National Science Foundation

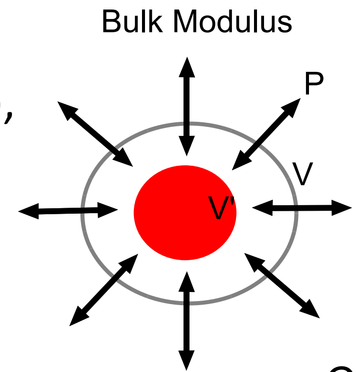
40% Stiffer Nano-Ceria at 33nm: But why?

Siu-Wai Chan, Columbia University, DMR 1206764

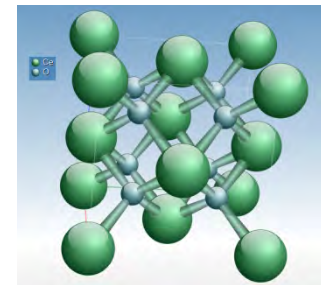
Outcome: The bulk modulus (B) reaches a maximum at 340GPa in 33nm-ceria (i.e. CeO_2), while for micron-size crystals B is 235GPa and for 6nm-ceria B is 180GPa.

Impact: Bulk Modulus is an intrinsic property and almost never a function of grain-size. Present findings require the science community to ask deeper questions of bonding physics and to re-examine the relation between bonding force and bond length more closely.

Possible Explanations: The core-shell model was used to explain a maximum in B with crystal-size in nano-PbS but no observation of any core-shell in nano-ceria from high resolution transmission electron microscopy. A number of models were discussed without satisfaction. Prof. Chan and students are working with theorists for better explanation and planning more definite experiments.

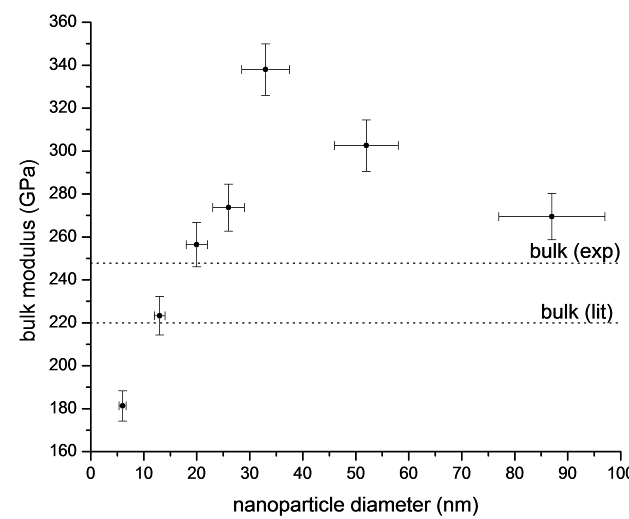


$$B = \frac{-\Delta P}{\Delta V/V}$$



Ce^{4+} in fcc & 8 O^{2-} in 8 tetrahedral sites

Left: schematic of Bulk modulus (B), Right: crystal structure of CeO_2. Below: B as a function of ceria crystallite diameter.



Applied Physics Letters, vol. 106, no. 16, 2015.

Visiting Bayside High School Students

Siu-Wai Chan, Columbia University, DMR 1206764

National Science Foundation

Outcome: High school students understand how materials science has impacted their daily lives and the possible career paths they can take if only they take enough STEM courses now in high school.

Impact: 100+ students get interested in materials science and at least understand there are everyday evidence, e.g. gorilla glass and Giga-hertz (10^9) transistors in their smart phones . Flexible and strong strains of optical fibers made from brittle glass are enabling fast telecommunication.

Explanations: The high school students are drawn in by the theatrical demonstration using liquid nitrogen and blow-torch in levitation and thermal resistance experiments where a corner of a space shuttle tile was heated to red-hot. After the demonstrations, they realized that the science they have been learning could one day materialize into something spectacular.

High school students showing interests in the team's demons

Levitation of a spinning strong magnet on top a cooled single crystal superconductor.

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Stability of Nano- Cu_2O Against Reduction: CeO_2-support & Crystal-size dependent

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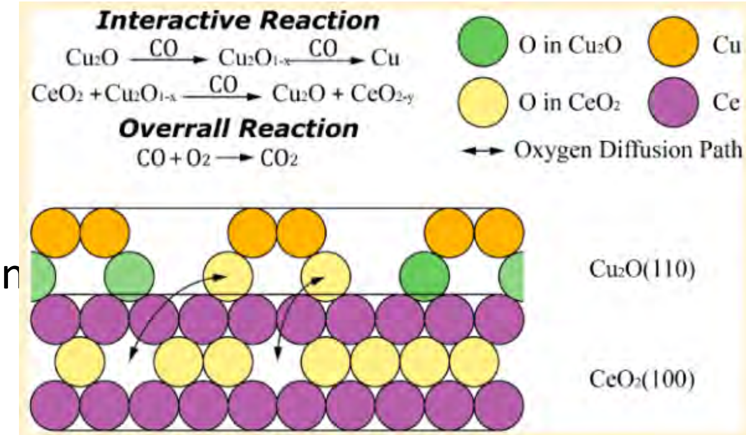
Outcome: A range of crystal-sizes of nano-Cu(I) oxide (aka Cu_2O or cuprite) was prepared. Nano-Cu_2O is reduced to Cu more easily when the crystal-size is smaller. Nano-ceria support was found to slow the reduction to copper with smaller ceria being more effective. The surface amorphous layer of Cu(II) oxide on nano-cuprite does provide an initial reduction protection.

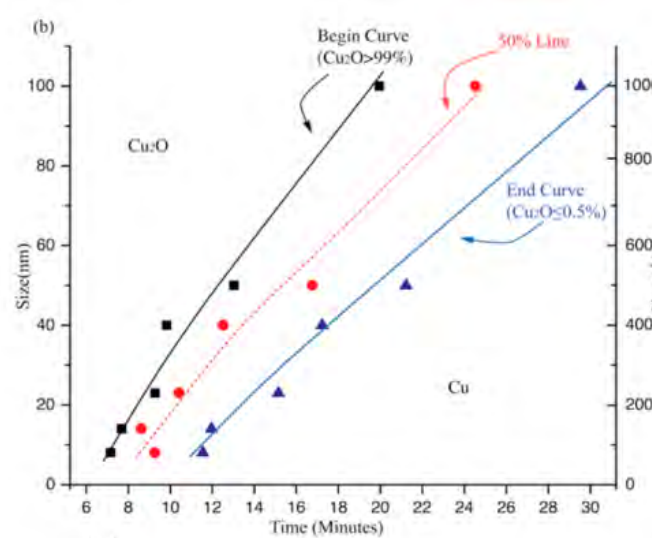
Impact: Reduction to copper deactivates cuprite catalytic capabilities. Nano-ceria support provides better stability. To improve catalytic performance, scientists need to understand how the stability against reduction depends on nano- Cu_2O crystal-size and those of its support, nano-CeO_2.

Explanations: **O**xygen ions migrate between the 2 oxide lattices stabilizing Cu(I) oxide nanoparticle from reduction to copper.

Journal of Physical Chemistry C, vol. 119, no. 31, pp. 17667–17672, 2015



Interactive reaction takes places when CeO2 is partially reduced by lending oxygen to prevent Cu+ from reducing



Time size reduction diagram constructed from the reduction profile

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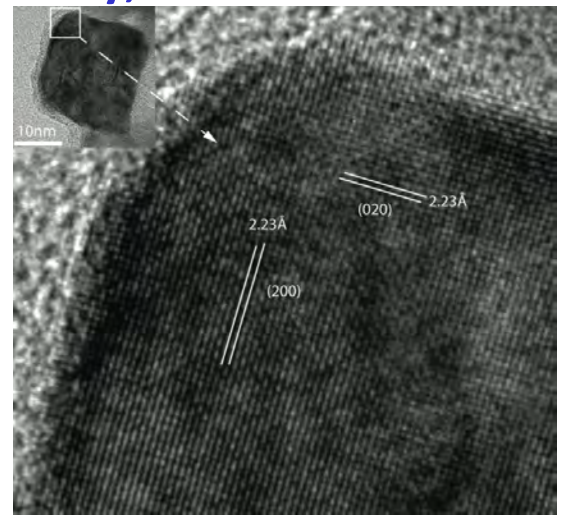
Lattice Expansion in Nano-Cu2O

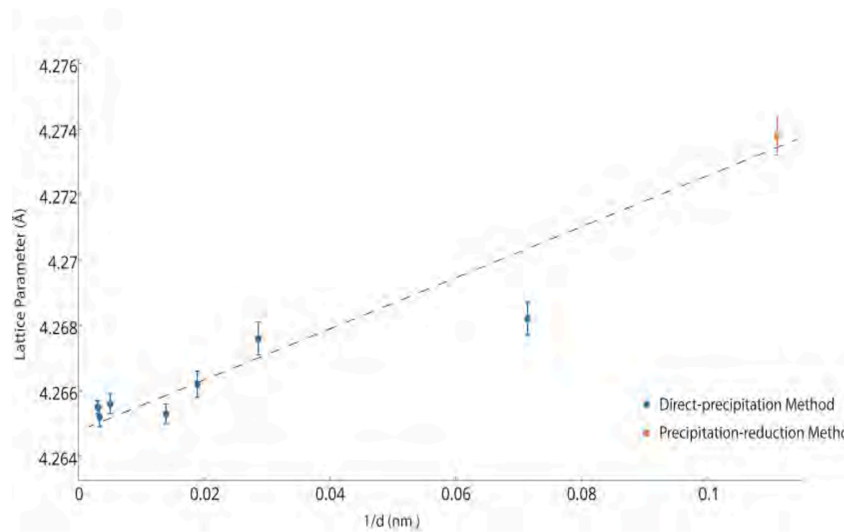
Siu-Wai Chan, Columbia University, DMR 1206764

Outcome: Nano-Cu(I) oxide crystals were synthesized in near mono-dispersed batches. The increasing lattice parameter with decreasing Cu_2O crystal-size was observed. Smaller nano-Cu_2O tends to have higher Cu^{2+} concentration. Results from X-ray Absorption Near-edge Spectroscopy (XANES) and X-ray diffraction give credence to the picture of an amorphous surface mono-layer CuO on nano-Cu_2O .



High-resolution transmission electron microscope imaging of a nano Cu(I) oxide crystal with cube shape

Impact: Redox reactions of copper oxide are dependent on the crystal structures at different sizes. Nano Cu_2O with higher Cu(II) content could effectively affect their catalytic performance in water-gas-shift-reaction. The expansion of lattice parameter by controlling the size of cuprite particles can be used for modifying oxygen diffusivity and the corresponding redox activities.



Increasing lattice parameter as Cu2O crystals size decreases.

Explanations: Longer Cu (II)-O bonds, compared to shorter Cu-O bonds in Cu_2O.

Int. J. Appl. Ceram. Technol., 1-6 (2015). DOI:10,111/ijac.12486

Nano ceria-hafnia crystal structure depends on crystal-size and concentration of Ce^{3+}

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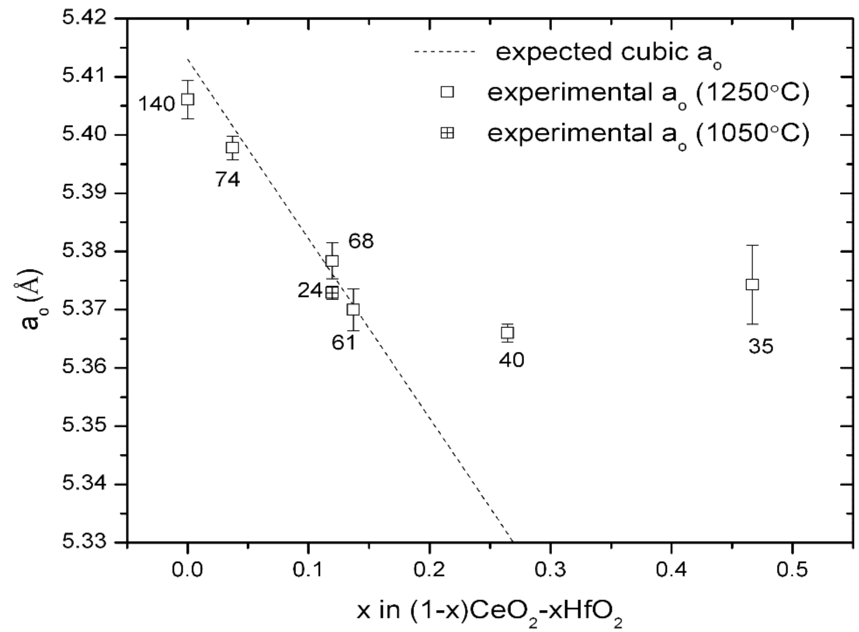
Outcome: Co-precipitated and calcined crystallites of $(1-x)CeO_2-xHfO_2$ show a solubility limit of $x \leq 0.14$ for hafnia in a structurally cubic solid solution with ceria when the crystallite size is 61 nm. Crystallites with a higher hafnia concentration in this sub-micron size range exhibit monoclinic XRD peaks.

Impact: Recent research has featured ceria-hafnia nanoparticles as redox catalysts. However, articles tend to focus on very small (<10 nm) crystallites with no consideration of phase stability as catalysts coarsen with use.

Possible Explanations: The limited solubility of hafnia in cubic solid solution with ceria is likely due to the lack of Ce^{3+} ions in the lattice as determined using XANES spectroscopy. Research in the twin system, ceria-zirconia, has shown the presence of Ce^{3+} ions to enhance phase stability.



Above: Lattice parameter (a_o) of cubic structure in $(1-x)CeO_2-xHfO_2$ crystallites as a function of x. Data point labels are crystallite size in nm. The dotted line shows expected a_o for structurally pure cubic solid solutions, while data points reflect an actual solubility limit of $x \leq 0.14$ for hafnia in solid solution with ceria in this sub-micron size range.

J. Alloys & Compounds, 644, pp. 996-1002, 2015,

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3D-Printing Crystal Unit Cells for Learning Materials Science

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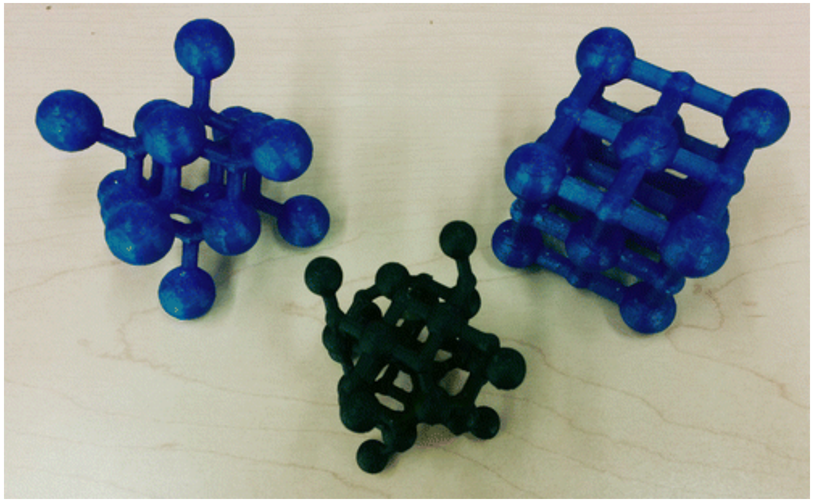

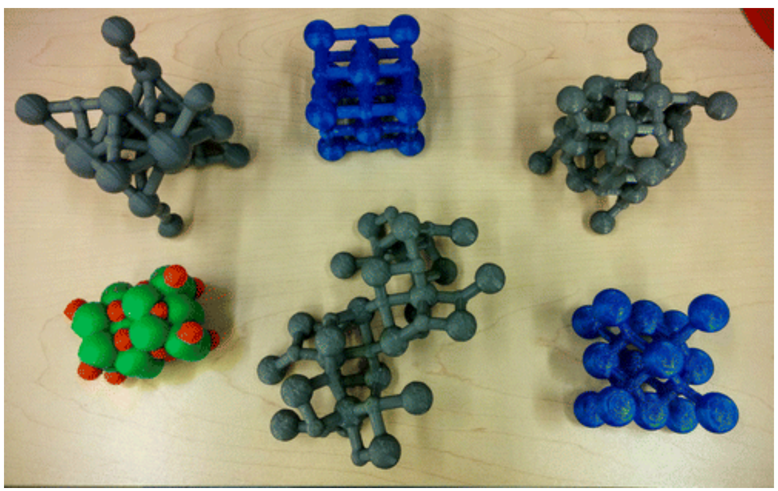

3D printed unit cells. Top image (from left to right): fluorite, tetragonal spinel, and rock salt. Bottom image (from top left clockwise): perovskite, rock salt, tetragonal spinel, fluorite, corundum, and space-filling tetragonal spinel featuring dual atom color.

Project outcome

Courses on materials universally include the study of crystal structure, which are highly visual 3D concepts. Traditionally, such topics are explored with 2D drawings or perhaps a limited set of difficult-to-construct 3D models. The rise of 3D printing, coupled with the wealth of freely available crystallographic data online, offers an elegant solution to the visualization problem. Here, we report a concise and up-to-date method to easily and rapidly transform actual crystallography files to 3D models of diverse unit cells for use as instructional aids.

Impact & benefits

Such 3D models are useful for class discussions, as compliments to a fully integrated course on materials science and engineering. 3D models are perhaps most useful to students who are kinesthetic or tactile learners, and such models could be used in conjunction with virtual visualizations, drawings, and verbal descriptions, so that students of all learning styles could have a comprehensive understanding of unit cells in materials science and engineering.

Background & explanation

The graduate student who helped to spearhead this, chemistry PhD candidate Philip Rodenbough, is supported by the NSF DMR Award.

Rodenbough, P. P.; Vanti, W. B.; Chan, S.-W. 3D-Printing Crystallographic Unit Cells for Learning Materials Science and Engineering. J. Chem. Educ. 2015, Article ASAP, doi: 10.1021/acs.jchemed.5b00597 .