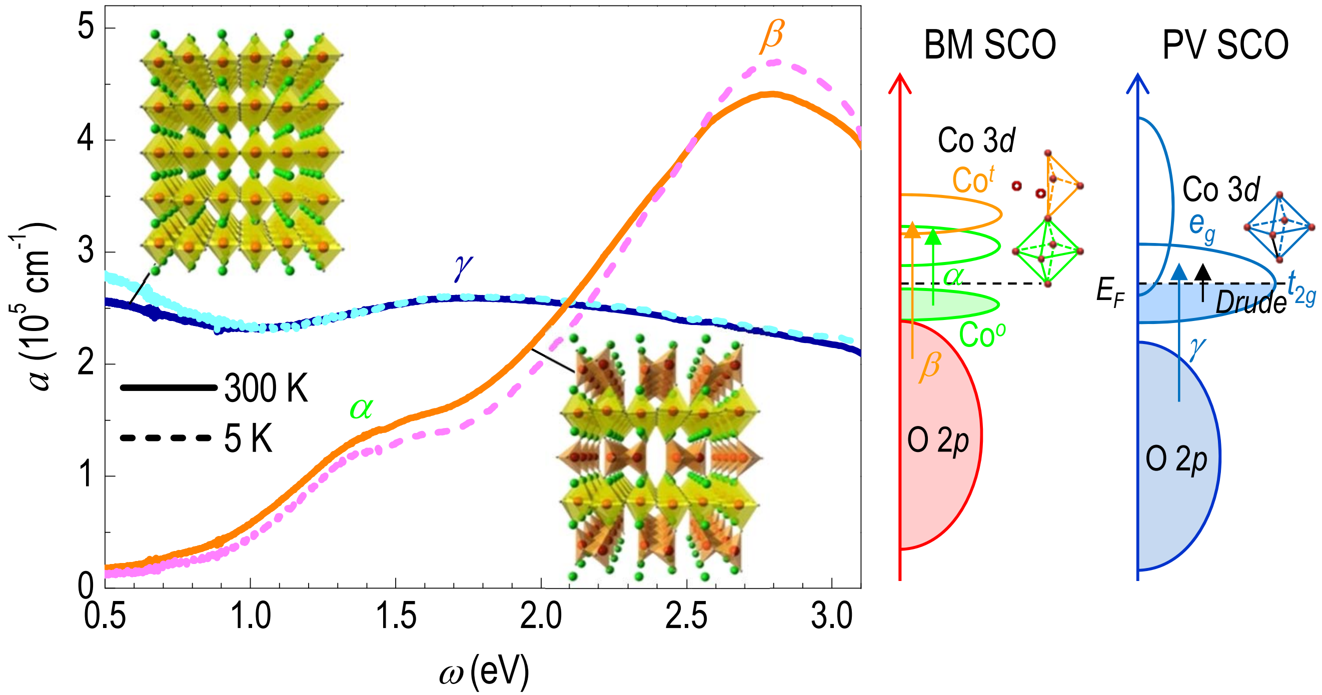
- Metallic transport behavior for P-SCO
  - Clear demonstration of successful stabilization of Co^{4+}.
  - Four orders of magnitude change in *dc*-conductivity already at 300 K.
  - Insulator-to-metal transition with incorporation of oxygen in $SrCoO_x$.
- A large Seebeck coefficient from BM-SCO.
- Positive Seebeck coefficient supports the *p*-type conduction (holes), also confirmed by Hall Measurements.
- Ferromagnetic ordering below ~250 K for P-SCO.

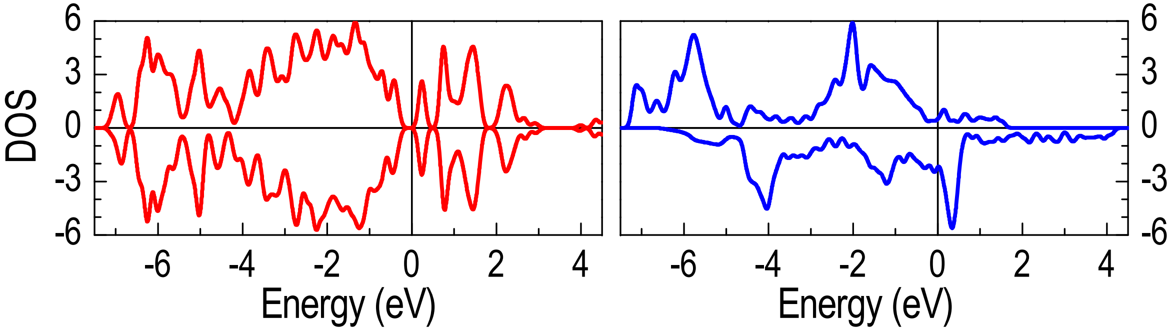
Topotactic transformation induced ***electronic*** and ***magnetic phase transitions***.

H. Jeen & W. S. Choi *et al. Nat. Mater.* 12, 1057 (2013)

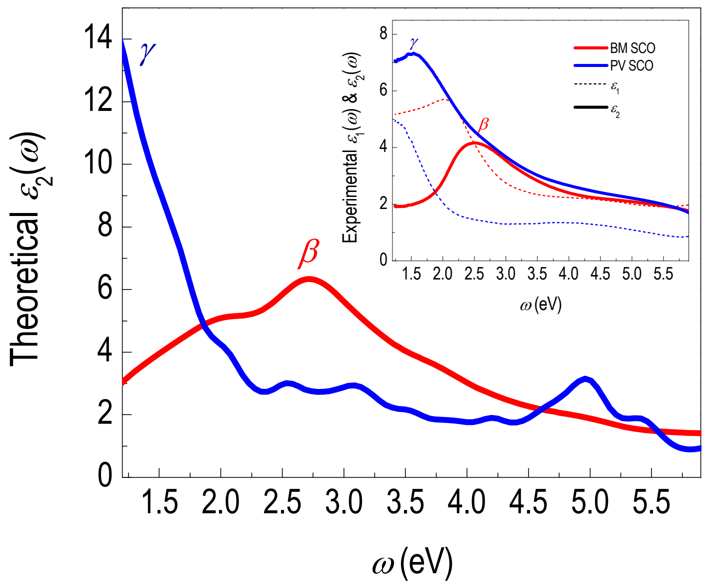
Optical properties and electronic structure

Distinct contrast in physical properties





- Insulator (BM) to metal (PV) transition is clearly shown.
- BM SCO: A low optical band gap insulator (~0.5 eV)
  - Typical BM phase oxides have >2 eV of band gap.
  - Advantageous for application: ionic (vacancy channel) + electronic conduction (in the vicinity of IMT)
- PV SCO: Metallic with Drude peak.

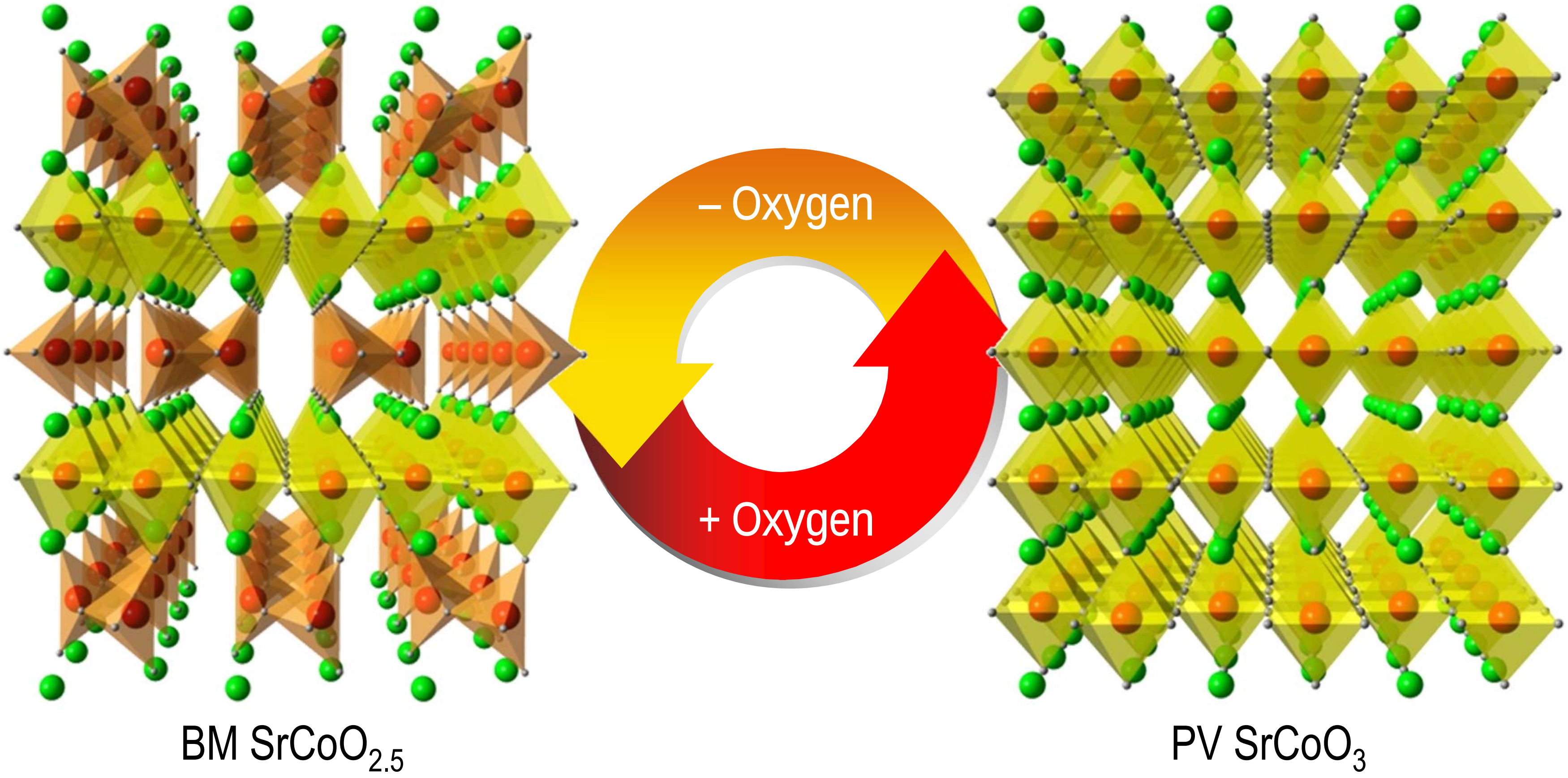


W. S. Choi *et al. Phys. Rev. Lett.* 111, 097401 (2013)

- Complicated electronic structure with both CoO_6 octahedral and CoO_4 teterahedral crystal field.
- First principles calculation reproduced the experimental peak features.

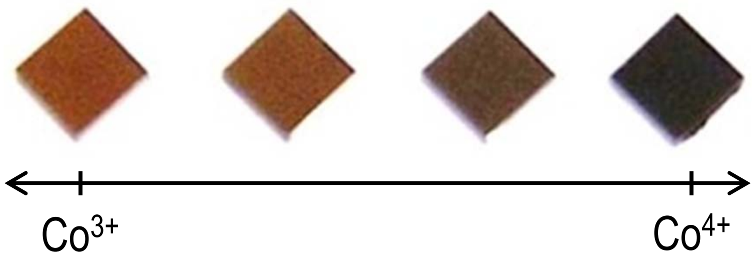
Topotactic transformation induced ***optical property change***.

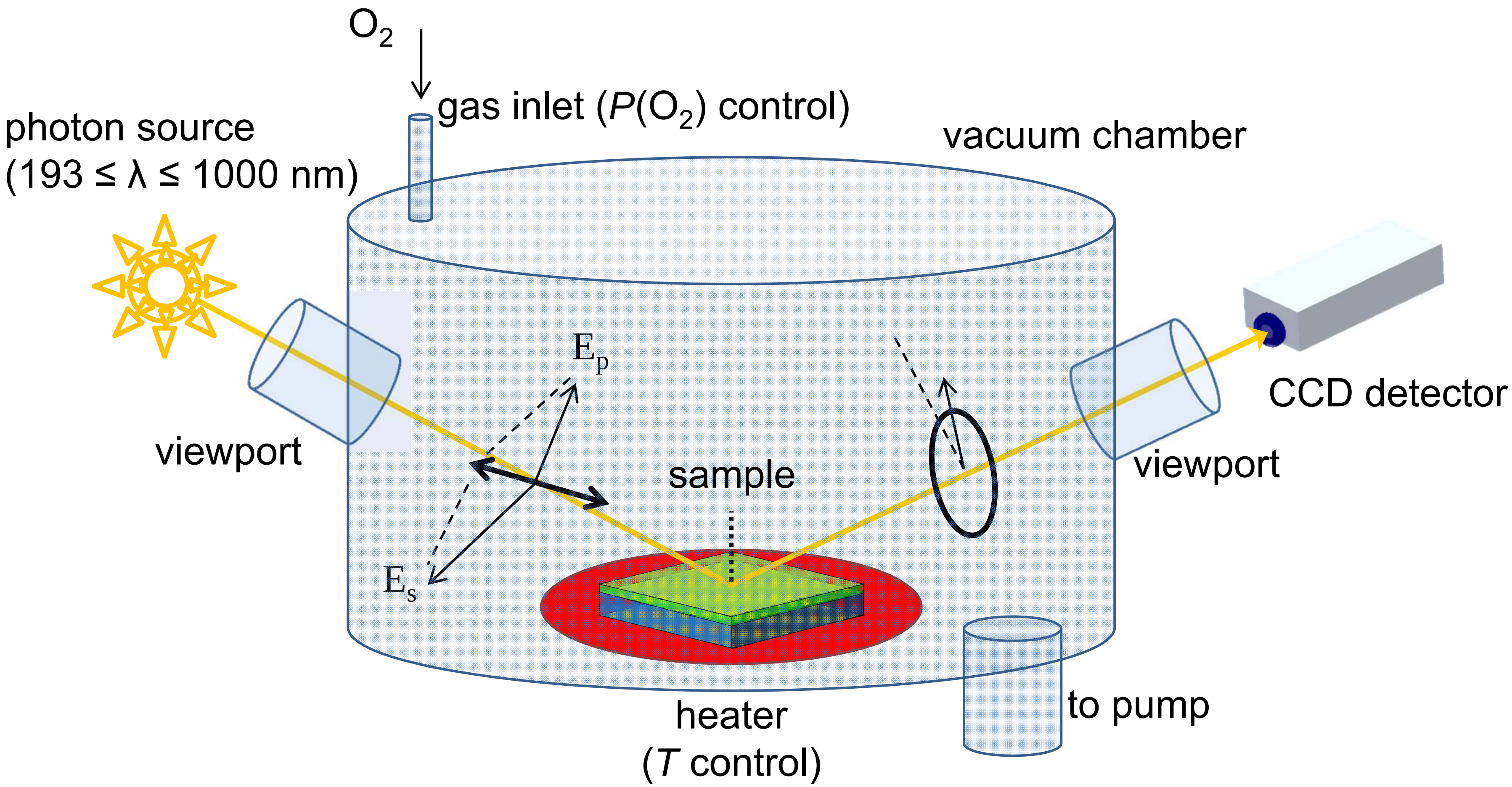
Fast and reversible phase transformation in SCO



Real-time observation of redox processes

Spectroscopic ellipsometry
for the electronic structure evolution
during topotatic phase reversal





in collaboration with Prof. Seo of University of Kentucky

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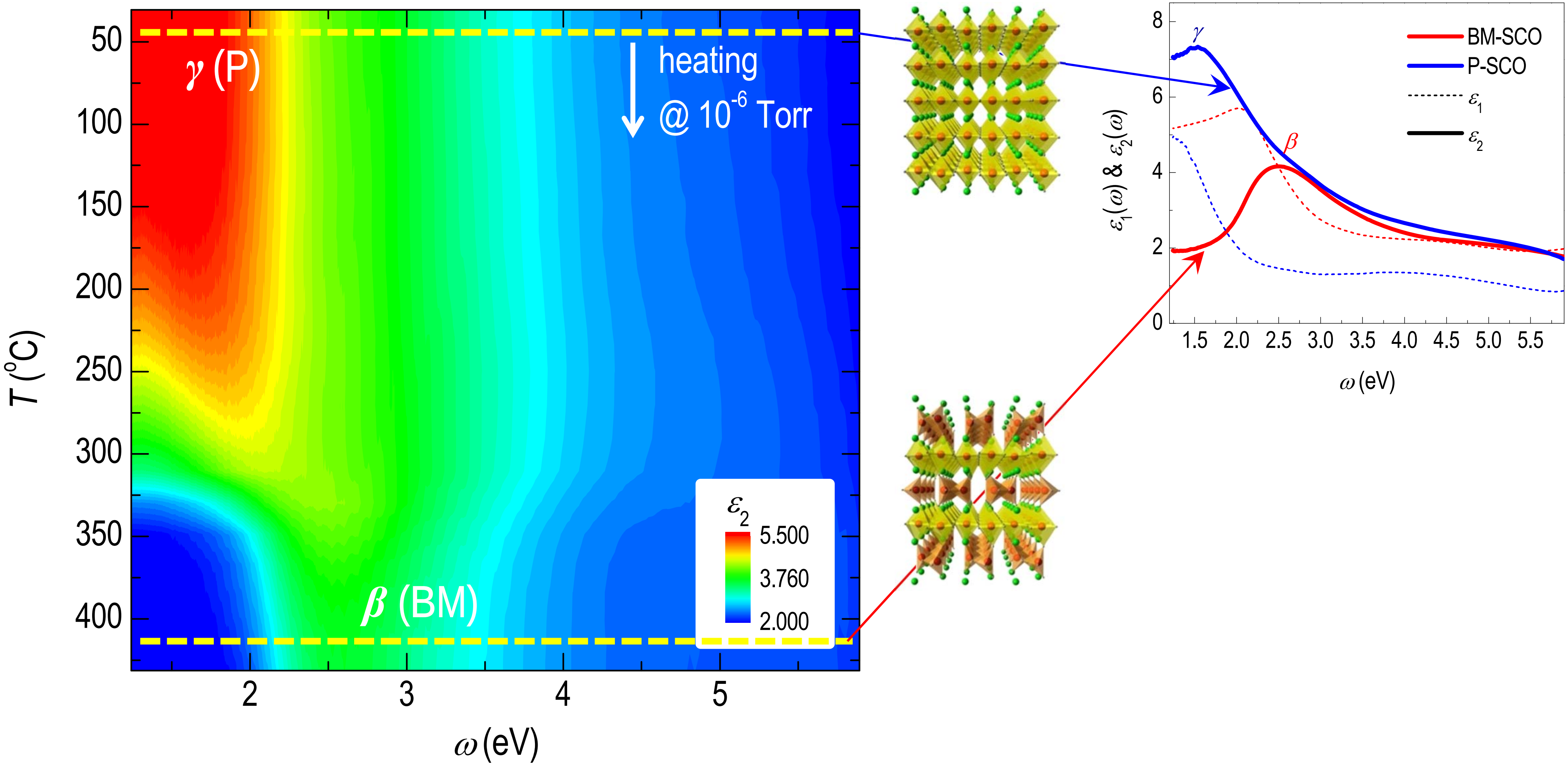
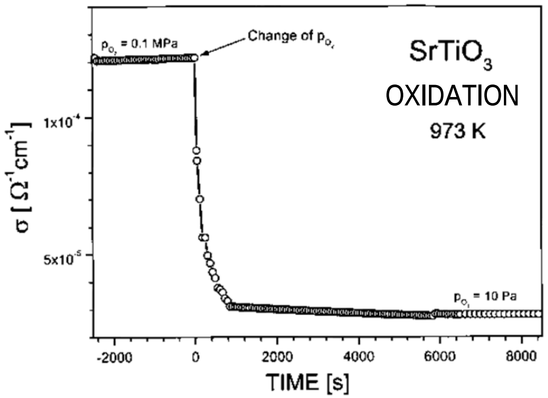
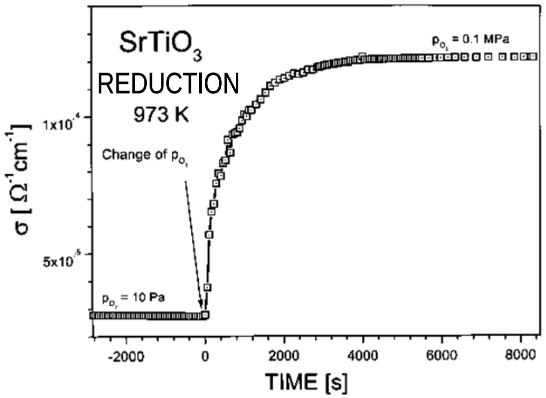
Electronic structure evolution







P. Pasierb *et al.*,
J. Phys. Chem. Solids 60, 1835 (1999)

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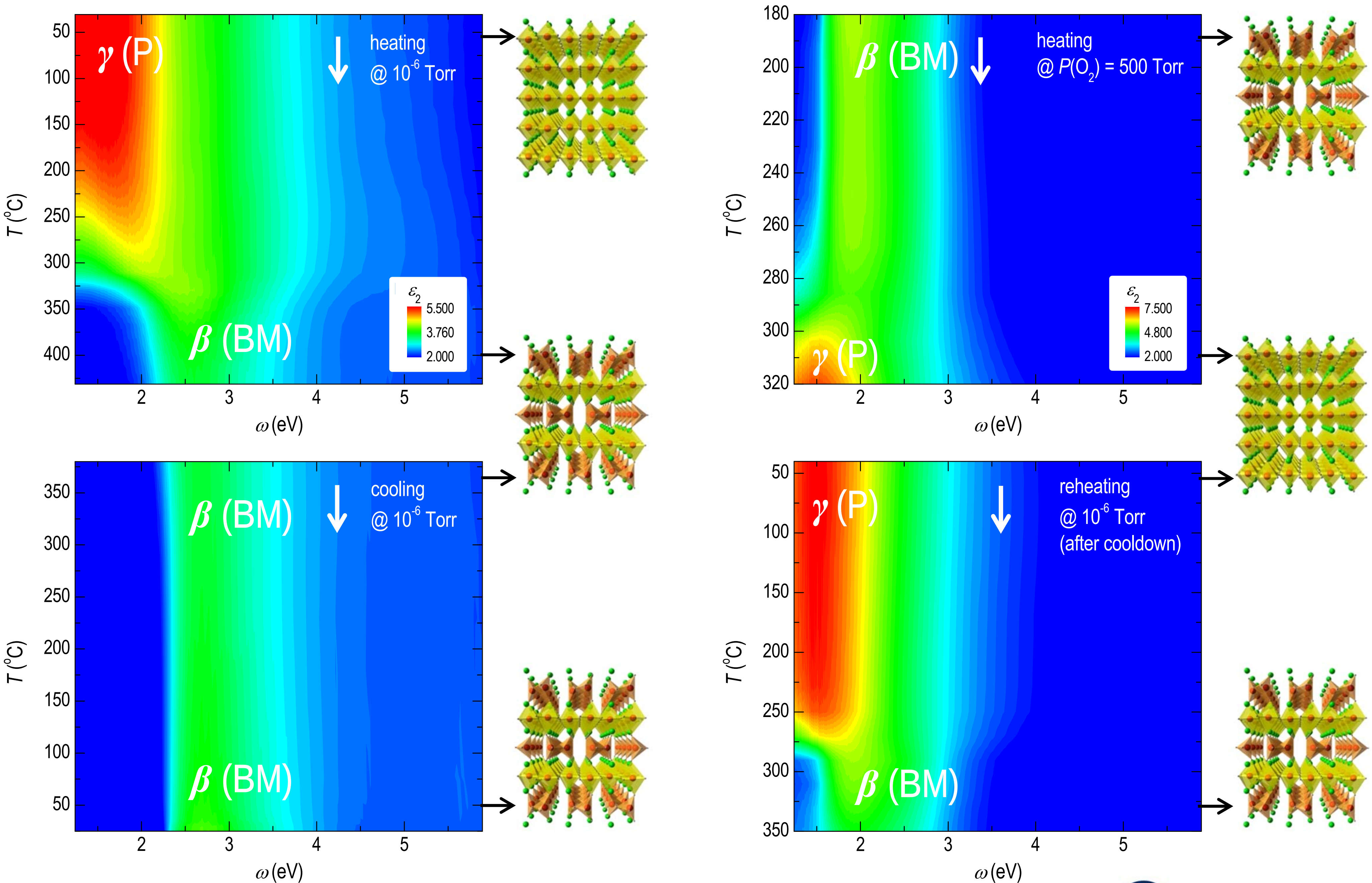
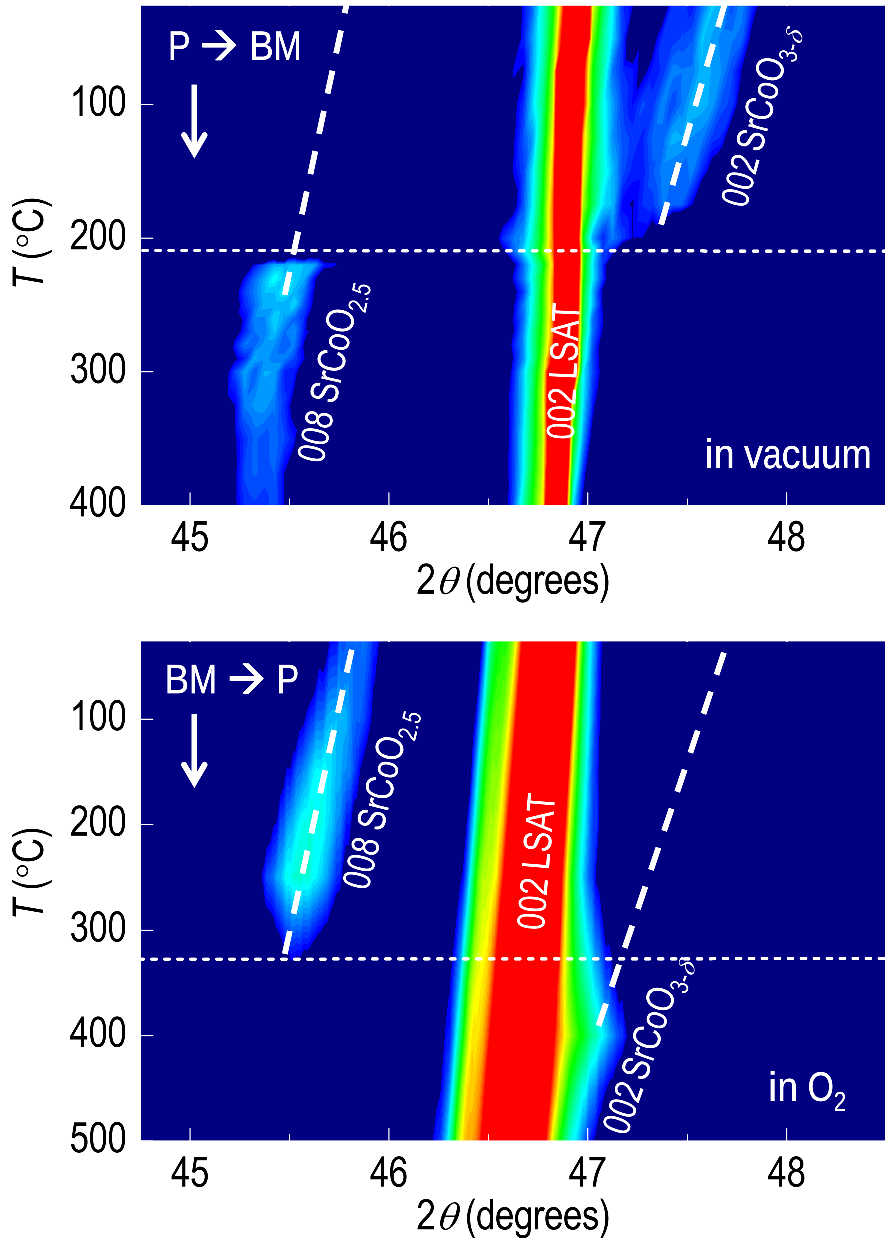
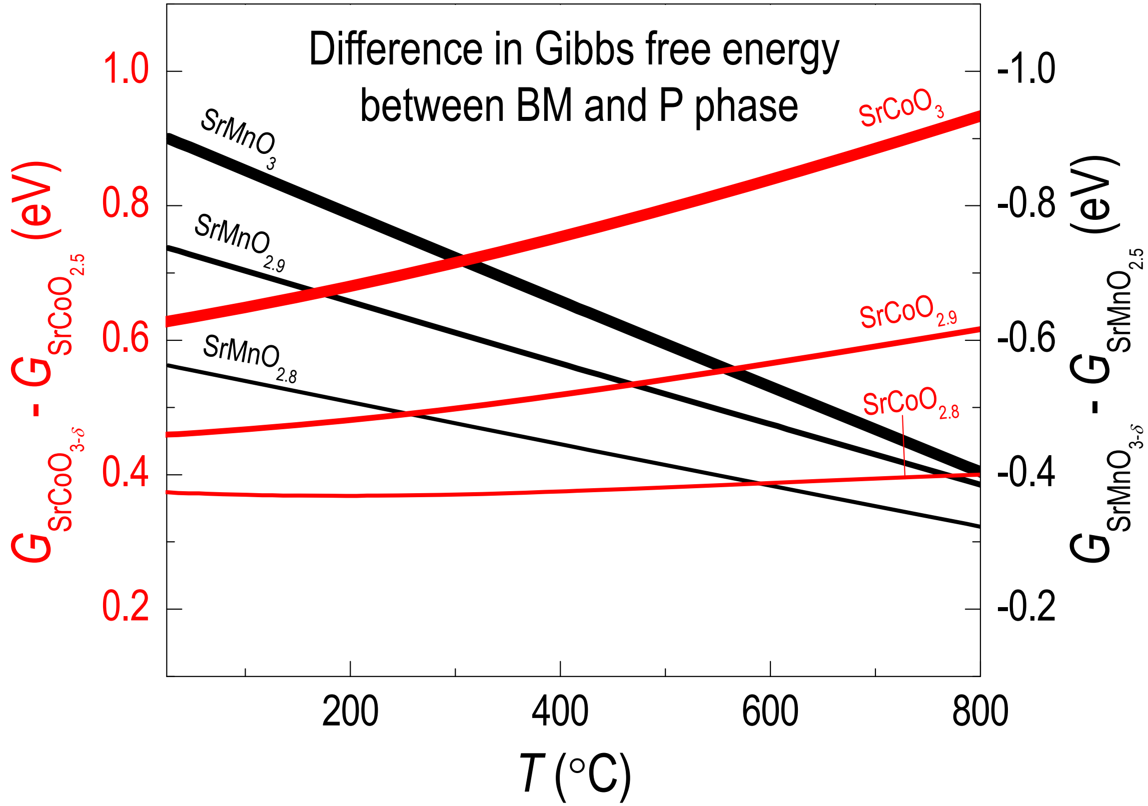
Real-time ellipsometry: BM ↔ PV



W. S. Choi *et al.* *Phys. Rev. Lett.* 111, 097401 (2013)

Real-time XRD: BM ↔ PV





- **Fast and reversible redox reaction** at relatively **low temperatures** for epitaxial SCO thin films.
- Sign and absolute value of the **Gibbs energy difference** provides crucial insight for custom tailoring of topotactic processes in multivalent oxides.
- Reduced energy difference at low temperatures was predicted for SCO.

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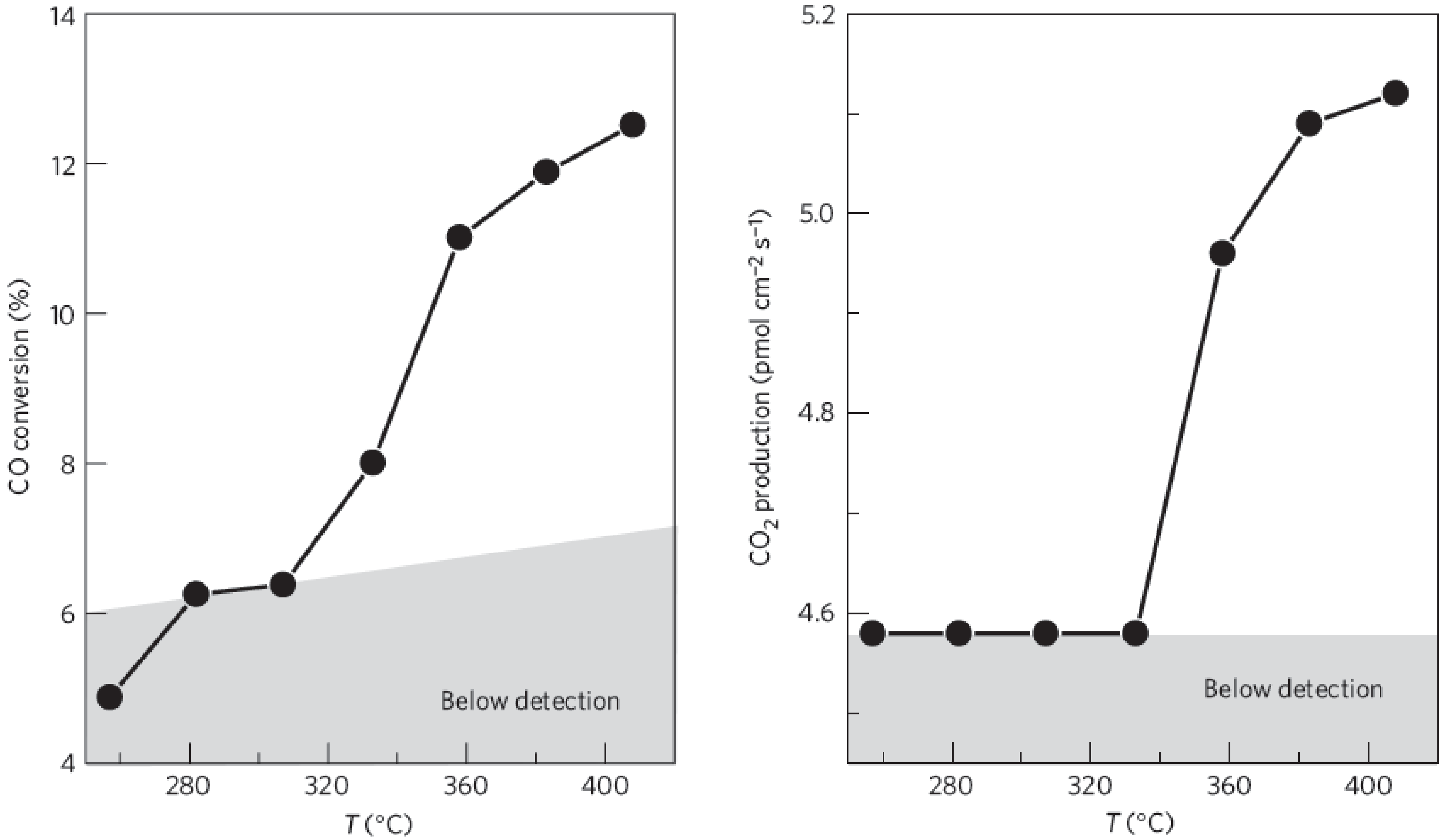
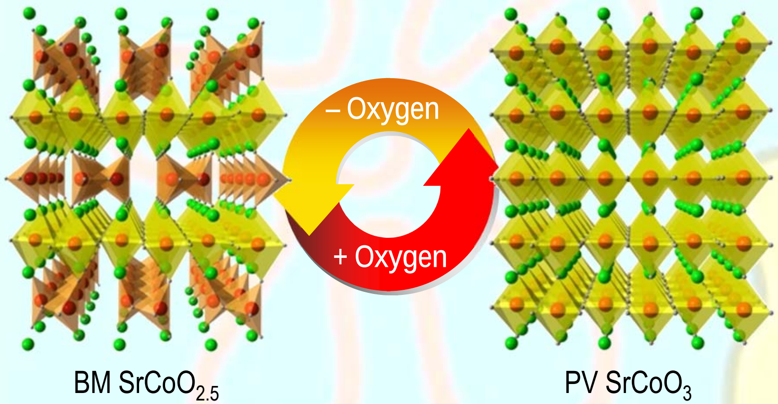
Catalytic activity



- The **redox reaction** at relatively **low temperatures** seems to enhance the catalytic activity of epitaxial SCO thin films (BM in this case).
- First evidence of catalytic activity shown form BM-SCO at relatively low temperature.

Epitaxial oxygen sponge $SrCoO_x$

- First PLE growth of **epitaxial brownmillerite** (BM) and **perovskite** (P) phases of **$SrCoO_x$ single crystalline thin films**!
- **Fast, reversible redox reactions** at **low temperatures**!
- The **topotactic phase transformation** accompanies various **physical property transitions**!



Adv. Mater. Early View doi:10.1002/adma.201302919 (2013).
Phys. Rev. Lett. **111**, 097401 (2013).
Nat. Mater. **12**, 1057 (2013).
Adv. Mater. **25**, 3651 (2013).