Characterizing oxides with low cation substitution

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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:

\[
\text{La}_{2-x}\text{Sr}_x\text{CuO}_4: \quad \text{Superconductivity}
\]

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

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

\[
\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3: \quad \text{Capacitors}
\]

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

*Referred to, on occasion, as subscript chemistry.
Examples: Tuning magnetic coupling in insulating spinels

The magnetic spinels, $\text{Zn}_{1-x}\text{Co}_x\text{Cr}_2\text{O}_4$: One end-member is frustrated and the other is a spiral magnet.

Examples: Tuning luminescence in a Ce$^{3+}$ 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 \([\textit{Phys Rev B.} \ 68 \ (2003) \ 205202; \ 71 \ (2005) \ 045201; \ 76 \ (2004) \ 115204; \ 78 \ (2008) \ 195205]\)


3. Perovskite oxides where aliovalent substitution of divalent Pd$^{2+}$ for quadrivalent Ce$^{4+}$ results in unusually active catalyst materials \([\textit{Chem. Mater.} \ 19 \ (2007) \ 1418; \ 20 \ (2008) \ 6567]\).
Cation substituted zinc oxides
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 $3.5 \times 10^{20}$ holes per cm$^3$. 
Cation-substituted ZnO: Magnetism

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

Prepared from oxalates: $(\text{Zn},t\text{M})\text{C}_2\text{O}_4\cdot2\text{H}_2\text{O}$ by rapidly heating to 800°C
Cell parameters follow the Végard law till the substitution limit is reached.

Co$^{2+}$ is slightly smaller than Zn$^{2+}$. 
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$^{2+}$]
No evidence of collective magnetism.

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

\( \Theta \) is large and negative implying that near-neighbor interactions are antiferromagnetic.

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

Motivation: What happens to ZnO upon Mg-substitution?

$(\text{ZnMg})\text{O}$ on SCAM, Laser ablation

[Graph showing transmittance and bandgap as functions of Mg content]

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.

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

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. SPALDIN$^1$

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/m$^2$, and piezoelectric constants, e$_{33}$ (e$_{31}$) of 1.64 (−0.58), 1.34 (−0.57), and 1.67 (−0.48) C/m$^2$ 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


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

Clean samples till $x = 0.15$, rock-salt MgO beyond.
Cation-substituted ZnO: Zn$_{1-x}$Mg$_x$O

Rietveld fits, including refinements of Zn:Mg ratios.
Cell and internal parameters to high precision.
The largest structural change is from the internal parameter $u$. 

$u = 0.375$

$c/a = 1.633$

$u = \frac{3}{8}; P_s = 0$
Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

Dipole along the $c$ direction:

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

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

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

Static polarization $P_s$ based on simple ionic charge model; shared reference state where all ZnO$_4$ tetrahedra have zero dipoles:

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

[decreases, Cf. Tsukazaki, DFT.]
Cation-substituted ZnO: Zn$_{1-x}$Mg$_x$O

Experiments versus DFT

Discrepancy in trend of $u$

Cation-substituted ZnO: Zn$_{1-x}$Mg$_x$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.
PDF analysis allows the positions Zn and Mg to be separately monitored.

Large error bars on distances associated with Mg from X-ray PDFs.
Enter neutrons:

Zn and Zn\(_{0.875}\)Mg\(_{0.125}\)O, the latter, specially formulated for ease of modeling: Zn\(_{7/8}\)Mg\(_{1/8}\)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.
Data can be modeled with an explicit 2x2x1 supercell for Zn$_{7/8}$Mg$_{1/8}$O.
Local MgO$_4$ coordination obtained from PDF closely matches DFT results on wurtzite structure MgO.
Cation-substituted ZnO: Zn$_{1-x}$Mg$_x$O

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

Stacking faults: Relative amounts not affected by substitution

$$\beta_i \cos \theta_i = \frac{\lambda}{D_v} + 4 \varepsilon \sin \theta_i$$
Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

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

<table>
<thead>
<tr>
<th>$x$</th>
<th>$D_v$ (nm)</th>
<th>$D_a$ (nm)</th>
<th>$\varepsilon$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>96(3)</td>
<td>69(3)</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>0.05</td>
<td>76(3)</td>
<td>57(3)</td>
<td>0.020(6)</td>
</tr>
<tr>
<td>0.10</td>
<td>70(2)</td>
<td>51(3)</td>
<td>0.028(5)</td>
</tr>
<tr>
<td>0.15</td>
<td>62(2)</td>
<td>47(2)</td>
<td>0.041(4)</td>
</tr>
<tr>
<td>0.20</td>
<td>33(1)</td>
<td>27(1)</td>
<td>0.099(7)</td>
</tr>
</tbody>
</table>

Some microstrain in Mg-substituted samples.

$D_v$: volume-weighted crystallite size
$D_a$: surface area-weighted crystallite size
$\varepsilon$: 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: Zn$_{1-x}$Mg$_x$O

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

$E_0$ : width of the tails of states in band gap

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

<table>
<thead>
<tr>
<th>$x$</th>
<th>$E_0$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>24.7</td>
</tr>
<tr>
<td>0.05</td>
<td>29.2</td>
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<tr>
<td>0.10</td>
<td>31.9</td>
</tr>
<tr>
<td>0.15</td>
<td>39.7</td>
</tr>
</tbody>
</table>
Cation-substituted ZnO: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

- $E_2^{\text{low}}$ (Gaussian)
- $E_2^{\text{high}}$ (Lorentzian)

Raman intensity (arb. units)

Raman shift (cm$^{-1}$)

$E_2^{\text{low}}$

$E_2^{\text{high}}$

$\omega$ (cm$^{-1}$)

$\Gamma$ (cm$^{-1}$)

$x$

$x$

$x = 0$

$x = 0.05$

$x = 0.10$

$x = 0.15$

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Nb-substituted perovskites $\text{SrTiO}_3$ and $\text{BaTiO}_3$
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 SrTiO$_3$ and BaTiO$_3$

What does structure tell us? Compare SrTi$_{0.875}$Nb$_{0.125}$O$_3$ and BaTi$_{0.875}$Nb$_{0.125}$O$_3$: 1/8$^\text{th}$ 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!
What about the very short range? \( \text{BaTi}_{0.875}\text{Nb}_{0.125}\text{O}_3 \) displays distortions in the first (Ti/Nb)-O neighbor:

Simulations of the first peak of \( \text{BaTiO}_3 \) for the different crystal structures.

Nb-substituted SrTiO$_3$ and BaTiO$_3$
Nb-substituted SrTiO$_3$ and BaTiO$_3$

Findings:

**SrTi$_{0.875}$Nb$_{0.125}$O$_3$:**

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$_3$ ...)

**BaTi$_{0.875}$Nb$_{0.125}$O$_3$:**

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$_3$

**BaTi$_{0.875}$Nb$_{0.125}$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 Pd$^{2+}$
Oxide catalysts with Pd$^{2+}$ substitution

Motivation: Reducing PGM use in catalysts

- More that 50% of Pt use is in automotive catalysis: 3-way converters
- + environmental problems with PGM release

Data from usgs.gov

More that 50% of Pt use is in automotive catalysis: 3-way converters.
Oxide catalysts with Pd$^{2+}$ substitution

Oxide catalysts with \( \text{Pd}^{2+} \) substitution

Motivation: Reducing PGM use in catalysts

Questions:

- Does Pd really go into the host as ions and come out as Pd°?
- Are there other (perhaps better) hosts?
Perovskite BaCeO$_3$ as a host:

Ba$^{2+}$ creates an oxide lattice that is highly oxidizing

Ce$^{4+}$/Ce$^{3+}$ are large and somewhat forgiving in terms of coordination.

BaCe$_{1-x}$Pd$_x$O$_{3-\delta}$ with $x = 0, 0.05, \text{ and } 0.10$

Samples prepared by solid state routes in O$_2$.

Neutron refinements [NPDF, Los Alamos] $\Rightarrow \delta \sim x$ so Pd in lattice is Pd$^{2+}$
DFT optimized structure of 2x2x2 perovskite cell with one Pd\textsuperscript{2+} substituting Ce\textsuperscript{4+} and one oxygen vacancy: \( x = 12.5 \) [Bennett and Rappe, Penn]

The oxygen vacancy prefers to be proximal to Pd\textsuperscript{2+} and leaves it nearly square planar.
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 Pd$^{2+}$ substitution

Pd core levels of the oxidized and reduced samples.

$\chi = 0.10$

Note the drop in counts for the reduced samples.

Ce is always Ce$^{4+}$

YFeO$_3$ exists as a stable perovskite or a metastable (sol-gel prep.) hexagonal compound with the YAIO$_3$ structure. 5-coordinate Fe$^{3+}$ in the hexagonal structure.
Oxide catalysts with Pd$^{2+}$ substitution

Even small Pd substitution strongly stabilizes the hexagonal compound, in keeping with the nature of d$^8$ Pd$^{2+}$. 
Neutron diffraction [NIST, BT-1] confirms the substitution.
Oxide catalysts with Pd$^{2+}$ substitution

Fe core levels unchanged with oxidation/reduction.

Pd core levels suggest ingress and egress under redox. Not all Pd$^{2+}$ reduced.
Oxide catalysts with $\text{Pd}^{2+}$ substitution

Pd nanoparticles seen after reduction in backscattering SEM and in TEM

$\text{YFeO}_3$ [10\%\text{Pd}] as-prepared

after 1$^{\text{st}}$ reduction
[also (c) and (d)]
Low light-off temperature. Effective catalyst despite low surface areas.

Oxidized compound, and even better catalyst

Questions ?