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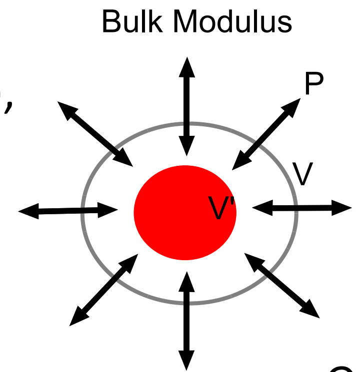
40% Stiffer Nano-Ceria at 33nm: But why?

Siu-Wai Chan, Columbia University, DMR 1206764

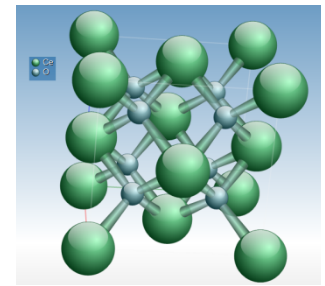
Outcome: The bulk modulus (B) reaches a maximum at 340GPa in 33nm-ceria (i.e. CeO_2), while for micron-size crystals B is 235GPa and for 6nm-ceria B is 180GPa.

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.

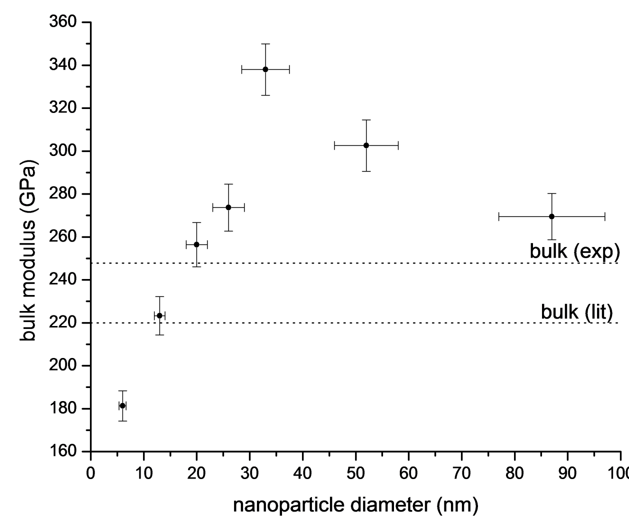


$$B = \frac{-\Delta P}{\Delta V / V}$$



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.



Visiting Bayside High School Students

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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 strains of optical fibers from brittle glass are made to enable fast telecommunication.

Explanations: The high school students are drawn in by the theatrical demonstration using liquid nitrogen and blow-torch fire for 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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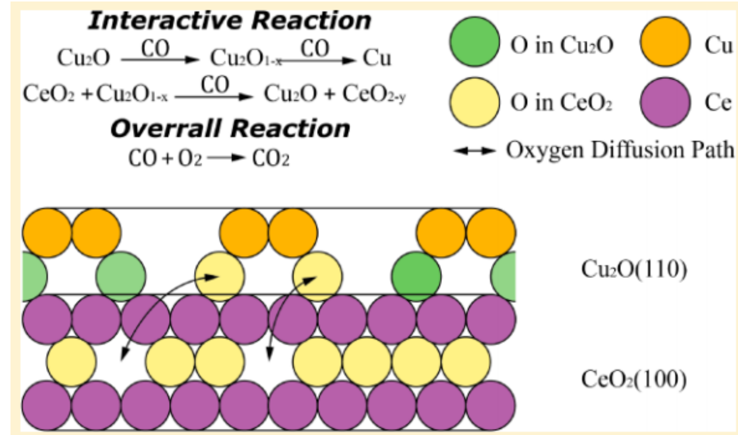
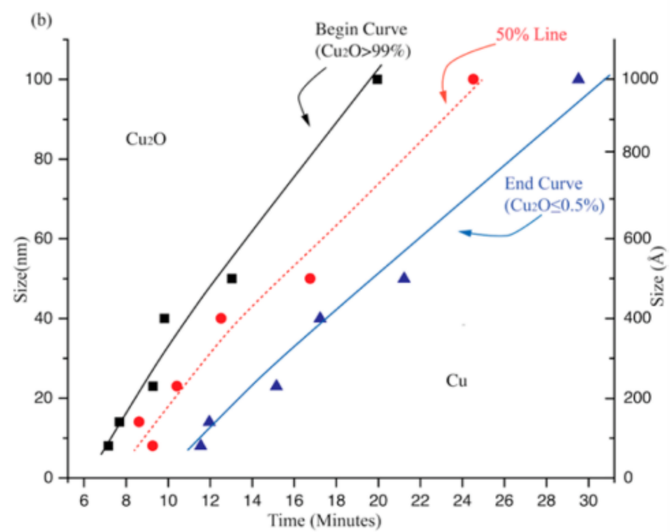
Outcome: A range of crystal-sizes of nano-Cu(I) oxide (aka Cu_2O or cuprite) was successfully prepared. Nano-Cu_2O is reduced to Cu more easily when the crystal-size is smaller. Nano-ceria support was found to slow the reduction to copper with smaller ceria being more effective. The surface amorphous layer of Cu(II) oxide on nano-cuprite does provide an initial reduction protection.

Impact: Reduction to copper deactivates cuprite catalytic capabilities. Nano Cu_2O with nano-ceria support is more stable. To improve catalytic performance, scientists need to understand how the reduction profile changes with the crystal-sizes of cuprite as well as those of the support, nano-ceria.

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



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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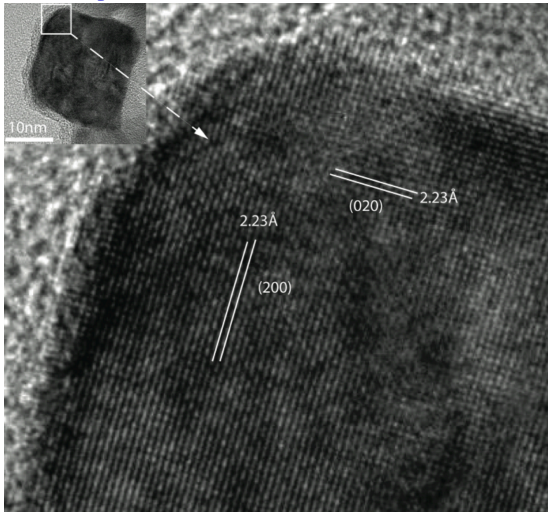
Lattice Expansion in Nano-Cu2O

Siu-Wai Chan, Columbia University, DMR 1206764

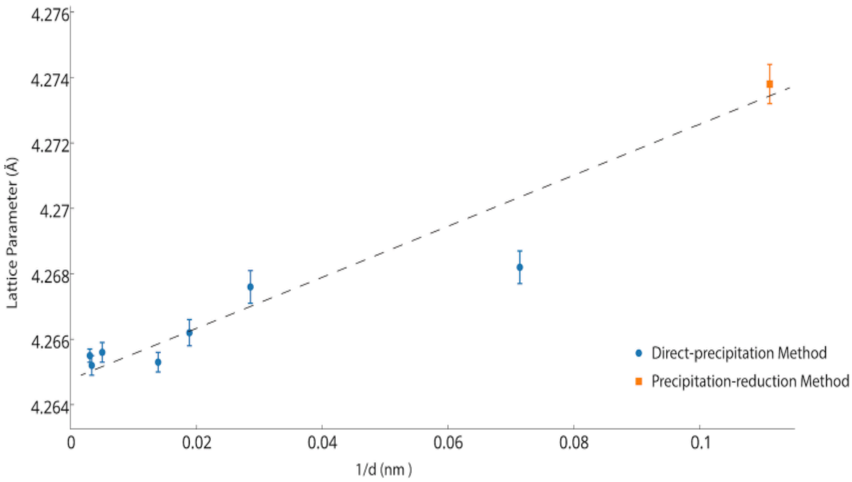
Outcome: Nano-Cu(I) oxide crystals were synthesized in near mono-dispersed batches. The increasing lattice parameter with decreasing Cu_2O crystal-size was observed. Smaller nano-Cu_2O tends to have higher Cu^{2+} concentration indicated the Cu^{2+}'s are located on the surface. Results from X-ray Absorption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

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.

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



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



Increasing lattice parameter as Cu2O crystals size decreases.

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3D-Printing Crystal Unit Cells for Learning Materials Science

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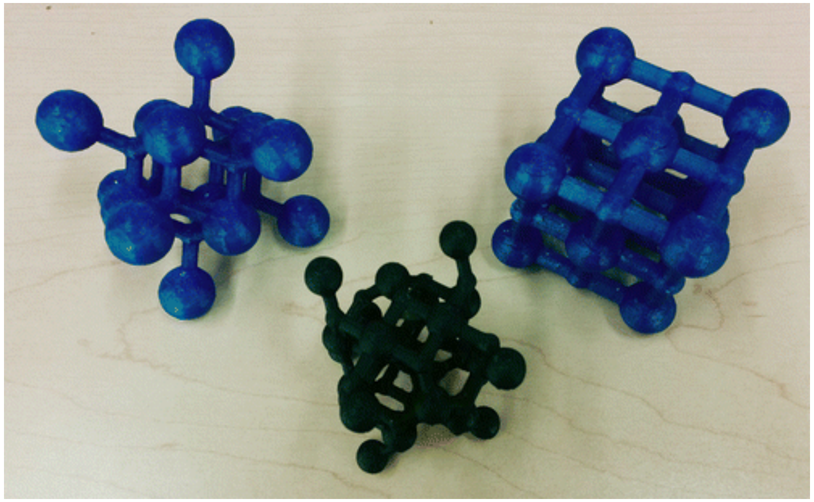

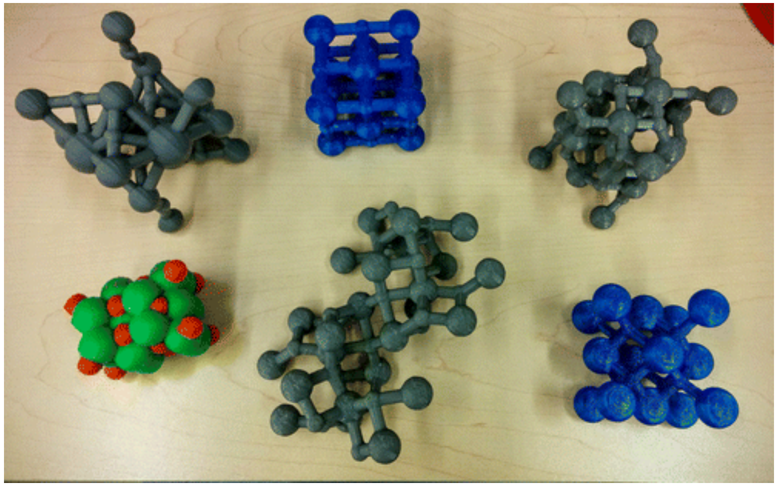

3D printed unit cells. Top image (from left to right): fluorite, tetragonal spinel, and rock salt. Bottom image (from top left clockwise): perovskite, rock salt, tetragonal spinel, fluorite, corundum, and space-filling tetragonal spinel featuring dual atom color.

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.

Reference: 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 .