

Materials 218/UCSB: Class I — An overview of some advanced inorganic materials

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By the end of this quarter, you should be able to figure out how to assemble together elements from the periodic table (where else !) into crystalline or amorphous inorganic solids in such a manner that the resulting material can serve a definite, predefined purpose. Towards this end, we will try and understand inorganic materials from a microscopic/atomic viewpoint — how they form, their structures, bonding, electronic structure . . . and how these manifest in material properties.

At every point, the emphasis shall be on why a particular material is suited for a specific application.

Space shuttle tiles

When the Space Shuttle re-enters the atmosphere, it must be able to withstand a great deal of heating on the surface — in fact the leading edges of the space shuttle turn red. The point of the tiles on the surface of the shuttle are to:

- To protect the Shuttle skin from being oxidized due to the combination of heat and the atmosphere — the material must resist oxidation
- To provide thermal insulation — the material must be a poor thermal conductor
- To *not* add a great deal of mass to the Shuttle – the material must be lightweight

The solution: Highly porous tiles made by sintering amorphous silica (SiO_2) fibers together.

- SiO_2 because it is already oxidized – cannot be oxidized further.
- SiO_2 has a large band gap and hence no electronic contribution to the thermal conductivity. The phonons are not very stiff because Si is heavy (*Cf.* C in diamond) so phonon contribution to thermal conductivity is also small and $\kappa = 1.4 \text{ Wm}^{-1}\text{K}$. In comparison, the thermal conductivity of Al is $247 \text{ Wm}^{-1}\text{K}$.
- The high porosity makes the material very lightweight. The air in the pores further decreases κ of the tile (κ of N_2 is about $0.01 \text{ Wm}^{-1}\text{K}$ at STP).
- Silica *ablates* which means that layers of atoms just strip of the surface at high T . This helps too.

Some discussion of these issues can be found in W. D. Callister, *Materials Science and Engineering, An Introduction*, John Wiley.

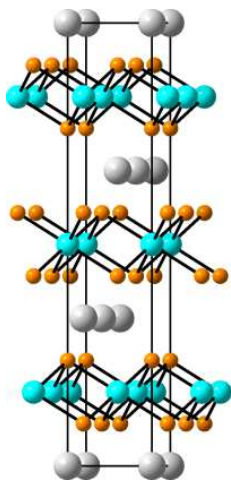
Cell phone batteries

A battery is a collection of cells. Cell phones (the cell refers to the network, not the power source) are usually powered by rechargeable Li ion batteries. In these systems, the layered oxide LiCoO_2 forms the positive electrode in the discharged state. In the charged state, Li^+ ions are removed from the LiCoO_2 host lattice with concomitant oxidation of Co from Co^{III} to something close to Co^{IV} .

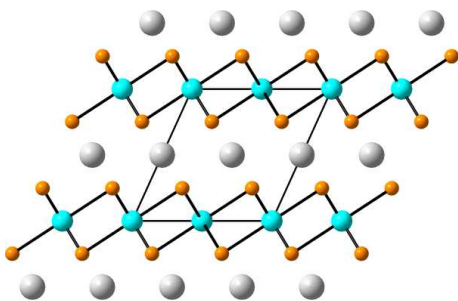
A great deal of insight into these materials has been obtained by performing *in-situ* studies of structural changes as the electrode is charged and/or discharged using high energy Synchrotron X-rays. In these experiments, the whole cell is placed in the sample holder of the Synchrotron X-ray diffractometer. See for example, Morcrette *et al.* *Electrochim. Acta* **47** (2002) 3137.

Here are some crystal structures drawn using coordinates given in the paper of Morcrette *et al.*:

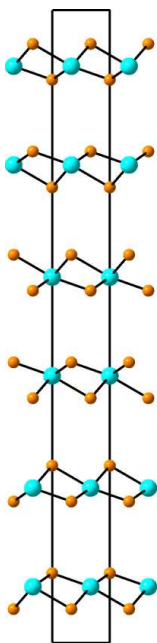
Rhombohedral LiCoO_2 (discharged): The grey atoms are Li, cyan are Co and orange, O.



Monoclinic $\text{Li}_{0.5}\text{CoO}_2$ (partially charged): Li are only half-occupied.



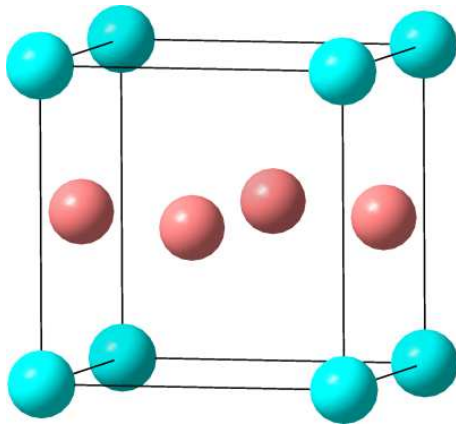
Rhombohedral CoO_2 (fully charged, irreversible):



While the battery in your cell phone no doubt does a good job, there are efforts worldwide to find new, cheaper materials with perhaps, a larger capacity than LiCoO_2 — if more than about 0.5 Li is removed from LiCoO_2 , the electrode is no longer fully reversible.

Jet turbine blades

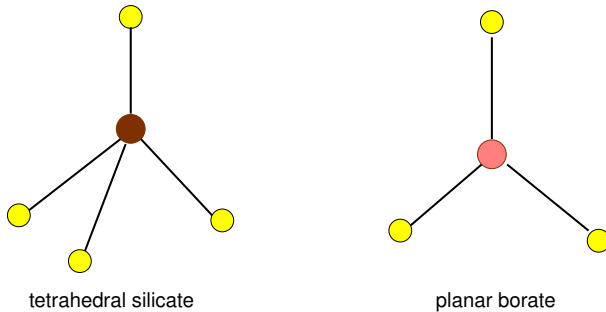
Increasingly, there are attempts to replace Ni-based turbine blades of jet engines with lighter, Ti-based ones since Ti is much less dense than Ni. For a review, see: F. Appel and R. Wagner, *Mater. Sci. Engg. R* **122** (1998) 187. The important 50:50 phase is the intermetallic $\gamma\text{-TiAl}$ which has the $L1_0$ crystal structure (ordered face-centered tetragonal). In the structure below, Ti are cyan and Al, pink:



The low density ($\rho \sim 3800 \text{ kg m}^{-3}$), high specific strength, high stiffness, strength retention at high T and resistance against combustion make this an attractive material. However, like most intermetallics (and unlike many alloys) $\gamma\text{-TiAl}$ suffers poor ductility and poor fracture toughness. The pure material therefore finds little use. However, two phase alloys in the slightly Ti-rich region of the phase diagram (mixtures of $\gamma\text{-TiAl}$ and $\alpha_2\text{-Ti}_3\text{Al}$, which has the ordered hexagonal $D0_{19}$ structure) do not suffer the problem of poor ductility, and these are finding increasing use.

Microwave casseroles

Both the SiO_4^{4-} and the BO_3^{3-} ions are *glass formers* and when one is added to the other, it is called a *network former*. However, while the former is tetrahedral and forms 3D networks, the latter is planar and forms sheets:

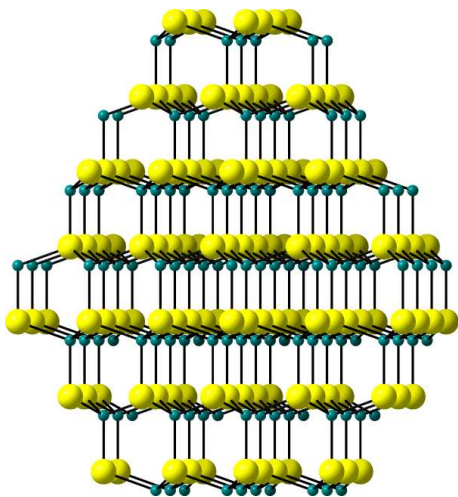


The addition of small amounts of borate (about 5 weight %) ions to a $\text{Na}_2\text{O}/\text{SiO}_2$ glass results in the thermal expansion coefficient of the glass becoming very small — nearly zero. This decrease in the thermal expansion coefficient arises because of the decrease in the average network dimensionality (Why ?) This

means that the glass (called borosilicate glass) becomes very good at handling rapid changes in temperature, or *thermal shock*. Borosilicate dishes are therefore quite capable of handling the rapid temperature changes associated with cooking using a microwave oven. In addition, both SiO_2 and B_2O_3 are poor microwave susceptors, so the dish itself is not heated by the microwaves. On the other hand, metals, polar materials, and materials with defects (most polycrystalline materials) are good microwave susceptors, and therefore cannot be used.

DNA quantum dot labels

Nanocrystals of CdSe share the properties of the parent solid (wide electronic bands, a rigid sp^3 hybridized lattice) with the properties of molecules (interaction with light *via* an electronic transition dipole). Since there is no tendency for non-radiative decay, when a CdSe quantum dot (nanocrystal) is photoexcited, it tends to luminesce with very high efficiencies. Nanocrystals are better photoemitters than the corresponding bulk material since the electron-hole pair created by photon absorption is spatially localized (exciton formation) within the confines of the nanocrystal. A drawing of an uncapped wurtzite CdSe quantum dot is displayed below:



To find out more about the photophysics of these systems, look at M. Nirmal and L. Brus, *Acc. Chem. Res.* **32** (1999) 407.

Because of its very small solubility product, CdSe nanocrystals turn out to be rather benign in a biological environment. In addition, their surfaces can be modified suitably that they pick up the ability to recognize specific sites in a cell. For example, certain DNA retain their natural ability to hybridize with complementary sequences even when tethered to quantum dots. Quantum dot luminescence can then be used as probe to monitor extent of DNA hybridization. For a recent review, see A. J. Sutherland, *Curr. Opin. Solid State Mater. Sci.* **6** (2002) 365. Quantum dots turn out to be better luminescence labels than organic dye molecules because they bleach less easily. Their useful lifetimes as labels is therefore much greater.