

Characterizing oxides with low cation substitution

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with (mostly):

Aditi Risbud (Molecular Foundry, Berkeley)

Young-II Kim (Yeongnam)

Katharine Page (Los Alamos), and

Jun Li (Rohm and Haas)



The game of x^*

Composition, along with pressure and temperature, are key variables in the study of the properties of crystalline solids, and in the development of functionality:

Examples:

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$: Superconductivity

$\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$: Colossal magnetoresistance, charge-ordering

$\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$: Piezoelectric tuning

$\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$: Capacitors

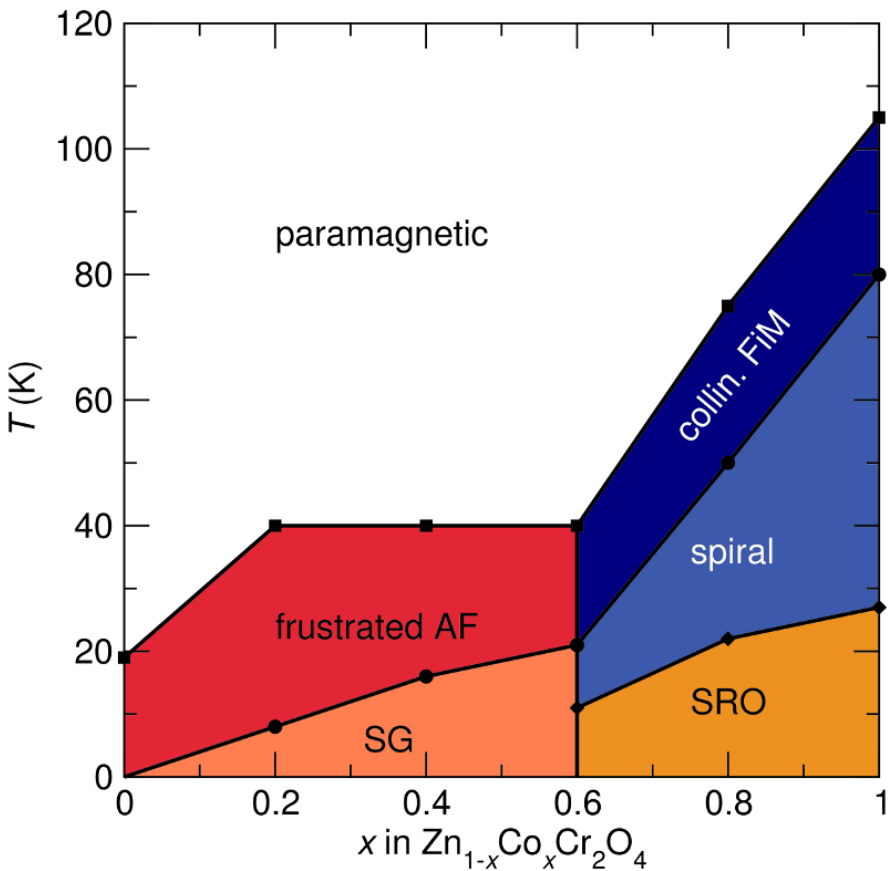
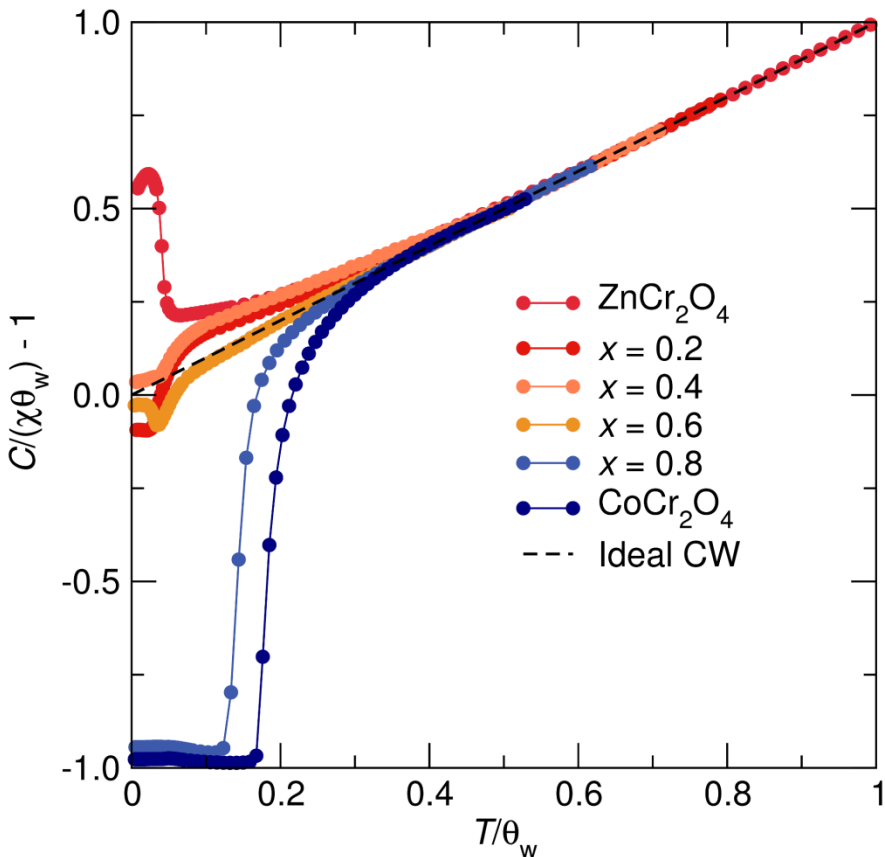
$\text{V}_{2-x}\text{Cr}_x\text{O}_3$: Insulator-metal transitions

*Referred to, on occasion, as subscript chemistry.



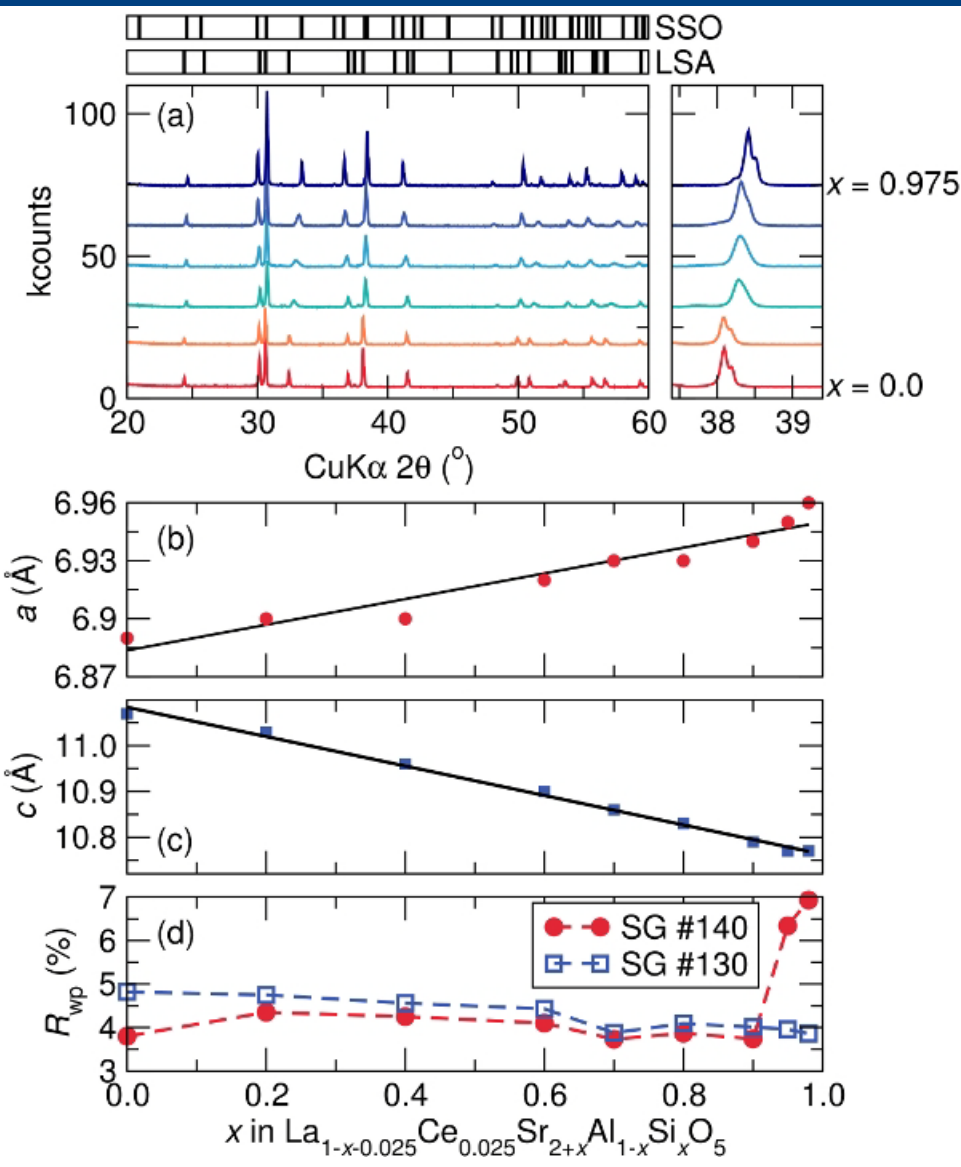
Examples: Tuning magnetic coupling in insulating spinels

The magnetic spinels, $Zn_{1-x}Co_xCr_2O_4$: One end-member is frustrated and the other is a spiral magnet.

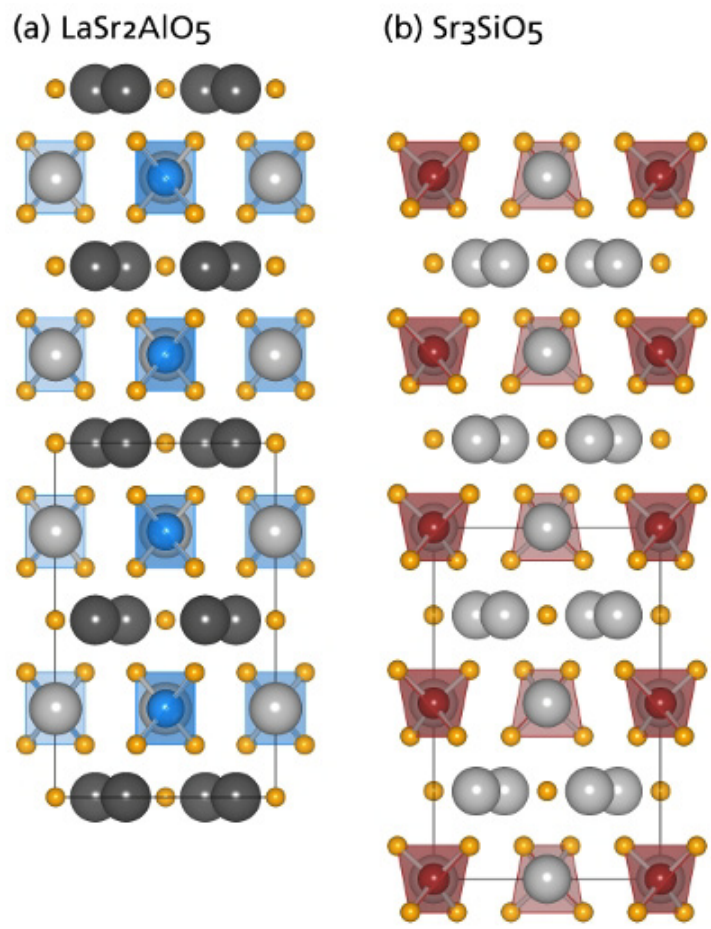


Melot, Drewes, Seshadri, Ramirez, *cond-mat*, 2008.

Examples: Tuning luminescence in a Ce³⁺ phosphor



Solid solutions between two end-members with distinct crystal structures.



Im, Fellows, DenBaars, Seshadri, *J. Mater. Chem.* (2009)

Outline:

1. Cation substituted zinc oxides: Isovalent substitution of divalent ions for Zn^{2+} influences magnetism, static polarization, and the band gap [*Phys Rev B*. **68** (2003) 205202; **71** (2005) 045201; **76** (2004) 115204; **78** (2008) 195205]
2. The perovskites SrTiO_3 and BaTiO_3 : Aliovalent substitution of Nb^{5+} for Ti^{4+} results in a delocalized metallic ground state in the case of SrTiO_3 but not in the case of BaTiO_3 [*Phys. Rev. Lett.* **101** (2008) 205502]
3. Perovskite oxides where aliovalent substitution of divalent Pd^{2+} for quadrivalent Ce^{4+} results in unusually active catalyst materials [*Chem. Mater.* **19** (2007) 1418; **20** (2008) 6567.]

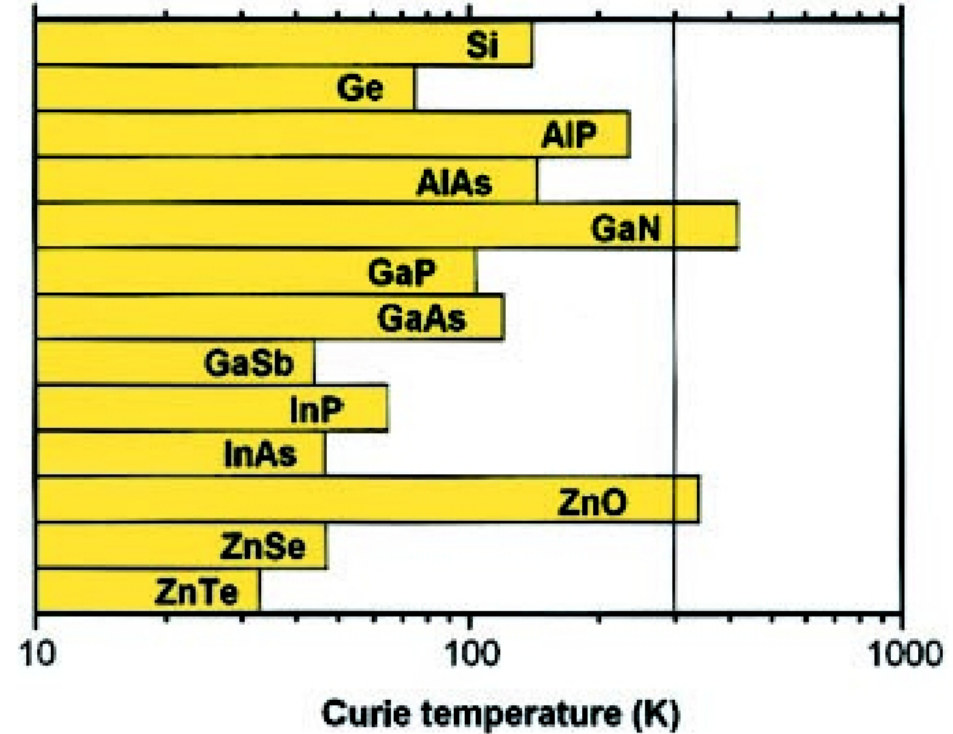


Cation substituted zinc oxides

Cation-substituted ZnO: Magnetism

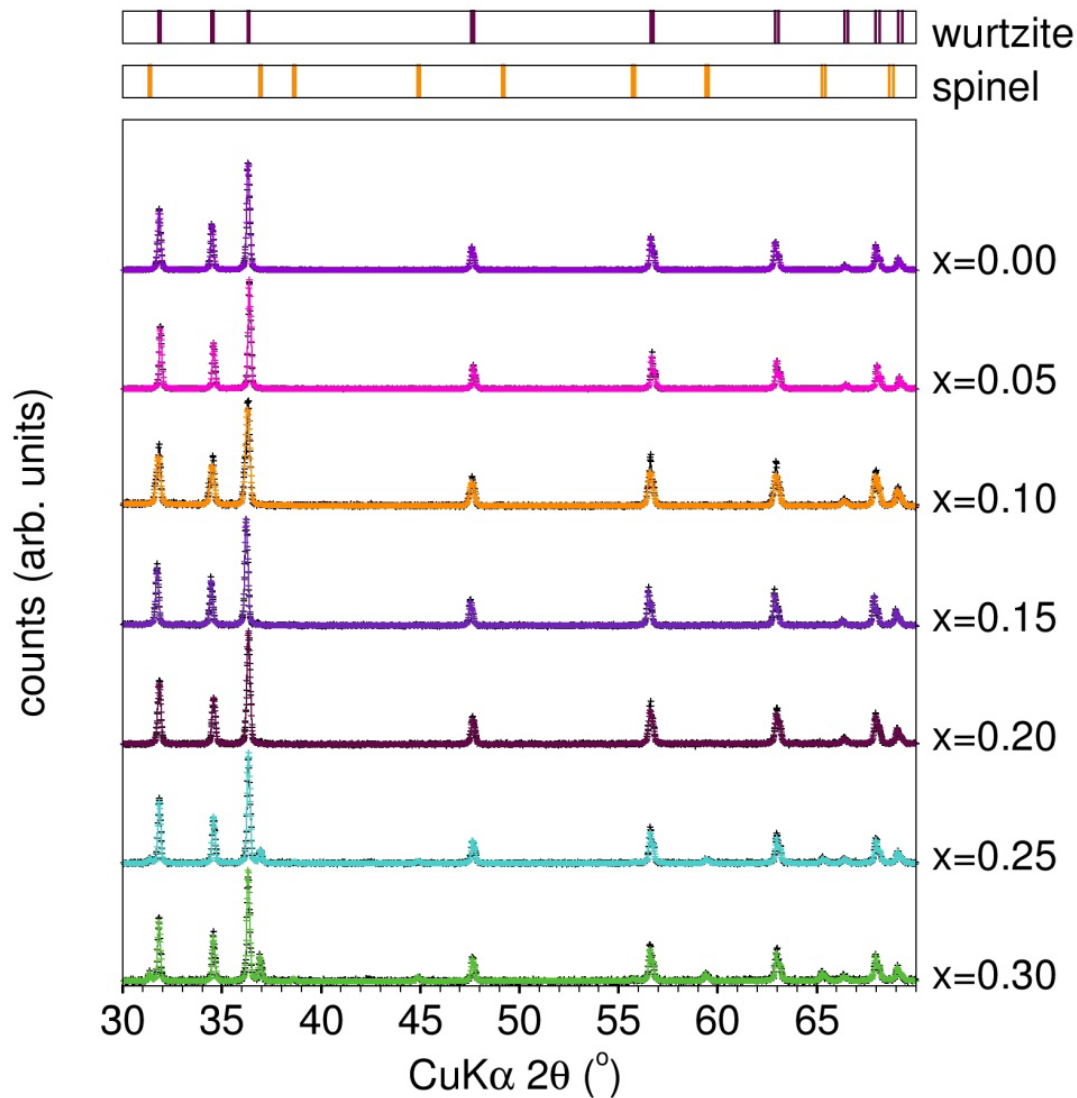
The suggestion: Hole doped wide band gap semiconductors can be rendered ferromagnetic through suitable cation substitution.

[Dietl, Ohno, Matsukura, Cibért, Ferrand, *Science* **287** (2000) 1019]



Computed values of the Curie temperature T_C for various p-type semiconductors containing 5% of Mn and 3.5×10^{20} holes per cm^3 .

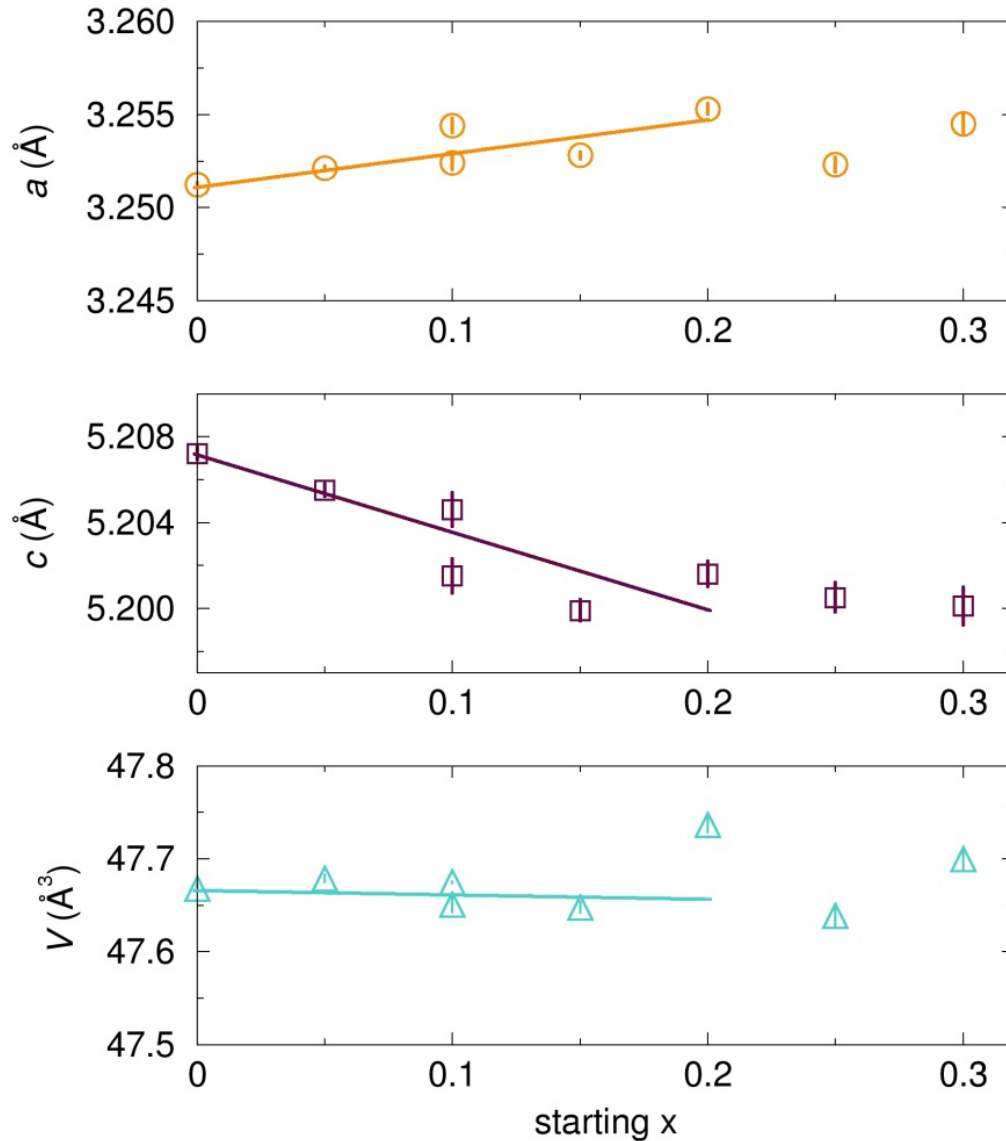
Cation-substituted ZnO: Magnetism



Bulk Co and Mn-substituted ZnO made using a precursor route. Clean phases $\text{Zn}_{1-x}\text{tM}_x\text{O}$ till $x = 0.15$ typically

Prepared from oxalates: $(\text{Zn}, \text{tM})\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ by rapidly heating to 800°C

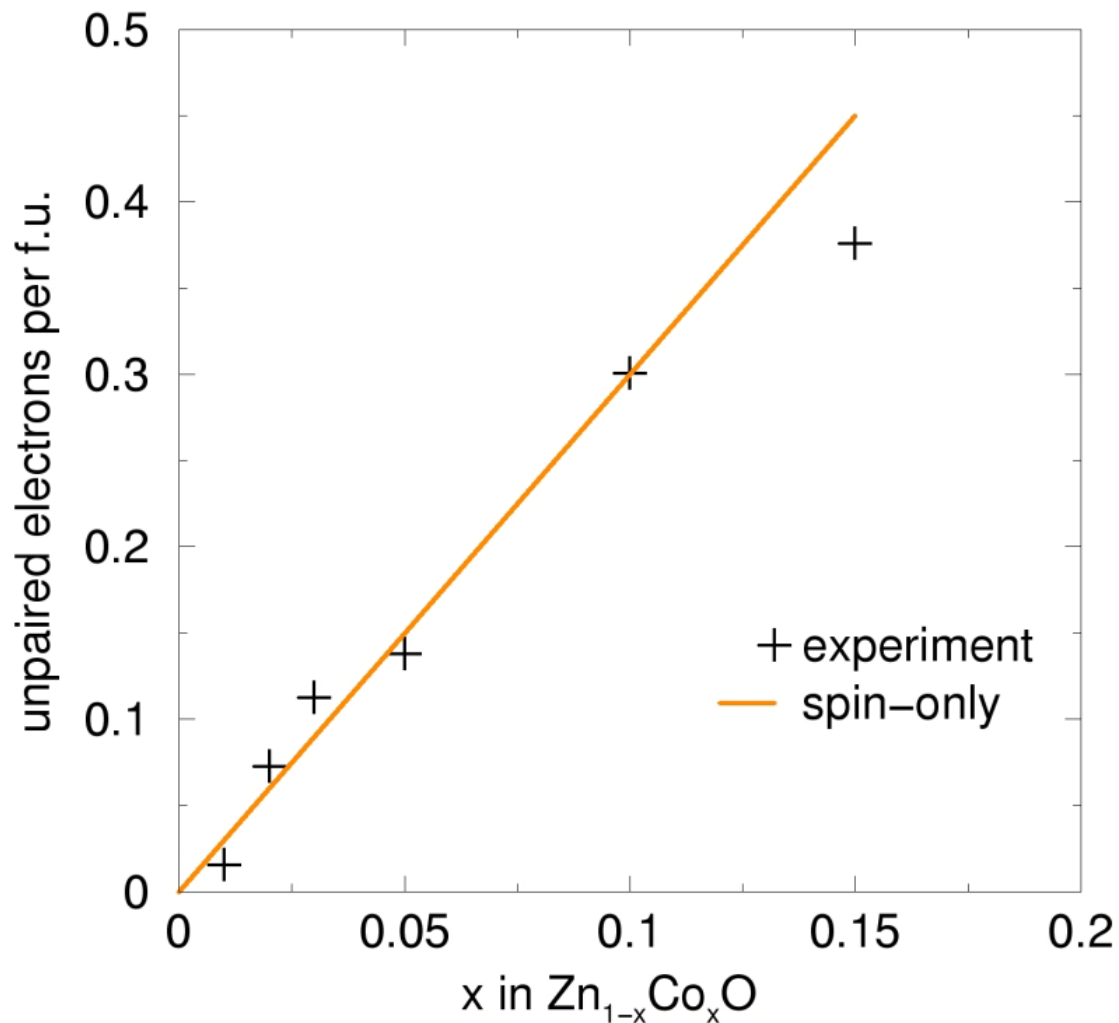
Cation-substituted ZnO: Magnetism



Cell parameters follow the Vegard law till the substitution limit is reached.

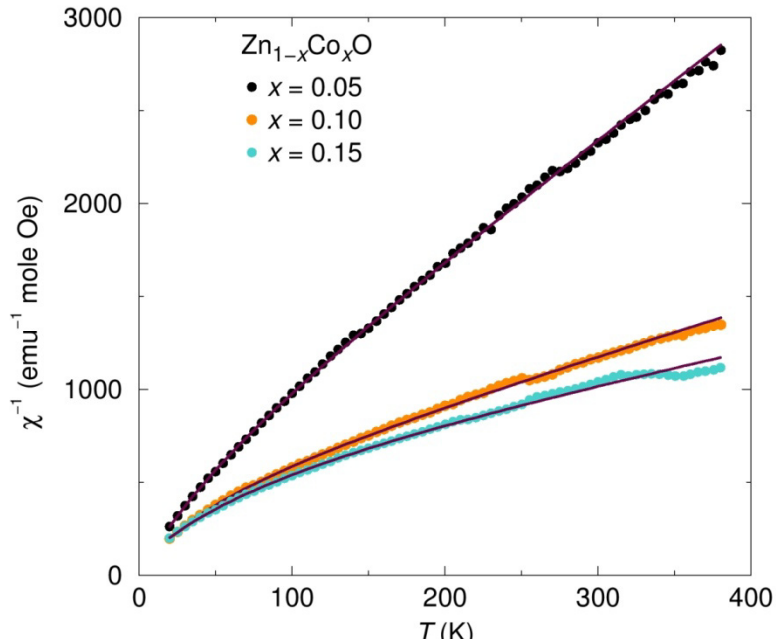
Co^{2+} is slightly smaller than Zn^{2+} .

Cation-substituted ZnO: Magnetism



Number of unpaired electrons obtained from the high- T Curie-Weiss slope (between 300 K and 350 K) correspond precisely to expectation for tetrahedral Co^{2+} [note $g = 1.54$ for Co^{2+}]

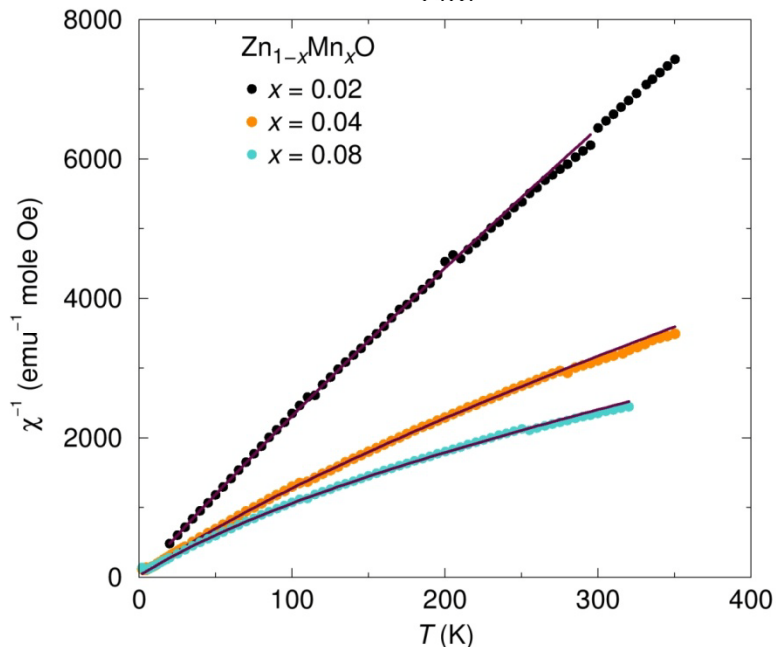
Cation-substituted ZnO: Magnetism



No evidence of collective magnetism.

Instead, $\chi = C_1/T + C_2/(T-\Theta)$ describes the magnetic susceptibility between 20 K and 400 K.

Θ is large and negative implying that near-neighbor interactions are antiferromagnetic.



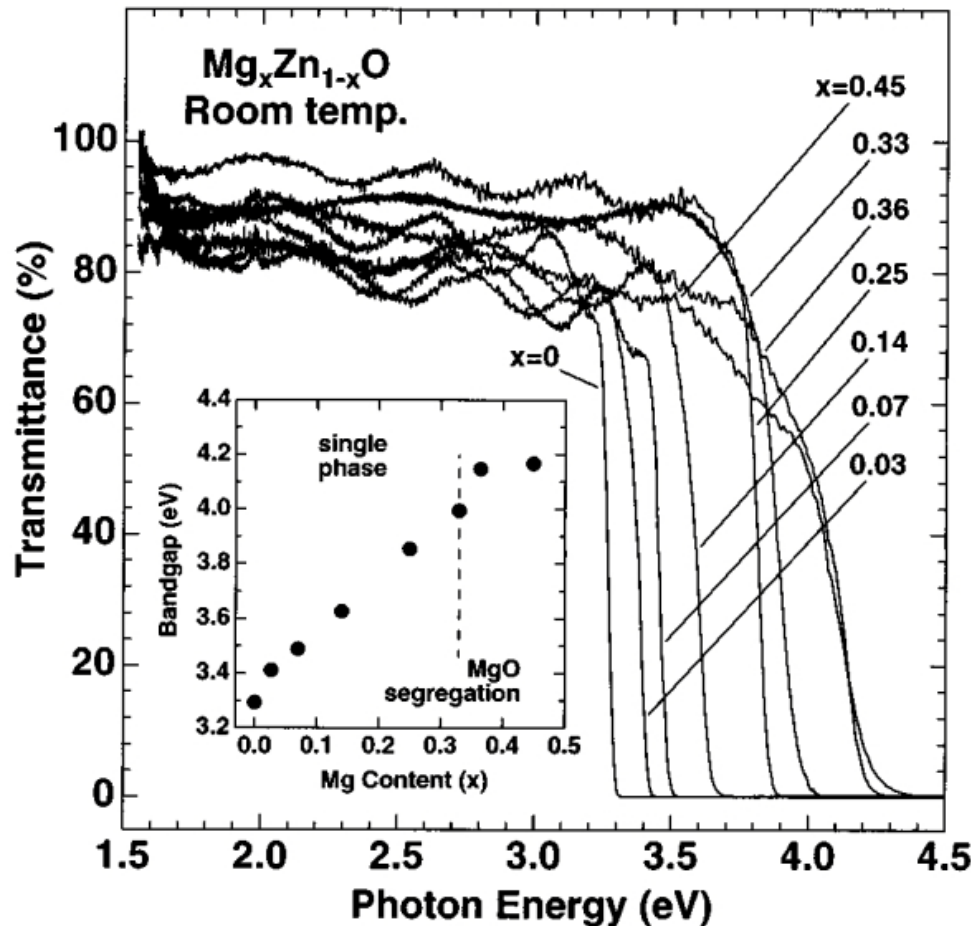
Risbud, Spaldin, Chen, Stemmer, Seshadri, *Phys. Rev. B.* **68** (2003) 205202; Lawes, Risbud, Ramirez, Seshadri, *Phys. Rev. B* **71** (2005) 045201.



Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

Motivation: What happens to ZnO upon Mg-substitution?

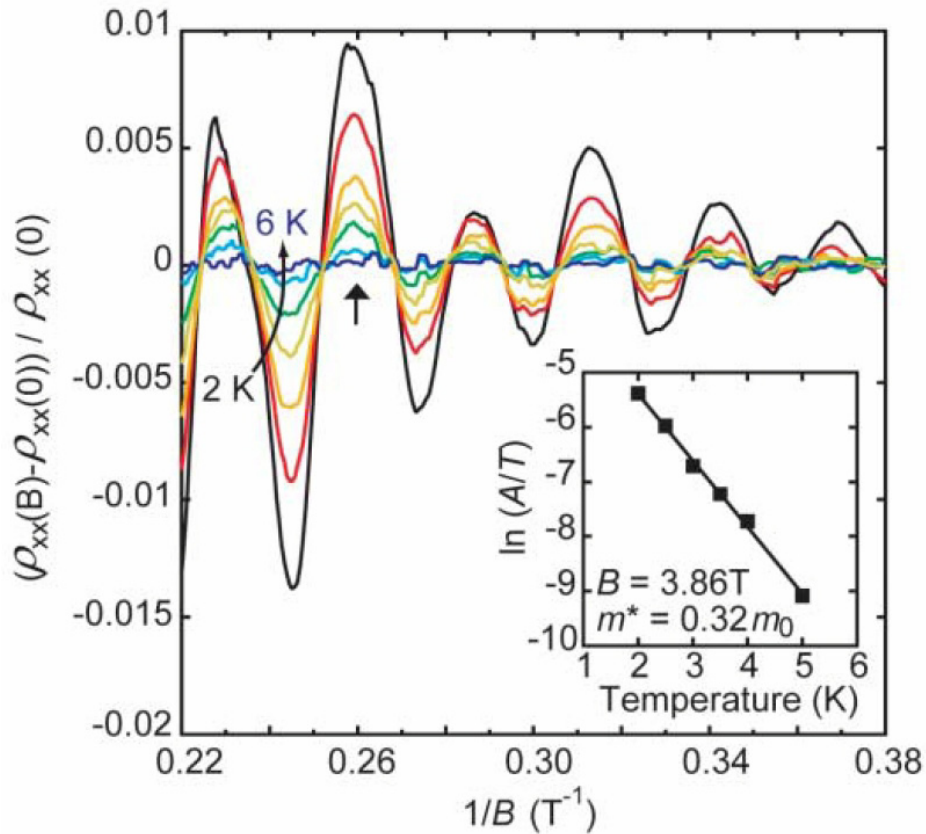
(ZnMg)O on SCAM,
Laser ablation



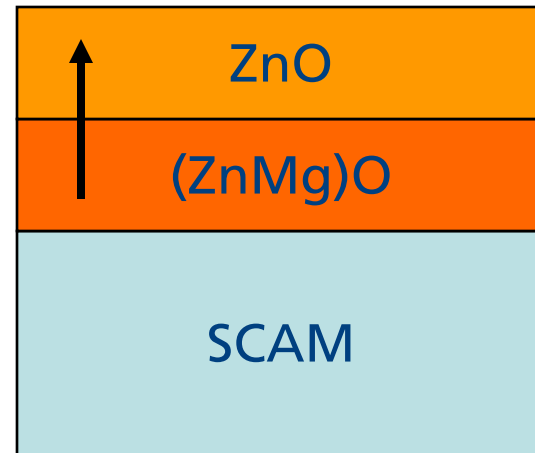
Ohtomo, Kawasaki, Koida, Masubuchi, Koinuma, Sakurai, Yoshida, Yasuda, Segawa, *Appl. Phys. Lett.* 72 (1998) 2466.

Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

Motivation: What happens to ZnO upon Mg-substitution?



Quantum Hall Effect observed at the 2DEG formed at the interface of unstrained (ZnMg)O and ZnO due to the polarization gradient.



Tsukazaki, Ohtomo, Kita, Ohno, Ohno, Kawasaki, *Science* 315 (2007) 1388.

Motivation: What happens to ZnO upon Mg-substitution?

Polarization, Piezoelectric Constants, and Elastic Constants of ZnO, MgO, and CdO

PRIYA GOPAL^{1,2} and NICOLA A. SPALDIN¹

1.—Materials Department, University of California, Santa Barbara, CA 93106-5050. 2.—E-mail: priyag@mrl.ucsb.edu

We report first-principles density functional calculations of the polarizations, piezoelectric stress constants, and elastic constants for the II-VI oxides MgO, ZnO, and CdO in the wurtzite structure. Using our pseudopotential self-interaction corrected implementation of density functional theory, we obtain polarization values of -0.060 , -0.022 , and -0.10 C/m², and piezoelectric constants, e_{33} (e_{31}) of 1.64 (-0.58), 1.34 (-0.57), and 1.67 (-0.48) C/m² for structurally relaxed MgO (with its in-plane lattice parameter fixed to that calculated for ZnO), ZnO, and CdO, respectively. The large polarization gradients between the end-point compounds in the MgO-ZnO-CdO system augur well for the production of large internal fields in ZnO-based polarization field effect transistors.



Our work: Polycrystalline $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ powders from oxalate precursors

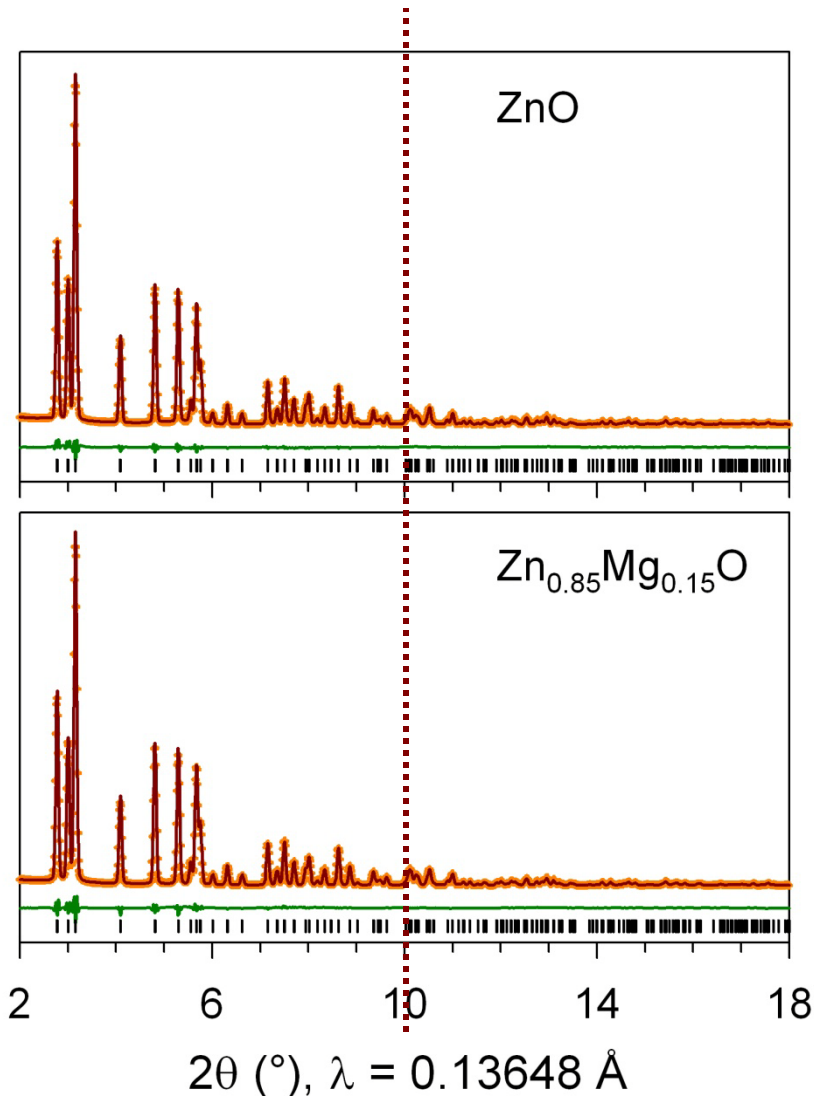
- Large [multi-gram] quantities for numerous studies: Optical, X-ray, IR, NMR, Raman, Neutrons, ...
- Possibility of detailed structural studies
- Successful in understanding diluted magnetic oxide semiconductors [*Phys. Rev. B* 71 (2005) 045201(1-5); *Phys. Rev. B* 68 (2003) 205202(1-7).]

$\text{Zn}_{1-x}\text{Mg}_x\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, heating in air at 550°C for 22 h \Rightarrow $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

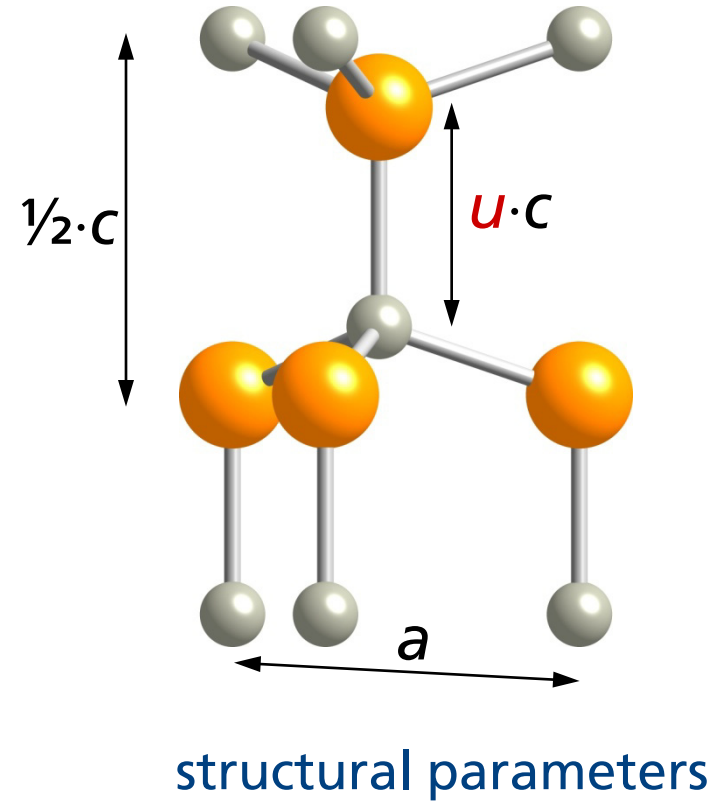
Clean samples till $x = 0.15$, rock-salt MgO beyond.



Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

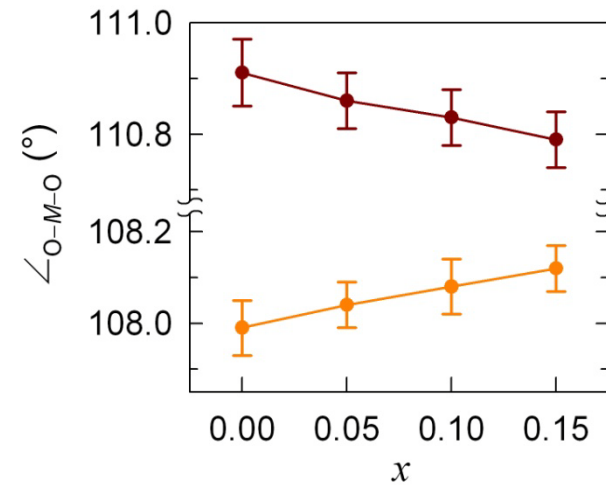
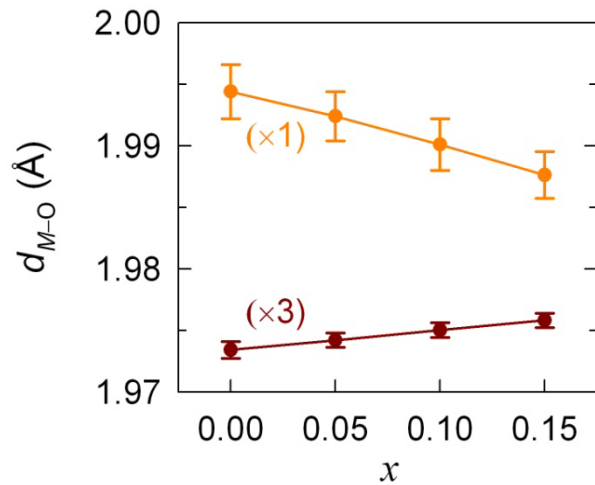
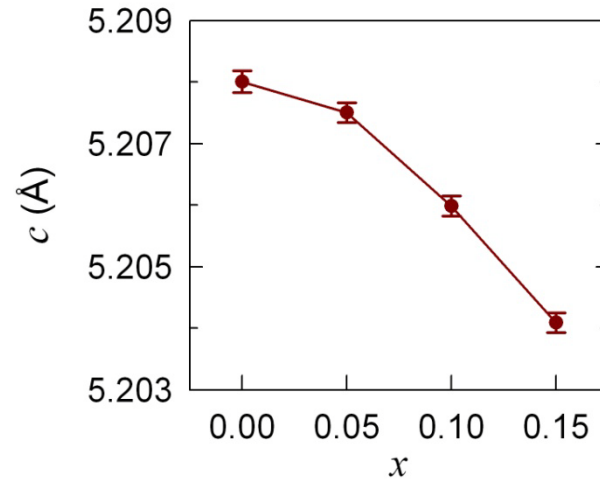
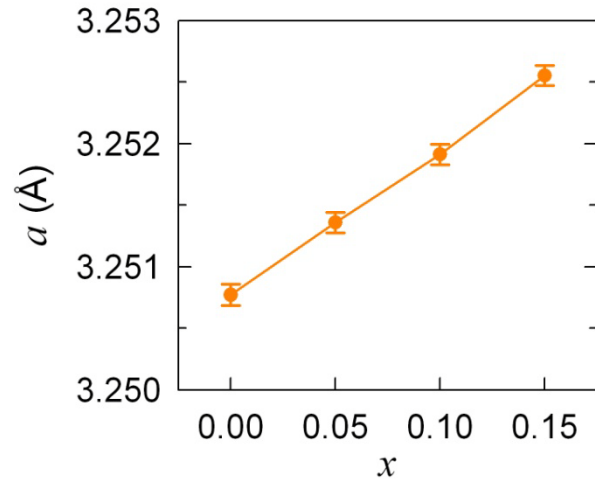


APS, 11-ID-B



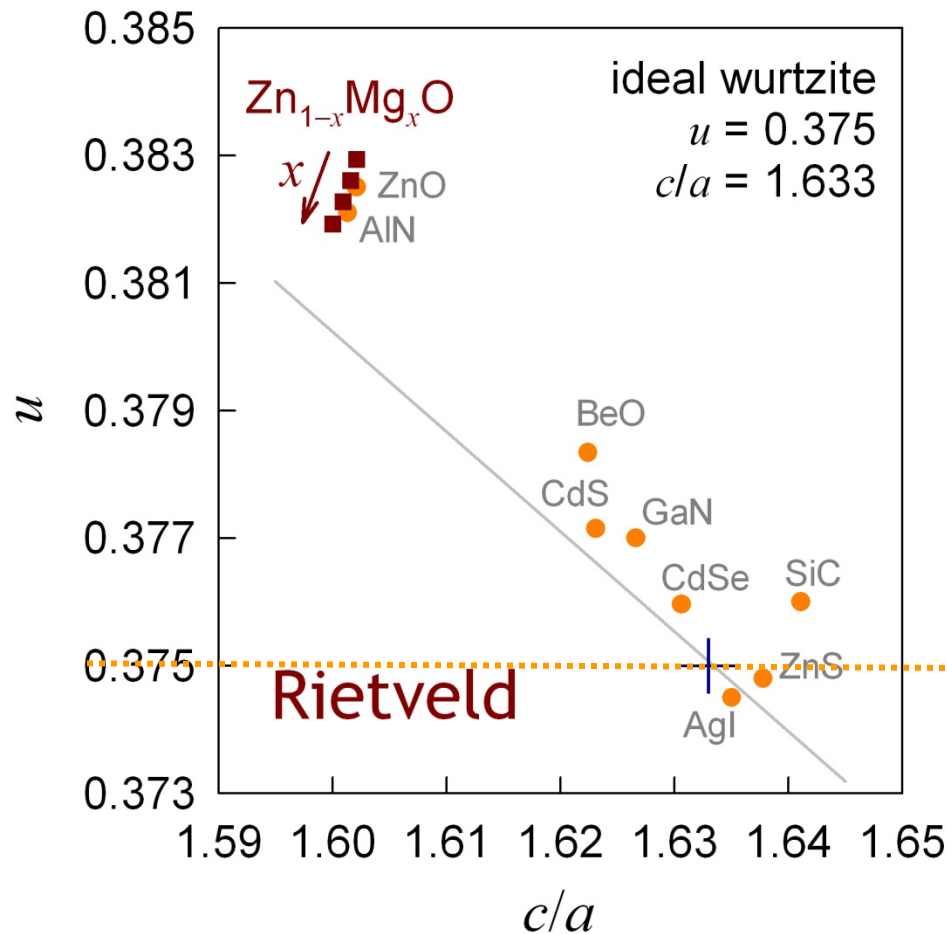
Rietveld fits, including refinements of Zn:Mg ratios.

Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$



Cell and internal parameters to high precision.

Cation-substituted ZnO: $Zn_{1-x}Mg_xO$



The largest structural change is from the internal parameter u .

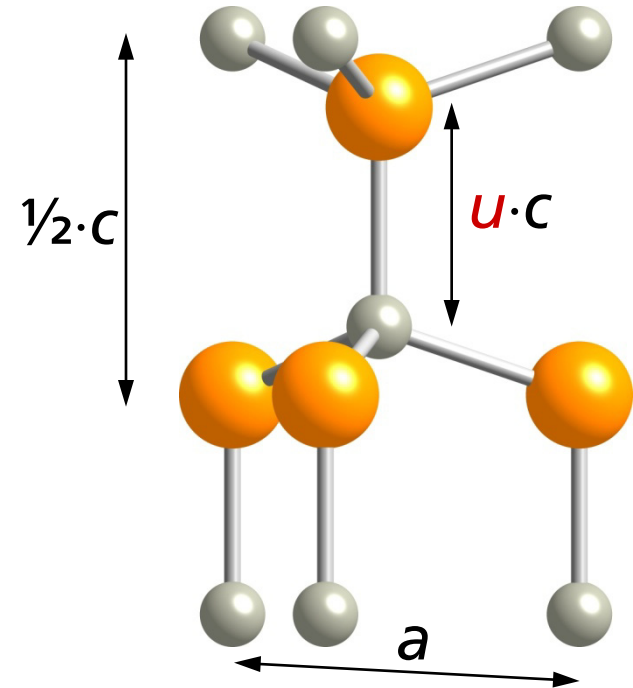
$$u = \frac{3}{8}; P_s = 0$$

Dipole along the c direction:

$$\mu(\text{Zn} - \text{O}_{\text{axial}}) = \frac{1}{4} \times (-2) \times u \times c$$

$$\mu(\text{Zn} - \text{O}_{\text{basal}}) = 3 \times \frac{1}{4} \times (-2) \times \left(u - \frac{1}{2} \times c\right)$$

$$P_s = \frac{\sum \mu}{V} = \frac{-2 \times \left(u - \frac{3}{8}\right) \times c}{\frac{\sqrt{3}}{4} a^2 \times c}$$



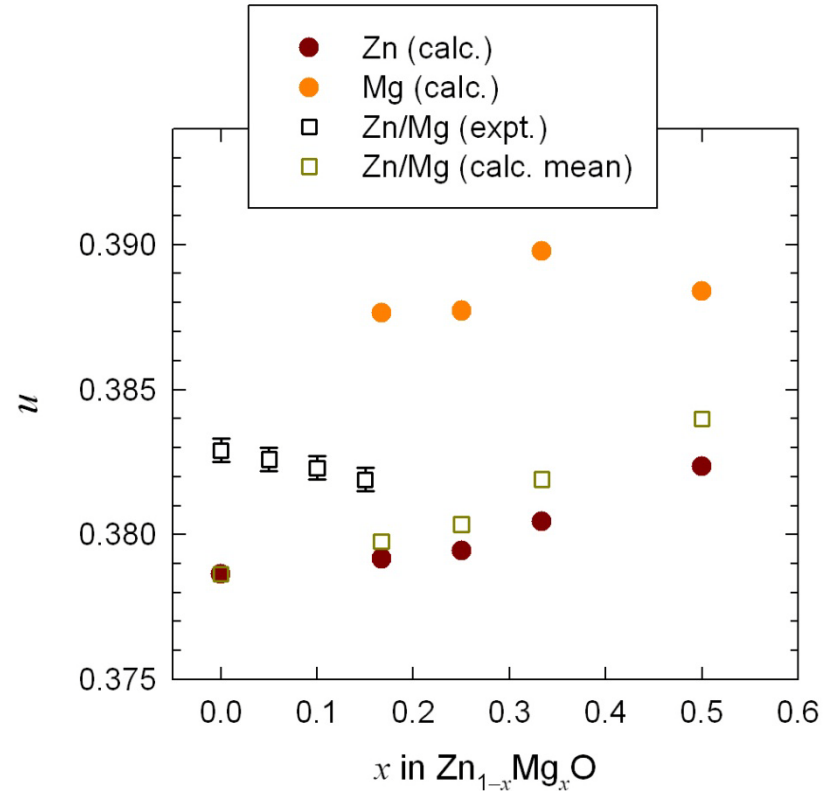
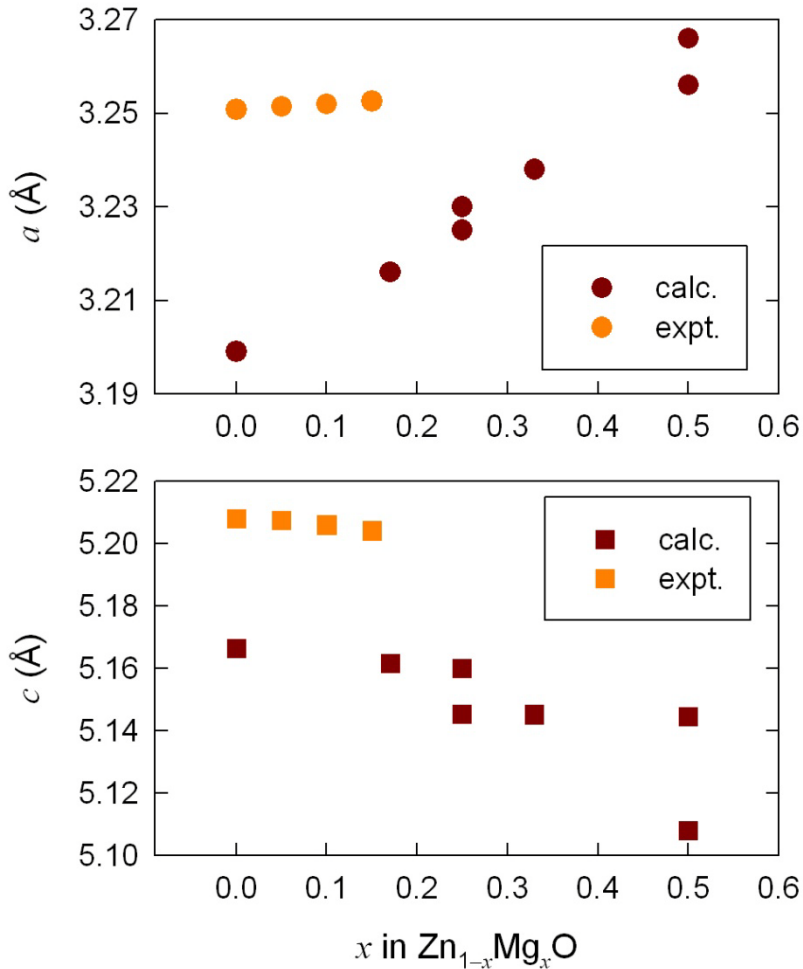
Static polarization P_s based on simple ionic charge model; shared reference state where all ZnO_4 tetrahedra have zero dipoles:

ZnO: $-5.6 \mu\text{C}/\text{cm}^2$ and $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$: $-4.8 \mu\text{C}/\text{cm}^2$

[decreases, Cf. Tsukazaki, DFT.]

Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

Experiments versus DFT

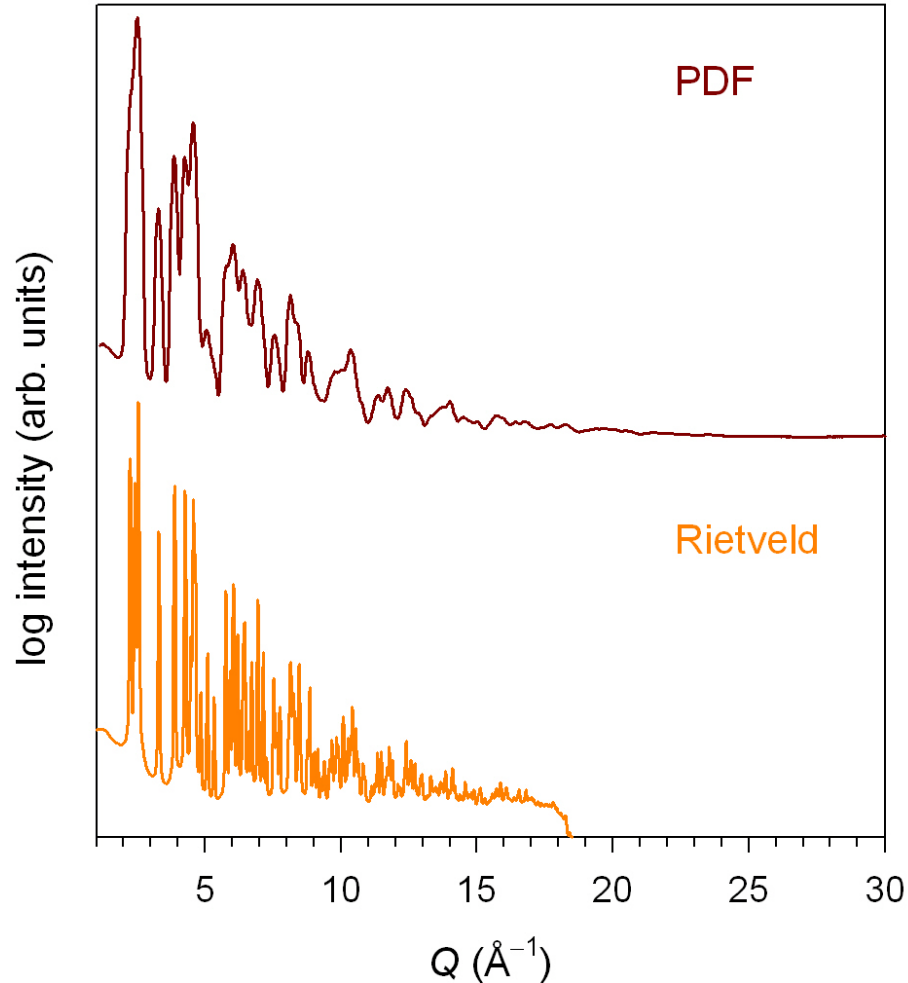


Discrepancy in trend of u

DFT: Malashevich, Vanderbilt, *Phys. Rev. B* 75 (2007) 045106; unpublished results.

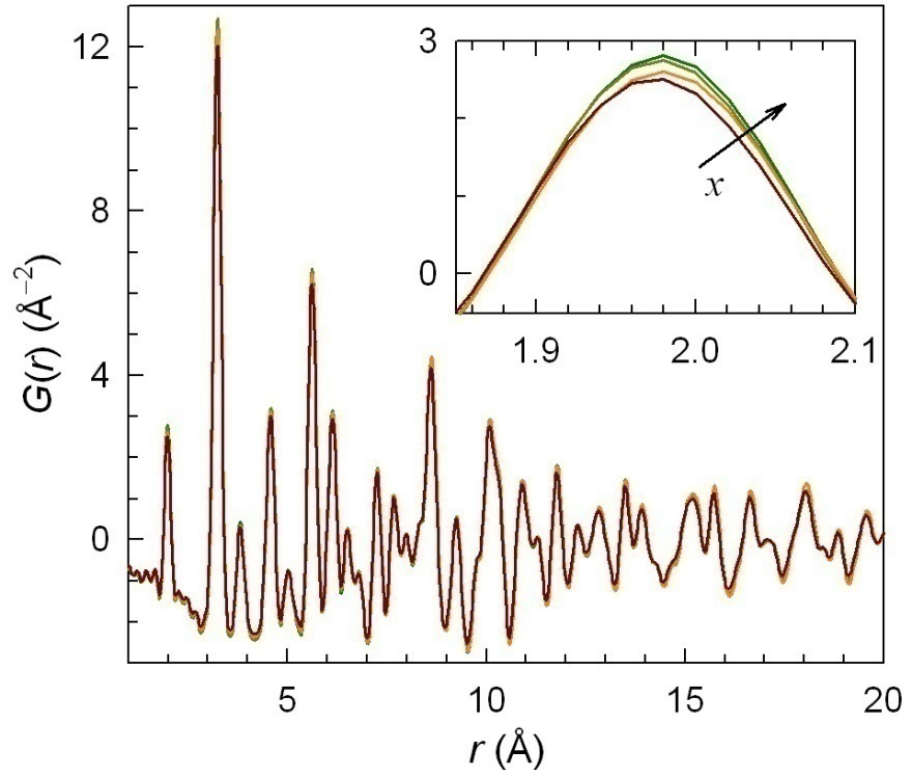
Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

The pair distribution function (PDF)

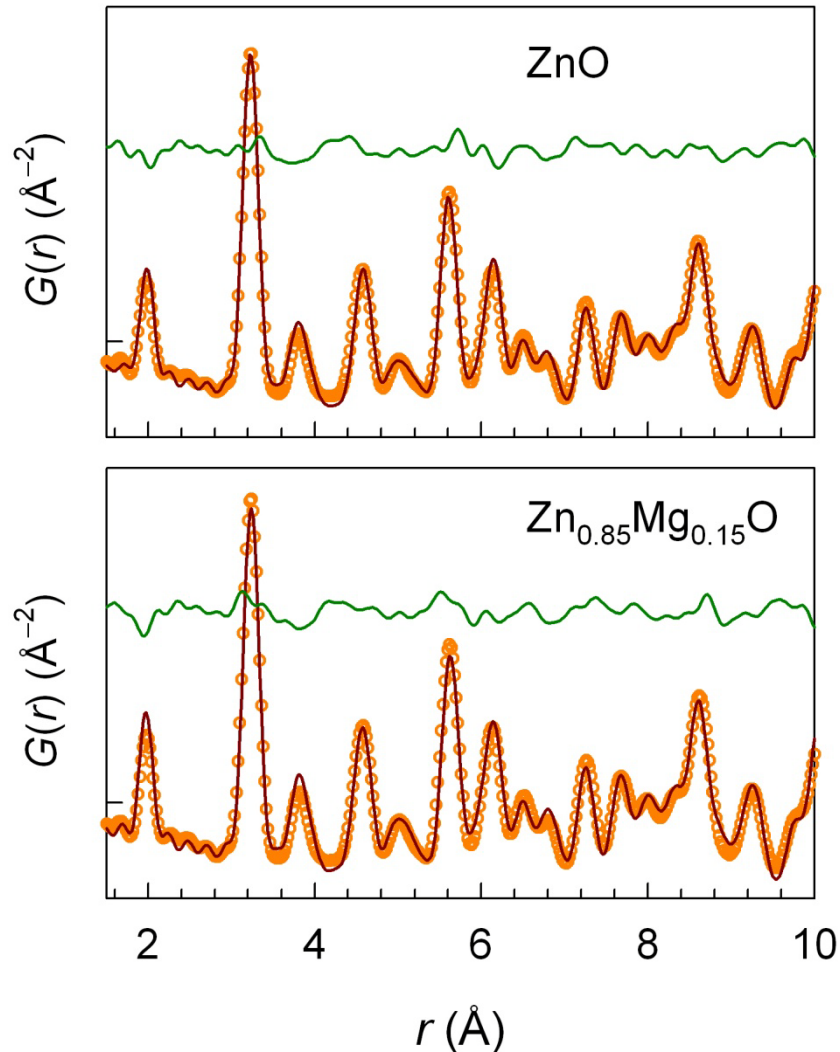


Data acquired at lower resolution but to higher Q: Bragg + diffuse

Fourier-transform and scale



Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

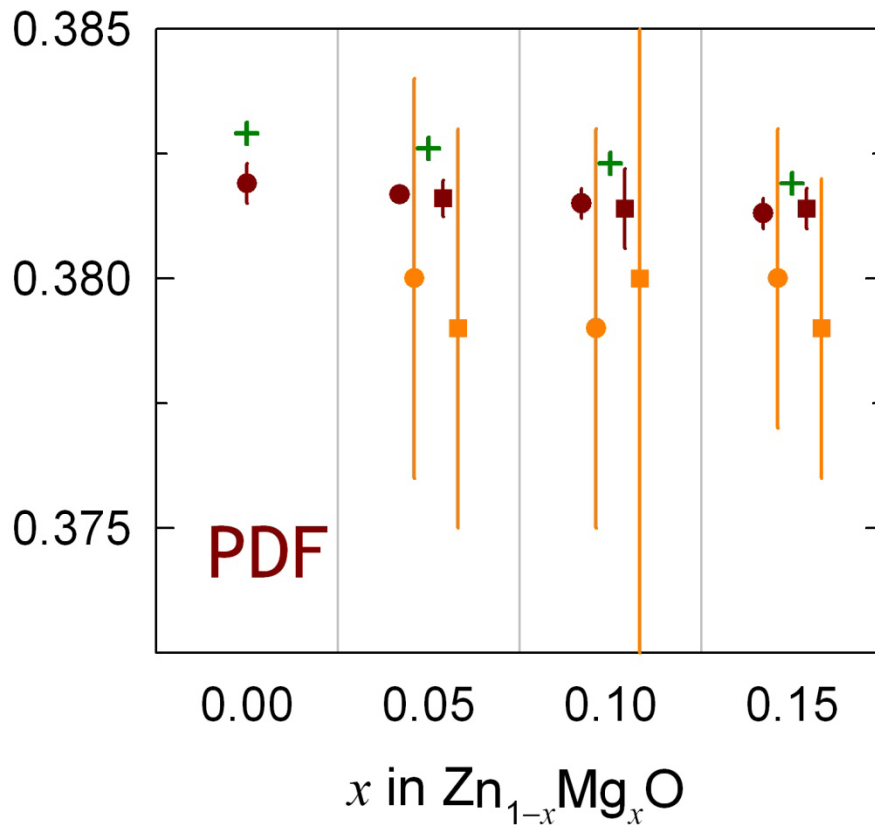


PDFs modeled using both average (crystallographic) and supercell descriptions.

Explicit Zn and Mg atoms in latter.

Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

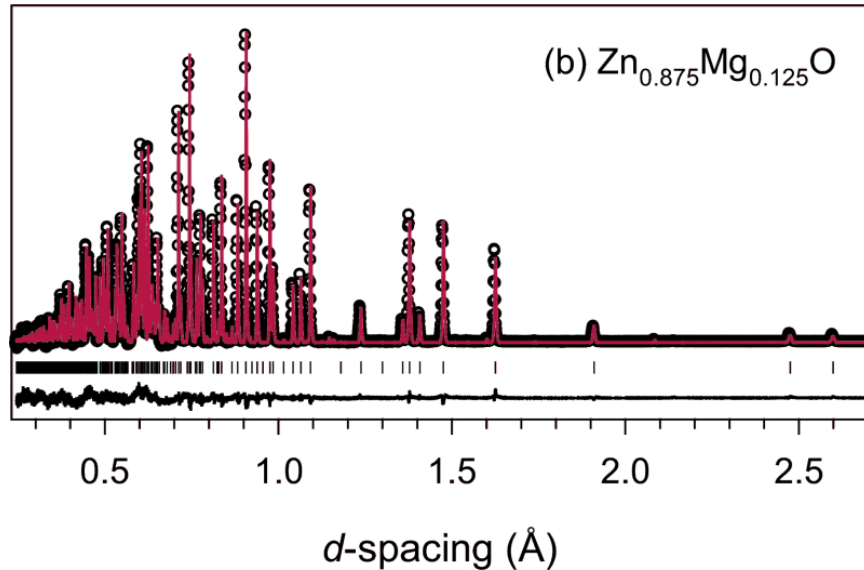
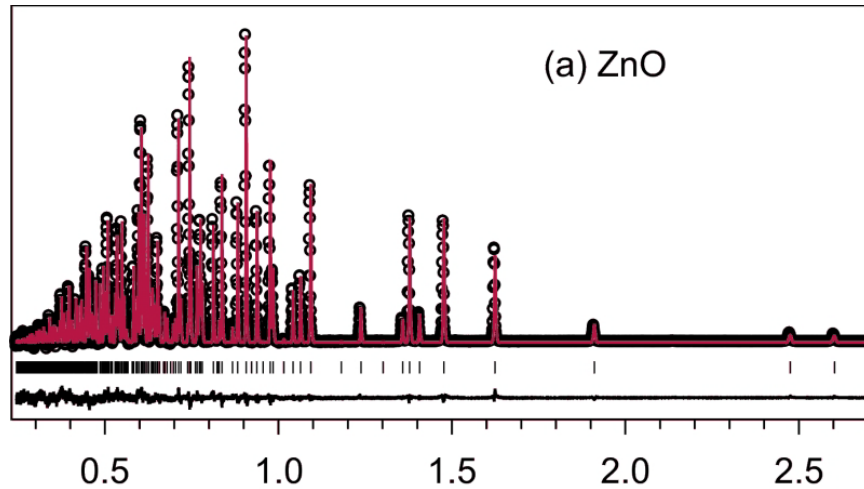
- Zn (simple cell)
- Mg (simple cell)
- Zn (supercell)
- Mg (supercell)
- + Zn/Mg (Rietveld)



PDF analysis allows the positions Zn and Mg to be separately monitored.

Large error bars on distances associated with Mg from X-ray PDFs

Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

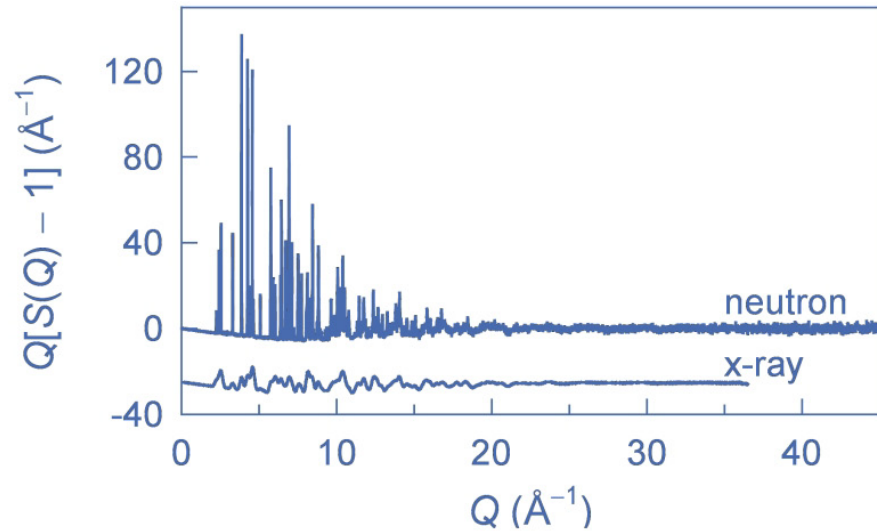


Enter neutrons:

Zn and $\text{Zn}_{0.875}\text{Mg}_{0.125}\text{O}$, the latter, specially formulated for ease of modeling: $\text{Zn}_{7/8}\text{Mg}_{1/8}\text{O}$.

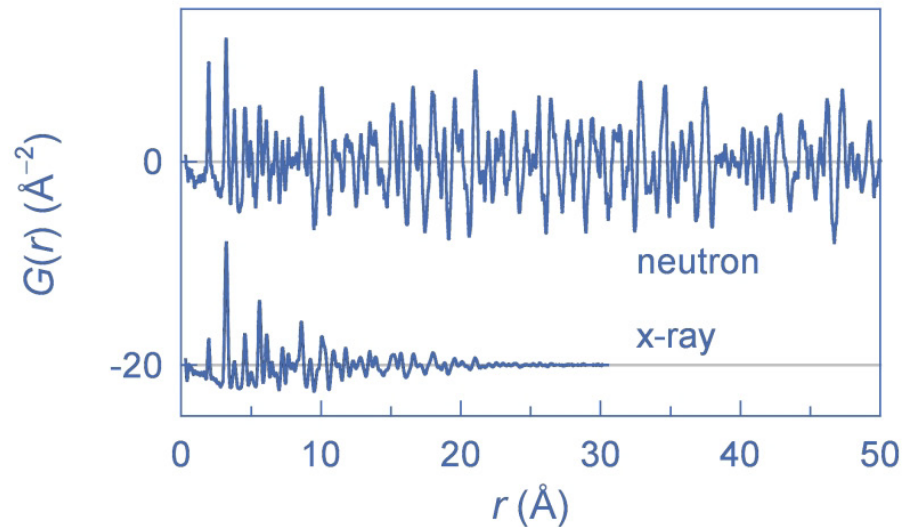
Rietveld analysis of TOF neutrons shown.

Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

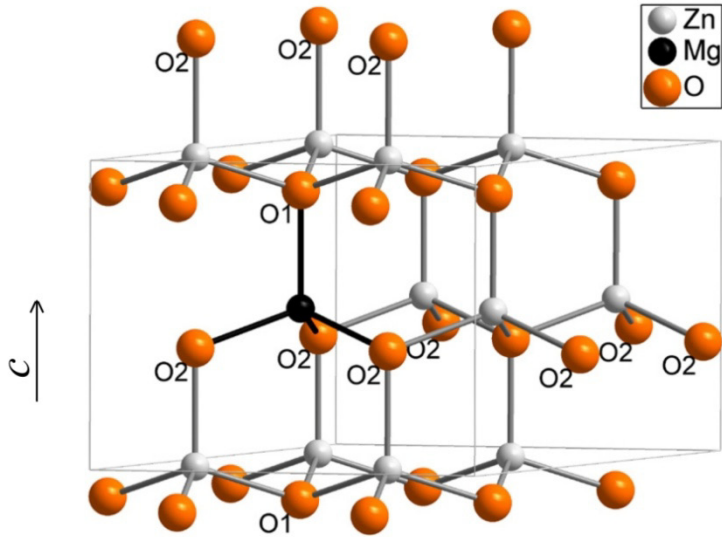


Why neutrons ?

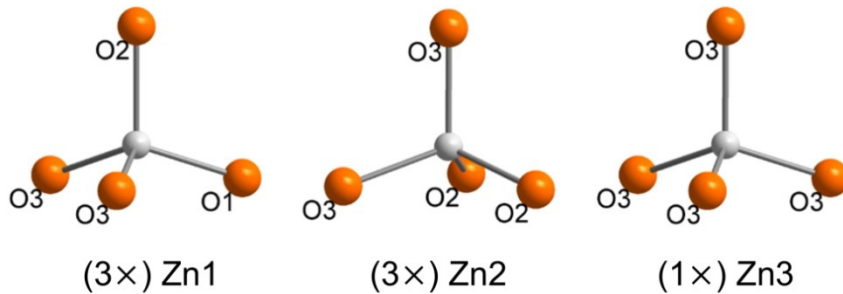
- Even scattering from all atoms
- Absence of form-factor fall-off.



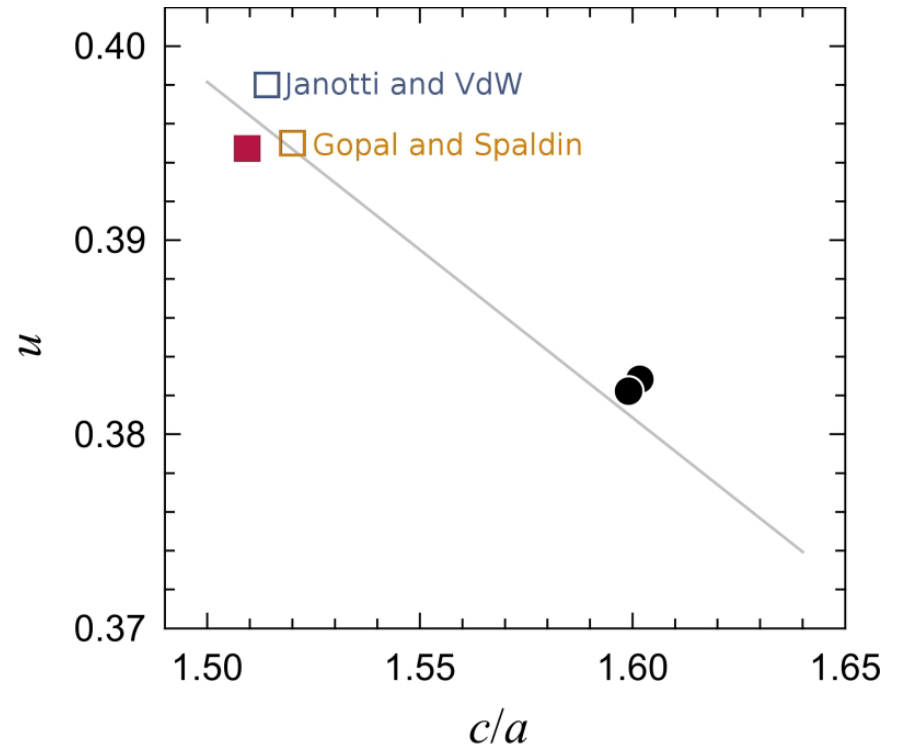
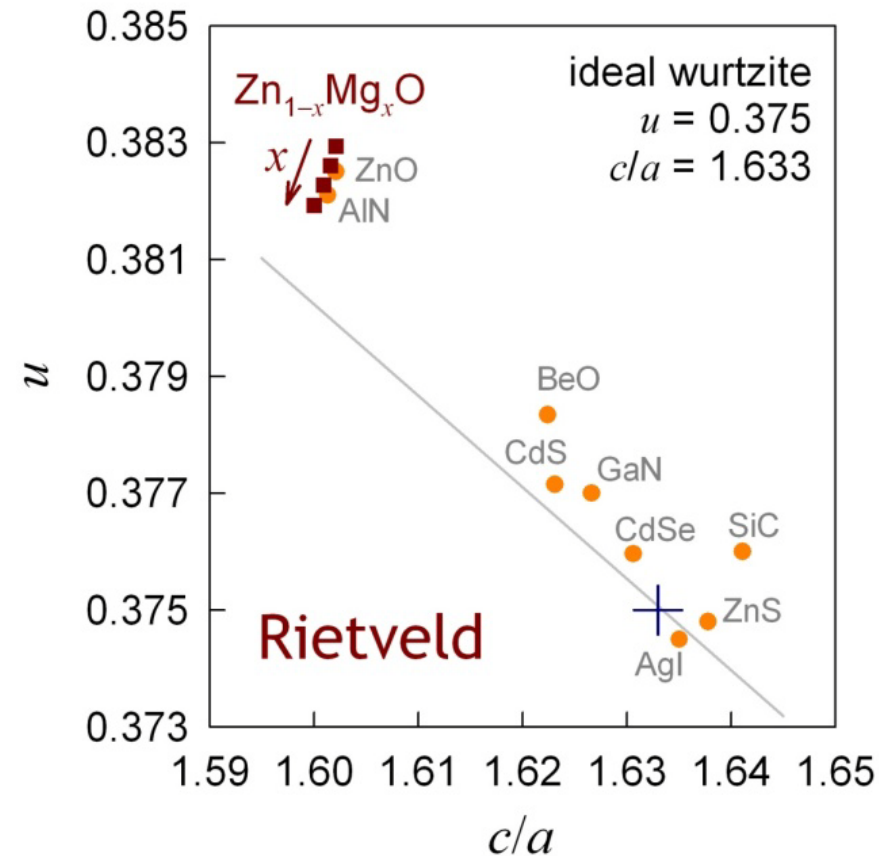
Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$



Data can be modeled with an explicit $2 \times 2 \times 1$ supercell for $\text{Zn}_{7/8}\text{Mg}_{1/8}\text{O}$



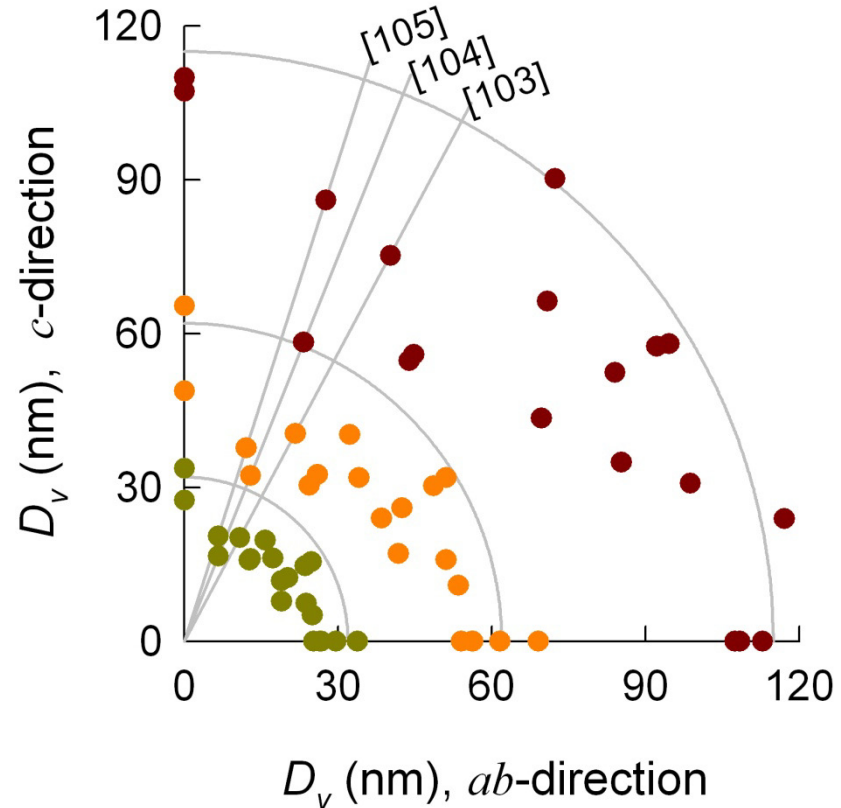
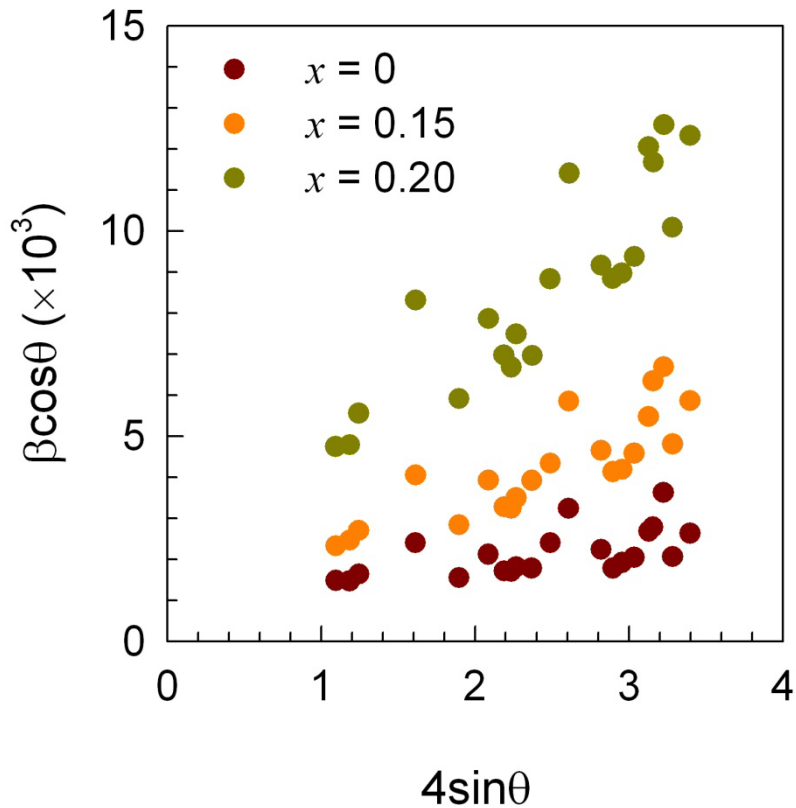
Cation-substituted ZnO: $Zn_{1-x}Mg_xO$



Local MgO_4 coordination obtained from PDF closely matches DFT results on wurtzite structure MgO.

Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

Williamson-Hall analysis of lab X-ray diffraction data [The computer program BREADTH]



$$\beta_i \cos \theta_i = \frac{\lambda}{D_v} + 4\varepsilon \sin \theta_i$$

Stacking faults: Relative amounts not affected by substitution

Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

Williamson-Hall analysis of lab X-ray diffraction data.

x	D_v (nm)	D_a (nm)	ε (%)
0	96(3)	69(3)	< 0.001
0.05	76(3)	57(3)	0.020(6)
0.10	70(2)	51(3)	0.028(5)
0.15	62(2)	47(2)	0.041(4)
0.20	33(1)	27(1)	0.099(7)

Some microstrain in Mg-substituted samples.

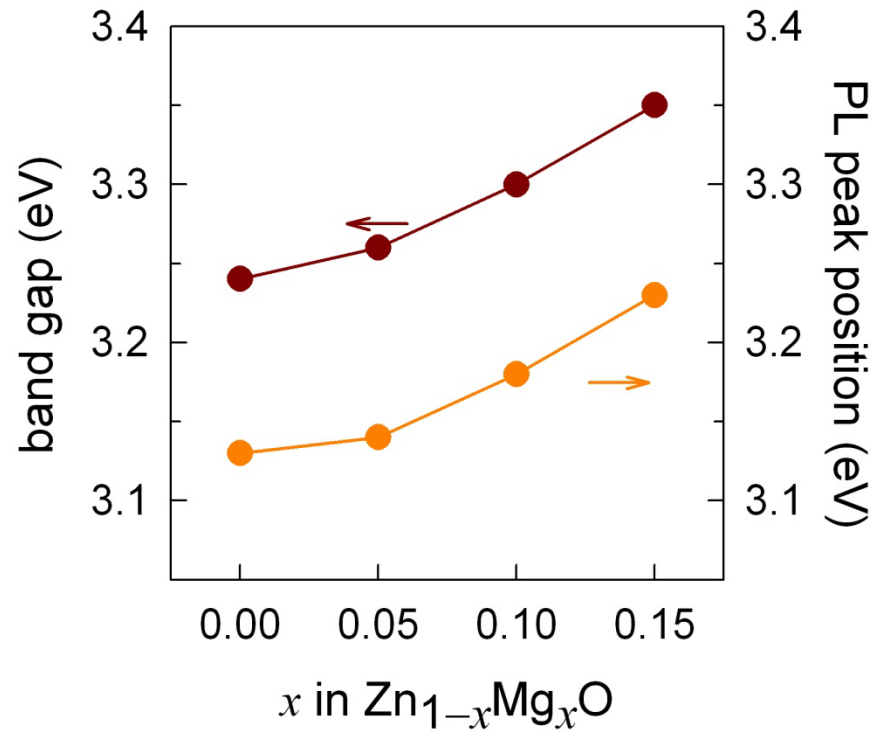
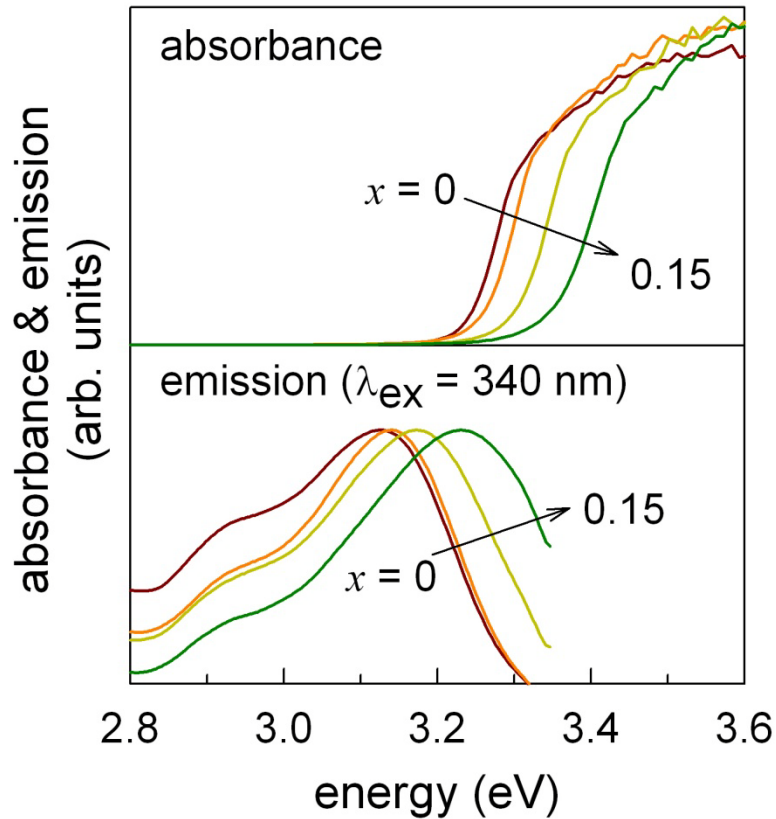
D_v : volume-weighted crystallite size

D_a : surface area-weighted
crystallite size

ε : strain

Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

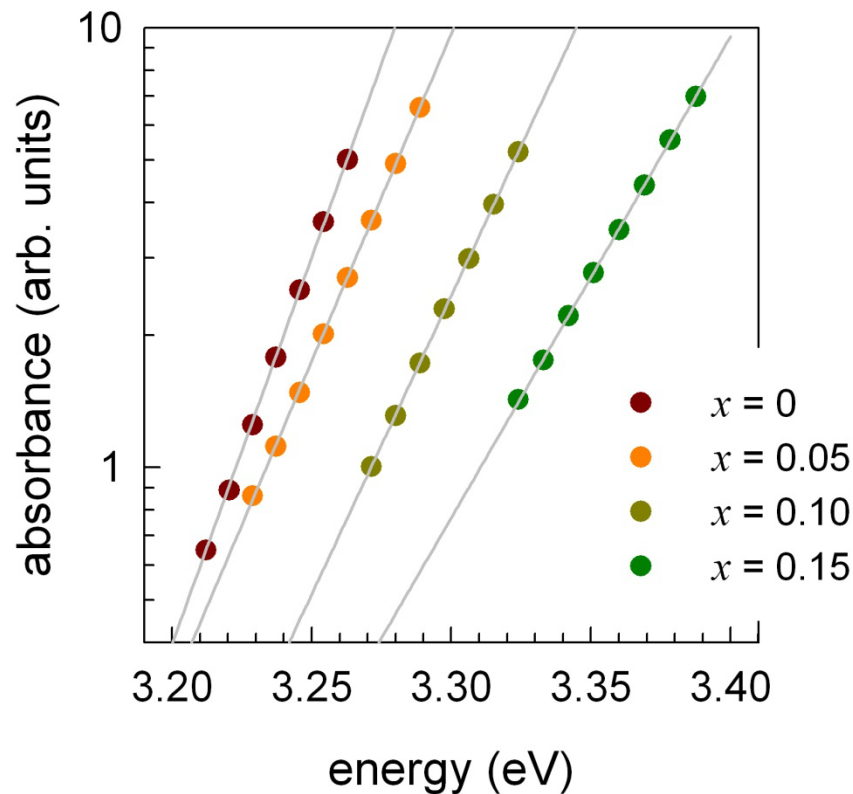
Band gap increase with x smaller than reported by Kawasaki *et al.*



Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

Following Pankove [*Phys. Rev.* **140** (1965) A2059]:

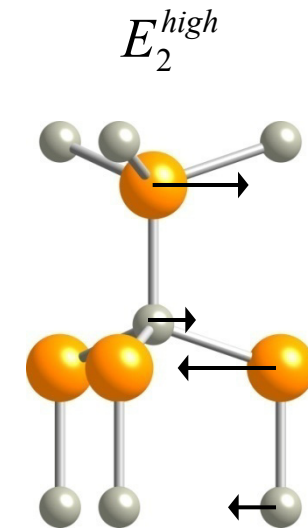
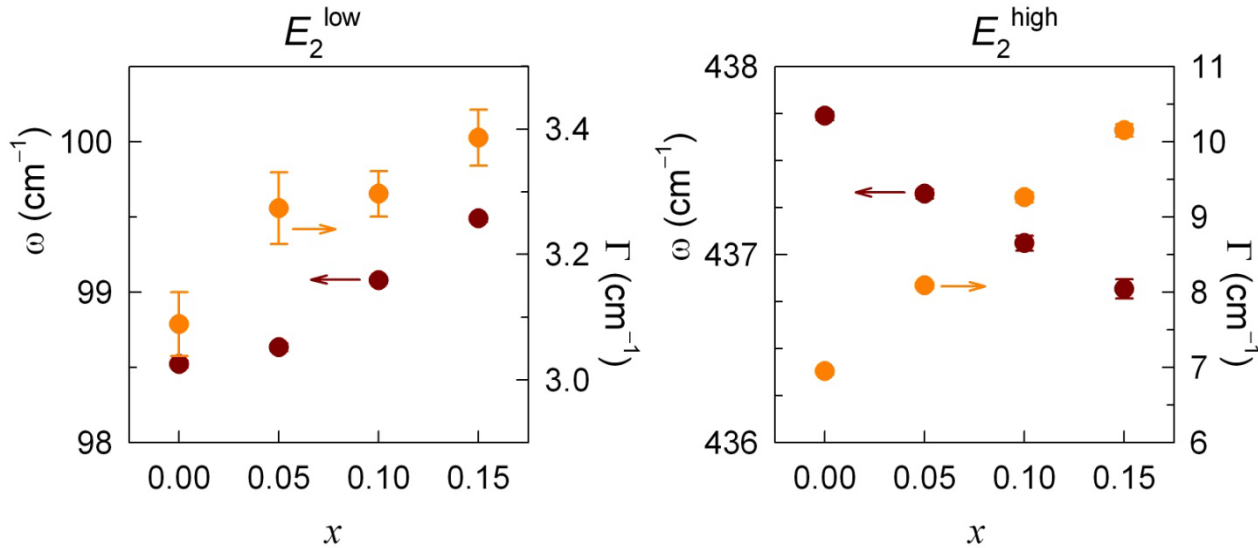
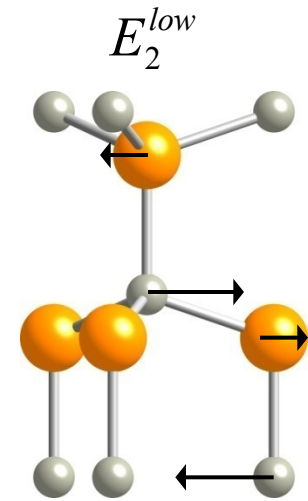
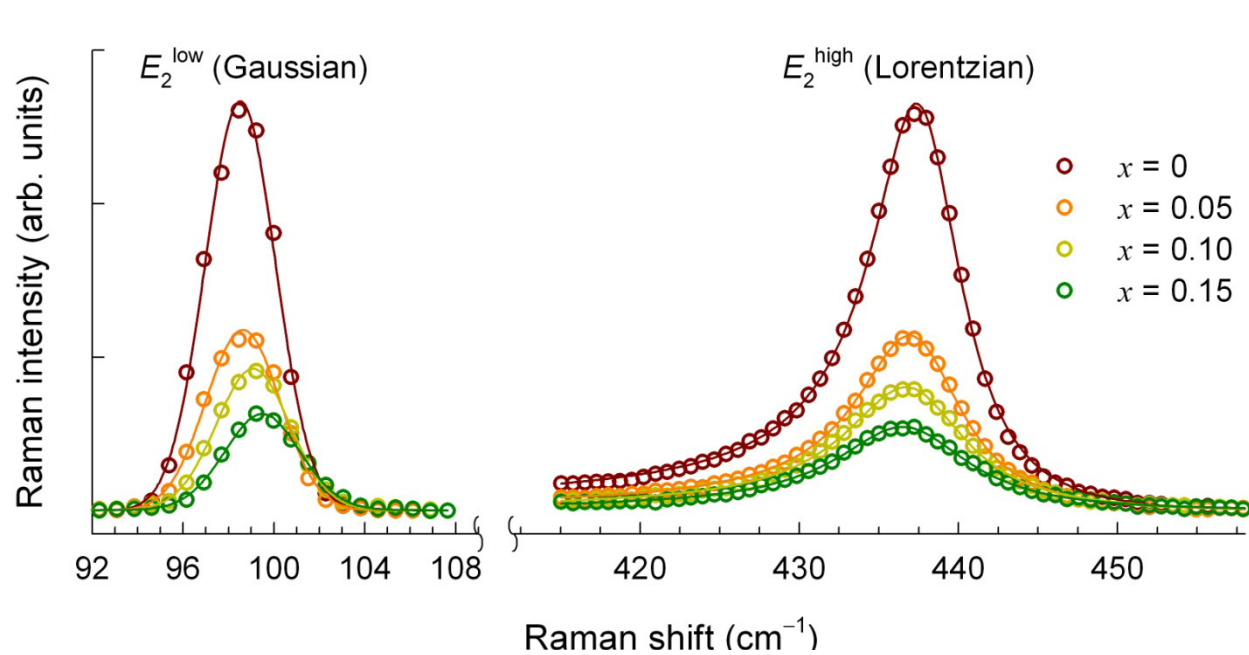
E_0 : width of the tails of states in band gap



$$A \propto \exp \frac{h\nu}{E_0}$$

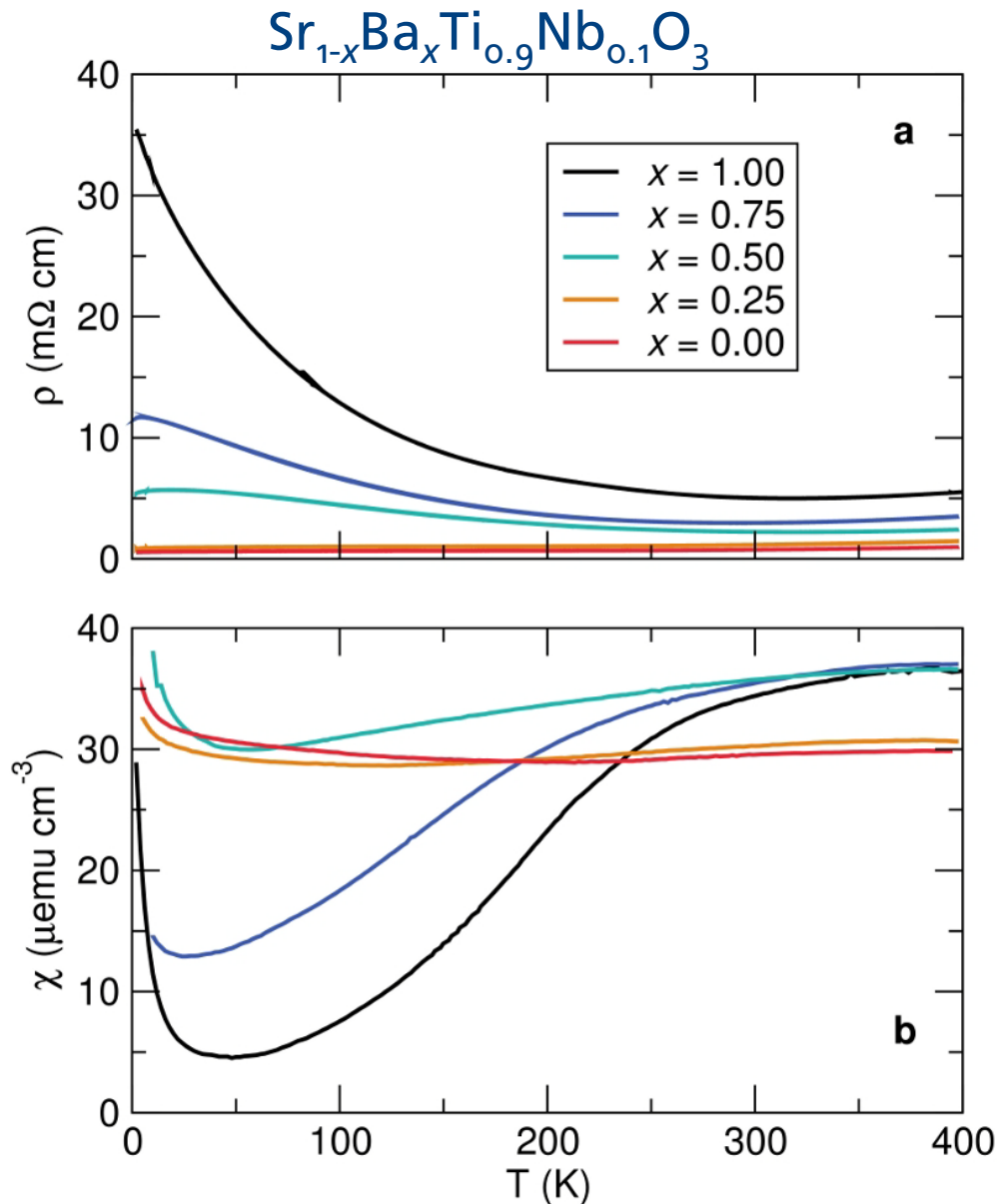
x	E_0 (meV)
0	24.7
0.05	29.2
0.10	31.9
0.15	39.7

Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$



Nb-substituted perovskites SrTiO_3 and BaTiO_3

Nb-substituted SrTiO_3 and BaTiO_3



SrTiO_3 and BaTiO_3 are band insulators.

Nb^{4+} -substitution (even small amounts) make SrTiO_3 metallic and even superconducting.

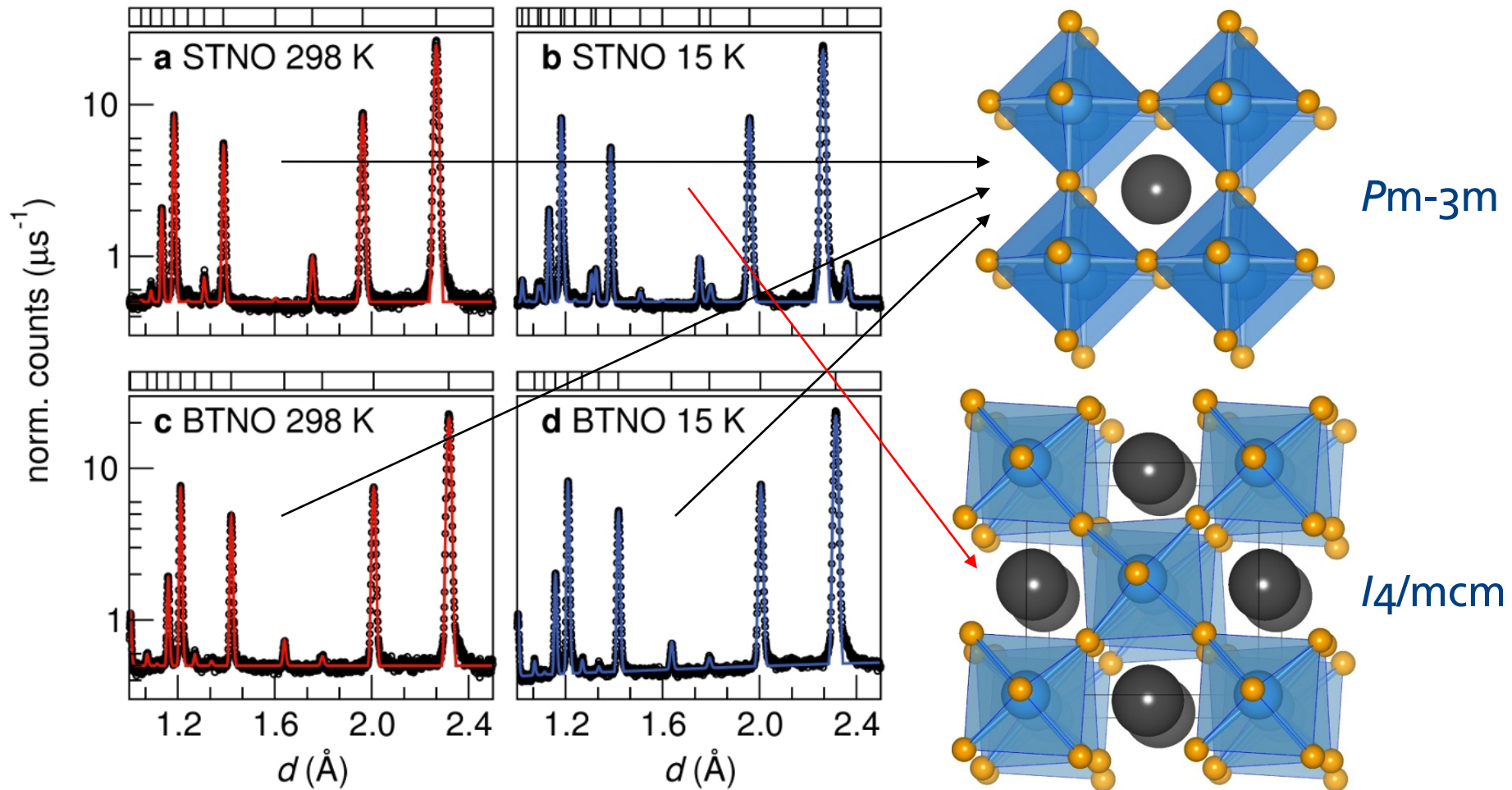
Not so BaTiO_3

Other differences as well, ferroelectricity *etc.*

Samples from T. Kolodiazhnyi, NIMS, Tsukuba

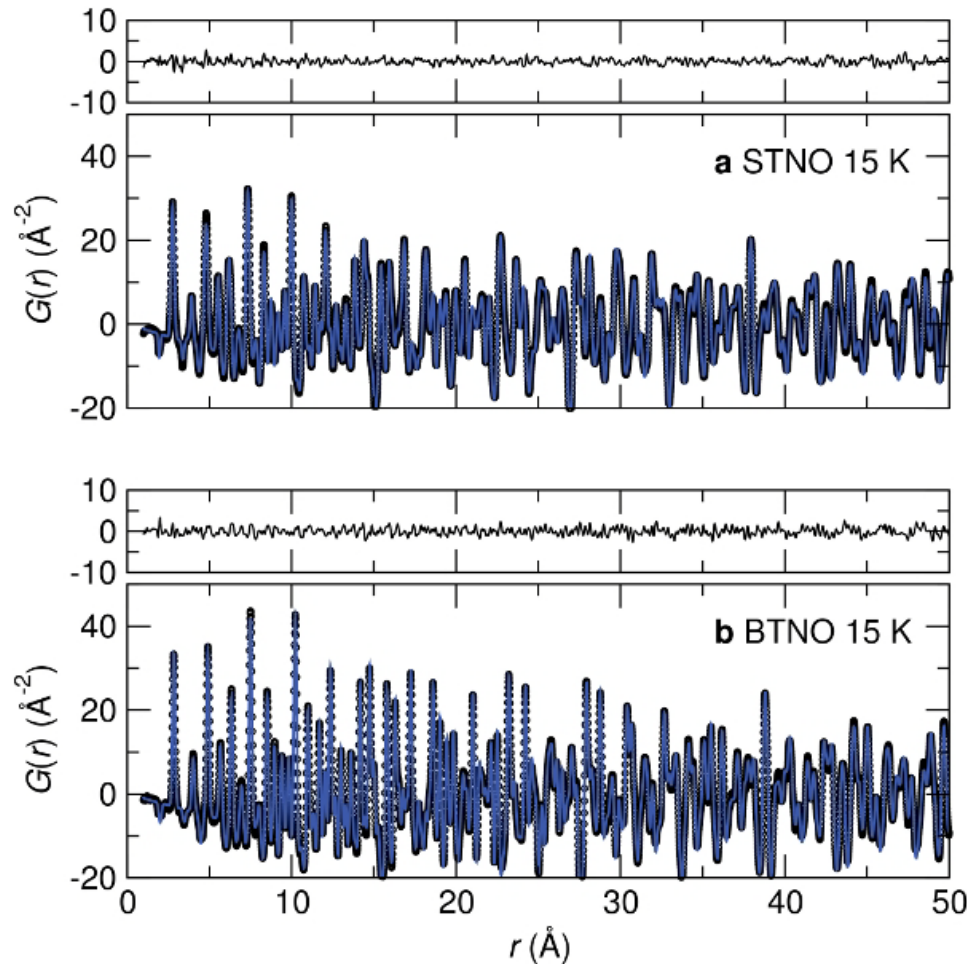
Nb-substituted SrTiO₃ and BaTiO₃

What does structure tell us? Compare SrTi_{0.875}Nb_{0.125}O₃ and BaTi_{0.875}Nb_{0.125}O₃: 1/8th substitution to aid modeling



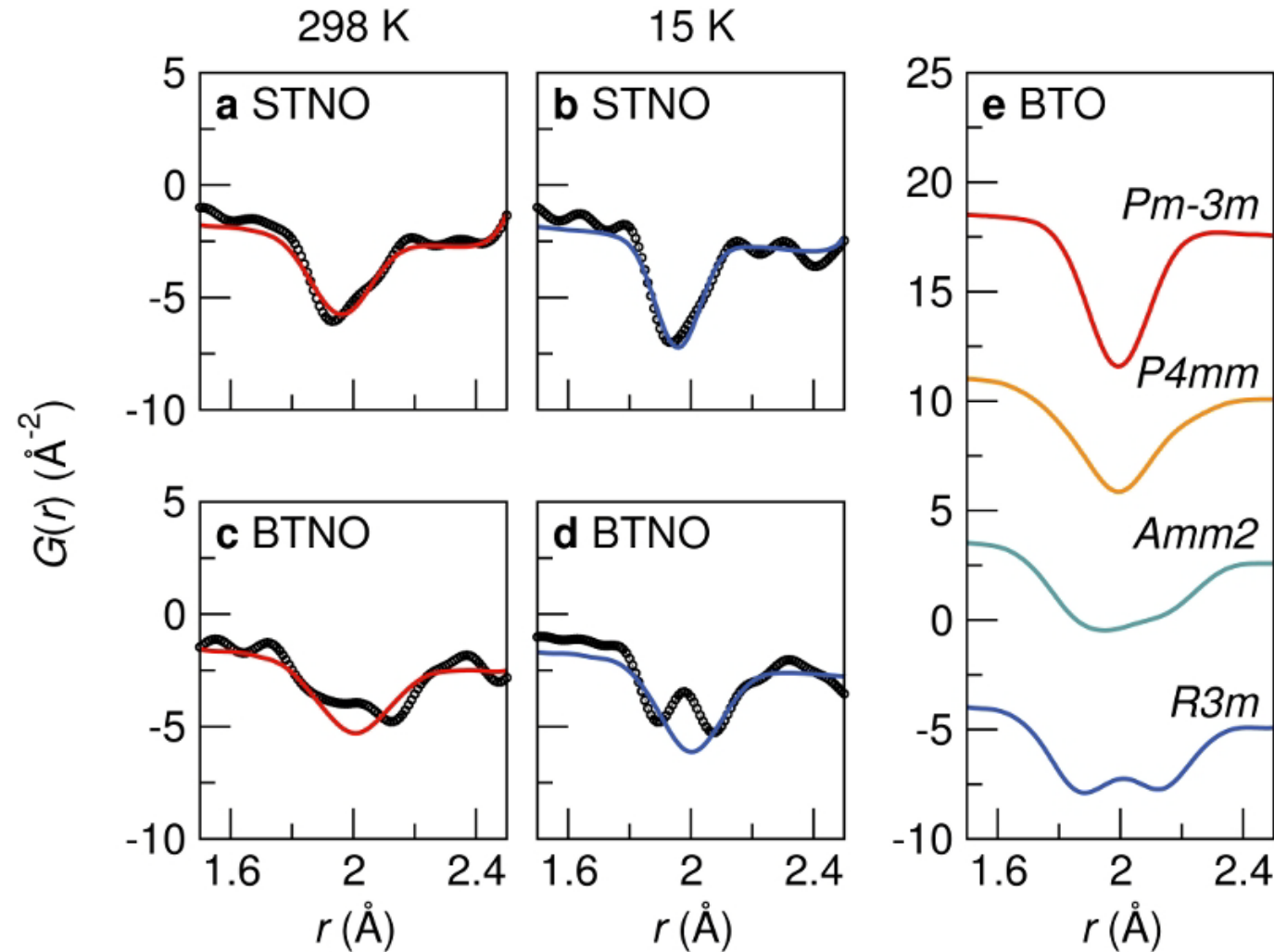
Nb-substituted SrTiO_3 and BaTiO_3

Pair distribution functions fit the average structure out to rather long vectors, very well !



Nb-substituted SrTiO₃ and BaTiO₃

What about the very short range ? BaTi_{0.875}Nb_{0.125}O₃ displays distortions in the first (Ti/Nb)-O neighbor:

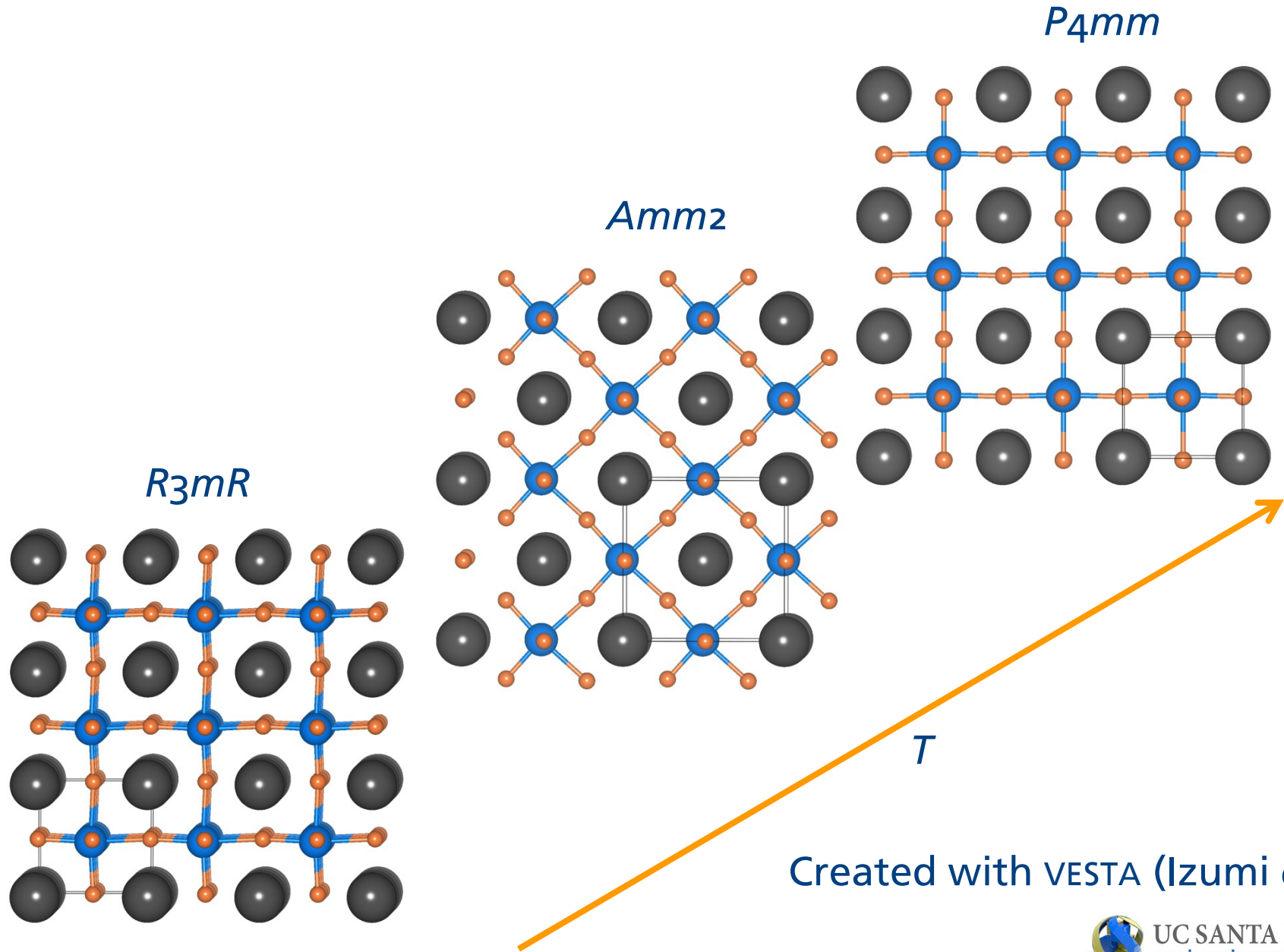


Simulations of the first peak of BaTiO₃ for the different crystal structures.

Page, Kolodiazhnyi, Proffen, Cheetham, Seshadri, *Phys. Rev. Lett.* **101** (2008) 205502.



Nb-substituted SrTiO_3 and BaTiO_3



Created with VESTA (Izumi *et al.*)

Nb-substituted SrTiO_3 and BaTiO_3

Findings:



Nb-substitution (on the perovskite *B* site) does not frustrate tilting. The ground state is tetragonal.

Tilting distortions do not result in an insulating ground state (*Cf.* SrRuO_3 , LaNiO_3 ...)

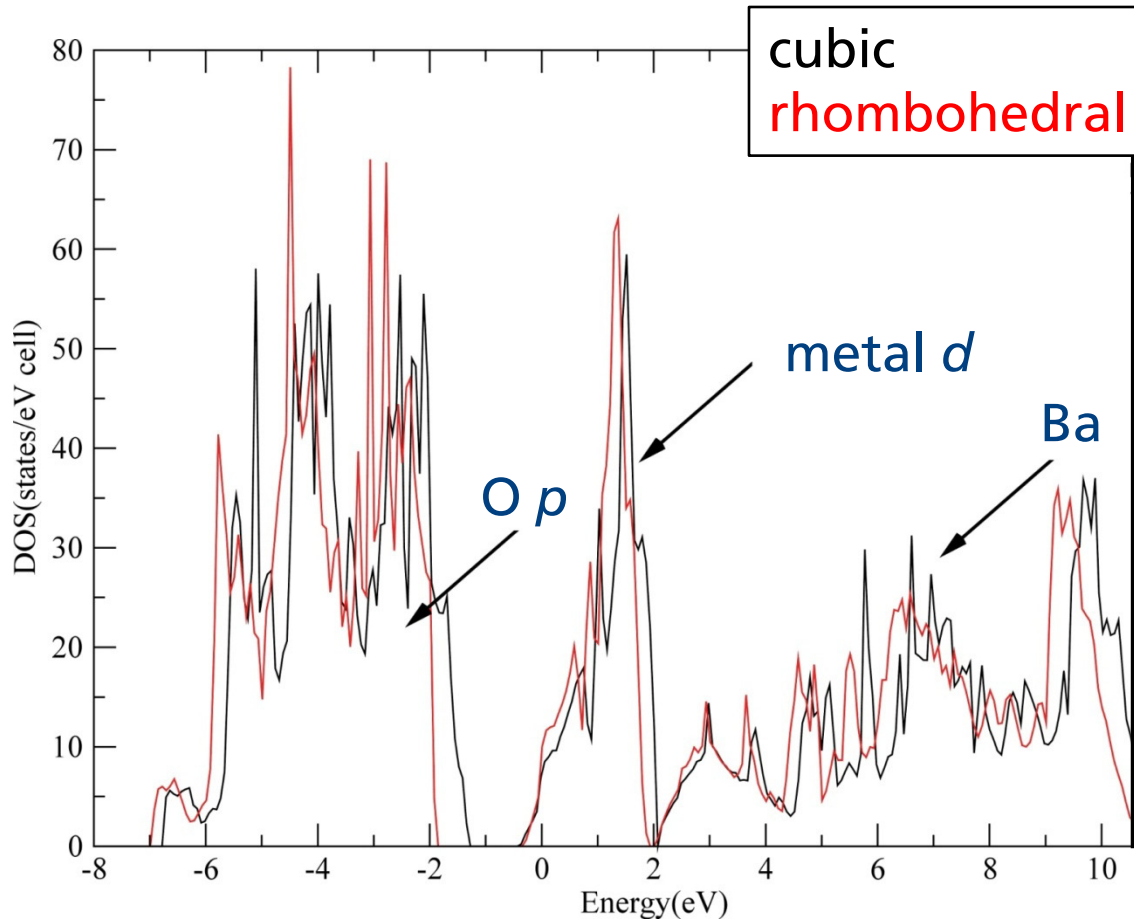


Nb-substitution (on the perovskite *B* site) frustrates long-range ordering of dipoles; additionally helped by dipole-dipole screening. Average structure is cubic.

Dipoles exist locally however. Incoherent off-centering might aid the insulating ground state.

Nb-substituted SrTiO_3 and BaTiO_3

$\text{BaTi}_{0.875}\text{Nb}_{0.125}\text{O}_3$: Densities of state for the cubic and rhombohedral structures (ordered Ti/Nb).



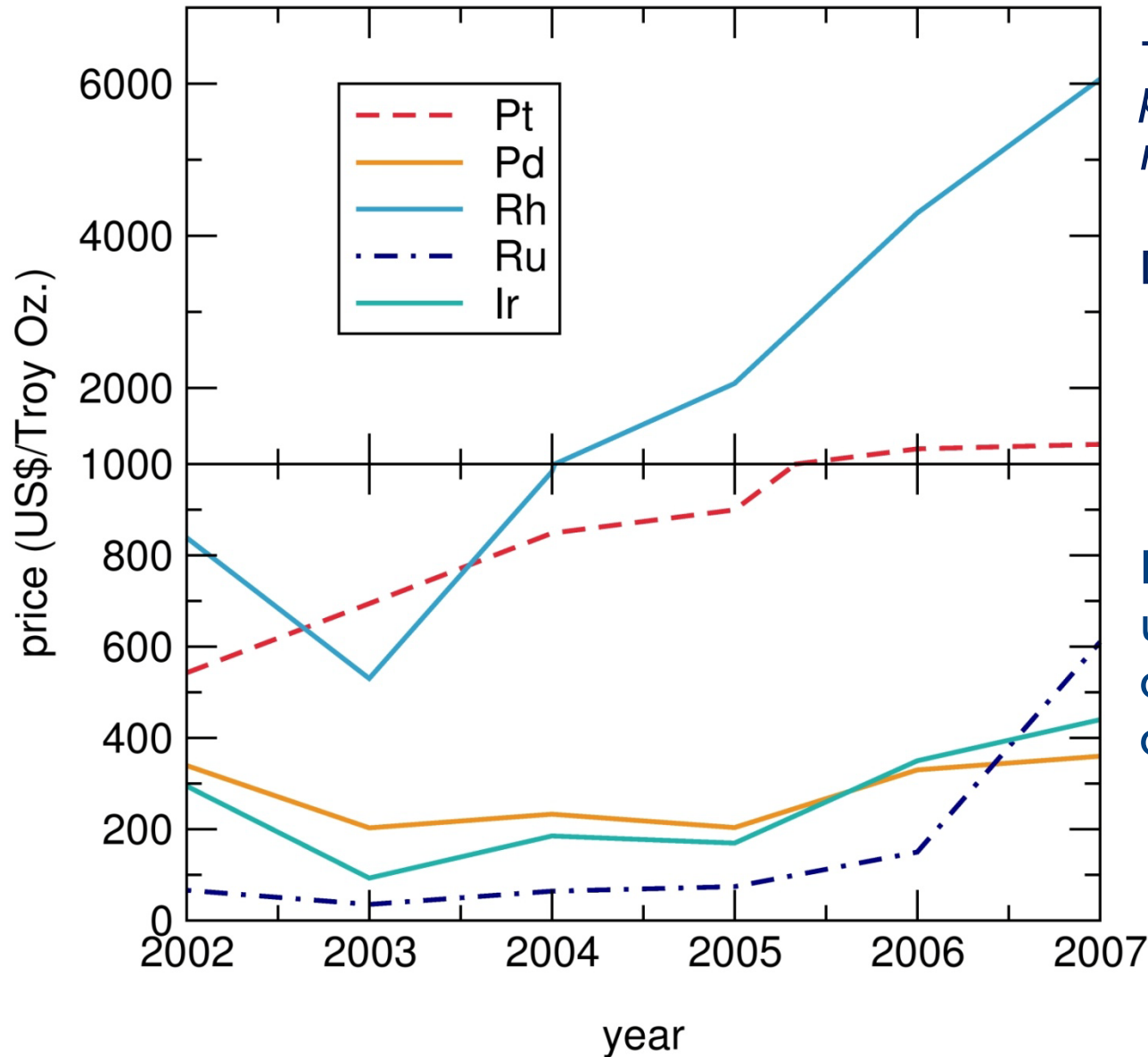
Narrowing of states but no gap. Incoherent off-centering required ?

(T. Saha-Dasgupta)

Perovskite oxides with divalent Pd²⁺

Oxide catalysts with Pd²⁺ substitution

Motivation: Reducing PGM use in catalysts



+ environmental problems with PGM release

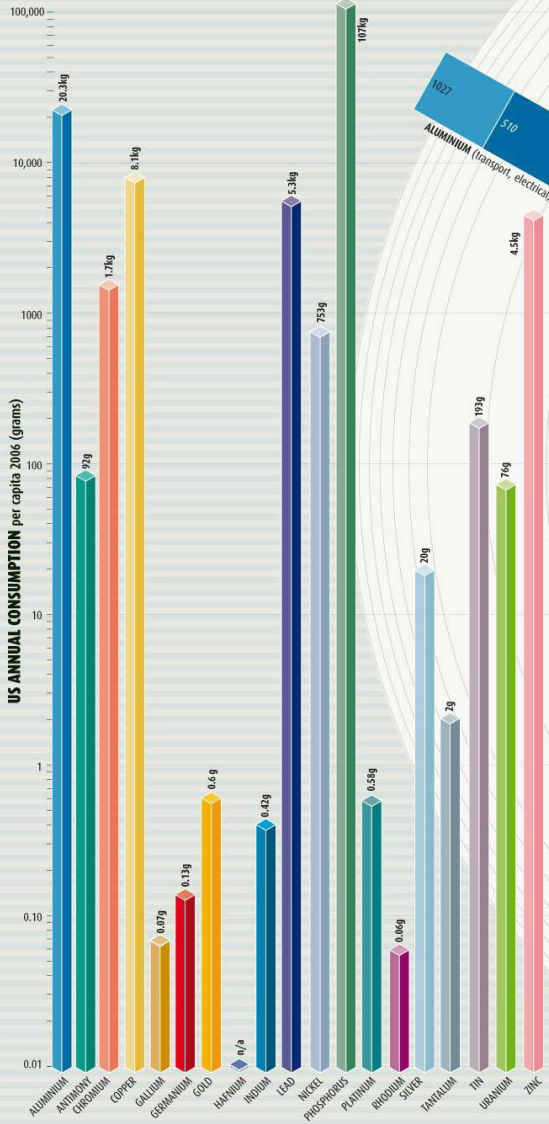
Data from usgs.gov

More than 50% of Pt use is in automotive catalysis: 3-way converters



Oxide catalysts with Pd²⁺ substitution

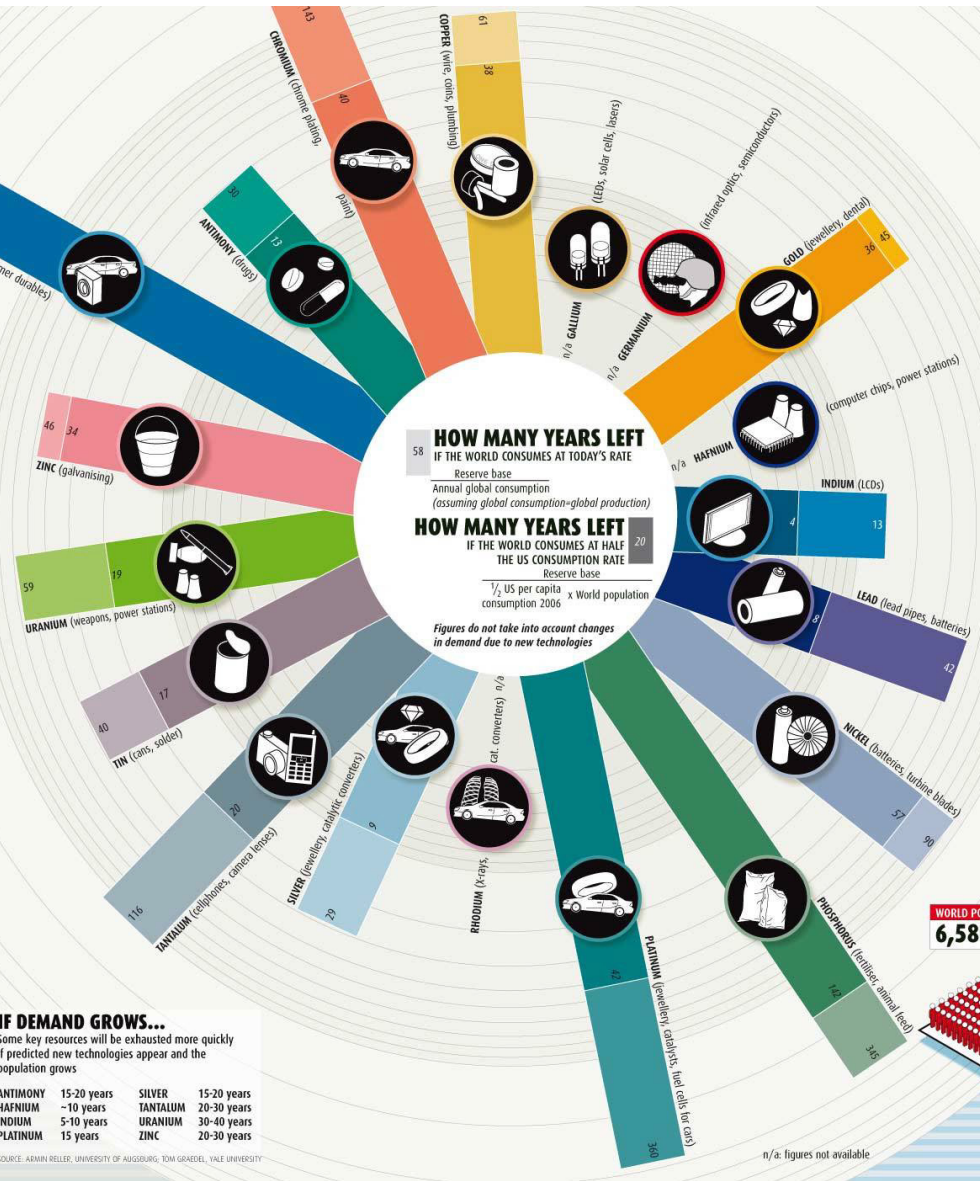
HOW LONG WILL IT LAST?



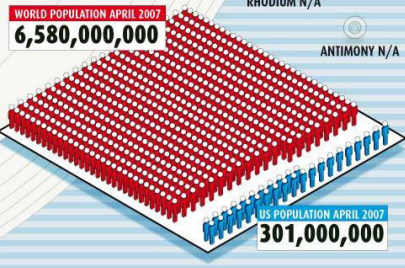
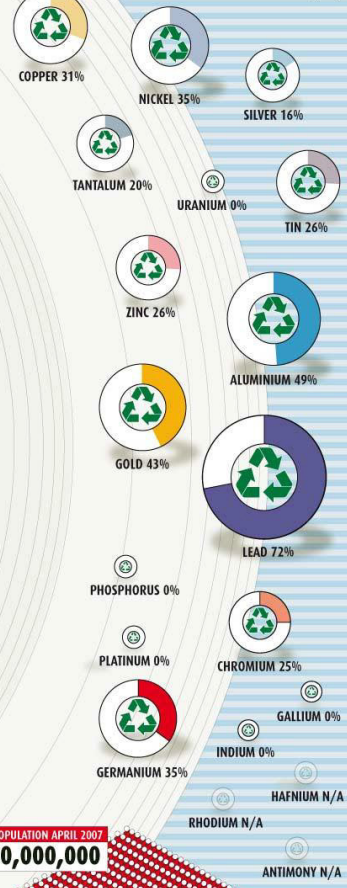
IF DEMAND GROWS...
 Some key resources will be exhausted more quickly if predicted new technologies appear and the population grows

ANTIMONY	15-20 years	SILVER	15-20 years
HAFNIUM	~10 years	TANTALUM	20-30 years
INDIUM	5-10 years	URANIUM	30-40 years
PLATINIUM	15 years	ZINC	20-30 years

SOURCE: ADMIN RELEA, UNIVERSITY OF ALBANY; TOM GARDNER, YALE UNIVERSITY

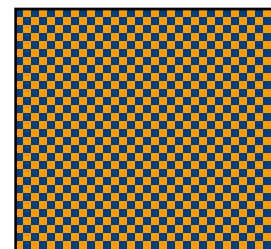
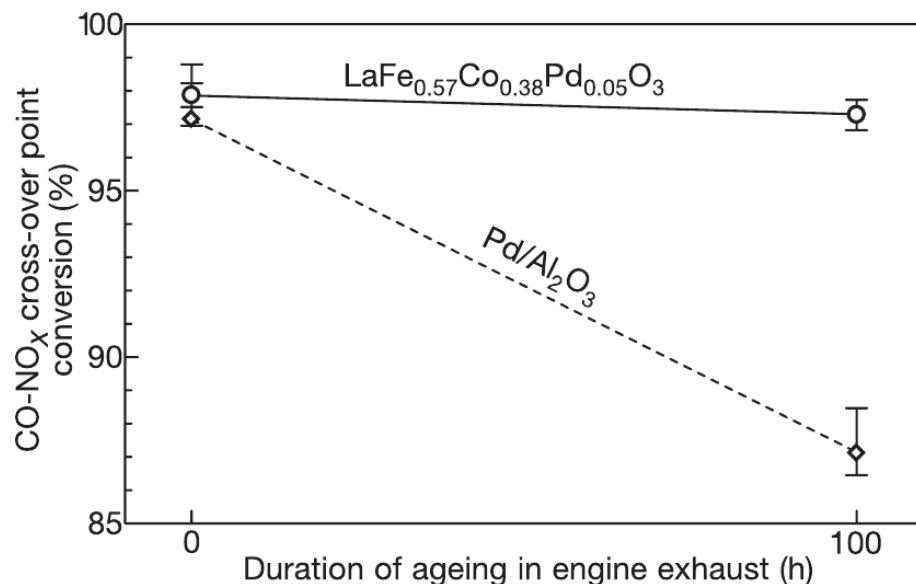


PROPORTION OF CONSUMPTION MET BY RECYCLED MATERIALS (%)

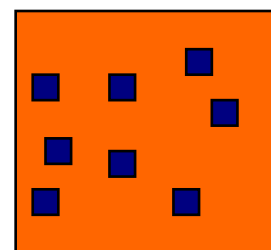


Oxide catalysts with Pd²⁺ substitution

Motivation: Reducing PGM use in catalysts



Oxidized state
(Pd²⁺ in lattice)



Reduced state
(supported Pd⁰
nanoparticles)

Nishihata, Mizuki, Akao, Tanaka, Uenishi, Kimura, Okamoto, Hamada, Self-regeneration of a Pd-perovskite catalyst for automotive emissions control, *Nature* **418** (2002) 164.



Questions:

- Does Pd really go into the host as ions and come out as Pd⁰ ?
- Are there other (perhaps better) hosts ?



Oxide catalysts with Pd²⁺ substitution

Perovskite BaCeO₃ as a host:

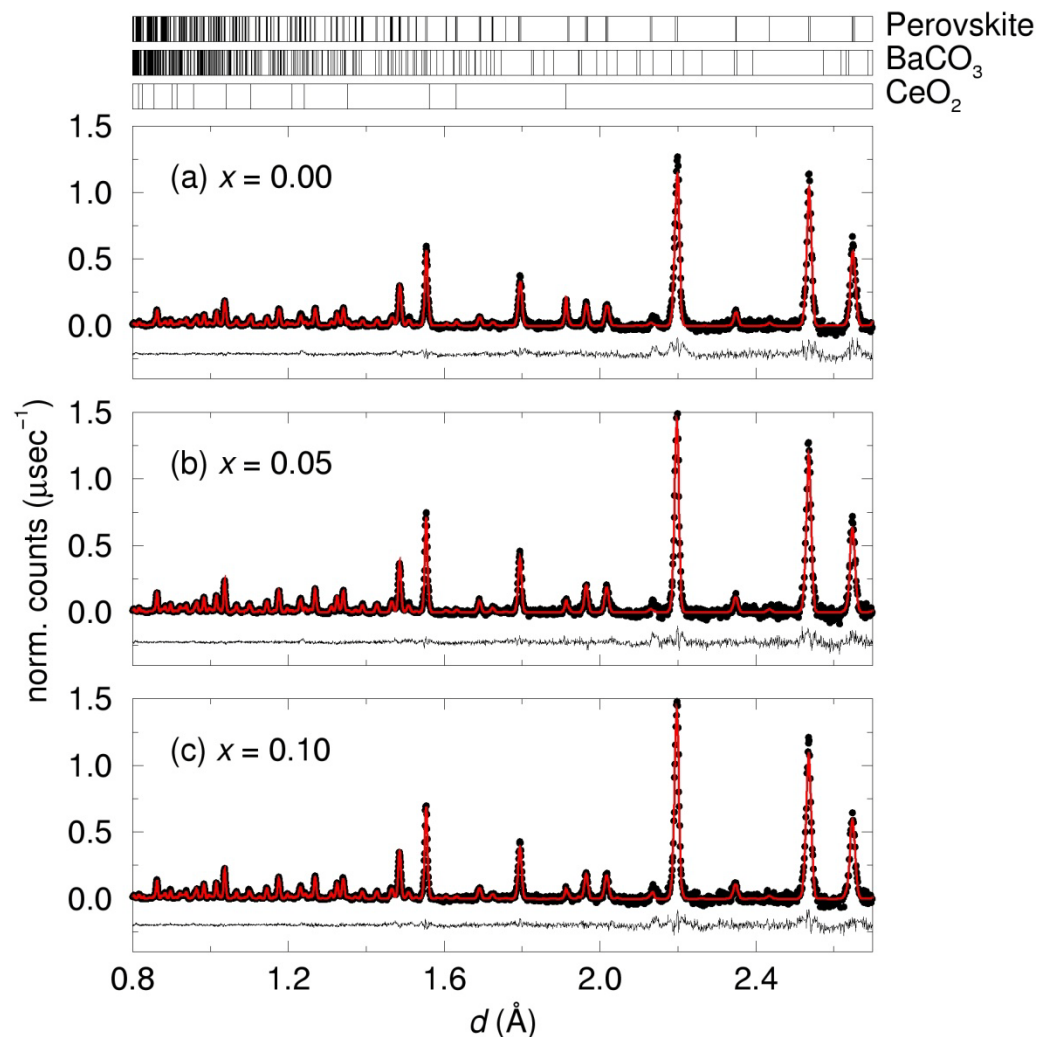
Ba²⁺ creates an oxide lattice that is highly oxidizing

Ce⁴⁺/Ce³⁺ are large and somewhat forgiving in terms of coordination.

BaCe_{1-x}Pd_xO_{3-δ}
with $x = 0, 0.05, \text{ and } 0.10$

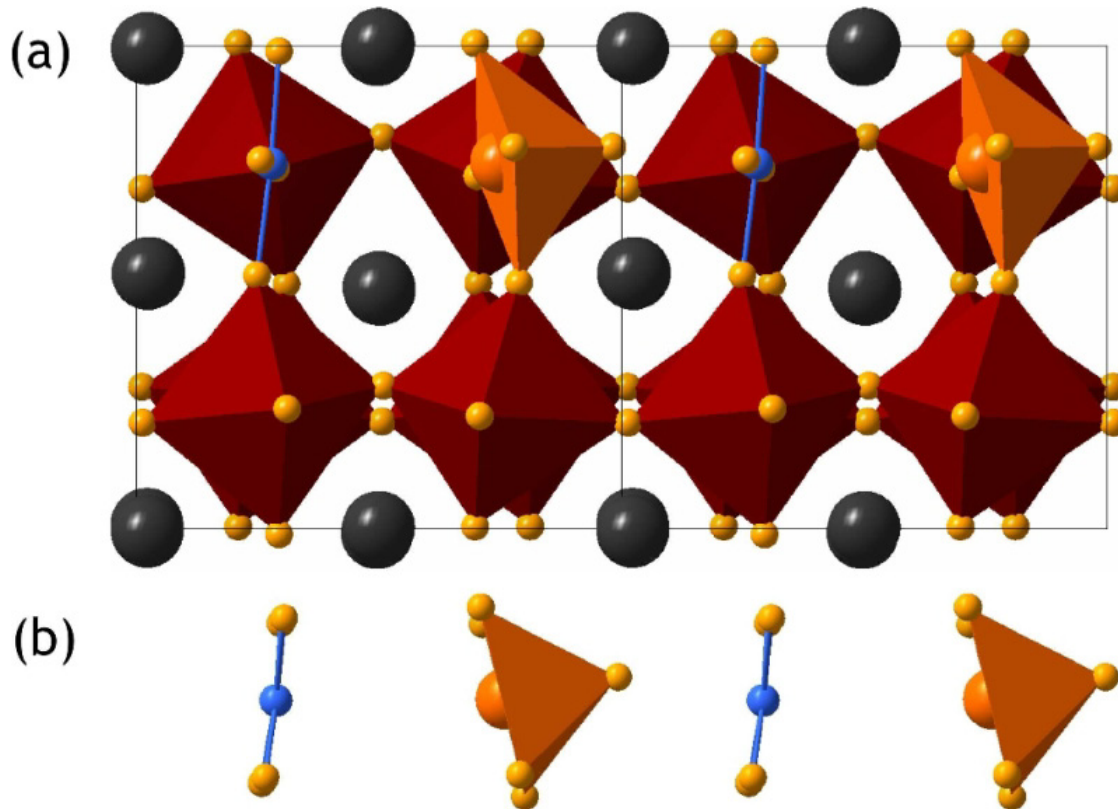
Samples prepared by solid state routes in O₂.

Neutron refinements [NPDF, Los Alamos] $\Rightarrow \delta \sim x$
so Pd in lattice is Pd²⁺



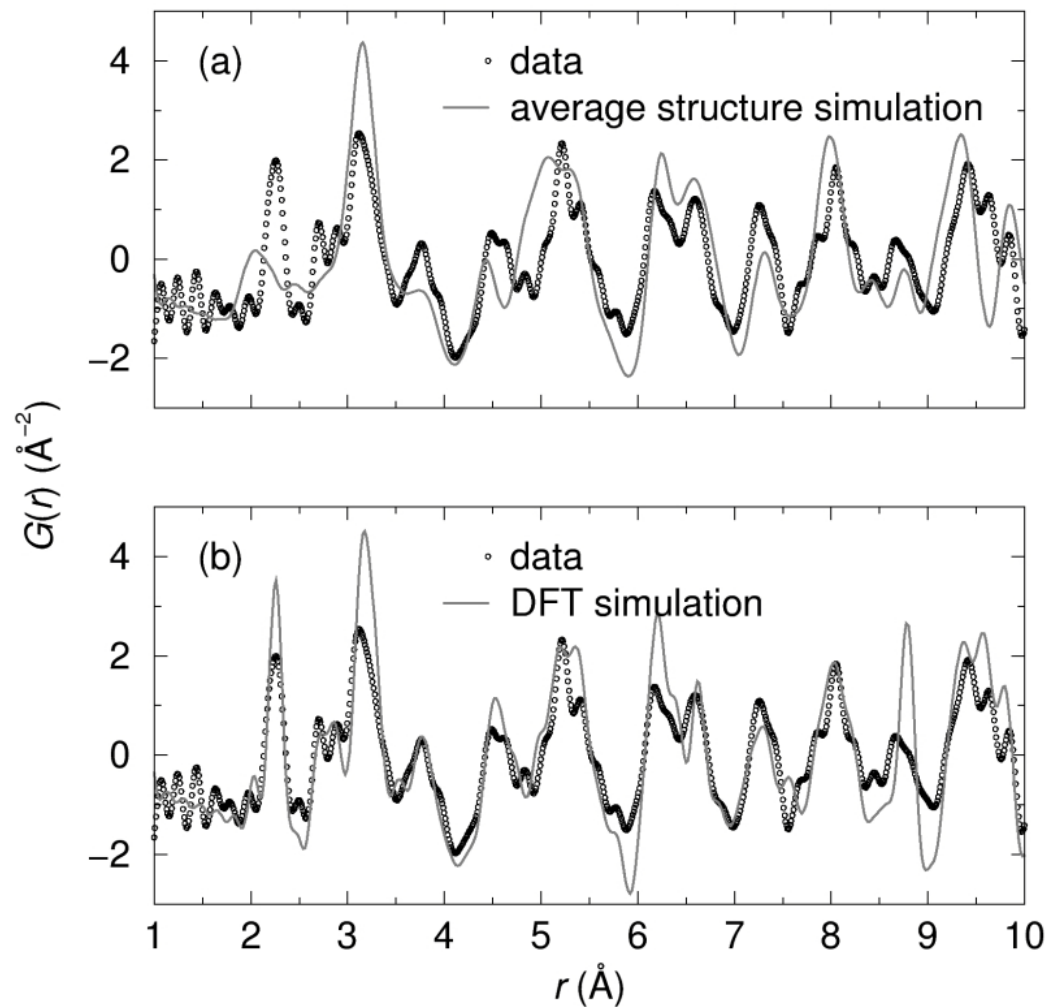
Oxide catalysts with Pd²⁺ substitution

DFT optimized structure of 2x2x2 perovskite cell with one Pd²⁺ substituting Ce⁴⁺ and one oxygen vacancy: $x = 12.5$ [Bennett and Rappe, Penn]



The oxygen vacancy prefers to be proximal to Pd²⁺ and leaves it nearly square planar.

Oxide catalysts with Pd²⁺ substitution



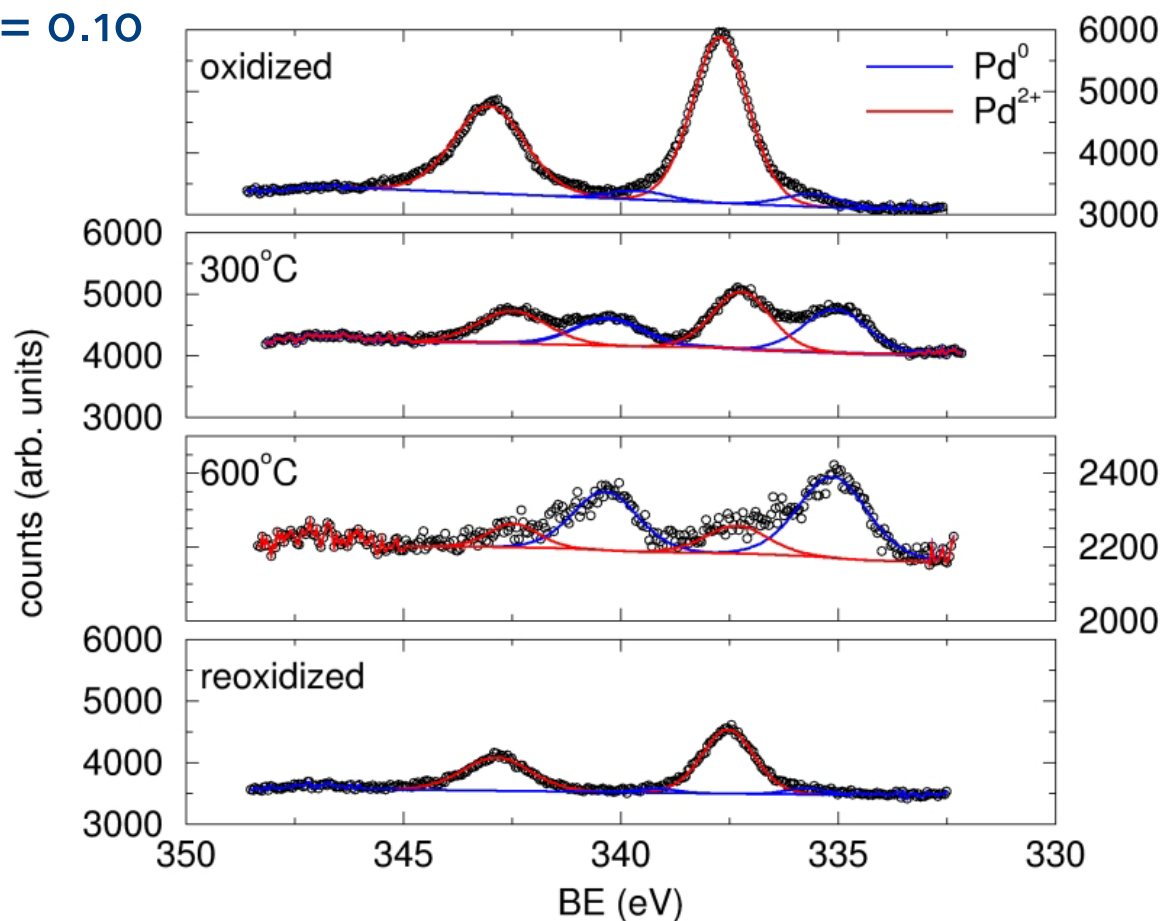
The neutron pair distribution function (PDF) for the $x = 0.10$ sample is well-modeled by the DFT structure, but not by the average structure.

Magnetic measurements suggest a diamagnetic system.

Oxide catalysts with Pd²⁺ substitution

Pd core levels of the oxidized and reduced samples.

$X = 0.10$



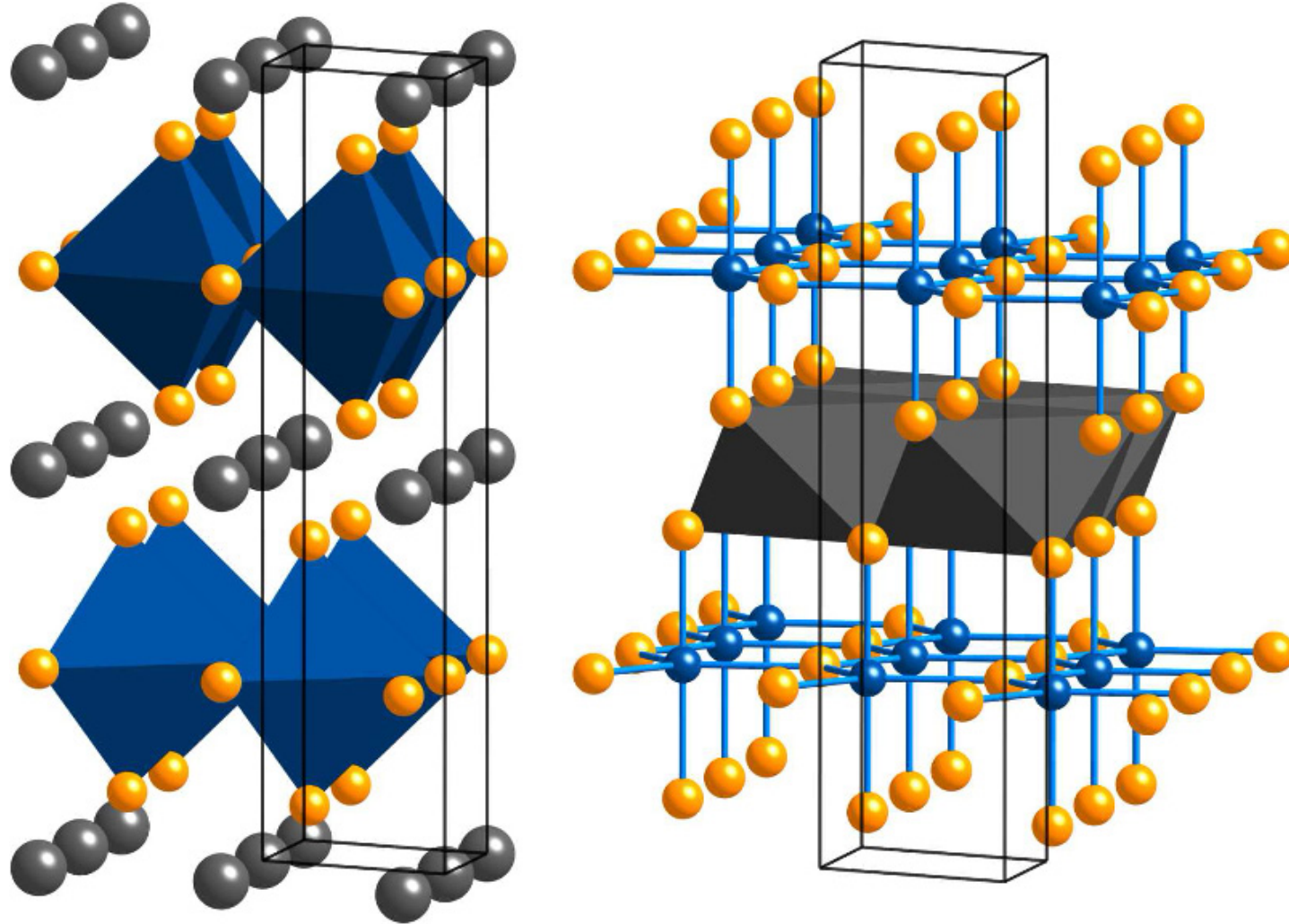
Note the drop in counts for the reduced samples.

Ce is always Ce⁴⁺

Li, Singh, Bennett, Page, Weaver, Zhang, Proffen, Rappe, Scott, Seshadri, *Chem. Mater.* 19 (2007) 1418-1426.

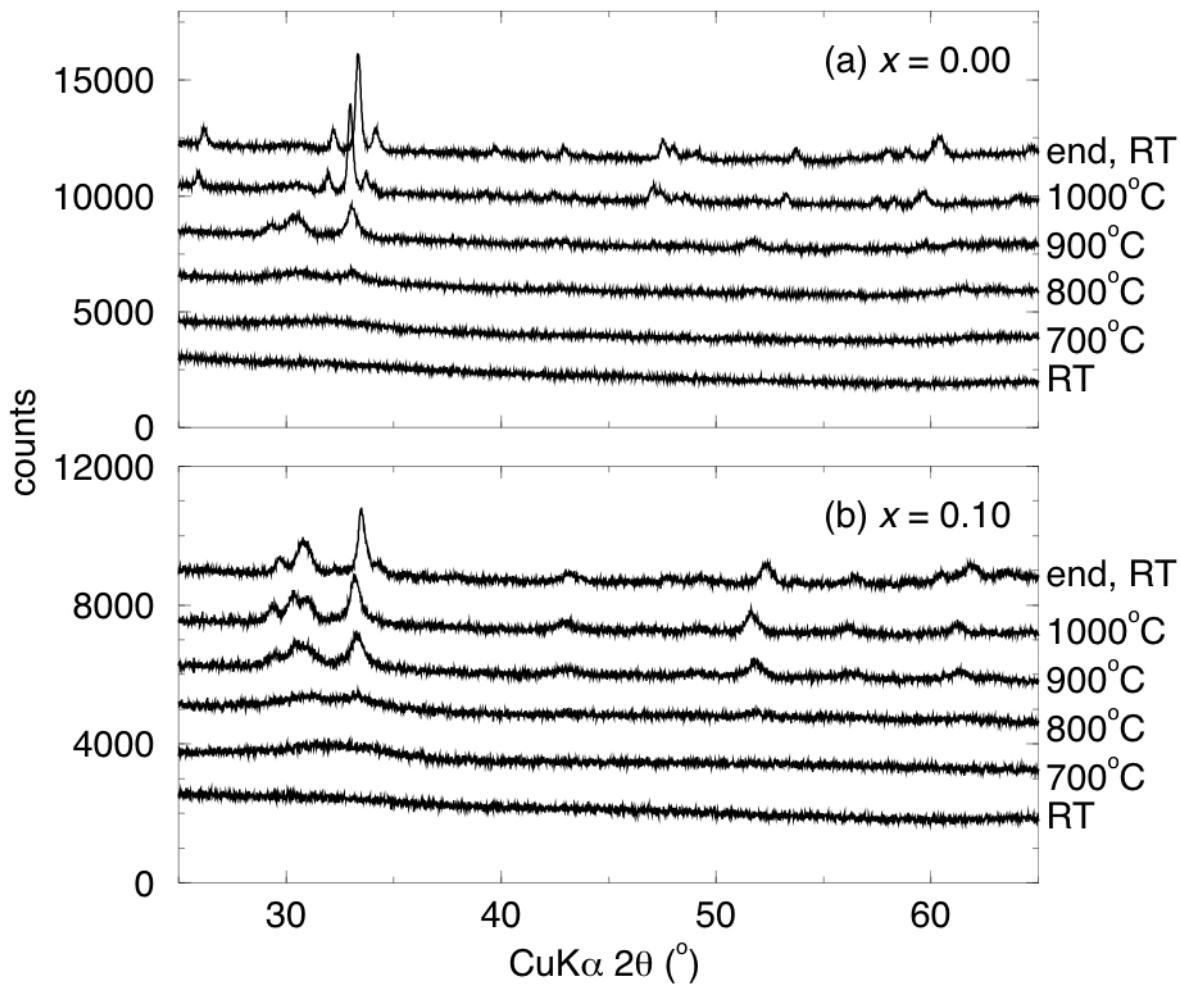


Oxide catalysts with Pd²⁺ substitution



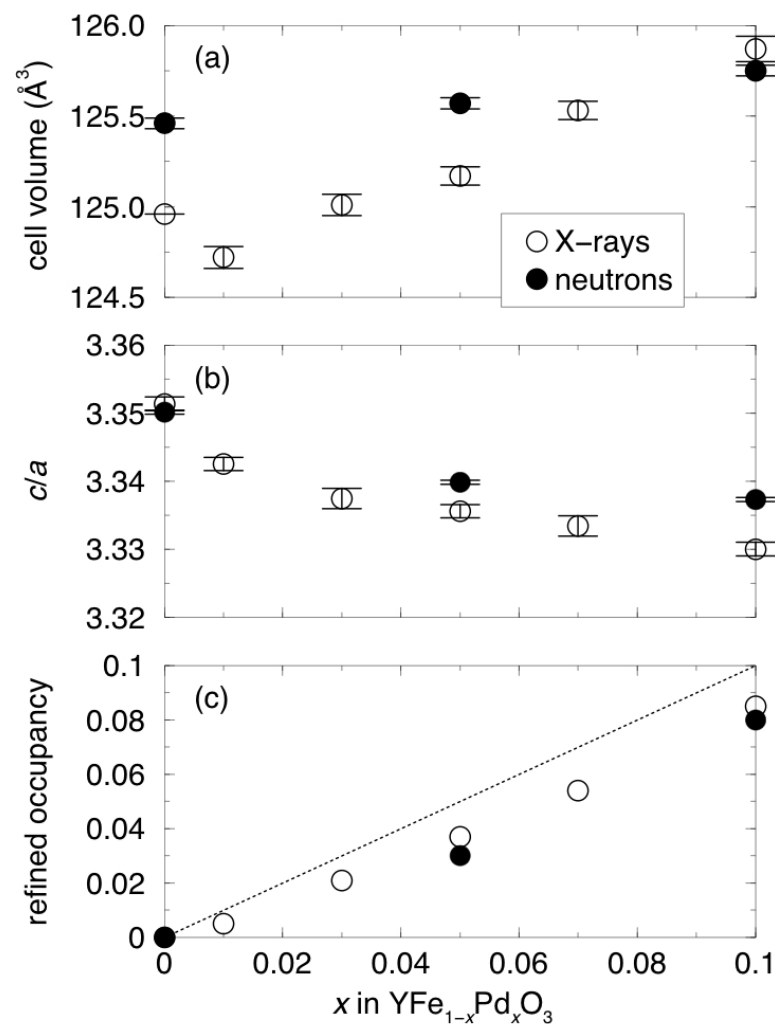
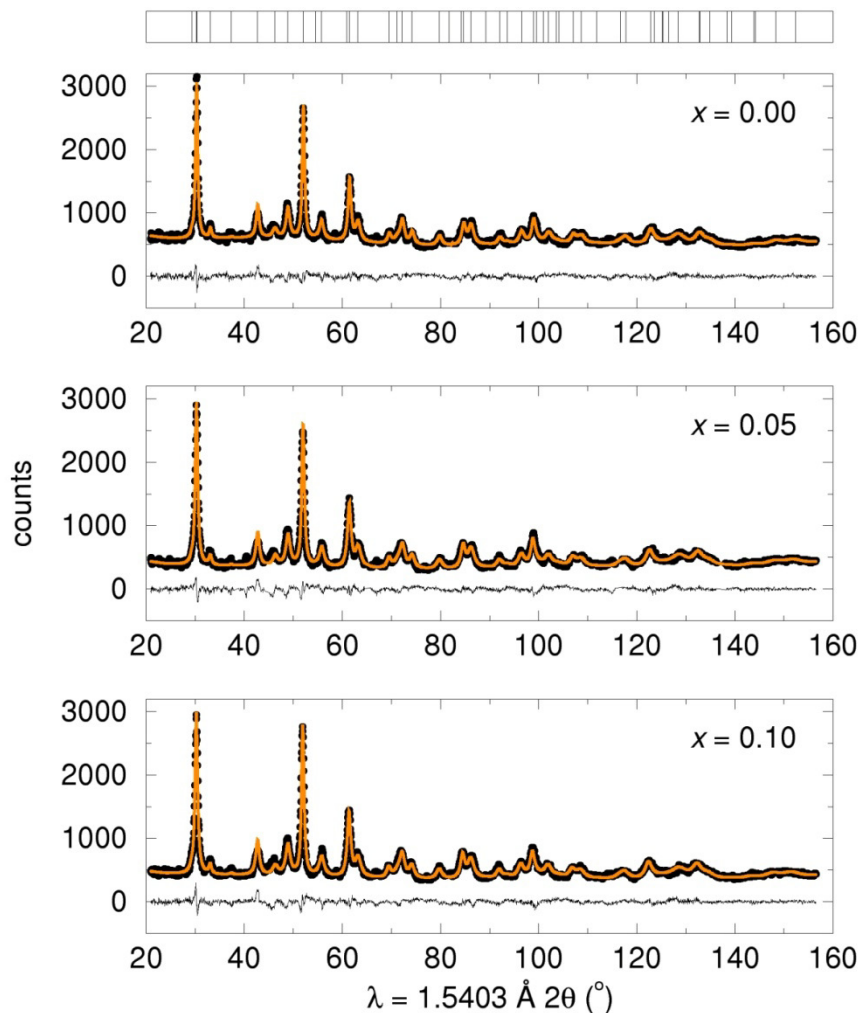
YFeO₃ exists as a stable perovskite or a metastable (sol-gel prep.) hexagonal compound with the YAlO₃ structure. 5-coordinate Fe³⁺ in the hexagonal structure.

Oxide catalysts with Pd²⁺ substitution



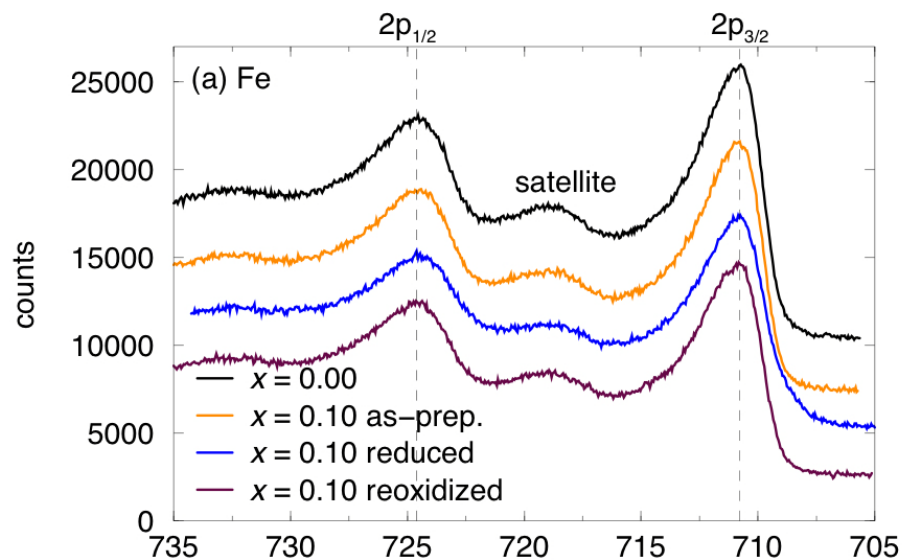
Even small Pd substitution strongly stabilizes the hexagonal compound, in keeping with the nature of d^8 Pd²⁺.

Oxide catalysts with Pd²⁺ substitution

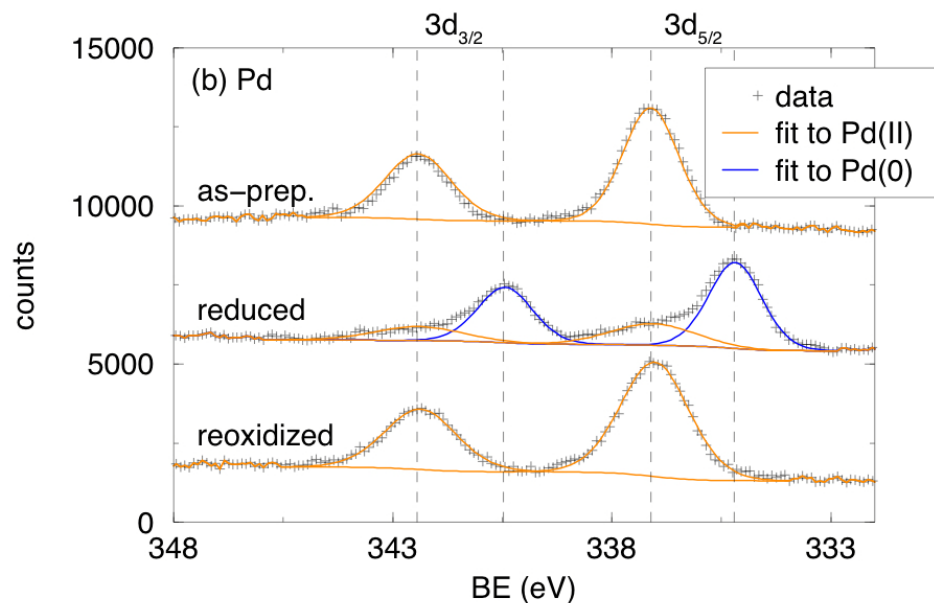


Neutron diffraction [NIST, BT-1] confirms the substitution.

Oxide catalysts with Pd²⁺ substitution



Fe core levels unchanged with oxidation/reduction.



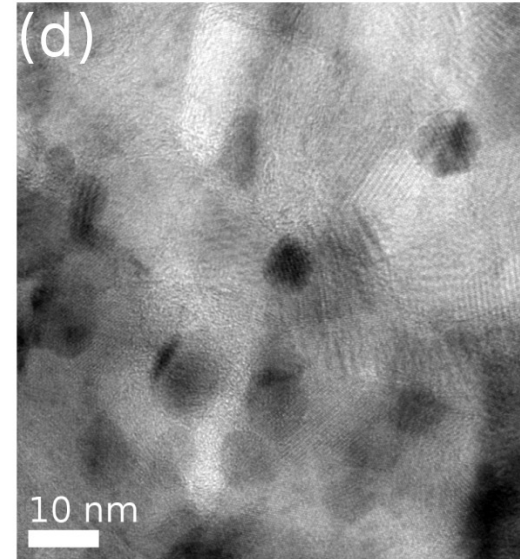
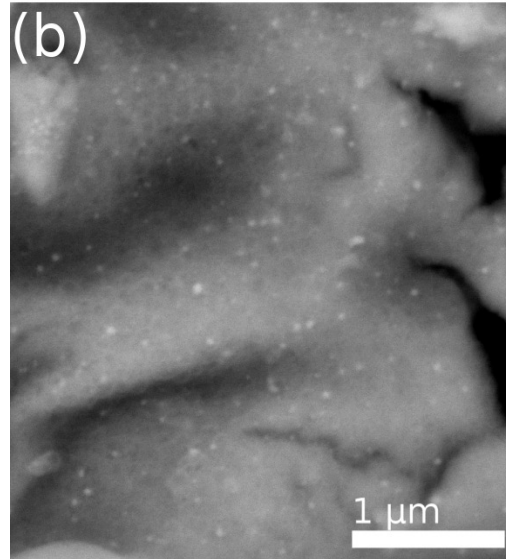
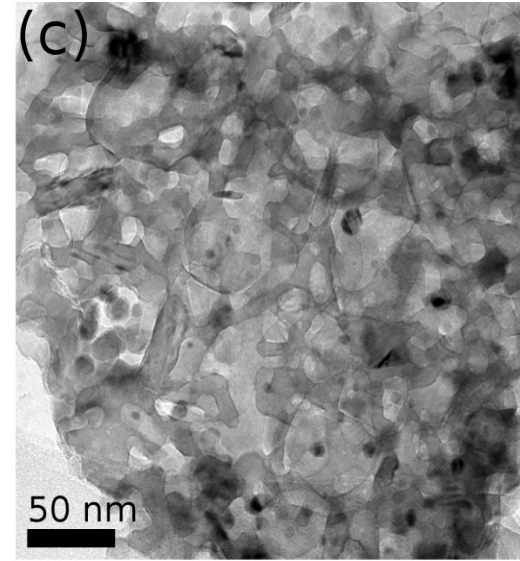
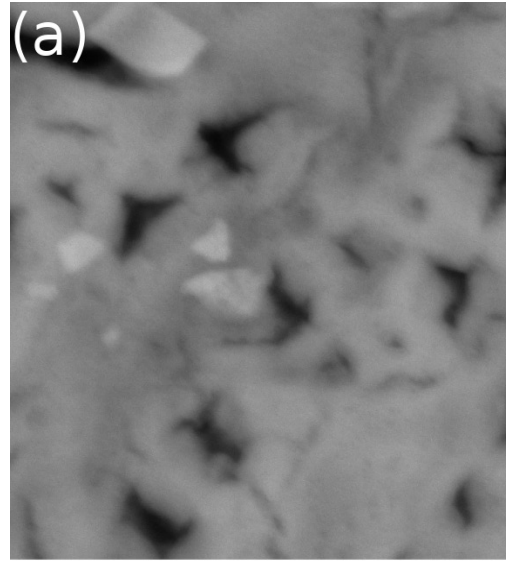
Pd core levels suggest ingress and egress under redox. Not all Pd²⁺ reduced.

Oxide catalysts with Pd²⁺ substitution

Pd nanoparticles seen
after reduction in
backscattering SEM and
in TEM

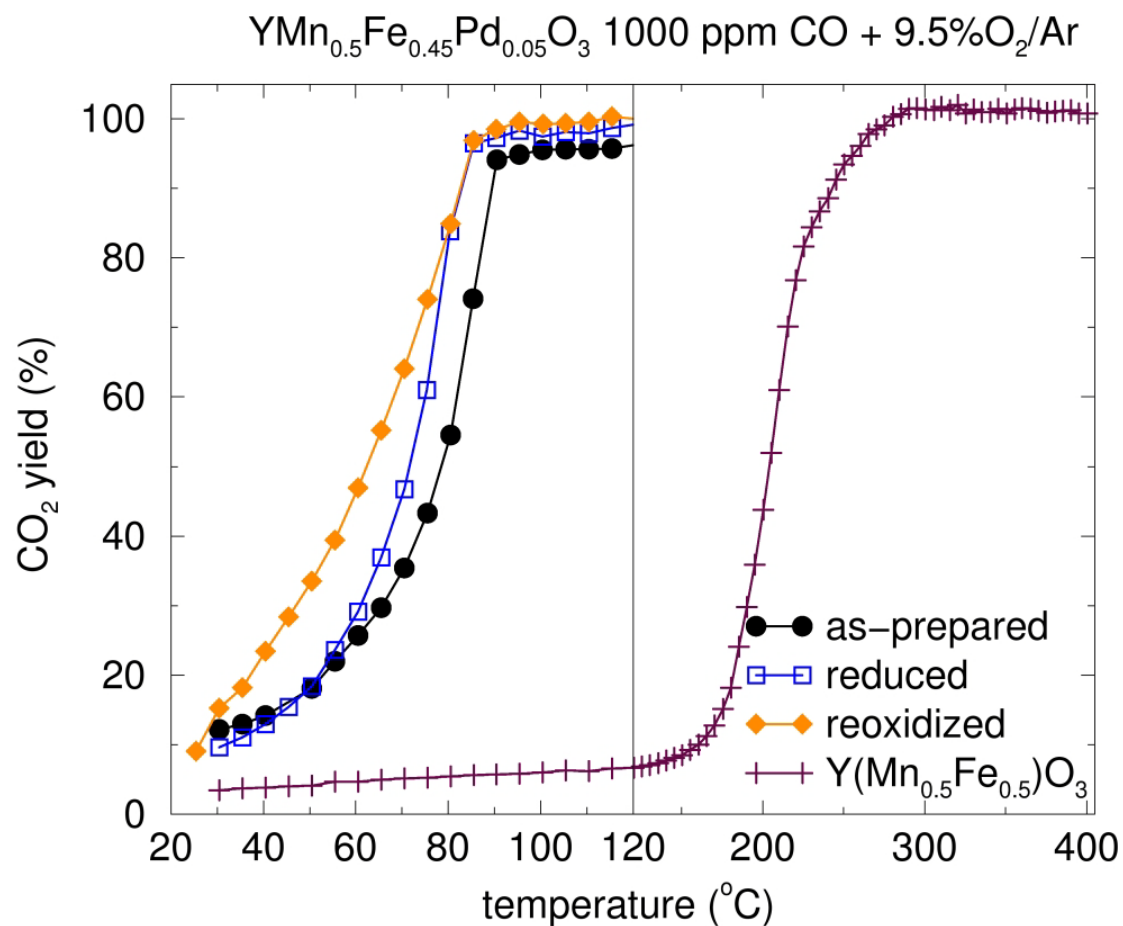
YFeO₃ [10%Pd] as-
prepared

after 1st reduction
[also (c) and (d)]



Oxide catalysts with Pd²⁺ substitution

Oxidized compound, and even better catalyst



Low light-off temperature. Effective catalyst despite low surface areas.

Li, Singh, Schladt, Stalick, Scott, Seshadri, *Chem. Mater.* 20 (2008) 6567–6576.

Questions ?