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Minerals of the Earth's Deep Interior

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# Minerals of the Earth's Deep Interior

David Schiferl\*, Yusheng Zhao, and Thomas J. Shankland

## Abstract

This is the final report of a three-year, Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). The project addresses the major geophysical issue of the nature of the seismic velocity and density discontinuity at 670 km depth (the boundary between upper and lower mantle with temperature about 1900 K and pressure about 23 GPa). A phase change at this depth would represent a relatively small barrier to mantle convection through the discontinuity, but compositional change would inhibit thermal convection throughout the mantle. To address this problem we measured equation of state parameters in mantle minerals as functions of high P-T using *single crystal* x-ray diffraction with a unique, new diamond-anvil cell (DAC) at simultaneous high temperature and pressure. Single-crystal diffraction improves absolute accuracy in lattice constants over those from powder diffraction by a factor of 5 to 10. We have measured equations of state of orthoenstatite  $MgSiO_3$  and hexagonal boron nitride  $hBN$ .

## Background and Research Objectives

The earth sciences community has thoroughly accepted the principle that plate tectonics--that is, the large scale movement of relatively rigid surface blocks arising from convective motions within the silicate outer half of the Earth's radius--is responsible for surface geological activity and the consequent hazards of volcanos and earthquakes. However, geophysical and geochemical data have not yet been interpreted well enough to resolve a fundamental question that has persisted for more than two decades: "Does the mantle convect as a whole or are there (at least) two separate layers that differ in composition?" The nature of the discontinuity in seismic velocity and density at 670 km depth that forms the boundary between upper and lower mantle is at the heart of the issue. A phase change at this depth presents a relatively small inhibition to mantle convection through the discontinuity. On the other hand, if the density jump arises from a compositional discontinuity, then thermally driven convection requires a thermal boundary layer of the order of 1000 K before thermal expansion could overcome a density increase of about 0.1 g/cc and permit exchange of material between upper and lower mantle. Two

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possible compositional changes are (a) from dominantly olivine stoichiometry,  $(\text{Mg},\text{Fe})_2\text{SiO}_4$ , to dominantly pyroxene stoichiometry,  $(\text{Mg},\text{Fe})\text{SiO}_3$ , i.e., a change of Mg/Si ratio and (b) iron enrichment from a fraction  $\text{Fe}/(\text{Mg}+\text{Fe})$  approximately 0.1 to almost 0.2. Whether either or a combination of both these changes take place remains highly controversial.

Composition, temperature, and density variations result from the patterns of mantle convection, and they influence seismic velocity structure. However, the necessary reliable *laboratory* data that can be used to unambiguously relate seismic velocities and densities across the mantle are still lacking. The single most important parameter for resolving these issues is thermal expansion  $\alpha$ , which comes from accurate measurements of lattice constants at simultaneous high temperature  $T$  and pressure  $P$  of candidate mantle minerals of known composition. We have used such measurements with newly developed high temperature-high pressure, single-crystal diffraction techniques.

At depths shallower than 670 km the high pressure polymorphs of olivine and pyroxene exist in spinel, garnet, and ilmenite structures; below 670 km they are perovskite and rock salt structure.  $(\text{Mg},\text{Fe})\text{SiO}_3$  in its high pressure perovskite form is believed to be Earth's most abundant mineral. We have obtained both lattice constants and atom positions at high temperature and pressure (up to 1100 K at 25 GPa) using the superior accuracy of single-crystal x-ray diffraction methods and a *unique* diamond-anvil cell (DAC) developed at LANL. Lattice constants obtained on well-controlled P-T paths provide accurate isothermal bulk moduli and thermal expansion coefficients along with their pressure and temperature derivatives for reliable extrapolation to  $T$  and  $P$  beyond our present experimental capability.

### **Importance to LANL's Science and Technology Base and National R&D Needs**

An extremely important point is that this research helps maintain Los Alamos capability in static high-pressure research, a technology that underlies stockpile stewardship. This technology is a vital complement to and calibration for dynamic methods such as ATLAS or shock wave techniques.

This project comprises one feature of the Earth and Environmental Sciences core competency. Issues for nuclear nonproliferation, such as discriminating between natural and artificial seismic sources and locating those sources more accurately, require understanding the nature of deep mantle paths for seismic wave propagation. Thus, this work fits larger missions by providing data for further developing models used for nonproliferation studies because deep seismic paths principally pass through the materials

of this project. In the course of this work we have developed new software for analyzing diffraction patterns that should have wide national distribution.

## Scientific Approach and Accomplishments

### Approach

The single-crystal x-ray diffraction experiments are done with a unique high-T, high-P DAC specially developed at Los Alamos for such measurements. This DAC can be used on a single-crystal Huber diffractometer with a rotating anode x-ray generator for determining lattice constants for T up to 1200 K and P up to 20 GPa. For higher temperatures as well as for the x-ray intensity measurements to determine atom positions, the intense x-rays from LANL Beam Line 10-2 at the Stanford Synchrotron Radiation Laboratory (SSRL) are needed to reduce measurement time and therefore pressure drifts during each run.

The diamond-anvil cells used in these experiments are special Merrill-Bassett cells constructed from materials chosen to provide accurate, stable pressures and homogeneous temperatures. The entire cell is in an externally heated cavity in a water-cooled vacuum oven that prevents graphitization of diamonds (at high T trace amounts of oxygen catalyze graphitization) and minimizes power required. While this external heating imposes considerable demands on the materials of the cell, it also allows very uniform and easily measured temperatures from thermocouples placed on different parts of the cell. By constructing the DACs from carefully chosen combinations of refractory materials (typically, Inconel 718, Udimet 700, Mo/Re, Re and tungsten carbide), we can hold pressures constant (to within about 0.2 GPa) for many hours even as T is varied. Pressures can be determined from the lattice constants of Au, or spectroscopically from the Sm:YAG Y-line fluorescence or the  $^{13}\text{C}/^{12}\text{C}$  diamond Raman system currently being developed. One advantage of high-T experiments is that the pressures are easily kept hydrostatic.

The unique high-T DAC is designed to mount on Huber diffractometers at Los Alamos or Beam Line 10-2 at SSRL while maintaining the full freedom of motion required to orient samples during single-crystal diffraction experiments. The cell design takes advantage of the small dispersion of Ag K-alpha radiation (24 keV) from the rotating anode generator at Los Alamos or the slightly higher energies (27 keV) used at synchrotron sources. The short x-ray wavelengths provide a sufficient number of reflections even though the angular apertures in the tungsten carbide cones that support the diamond anvils are limited to only 60 degrees to maintain mechanical strength.

Although most high-T, high-P x-ray diffraction studies have involved powder diffraction, we concentrate on single-crystal methods, which offer many advantages. Accuracy in the lattice constants is improved by a factor of 5 to 10; statistical errors are much smaller, and systematic errors due to instrument or sample misalignment are easily detected and corrected. Reflections are much more intense so that data can be collected much more quickly. It is possible to obtain reliable intensities for determining atom positions as well. Two new features beyond normal high-pressure, single-crystal diffraction techniques that we will incorporate are: (a) an improved algorithm developed by L. W. Finger for determining lattice constants to about 1 part in 15000 by fitting peak positions (already in our diffractometer control programs at Los Alamos), and (b) intense synchrotron x-ray sources and image plates to collect data in short times.

In addition to Los Alamos facilities we have collaborated with colleagues at SUNY Stony Brook to use their large-volume, high-temperature press at the National Synchrotron Light Source at Brookhaven National Laboratory.

#### Accomplishments

Modifications to the DAC were made to ensure stable high pressure at simultaneous high temperatures. Along with 7 points for silicate perovskite we determined pressure and temperature derivatives of the bulk modulus and thermal expansion for orthoenstatite  $MgSiO_3$ , up to 1000 K at 1.5 GPa, with P up to 4.5 GPa at lower T. This result breaks previous records for single-crystal diffraction at high T and P and defines a new state of the art. Further, we conducted large-volume pressure-diffraction experiments up to 10 GPa and 1300 K using a synchrotron x-ray radiation source. Experimental data on two other materials,  $hBN$  and  $NaAlSi_2O_6$  jadeite, improve our understanding of thermoelasticities of materials and can be applied to modeling P-T systematics and mantle mineralogy.

As an example, using the unique diamond-anvil pressure cell and analytical software, we extended the pressure and temperature range for single crystal x-ray diffraction to record high levels. In the first use of this apparatus we measured thermoelastic properties for the equation of state of the  $MgSiO_3$  end member of the orthopyroxene series at temperatures to 1000 K and pressures to 4.5 GPa, conditions that apply to the uppermost mantle. Comprising about 20 to 30 molar percent of rocks considered to comprise the upper mantle, orthopyroxene is the second most abundant mineral (after olivine) in the first few hundred km. It is also a significant component of crustal rocks. Unit cell volumes at different temperatures and pressures from this work combined with data at ambient temperature and pressure were fitted to a thermoelastic equation of state based on the Birch-Murnaghan equation [Figure 1]. The resulting thermoelastic parameters are: thermal expansivity  $\alpha_v = 2.86(3) \cdot 10^{-5} + 0.72(16) \cdot 10^{-8}$

T, isothermal bulk modulus  $K_{T0} = 102.8(2)$  GPa, pressure derivative  $K_{T0}' = 10.2(1.2)$ , and temperature derivative  $(\partial K/\partial T)_P = -0.037(5)$  GPa/K. The importance of covering a sizeable regime in pressure-temperature is shown in the ability to make independent cross checks for consistency. Thus, the pressure derivative calculated from thermodynamics relation  $(\partial \alpha_v/\partial P)_T = -3.5 \cdot 10^{-6}$  K<sup>-1</sup> GPa<sup>-1</sup>, agrees well with the independently measured  $\Delta \alpha_v/\Delta P = -3.2 \cdot 10^{-6}$  K<sup>-1</sup> GPa<sup>-1</sup>.

We reported the first measurement of a complete set of thermoelastic equation of state of a clinopyroxene mineral. We conducted an *in situ* synchrotron x-ray diffraction study of jadeite at simultaneous high pressures and high temperatures. A modified Rietveld profile refinement program has been applied to refine the diffraction spectra of low symmetry and multiple phases observed in energy dispersive mode. Unit cell volumes, measured up to 8.2 GPa and 1280 K, are fitted to a modified high-temperature Birch-Murnaghan equation of state. The derived thermoelastic parameters of jadeite are: bulk modulus  $K = 124.5$  GPa with assumed pressure derivative of bulk modulus  $K' = \partial K/\partial P = 5.0$ , temperature derivative of bulk modulus  $\partial K/\partial T = -1.65 \times 10^{-2}$  GPa K<sup>-1</sup>, and volumetric thermal expansivity  $\alpha = a + bT$  with values of  $a = 2.56 \times 10^{-5}$  K<sup>-1</sup> and  $b = 0.26 \times 10^{-8}$  K<sup>-2</sup>. We also derived thermal Grüneisen parameter  $\gamma_{th} = 1.06$  for ambient conditions; Anderson-Grüneisen parameter  $\delta_{T0} = 5.02$ , and pressure derivative of thermal expansion  $\partial \alpha/\partial P = -1.06 \times 10^{-6}$  K<sup>-1</sup> GPa<sup>-1</sup>. From the  $P$ - $V$ - $T$  data and the thermoelastic equation of state, thermal expansions at five constant pressures of 1.0, 2.5, 4.0, 5.5, and 7.5 GPa are calculated. The derived pressure dependence of thermal expansion is:  $\Delta \alpha/\Delta P = -0.97 \times 10^{-6}$  K<sup>-1</sup> GPa<sup>-1</sup> [Figure 2] in good agreement with the thermodynamic relations.

A synchrotron x-ray diffraction study on hexagonal boron-nitride (*h*BN) was conducted at simultaneous high pressures and temperatures. The pressure applied to the sample is pseudo-hydrostatic up to 9.0 GPa and the temperature was homogeneous in the range of 300 K to 1280 K. A modified Rietveld profile refinement has been applied to these diffraction spectra of low symmetry and multiple phases observed in the energy-dispersive mode. Thermoelastic parameters of *h*BN were derived by fitting a modified high-temperature Birch-Murnaghan equation of state. The results are: bulk modulus  $K = 17.6$  GPa, pressure derivative  $K' = \partial K/\partial P = 19.5$ , temperature derivative  $\partial K/\partial T = -0.69 \times 10^{-2}$  GPa/K, volumetric thermal expansivity  $\alpha =$

$a + bT$  with values of  $a=4.38 \times 10^{-5} \text{ K}^{-1}$  and  $b=1.75 \times 10^{-8} \text{ K}^{-2}$ , respectively. It is observed that the thermal expansion and compression along different crystal axes are significantly different. The crystal  $c$ -axis is much more expandable and compressible than the  $a$ -axis. This is attributed to the layered structure of the  $h$ BN. Because the thermoelastic equations of state of  $h$ BN and NaCl are quite different, the unit cell volumes of these two materials, derived from the same diffraction pattern, can be used to derive the experimental  $P$ - $T$  conditions. The large intersection angle of isochoric lines of these phases in  $P$ - $T$  space ensures a determination of  $P$ - $T$  with satisfactory precision [Figure 3]. The application and limitations of this method in obtaining experimental pressure and temperature using diffraction data and thermoelastic equations of state of multiple phases are discussed below.

The accomplishments described above came about in part because we have made important advances in some of the underlying high pressure technology as a part of this work. We have developed the two best pressure sensor systems for use at high pressure and temperature: the  $^{13}\text{C}/^{12}\text{C}$  diamond Raman sensor system and the Sm:YAG Y1 fluorescence system with a 10-line fit. A considerable amount of work has been required to make these both easy to use and accurate. The  $^{13}\text{C}/^{12}\text{C}$  diamond Raman sensor system is especially good for aqueous samples. It has long been known that the Raman peak of a  $^{12}\text{C}$  diamond chip under hydrostatic pressure in the sample chamber of a diamond cell emerges from the Raman spectra of the diamond anvils (under uniaxial stress) above 13 GPa. We discovered that the Raman spectrum of  $^{13}\text{C}$  diamond can be observed up to 13 GPa in a diamond-anvil cell. Thus, by placing  $^{13}\text{C}$  and a  $^{12}\text{C}$  diamond chip in the sample chamber, pressures can be measured for any sample chemically compatible with a high  $P$ - $T$  diamond-anvil cell. The pressures can be measured to better than 0.3 GPa over the entire range 0 - 25 GPa at 10 - 1200 K.

The Y1 peak of Sm:YAG can be used to measure pressures in a manner similar to that of the more familiar ruby fluorescence method. Sm:YAG provides a useful signal even above 1100 K, while ruby cannot be used above about 700 K. While not compatible with as many samples as the  $^{13}\text{C}/^{12}\text{C}$  diamond Raman sensor system, Sm:YAG provides much stronger signals. We have finally developed a procedure for accurately determining the Y1 positions at high  $P$ - $T$ , by fitting the ten nearest peaks around the Y1 peak position. Because the relative intensities, widths and positions of all the peaks shift markedly with temperature, developing a robust algorithm for determining pressures has proved to be no small labor. Pressures can be measured with the new 10-line fitting procedure to better than 0.4 GPa up to at least 19 GPa at 1100 K.

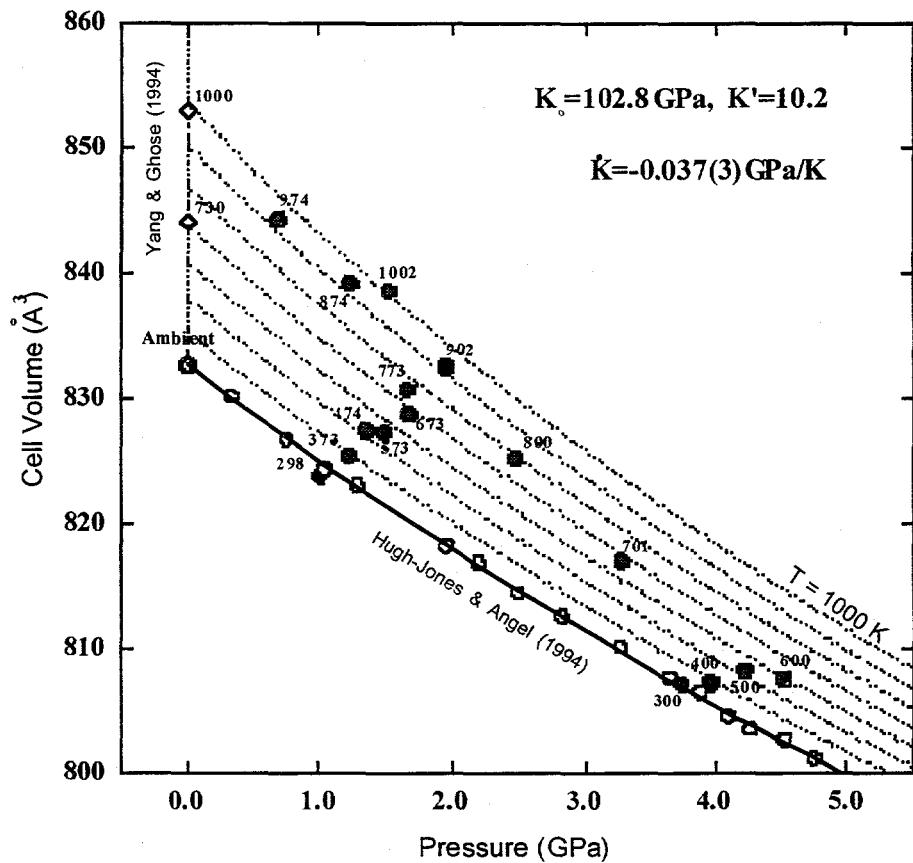
In a thorough study, we have also shown that no deviatoric stresses are caused by the high viscosity silicone fluid used to hold the crystals in place in the high  $P$ - $T$  single-crystal x-ray experiments, and that this fluid can serve as a new hydrostatic pressure medium.

The DOE designated these facilities as Technology Deployment Center/User Facilities. They are the Extreme Pressure and Temperature Diamond-Anvil Cell Laboratory and the Advanced X-Ray Diffraction Laboratory.

## Publications

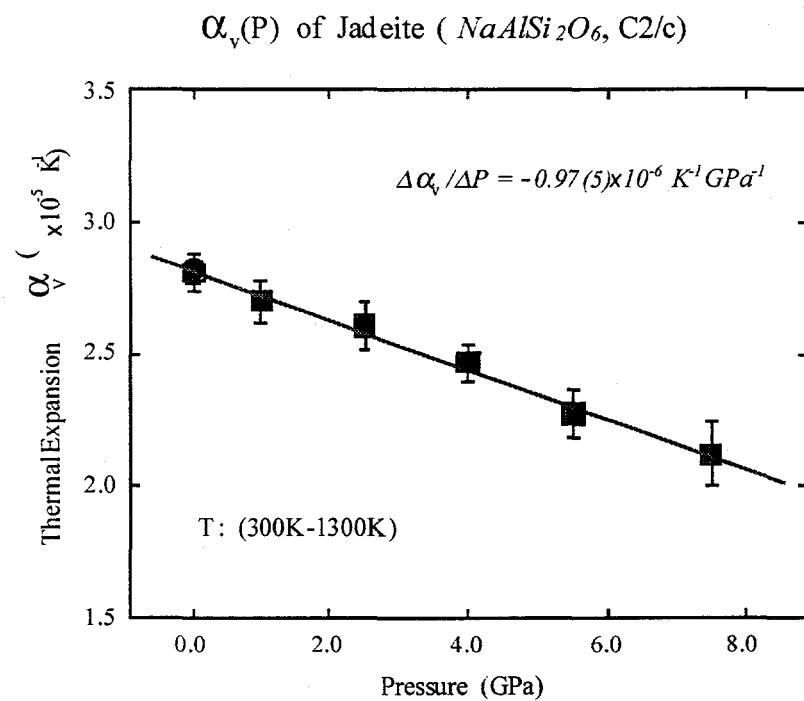
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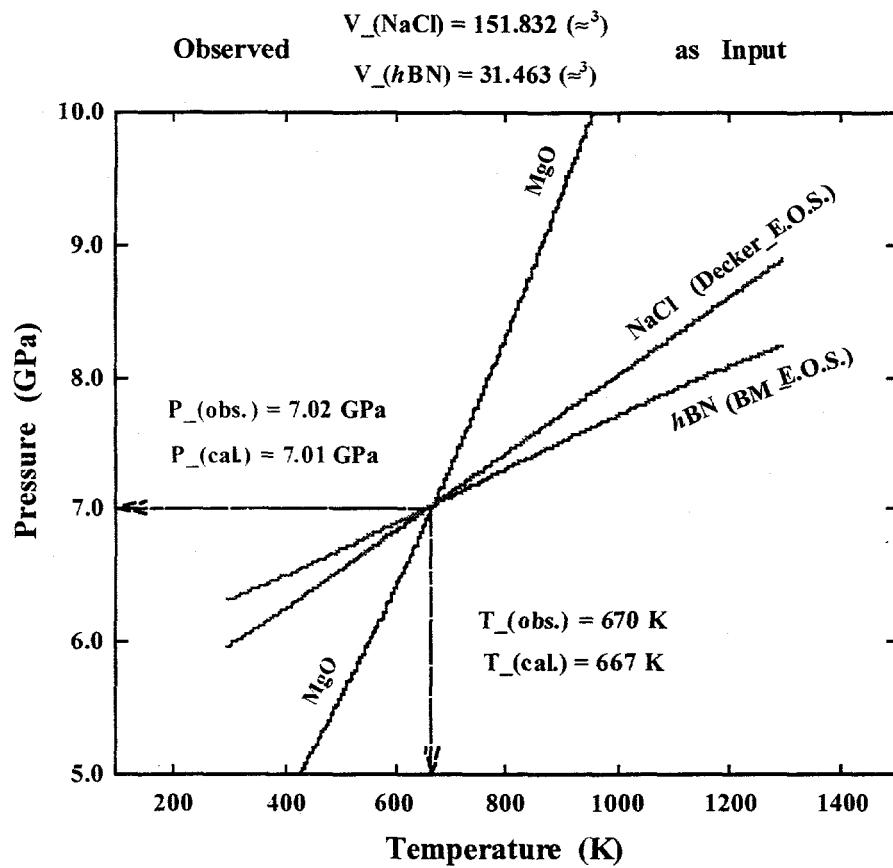
## Compression of $\text{MgSiO}_3$ Orthoenstatite @ High Temperatur



**Figure 1.** The cell volume  $V(P,T)$  of the orthoenstatite against pressure. The temperatures (K) are labeled next to the data points in the diagram. The dotted lines represent the fitted isothermal compressions with temperature steps of 100 K from 300 ~ 1000 K.

**Figure 2.** Thermal expansions of jadeite  $\text{NaAlSi}_2\text{O}_6$  plotted as a function of pressure. The slope of the fitted straight line represents pressure derivative of thermal expansion,  $\Delta\alpha/\Delta P$ . Solid circle is the regression result for thermal expansion at atmospheric pressure  $\alpha_0$ .





**Figure 3.** Determination of pressure and temperature from the observed cell volume  $V_{\text{obs}}(\text{NaCl})$  and  $V_{\text{obs}}(\text{hBN})$  and their thermoelastic equations of state. The intersection point ( $P_{\text{cal.}}$ ,  $T_{\text{cal.}}$ ) of isochoric of NaCl, hBN, and MgO closely matches experimental ( $P_{\text{obs.}}$ ,  $T_{\text{obs.}}$ ) conditions.