Lecture 18

Characterization of minerals and functional materials under high pressure and high temperature

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1. High Pressure Methods in Geophysics and Materials
2. History of High Pressure Physics
3. Large Volume Press Apparatus
4. Diamond Anvil Cell
5. High Pressure Techniques in Geophysics
6. High Pressure Techniques in Materials Science
High pressure Geophysics and Earth Interior

Imagining Earth’s Interior

(From http://www.gsecars.org/)
The unit cells obtained in the phases predicted theoretically (i.e., 3.745 Å for cubic BC and 3.642 Å for nearly cubic BC3) are slightly larger than that of a diamond (3.5667 Å) (Lowther J E 2005 *J. Phys. Condes. Matter.* 17 3221).
How do we study minerals and materials at HP-HT?

Pressure and Temperature generating apparatus
- Piston cylinder
- Multi-anvil press
- Diamond anvil cell
- Shock experiments

Piston-cylinder apparatus
- pressures up to 5 GPa

Calculation
- Macroscopic methods
- Atomistic methods
Prehistory

Percy Williams Bridgman was an American physicist who won the 1946 Nobel Prize in Physics for his work on the physics of high pressures. He also wrote extensively on the scientific method and on other aspects of the philosophy of science.

Bridgman entered Harvard University in 1900, and studied physics through to his Ph.D. In 1905, he began investigating the properties of matter under high pressure. A machinery malfunction led him to modify his pressure apparatus; the result was a new device enabling him to create pressures eventually exceeding 10 GPa. This was a huge improvement over previous machinery, which could achieve pressures of only 0.3 GPa. This new apparatus led to an abundance of new findings, including on the effect of pressure on electrical resistance, and on the liquid and solid states. Bridgman is also known for his studies of electrical conduction in metals and properties of crystals. He developed the Bridgman seal and is the eponym for Bridgman’s thermodynamic equations (Wikipedia, 2009).

Percy Williams Bridgman (1882 – 1961)

Bridgman made many improvements to his high pressure apparatus over the years, and unsuccessfully attempted the synthesis of diamond many times.
Large Volume Press
Large Volume Press (LVP)

The octahedra before experiment.

The octahedra after experiment.

The octahedra after experiment.
Generation of pressures to similar to 60 GPa in Kawai-type apparatus and stability of MnGeO₃ perovskite at high pressure and high temperature (1000 degrees C) has been reported recently (Yamazaki et al., AMERICAN MINERALOGIST, 91, 1342 (2006))
Diamond is remarkable not only because it is the hardest known material, but also because it is highly transparent to many ranges of electromagnetic radiation. These attributes of diamond have led to its present widespread use in high-pressure minerals physics and in high-pressure materials science. Lawson and Tang (1950) at the University of Chicago first employed diamonds in a high-pressure x-ray experiments.
The operation of the diamond anvil cell relies on a simple principle:

Pressure = Force/Area

Schematic cross section diagram of the opposed diamond anvil configuration showing the gasket, a thin metal sheet with a small hole in it, placed between the anvil faces. The hole, containing the sample, is precisely centered over the anvil faces to prevent blow-out as the anvils are squeezed together to deform the gasket and decrease the sample volume.

High pressure can be achieved by applying a moderate force on a sample with a small area, rather than applying a large force on a large area. In order to minimize deformation and failure of the anvils that apply the force, they must be made from a very hard and virtually incompressible material, such as diamond.
Principle of DAC
**History:** The laser-heated diamond-anvil cell (LH-DAC) is the only experimental tool able to create extreme static pressures \((P > 100 \text{ GPa})\) and temperatures \((T > 3000 \text{ K})\) and it has therefore a major impact in high-pressure research and geophysics. In 1968 Taro Takahashi and William Basset observed a phase transition that resulted from laser heating under pressure in a diamond anvil cell. Using a ruby laser, they successfully converted graphite to diamond (Bassett, *Rev. Sci. Instrum.* **72**, 1270, 2001). First paper on laser heating was published in 1974: application of the YAG laser by Ming and Basset made it possible to convert \((\text{Fe, Mg})_2\text{SO}_4\) into \((\text{Fe, Mg})\text{O} + \text{SO}_2\) (stishovite) (Ming, Bassett, *Rev. Sci. Instrum.* **45** 1115, 1974). Now, LH-DAC is one of the most fundamental tools in the arsenal of high-pressure mineral physics research as it is the only device that can access the entire range of pressures and temperatures encountered in Earth interiors.
Laser Heating in DAC

Principles: Laser heating is based on the principle of absorption of infrared laser light by the sample after the light has passed through one or both of the diamond anvils with only minor intensity loss. It simplified the sample assemblage in the DAC by heating a portion of the sample that is only tens of microns across and well isolated from the anvils. When laser heating is used, the pressure and temperature limitations due to the temperature-induced failure of diamonds and mechanical parts are no longer a problem. Temperatures up to several thousand degrees and pressures up to megabars have been achieved.
Apparatus to Study the Interior of the Earth

Pressure at the center of the: Earth = 300 GPa; Uranus = 600 GPa; Saturn = 1400 GPa; Jupiter = 2000 GPa

Seismological images of the Earth's mantle reveal three distinct changes in velocity structure, at depths of 410, 660 and 2,700 km. The first two are best explained by mineral phase transformations, whereas the third—the D" layer—probably reflects a change in chemical composition and thermal structure.

Average elastic parameters as a function of depth. The P-wave velocity $V_p$, S-wave velocity $V_S$, and density $p$ are determined from seismological analysis. The figure is based on the Primary Reference Earth Model (PREM). PREM was created in 1981 (Dziewonski and Anderson, Phys. Earth. Planet. Int., 25, 297).
Bernal was the first to propose that rapid increases in seismic velocity in the mantle might be due to phase transformations rather than a change in composition. Experiments in the mid-1960s showed that the olivine component of peridotite undergoes successive pressure-dependent transformations to the spinel structure (ringwoodite), and ultimately breaks down to form (Mg,Fe)SiO₃ perovskite plus (Mg,Fe)O:

\[
(Mg,Fe)_2SiO_4 = (Mg,Fe)_2SiO_4 \quad \text{Pressure, 13-14 GPa; depth, 410 km}
\]

\textit{Olivine} \hspace{1cm} \textit{Wadsleyite}

\[
(Mg,Fe)_2SiO_4 = (Mg,Fe)_2SiO_4 \quad \text{Pressure, 18 GPa; depth, 520 km}
\]

\textit{Wadsleyite} \hspace{1cm} \textit{Ringwoodite}

\[
(Mg,Fe)_2SiO_4 = (Mg,Fe)SiO_3 + (Mg,Fe)O \quad \text{Pressure, 23 GPa; depth, 660 km}
\]

\textit{Ringwoodite} \hspace{1cm} \textit{Perovskite} \hspace{1cm} \textit{Magnesiowustite}
Divisions in the Earth's Mantle

With increasing pressure, upper mantle minerals such as $(\text{Mg,Fe})_2\text{SiO}_4$ olivine, garnet, and pyroxene transform to denser mineral phases. These transformations are associated with major jumps in seismic velocity, called discontinuities, at depths of 410 and 660 km.

Transformations to a perovskite-structured phase with the formula $(\text{Mg,Fe})\text{SiO}_3$ is generally associated with the major seismic discontinuity at 660 km depth. This phase, along with $(\text{Mg,Fe})\text{O}$ and perovskite-structured $\text{CaSiO}_3$, are thought to account for the bulk of the lower mantle deeper than 660 km.

Mineral volume fractions for the top 1000 km of a pyrolite mantle. Pyrolite is a theoretical rock considered to be the best approximation of the composition of Earth's upper mantle (from Frost, Elements, 2008).
Minerals in Earth’s mantle

\[ (\text{Mg,Fe,Al})-\text{MgSiO}_3 \text{ perovskite} \]

\[ (\text{Mg,Fe})\text{O} - \text{ferropericlase} \]

\[ (\text{Mg,Fe,Al,Ca})-\text{silicates} \]
Olivine

Atomic Structure of Olivine: Mg$_2$SiO$_4$
There appears to be 3 minerals that are most important in the lower mantle because of their abundance.

Magnesium-silicate perovskite: 
(Mg,Fe)SiO$_3$

Stishovite, SiO$_2$

Magnesio-wüstite: (Mg,Fe)O

http://www.geo.arizona.edu/xtal/geos306/fall09-13.htm
A perovskite is any material with the same type of crystal structure as calcium titanium oxide \((\text{CaTiO}_3)\), known as the perovskite structure. Perovskites take their name from this compound, which was first discovered in the Ural mountains of Russia by Gustav Rose in 1839 and is named after Russian mineralogist, L. A. Perovski (1792-1856).
Example of the perovskite mineral

The general formula for a perovskite is $\text{ABO}_3$ where A and B are cations. The A cations occupy every hole which is created by 8 BO$_6$ octahedra, giving the A cation a 12-fold oxygen coordination, and the B-cation a 6-fold oxygen coordination. In the example shown below, (SrTiO$_3$, download cif) the Sr atoms sit in the 12 coordinate A site, while the Ti atoms occupy the 6 coordinate B site. There are many ABO$_3$ compounds for which the ideal cubic structure is distorted to a lower symmetry (e.g. tetragonal, orthorhombic, etc.)
The relative ion size requirements for stability of the cubic structure are quite stringent, so slight buckling and distortion can produce several lower-symmetry distorted versions, in which the coordination numbers of A cations, B cations or both are reduced.
Magnesio-wüstite: (Mg,Fe)O

Marquardt, Speziale, et al, 2009
Stishovite, SiO$_2$

**Stishovite**: Distorted hcp array of oxygens with Si in the octahedral voids. Synthesized by Stishov and Popova in the late 1950's.

Stishovite (after Sergey M. Stishov and Popova, a renowned Russian high-pressure physicist who first synthesized this mineral) is an extremely hard, dense tetragonal form (polymorph) of silicon dioxide. Stishovite was first found at Meteor Crater, Arizona in 1960's and named after Stishov (who synthesized it earlier the same year) by Edward C. T. Chao.

Undergoes a displacive phase transition around 50 GPa that is driven by more efficient packing of the O atoms.
Stishovite, SiO$_2$

Deep mantle, meteorite impact, and other ultrahigh-pressure settings may result in a more densely-packed SiO$_2$-structure, with silicon in octahedral (6-fold) coordination with oxygen. This is the structure basis for stishovite, which is isostructural with rutile (TiO$_2$, in which Ti is in octahedral coordination).

This is a part of the unit cell for stishovite, showing the coordination of silicon and oxygen. The oxygen is in hexagonal closest packing; in the full unit cell and mineral structure, half of the possible octahedral positions are occupied by silicon.

Stishovite has a tetragonal structure, with strips of edge-sharing octahedra that run parallel to the c-axis.
World of SiO$_2$
The variation in sound velocity with depth for various key mantle minerals: olivine (Ol), diopside (Cpx), enstatite (Opx), garnet (Gt), majorite-garnet solid solution (Mj50), wadsleyite (Wd), ringwoodite (Rw), magnesiowüstite (Mw), Mg-silicate perovskite (Pv). Increases in temperature for an adiabatic gradient are taken into account. The reference model PREM (Dziewonski and Anderson 1981) is shown for reference. The length of an adiabat indicates approximately the maximum pressure stability of any given phase. (From Bass, *Elements*, 2008).
A phase transition of MgSiO₃ perovskite, the most abundant component of the lower mantle, to a higher-pressure (125 GPa, 2000K) form called post-perovskite was recently discovered for pressure and temperature conditions in the vicinity of the Earth’s core–mantle boundary.

Crystal structure of the post-perovskite phase of (Mg,Fe)SiO₃. The structure consists of layers of linked silicon octahedra (yellow). Red spheres at vertices of SiO₆ octahedra are oxygen ions, and blue spheres are magnesium and iron ions.

The lower mantle extends from a depth of 660 km to a depth of 2,890 km, with the D" region extending about 200 km above the core (Duffy, *Nature* **451**, 269 (2008))
Do we know everything about Earth Interior?

Whole mantle shear velocity heterogeneity

Iso-velocity contours: +/- 0.7%

Grand [2002]

(From http://www.gsecars.org/)
Do we know everything about Earth Interior?

Figure: Science Perspective (Garnero)

(From http://www.gsecars.org/)
In chemistry, activation energy is a term introduced in 1889 by the Swedish scientist Arrhenius, that is defined as the energy that must be overcome in order for a chemical reaction to occur.

Computed phase boundary between carbon + nitrogen and the dense phases of C\textsubscript{3}N\textsubscript{4}: willemite-type phase w-C\textsubscript{3}N\textsubscript{4} (blue line) and β-C\textsubscript{3}N\textsubscript{4} (red line). The phase diagram of carbon is shown for comparison by dashed lines.
Synthesis of Diamond

An independent diamond synthesis was achieved on February 16, 1953 in Stockholm by the ASEA (Allmänna Svenska Elektriska Aktiebolaget), one of Sweden's major electrical manufacturing companies. Starting in 1949, ASEA employed a team of five scientists and engineers as part of a top-secret diamond-making project code-named QUINTUS. The team used a bulky split-sphere apparatus designed by Baltzar von Platen and Anders Kämpe. Pressure was maintained within the device at an estimated 8.4 GPa for an hour. A few small diamonds were produced, but not of gem quality or size. The work was not reported until the 1980s.

Hall achieved the first commercially successful synthesis of diamond on December 16, 1954, and this was announced on February 15, 1955. His breakthrough was using a "belt" press, which was capable of producing pressures above 10 GPa and temperatures above 2000 °C. The "belt" press used a pyrophyllite container in which graphite was dissolved within molten nickel, cobalt or iron. Those metals acted as a "solvent-catalyst", which both dissolved carbon and accelerated its conversion into diamond. The largest diamond he produced was 0.15 mm across; it was too small and visually imperfect for jewelry, but usable in industrial abrasives. Hall's co-workers were able to replicate his work, and the discovery was published in the major journal Nature. He was the first person to grow a synthetic diamond with a reproducible, verifiable and well-documented process.
Synthesis of Diamond

A charter member of General Electric Corp.'s Project Superpressure in the early 1950s, Hall specialized in designing components for the high-powered presses needed to make diamonds. While other members of Project Superpressure worked with a new, three-story-high press, Hall worked with a leaky, older press but found success by designing an elegant carbide belt that held the sample cell of graphite and other materials, subjected to 70,000 atmospheres of pressure.

When he broke the cell open on December 16, 1954, he later wrote, "My hands began to tremble; my heart beat rapidly; my knees weakened and no longer gave support. My eyes had caught the flashing light from dozens of tiny triangular faces of octahedral crystals ... and I knew that diamonds had finally been made by man."

H. Tracy Hall with a diamond press he designed.

Industrial diamond consumption grew rapidly after Hall's invention. In 1954, some 14 million carats of industrial diamonds were used, all of them from natural sources. By the mid-1990s, that had grown to more than 500 million carats, 90% manufactured, according to the Industrial Diamond Association.
Synthesis of Gem Quality Diamond

Synthetic gem-quality diamond crystals were first produced in 1970 by GE, then reported in 1971. The first successes used a pyrophyllite tube seeded at each end with thin pieces of diamond. The graphite feed material was placed in the center and the metal solvent (nickel) between the graphite and the seeds. The container was heated and the pressure was raised to about 5.5 GPa. Initially a week-long growth process produced gem-quality stones of around 5 mm (1 carat or 0.2 g), and the process conditions had to be as stable as possible.

The De Beers Diamond Research Laboratory has grown stones of up to 25 carats (5.0 g) for research purposes. Stable HPHT conditions were kept for six weeks to grow high-quality diamonds of this size. For economic reasons, the growth of most synthetic diamonds is terminated when they reach a weight of 1 carat (200 mg) to 1.5 carats (300 mg).

In the 1950s, research started in the Soviet Union and the US on the growth of diamond by pyrolysis of hydrocarbon gases at the relatively low temperature of 800 °C. This low-pressure process is known as chemical vapor deposition (CVD). William G. Eversole reportedly achieved vapor deposition of diamond over diamond substrate in 1953, but it was not reported until 1962. Diamond film deposition was independently reproduced by Angus and coworkers in 1968 and by Deryagin and Fedoseev in 1970. Whereas Eversole and Angus used large, expensive, single-crystal diamonds as substrates, Deryagin and Fedoseev succeeded in making diamond films on non-diamond materials (silicon and metals), which led to massive research on inexpensive diamond coatings in the 1980s (Wikipedia, 2009).
Synthesis of New Diamond–like materials from B-C-N triangle under HPHT

The composition triangle in the B-C-N system.
In 1965, Wentorf reported the synthesis of a new boron form at pressures above 10 GPa and temperatures above 1500 C. The existence of this material was not confirmed until recently.

An orthorhombic (space group Pnnm) boron phase was synthesized at pressures above 9 GPa and high temperature, and it was demonstrated to be stable at least up to 30 GPa. The structure, determined by single-crystal x-ray diffraction, consists of B_{12} icosahedra and B_{2} dumbbells. The charge density distribution obtained from experimental data and ab initio calculations suggests covalent chemical bonding in this phase. Strong covalent interatomic interactions explain the low compressibility value (bulk modulus is K300 ¼ 227 GPa) and high hardness of high-pressure boron (Vickers hardness HV ¼ 58 GPa), after diamond the second hardest elemental material.

Borazon is a brand name of a cubic form of boron nitride (cBN). It is one of the hardest known materials, along with various forms of diamond and boron nitride. Borazon is a crystal created by heating equal quantities of boron and nitrogen at temperatures greater than 1800 °C at 7 GPa. Borazon is the only substance other than those listed above that can scratch a diamond (although lasers can cut diamond). A diamond will also scratch Borazon (Wikipedia, 2009).

Borazon was first produced in 1957 by Robert H. Wentorf, Jr., a physical chemist working for the General Electric Company. In 1969, General Electric adopted the name Borazon as its trademark for the material.
Synthesis of Novel Binary Materials

• B-C system: The unit cells obtained in the phases predicted theoretically (i.e., 3.745 Å for cubic BC and 3.642 Å for nearly cubic BC3) are slightly larger than that of a diamond (3.5667 Å) (Lowther J E 2005 *J. Phys. Condes. Matter* 17 3221).

• Graphitic and cubic BC₃ phases are predicted to be superconductors with a relatively high superconducting temperature (*T_c* ~ 22 -50 K): Moussa, Cohen, *Phys. Rev. B* 77 8 (2008)

Computed phase boundary between carbon + nitrogen and the dense phases of C$_3$N$_4$: willemite-type phase w-C$_3$N$_4$ (blue line) and β-C$_3$N$_4$ (red line). The phase diagram of carbon is shown for comparison by dashed lines.

In chemistry, activation energy is a term introduced in 1889 by the Swedish scientist Arrhenius, that is defined as the energy that must be overcome in order for a chemical reaction to occur.
Synthesis of Dense Nitrides

- Prediction of the dense $C_3N_4$ phase stimulated a search for new nitrides of the groups 4 and 14 elements. A cubic phase of silicon nitride with a spinel structure, $\gamma$-$Si_3N_4$ has been synthesized by Zerr et al. (Zerr et al. *Nature* 400, 340 (1999)) in a LHDAC. The $\gamma$-$Si_3N_4$ is known today as a material with unique combination of advanced properties and it can be produced in large amounts at reasonable costs using detonation synthesis routes. High-pressure research on the other group 4 elements also led to discovery of another, previously unknown family of binary nitrides of the group 4 elements, having Th$_3$P$_4$-type structure, c-$Zr_3N_4$ and c-$Hf_3N_4$ (Zerr et al., *Nature Mater.* 2, 185 (2003)).

- It is known today that the wear resistance of c-$Zr_3N_4$ is 10 times better than that of titanium mononitride. Further, the hardness of dense c-$Zr_3N_4$ appears to exceed 30 GPa which is about 2.5 times higher than that of the corresponding mononitrides.

Optical image of a platelet of elemental Hf embedded in the nitrogen pressure medium at 18 GPa before heating. Metallic hafnium does not transmit the visible light. (Right) The same sample after heating to 2800 K showing reaction of Hf and N$_2$. The hole diameter, containing the sample and pressure media, is about 150 $\mu$m.
Structure of $g$-C$_3$N$_4$ phases

The second graphitic phase, $g$-C$_3$N$_4$, was prepared by solid-state reaction between cyanuric chloride or its fluoro analogue and lithium nitride [8,15]

$$C_3N_3Cl_3 + 3Li_3N \rightarrow g$-C$_3$N$_4 + 3LiCl$$


Synthesis of cubic $\text{C}_3\text{N}_4$ phase at HPHT

\[
a = 3.878 \pm 0.001 \, \text{Å}, \text{ density } 2.62 \, \text{g/cm}^3
\]

Synthesis of New Cubic BCx Phases under HPHT

Electronic charge distribution in graphitic BC$_3$ (from Lowther et al., PRB, 2009).

Possible structures of BCx phases (from (Lowther, 2005)).
Synthesis of cubic-BC$_4$ phase at 37 GPa

X-ray diffraction of the graphitic BC$_4$ (g-BC$_4$(I)) as the starting material, where the broad peak around 2.384 Å is from the B$_4$C.

The ambient x-ray diffraction pattern of a post-lasered BC$_4$ (c-BC$_4$(II)) phase recovered from 37 GPa. Two weak and broad peaks at 3.736 and 2.347 are from the B$_4$C in the starting material.

Phase Transitions in BC$_4$

$g$-BC$_4$ (I) – hexagonal (graphite-related phase)

Factors that could effect the lattice parameter of the diamond-like BC$_{\text{x}}$ phases

- Structure defect: Higher the vacancy, larger the lattice parameter
- Synthesis pressure: Higher the synthesis P, Smaller the lattice parameter

$g$-BC$_4$ (II) – hexagonal (graphite-related phase)

44 GPa, 1984 K

$c$-BC$_4$ – cubic (diamond-like phase)

24 GPa, 2020 K

Electron microprobe analysis of the recovered BC$_{\text{x}}$ sample was performed using JEOL Hyperprobe JXA-8500F at UH.

The result obtained from EMP measurements gives a C/B ratio of around 4 ($C/B = 3.91 \pm 0.26$).
Raman Spectroscopy of cubic BC\textsubscript{4}

Raman spectrum (532 nm) of \textit{c}-BC\textsubscript{4} phase: integration time was 4 min, laser power was 2 mW.

(a) Optical image of the \textit{c}-BC\textsubscript{4} phase and (b) a map of the Raman peak intensity at 1193 cm\textsuperscript{-1} shown in a yellow colour scale.

Mahalo