High-pressure characterization techniques & their applications for materials in extreme environments

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1. Introduction of the Field

Advancements in the field of materials science, physics, engineering, and chemistry call upon materials to perform under extreme environments, such as great sub surfaces, outer planets, or deep seas, with drastic conditions including high pressure, raised temperature, strong electric or magnetic fields, high radiation flux, thermal or mechanical shock, or extremely destructive chemistry. The ability to simulate such climates opens the door for scientific investigation of previously unexplored and inaccessible regions. Understanding the response of materials when subjected to the conditions is critical in creating appropriate experiments with suitable tools and techniques. The impact of such extreme conditions can vary many material properties, inducing advantageous phase transformations, and even synthesizing novel advanced materials. Pressure and temperature are interesting conditions to examine, as their values can change so drastically depending upon environmental location; at the Earth's surface, pressure and temperature are recorded as 10^{-4} GPa and 298 K respectively, while at 6400 km below the Earth's surface, pressure and temperature are recorded as 364 GPa and 5000K respectively.[1] The simulation of the non-ambient conditions found below the Earth's surface has led to the discovery of a new class of iron oxide compounds, namely the Fe_4O_5 polymorph.[2] Because iron and oxygen compromise two of the most abundant and important elements on Earth, investigation of this newly discovered compound is crucial for propelling the understanding of phases present within the Earth's interior.[3] This proposal explores the materials science interest in the synthesis of a novel material and its response to extreme environments by examining high-pressure and high-temperature conditions of 65 GPa and 2800 K via characterization techniques Raman spectroscopy and X-ray diffraction.

2. Fundamentals Background

Pressure, or the perpendicular force applied to the area of a surface, is a thermodynamic variable that can be used to describe a condition for the state of a system.[4] Pressure is an intensive

state function, meaning that it describes a current condition of a point within a system. High-pressure conditions can alter atomic and molecular interactions.[5] By increasing the pressure applied to a material, atomic volume is decreased such that there is a shortening of interatomic distance. As a result of this volume contraction, atoms are brought closer together creating a larger overlap between electronic orbitals. For example, the transition of layered hexagonal graphite with sp^2 C-C bonding to synthetic polycrystalline cubic diamond with sp^3 C-C bonding under high pressure results in a decrease of the interatomic distance between layers.[6,7] Consequently, the newly formed diamond becomes more energetically favorable, as the applied pressure reduces the previously-high energy activation barrier.[6,7]

Alterations to the hybridization of outer electronic orbitals creates higher repulsive energies, permitting the exploration of once previously inaccessible areas of potential energy. It is possible that electrons can change the ordering of outer atomic orbitals by relocation from occupied to unoccupied regions. Simultaneously, chemical bonding is modified as once weak Van der Waals and hydrogen bonds become stronger ionic or covalent bonds. For example, when subjected to high pressures around 11 GPa, curium pyrrolidine-dithiocarbamate reports alterations to the bonding nature where reductions in the distance between curium(III) and coordinating ligand sulfur atoms, and changes in the involvement of the half-filled 5*f* shell result in a strengthened degree of covalency between metal-ligand bonds.[8] Curium, a highly radioactive inert element in the actinide series, is discovered to have drastically different magnetic interactions within the crystal structure after being subjected to manipulation via pressurization.[9,10] The reduction of interatomic distance can also result in other material changes besides stability, including chemical reactivity and electronic properties. These reductions can establish extraordinary bonding, creating compounds that were once unattainable at ordinary atmospheric conditions. Similarly, alterations to bonding

distances can lead to changes in band structures. Overlaps in band structures, and their resulting broadened effect, can induce a conversion from insulators to conductors.[7]

Much like pressure, temperature is also a crucial thermodynamic variable. This intensive state function is used to describe the trend of systems giving up energy to nearby surroundings via an exchange of heat.[4] In general, increases in temperature cause materials to become more soft, ductile, and weak.[11] While classes of products such as metals, ceramics and polymers vary in atomic bonding types, it is understood that most materials experience a decrease in the modulus of elasticity, or Young's modulus, with increasing temperature.[11] Alterations to temperature can similarly generate desirable phase transformations with techniques such as annealing and tempering resulting in reductions to internal stress and promotions to toughness.[11]

From a thermodynamic perspective, inducing a transformation via high-pressure or high-temperature results in the formation of a metastable phase. A phase, or portion of a system with uniform characteristics, was originally proposed by J.W. Gibbs in examination of a larger system.[11,12] When there is an adjustment to a system, for example through pressure or temperature, there is a change to the internal energy, or Gibbs free energy. As a result, a metastable phase will be of a non-equilibrium state with higher Gibbs free energy than that of a stable phase.[13] Thus analyzing the effects of both high-temperature and high-pressure on material properties is key in understanding the transformation of material phases and the synthesis of novel products.[1]

Iron oxide, an important complex material involved in many geological processes, is the prime example of a material that undergoes phase transformations when subjected to high-pressure and high-temperature. At ambient conditions, several different types of iron oxides exist with various ferrous (Fe^{+2}) and ferric (Fe^{+3}) iron ratios, including wustite (FeO), hematite (Fe_2O_3), and magnetite (Fe_3O_4).[2] While iron oxides are usually investigated because of their magnetic properties and use in semiconductors, catalysts, and pigments, Fe_3O_4 is heavily explored because of its mixed

valence chemistry and spinel structure.[14-16] In 2011, research by Lavina et al. that was investigating the highly-debated structure and diffraction peaks of Fe_3O_4 discovered, for the first time, the new iron oxide phase Fe_4O_5.[17] Although initial experimentation predicted Fe_4O_5 stability within the upper mantle at pressure values up to about 30 GPa, recent investigation has discovered that Fe_4O_5 stability can withstand pressure values up to about 40 GPa.[17,18] Further study of Fe_4O_5 is integral in not only alleviating uncertainty regarding response to high-pressure and high-temperature conditions, but also in advancing the fundamental iron-oxygen phase diagram.[17]

3. High-Pressure & High-Temperature Instrumentation Background

Research of high-pressure extreme conditions has proven difficult since the progress of high-pressure instrumentation has lagged behind other techniques, such as those used for catalysis or high-temperature applications.[19] Because high-pressure devices, including press machines and compressors, are often expensive and small, research is often complemented by theoretical modeling including classical molecular dynamics (CMD) and ab initio molecular dynamics (AIMD).[19,20] For experimental high-pressure methods, there are two types of pressure, dynamic and static, that vary the applicable testing apparatuses. Dynamic pressure, which can be generated through laser-generated shock wave technology, can range from 100-700 GPa with volumes of 1-10 cm^3.[19] In the exploration of nano diamonds, scientists have utilized pulsed high-power lasers that can achieve high-pressures, sometimes even along the TPa scale, and high-temperatures, along the 10^5 K scale, for short bursts of time.[19,20] Static pressure, which can be generated through piston-cylinders or Bridgman-anvils, can range from 0.1-1 GPa with larger volumes of 0.01-1 m^3 or from 3-15 GPa with smaller volumes of 0.1-10 cm^3.[19] In particular, Bridgman-anvil cells can produce significantly higher applied pressures depending on the type of anvil cell used, with hard alloy anvils applying 5-7 GPa, SiC anvils applying 20-70 GPa, and diamond anvils applying 100-300 GPa.[19] Research by Ming and Bassett discovered a new technique for combining ultrahigh static

pressures, ranging up to 300 GPa, and temperatures, ranging up to 6000 K, through the creation of the laser-heated DAC (LH-DAC).[5,21,22] As a result, the DAC is one of the most compelling techniques for high-pressure research worthy of further investigation.

Diamond, which is typically limited in size from ⅓ to ½ carat, is used in anvil cells because of hardness, transparency, chemical inertness, electrical and magnetic compatibility, and thermal conductivity.[20,23] Typically, diamonds used in the DAC are expertly cut along specific crystallographic planes, with preference being parallel to the (100) plane.[22,23] In particular, the transparency of diamond to infrared, visible, and ultraviolet radiation below 5 eV and to X-ray above 10 keV makes it an excellent material to be used with clear windows for in-situ spectroscopy, diffraction and imaging techniques.[20,23] Furthermore, the light weight and small nature of both diamonds and the DAC enable ease of transportation between laboratories.[20]

The primary concept behind the DAC technique uses the cutlets of two opposing gem-quality diamond anvils to compress a small sample (typically 100 μg or less).[20,23] When a force is applied to the piston diamond, as shown in **Figure 1**, these two anvils are sandwiched between a pre-indented metallic gasket (typically 200-300 μm thick).[20,22] A pressure is applied, usually through translational screws, that ensures the perfect alignment of the two coaxial anvils and parallel cutlets.[22-26] In response to the pressure, the small sample hole, which lies between two tiny cutlets, is sealed and forms a high-pressure chamber.[20,22] Generally, a pressure transmitting medium (PTM) is also enclosed into the chamber with the specimen in an attempt to homogenize any applied stresses and promote hydrostatic activity.[20] Selecting the appropriate PTM for investigation is crucial as

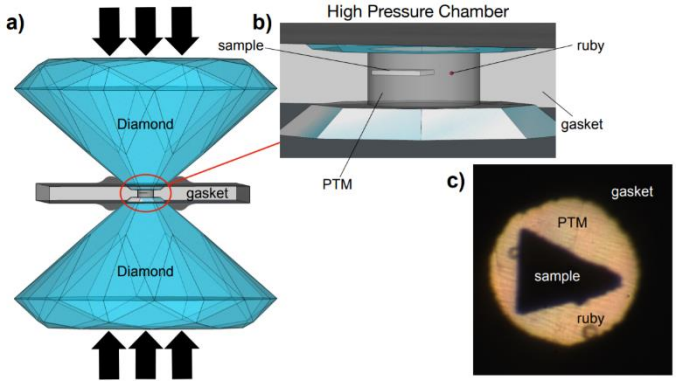

Figure 1: (a) Concept behind DAC technique. **(b)** High-pressure chamber. **(c)** Top view real image of loaded high-pressure chamber.[22]

compatibility with the sample and experimental conditions must be guaranteed to avoid issues related to heat and material loss, chemical reactivity and deviatoric stress.[22,23,27]

The primary concept behind the LH-DAC uses a laser to spot heat the sample through the transparent diamond window while simultaneously avoiding unwanted interactions with the DAC, anvils and gasket.[22,23] LH-DAC enables researchers to achieve ultrahigh static pressure and temperature values without the risk of rapid graphitization of diamond or damage to the anvil cells.[28] The specimen material type dictates the experimental laser type, where transparent materials use a CO_2 laser while opaque materials use either an Nd:YAG (Nd^{3+} doped yttrium aluminum garnet) or an Nd:YLF (Nd^{3+} yttrium lithium fluoride) near-infrared (IR) laser.[22] Lasers within the LH-DAC are tightly focused and a double-sided "hot plate" laser-heating system is used to irradiate a sample from both sides, ensuring that consistent temperatures minimize axial thermal gradients within sample data.[22,29]

Temperature measurements in the LH-DAC are taken through spectral radiometry, where the thermal radiation signal is fitted to Planck's radiation function.[23] To minimize thermal gradients, new research employs a peak-scaling method to create a temperature map.[22,30-32] By using a pseudo-Planck curve and data from a spectrometer, the light collected within a particular region is averaged to produce a monochromatic image.[22] Pressure measurements in the LH-DAC are taken through a primary/absolute or secondary scale. The absolute scale is established by the piston cylinder, shock wave measurements, or density and elasticity measurements.[20] Research by Smith et al. discovered a more accurate way of determining an absolute scale by utilizing integration of the isothermal bulk modulus to determine true thermodynamic pressure via spectroscopy, ultrasonic, and Brillouin scattering measurements.[33] The secondary scale can either be fixed or continuous, and is determined from calibration of internal given standards that are loaded with the specimen into the high-pressure

chamber.[20] Typically, ruby will be used as the material standard in high-pressure conditions and gold or platinum will be used as the material standard in ultrahigh-pressure conditions.[20, 34]

4. Characterization Techniques

In considering the various types of high-pressure and high-temperature research methods suitable for basic and applied materials science research, it becomes clear that several in-house laboratory and synchrotron characterization techniques are available to be used in-situ with LH-DAC. A few of the high-pressure and high-temperature techniques can include Raman spectroscopy, Brillouin scattering, Nuclear Magnetic Resonance (NMR), X-ray diffraction (XRD), and X-ray absorption (XAS).[22,23] In this proposal, the applied characterization techniques will include Raman spectroscopy and XRD.

Raman spectroscopy is a technique most used for materials characterization. This technique is often applied in exploration of condensed matter to investigate structural and dynamic properties by discerning the spectra pattern of a material from characteristic wavelengths.[5,28] When combined with LH-DAC, Raman can gather critical information on phonon spectra and electron-phonon interactions to understand the lattice vibrations of a sample after being subjected to extreme conditions.[28] However, it is worth noting that use of Raman in both high-pressure and high-temperature conditions is rare not only for typical LH-DAC investigations but also for Fe_4O_5 specifically. Because Raman methods can pose innovative means of exploring high-pressure and high-temperature conditions, risks are associated with the technique. In particular, Raman may include unreliable data, poor resolution, and excessive noise, all of which can be solved by ensuring that the excitation laser spot is smaller than the heat laser spot, the camera and monitor is focused when collecting scattering measurements, and a filter is applied to the Nd:YLF laser heating system that diminishes background thermal emission.[28]

XRD is a technique most used for examining the crystal structure of materials since synchrotron sources provide powerful, polarized X-ray radiation.[23] When combined with LH-DAC, XRD can execute time-resolved characterization of samples to understand the structural and chemical evolution after being subjected to extreme conditions.[22] To minimize thermal gradients within sample data, X-ray beams should be clean and well collimated, and specimen sizes should be small and well contained.[22] It is worth noting that XRD can be used for both single crystal samples and polycrystalline samples, where the former uses diffraction spots to understand crystal orientation while the latter uses overlapping diffraction rings to understand random crystal orientation.[23] While noise from diffraction spots is often considered to be an issue, various software packages, such as Fully Automatic Beam Line Experiment (FABLE), assist in processing and cataloging diffraction spots by regarding crystallites as separate crystals with individual crystallographic orientations.[23] Other techniques for improving resolution, namely reducing undesired shadow signals, include allowing temperature measurements to only be collected from the upstream side, thus blocking diffraction from optical components, and using transparent mirrors to pass X-ray beams from both sides, thus allowing for the collection of temperature measurements without inducing scattering.[22] Other strategies have resolved issues related to signal and detector time by mounting LH-DAC systems directly on undulator beamlines.[22]

5. Synthesis, Testing & Data Analysis/Refinement

Following the research of Lavina et al., the discoverer of Fe_4O_5, the experiment is conducted in a diamond anvil cell through the breakdown of siderite ($FeCO_3$) at 10 GPa and 1800K.[17] This method enables the material to behave like a single crystal where the *c* axis is nearly parallel to the load axis, thus giving a large compressibility potential.[17] The experimental setup for LH-DAC incorporates a double-sided Nd:YLF laser heating system with a pressure of 65 GPa and a temperature of 2800 K, conditions that have not been previously explored for Fe_4O_5.

In-situ XRD measurements are conducted using an X-ray beam of 30 keV focused to 5×5 μm along an 0.393545 Å wavelength.[17] For in-situ XRD characterization, samples are loaded directly into the specimen chamber with a ruby pressure gauge and Ne PTM.[17,18] Data will be analyzed and modeled theoretically using the General Structure Analysis System (GASS), where single-phase patterns will be used to generate comprehensive diffraction images.[17] The results from this experiment will feed into further refinement of the iron oxide phase diagram, as the entire Fe_4O_5 compound still includes perplexing regions. As demonstrated in previous research, varying the experimental pressure and temperature conditions provides the data necessary to develop a more accurate understanding of Fe_4O_5 stability.[17,18]

In-situ Raman spectroscopy uses the LH-DAC in the continuous donut TEM_{01} mode.[28] Raman measurements are taken through an Acton SpctraPro500i spectrograph that is equipped with a thermally cooled charge-coupled device (CCD) camera. Following the research of Zhou et al., the spectrograph uses a 350 mm focal length and 0.05 nm wavelength resolution at 435.8 nm, and the excitation laser uses a 200 mW Ar^+ ion laser.[28] Data is collected via the spectral radiometry technique and the Raman system technique that permits analysis of Raman spectra and visually-monitored images.[28] The results of this experiment will feed into further refinement by confirming any pressure-induced shifts worthy of further investigation.[20]

6. Summary

The exploration of the iron oxide Fe_4O_5 represents an underexplored means of utilizing advanced characterization techniques to investigate materials under extreme conditions. This proposal researches the effects of high-temperature and high-pressure on the synthesis of a metastable polymorph with a laser-heated diamond anvil cell. Analysis of unexplored experimental conditions furthers the understanding of the innovative tools available for advanced materials science research.

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