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14. ABSTRACT We report on our progress in developing new techniques and experiments for studies of fast chemical transformations in energetic materials under conditions of high pressure and temperature. We have developed a new ultrafast mid-to-near infrared (IR) system equipped with modulated and/or continuous wave laser heating, and completed an absorption system for measuring in situ materials at high pressures and temperatures. The systems utilize ultrafast pulse amplifying instrument (Coherent Legend Elite) in combination with an optical parametric amplifier (OPA) for generation of a range of short pulsed frequencies used to study the dynamics of chemical					
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Report Title

Final Report: Probing of Fast Chemical Dynamics at High Pressures and Temperatures using Pulsed Laser Techniques

ABSTRACT

We report on our progress in developing new techniques and experiments for studies of fast chemical transformations in energetic materials under conditions of high pressure and temperature. We have developed a new ultrafast mid-to-near infrared (IR) system equipped with modulated and/or continuous wave laser heating, and completed an absorption system for measuring in situ materials at high pressures and temperatures. The systems utilize ultrafast pulse amplifying instrument (Coherent Legend Elite) in combination with an optical parametric amplifier (OPA) for generation of a range of short-pulsed frequencies used to study the dynamics of chemical systems, as well as the newly purchased pulsed broadband source (Leukos Pegasus).

Experimental progress has excelled in the study of high-energy density materials (HEDMs), with promising results coming from the nitrogen-hydrogen mixtures. Results conclude that at high pressures (>47 GPa) a nitrogen backbone structure is formed and stabilized by surrounding hydrogen atoms, in deep contrast to compressed pure nitrogen at these pressures. Moreover, we show through the use of photon or multi-photon absorption that we can generate similar compounds at significantly lower pressures (~ 10 GPa). The metastability of these compounds was found to be fairly large, some even recoverable at ambient pressures and colder temperatures. To enhance our understanding of $N_2:H_2$ systems, alterations in the ratio of nitrogen to hydrogen mixture have been studied, specifically on high-hydrogen mixtures. In addition to HEDMs we have also studied noble gases under extreme conditions using combined compression and short-duration laser heating to study the evolution and dynamics of planets and stars.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
02/28/2013 28.00	Michael R. Armstrong, Jonathan C. Crowhurst, Sorin Bastea, William M. Howard, Joseph M. Zaug, Alexander F. Goncharov. Prospects for achieving high dynamic compression with low energy, <i>Applied Physics Letters</i> , (09 2012): 0. doi: 10.1063/1.4751107
02/28/2013 30.00	Elissaios Stavrou, Muhtar Ahart, Mohammad F. Mahmood, Alexander F. Goncharov. Probing the different spatial scales of Kel F-800 polymeric glass under pressure, <i>Scientific Reports</i> , (02 2013): 0. doi: 10.1038/srep01290
02/28/2013 29.00	John S. Tse, Hui Wang, Jianjun Yang, Alexander F. Goncharov, Viktor V. Struzhkin, Ross T. Howie, Eugene Gregoryanz. Bonding, structures, and band gap closure of hydrogen at high pressures, <i>Physical Review B</i> , (01 2013): 0. doi: 10.1103/PhysRevB.87.024101
03/23/2014 31.00	Yu.A. Freiman, A. Grechnev, S.M. Tretyak, A. F. Goncharov, R.J. Hemley. Sound velocities in solid hydrogen under pressure, <i>Low Temperature Physics</i> , (01 2013): 548. doi:
03/23/2014 35.00	Ross T. Howie, Eugene Gregoryanz, Alexander F. Goncharov. Hydrogen (deuterium) vibron frequency as a pressure comparison gauge at multi-Mbar pressures, <i>Journal of Applied Physics</i> , (08 2013): 73505. doi: 10.1063/1.4818606
03/23/2014 32.00	A.F. Goncharov, R.T. Howie, E. Gregoryanz. Hydrogen at extreme pressures, <i>Low Temperature Physics</i> , (02 2013): 523. doi:
03/24/2014 33.00	Yu.A. Freiman, A. Grechnev, S.M. Tretyak, A.F. Goncharov, C.S. Zha, Russell J. Hemley. Sound velocities of hexagonal close-packed H ₂ and He under pressure, <i>Physical Review B</i> , (12 2013): 214501. doi:
03/24/2014 36.00	Sergey S. Lobanov, Pei-Nan Chen, Xiao-Jia Chen, Chang-Sheng Zha, Konstantin D. Litasov, Ho-Kwang Mao, Alexander F. Goncharov. Carbon precipitation from heavy hydrocarbon fluid in deep planetary interiors, <i>Nature Communications</i> , (09 2013): 0. doi: 10.1038/ncomms3446
03/24/2014 37.00	W.W. Zhang, A.R. Oganov, A.F. Goncharov, Q. Zhu, S.E. Boulfelfel, A.O. Lyakhov, E. Stavrou, M. Somayazulu, Z. Konopkova, V.B. Prakapenka. Unexpected stoichiometries of stable sodium chlorides, <i>Science</i> , (12 2013): 1502. doi:
08/30/2011 3.00	Alexander F. Goncharov, Vitali B. Prakapenka, Viktor V. Struzhkin, Innokenty Kantor, Mark L. Rivers, D. Allen Dalton. X-ray diffraction in the pulsed laser heated diamond anvil cell, <i>Review of Scientific Instruments</i> , (11 2010): 1. doi: 10.1063/1.3499358
08/30/2011 8.00	Natarajan Subramanian, Alexander F. Goncharov, Viktor V. Struzhkin, Maddury Somayazulu, Russell J. Hemley. Bonding changes in hot fluid hydrogen at megabar pressures, <i>Proceedings of the National Academy of Sciences(US)</i> , (02 2011): 1. doi:
08/30/2011 7.00	Alexander F. Goncharov, N. Subramanian, T. R. Ravindran, Maddury Somayazulu, Vitali B. Prakapenka, Russell J. Hemley. Polymorphism of dense, hot oxygen, <i>The Journal of Chemical Physics</i> , (08 2011): 1. doi: 10.1063/1.3626860

- 08/30/2011 6.00 Alexander F. Goncharov, Russell J. Hemley, Ho-kwang Mao. Vibron frequencies of solid H₂ and D₂ to 200 GPa and implications for the P–T phase diagram, *The Journal of Chemical Physics*, (05 2011): 1. doi: 10.1063/1.3574009
- 08/30/2011 5.00 Andrew Kung, Alexander F. Goncharov, Chang sheng Zha, Peter Eng, Wendy L. Mao. Compressional, temporal, and compositional behavior of H₂-O₂ compound formed by high pressure x-ray irradiation, *The Journal of Chemical Physics*, (06 2011): 1. doi: 10.1063/1.3599479
- 08/30/2011 4.00 Alexander Goncharov, Timothy Strobel, Christopher Seagle, Zhenxian Liu, Maddury Somayazulu, Viktor Struzhkin, Russell Hemley. High-pressure study of silane to 150 GPa, *Physical Review B*, (04 2011): 1. doi: 10.1103/PhysRevB.83.144102
- 08/30/2012 13.00 Yasmin Kadry, Mohammad F. Mahmood, Alexander F. Goncharov, Jennifer Ciezak-Jenkins, R. Stewart McWilliams. Structural and chemical properties of the nitrogen-rich energetic material triaminoguanidinium 1-methyl-5-nitriminotetrazolate under pressure, *The Journal of Chemical Physics*, (08 2012): 0. doi: 10.1063/1.4732097
- 08/30/2012 23.00 Alexander F. Goncharov, Russell J. Hemley, Ho-kwang Mao. Vibron frequencies of solid H₂ and D₂ to 200 GPa and implications for the P–T phase diagram, *The Journal of Chemical Physics*, (05 2011): 0. doi:
- 08/30/2012 20.00 J. G. O. Ojwang, R. Stewart McWilliams, Xuezhong Ke, Alexander F. Goncharov. Melting and dissociation of ammonia at high pressure and high temperature, *The Journal of Chemical Physics*, (08 2012): 0. doi: 10.1063/1.4742340
- 08/30/2012 18.00 Ross Howie, Christophe Guillaume, Thomas Scheler, Alexander Goncharov, Eugene Gregoryanz. Mixed Molecular and Atomic Phase of Dense Hydrogen, *Physical Review Letters*, (03 2012): 0. doi: 10.1103/PhysRevLett.108.125501
- 08/30/2012 17.00 Alexander F. Goncharov. Raman Spectroscopy at High Pressures, *International Journal of Spectroscopy*, (10 2012): 0. doi: 10.1155/2012/617528
- 08/30/2012 16.00 Javier A. Montoya, Alexander F. Goncharov. Finite element calculations of the time dependent thermal fluxes in the laser-heated diamond anvil cell, *Journal of Applied Physics*, (06 2012): 0. doi: 10.1063/1.4726231
- 08/30/2012 15.00 Douglas Allen Dalton, M. Somayazulu, Alexander F. Goncharov, Russell J. Hemley. Static Compression of Tetramethylammonium Borohydride, *The Journal of Physical Chemistry A*, (10 2011): 0. doi: 10.1021/jp204642b
- 08/31/2012 24.00 Alexander F. Goncharov, N. Subramanian, T. R. Ravindran, Maddury Somayazulu, Vitali B. Prakapenka, Russell J. Hemley. Polymorphism of dense, hot oxygen, *The Journal of Chemical Physics*, (08 2011): 0. doi:
- 10/05/2010 1.00 A. Goncharov, J. Montoya, N. Subramanian, V. Struzhkin, A. Kolesnikov, M. Somayazulu, R. Hemley. Laser heating in diamond anvil cells: developments in pulsed and continuous techniques, (10 2010): . doi:
- 10/05/2010 2.00 N. Subramanian, V. Struzhkin, A. Goncharov, R. Hemley. A virtual experiment control and data acquisition system for in situ laser heated diamond anvil cell Raman spectroscopy, *Review of Scientific Instruments*, (08 2010): . doi:
- 12/17/2014 38.00 Motohiko Murakami, Alexander F. Goncharov, Naohisa Hirao, Ryo Masuda, Takaya Mitsui, Sylvia-Monique Thomas, Craig R. Bina. High-pressure radiative conductivity of dense silicate glasses with potential implications for dark magmas, *Nature Communications*, (11 2014): 0. doi: 10.1038/ncomms6428

TOTAL: 26

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Nicholas Holtgrewe**, Alexander Goncharov, Mohammad F. Mahmood, Synthesis of Energetic Nitrogen and Hydrogen Compounds Using High Pressure and Multiphoton Absorption, Poster at the Gordon Research Conference on High Pressure at University of New England, Biddeford, Maine, June 22-27, 2014.

Alexander Goncharov, Invited talk: Exotic chemistry rules at high pressures, Gordon Research Conference on High Pressure at University of New England, Biddeford, Maine, June 22-27, 2014.

Alexander Goncharov, High-pressure synthesis of novel materials with new bonding patterns and unusual stoichiometries, Invited talk at 2014 IUCr Congress and General Assembly, August 2014, Montreal, Canada.

Alexander Goncharov, Elissaios Stavrou*, Sergey Lobanov, Artem R Oganov, Valery Rosen, Artem Chanyshv, Konstantin Litasov, Zuzana Konopkova, Kirill Zhuravlev, Vitali Prakapenka, Structure of methane and ethane at high pressures, 2014 IUCr Congress and General Assembly, Poster.

Number of Presentations: 4.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
08/30/2011 9.00	Alexander F. Goncharov, Viktor V. Struzhkin, M. Somayazulu, Russell J. Hemley, N. Subramanian. Probing Hydrogen at Extreme Conditions by Raman Spectroscopy, Proceedings of the 55th DAE Solid State Physics Symposium 2010. , . : ,
08/31/2012 27.00	Alexander F. Goncharov, D. Allen Dalton, R. Stewart McWilliams, Mohammad F. Mahmood. Development of ultrafast spectroscopic techniques to study rapid chemical and physical changes in materials under extreme pressure and temperature conditions, Mater. Res. Soc. Symp.. 20-JAN-11, . : ,
TOTAL:	2

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

<u>Received</u>	<u>Paper</u>
08/30/2011 10.00	Douglas Allen Dalton, M. Somayazulu, Alexander. F. Goncharov, Russell J. Hemley. Static compression of tetramethylammoniumborohydride (TMAB), Journal of Physical Chemistry (08 2011)
08/30/2011 11.00	R.S. McWilliams, M.F. Mahmood, Y. Kadry, A.F. Goncharov, J. Ciezak-Jenkins. Structural and chemical properties of the nitrogen-rich energetic material Triaminoguanidinium 1-methyl-5-nitriminotetrazolate (TAG-MNT) under pressure, Journal of Chemical Physics (08 2011)
08/30/2011 12.00	Javier A. Montoya, Alexander F. Goncharov. Finite element calculations of the time dependent thermal fluxes in the laser-heated diamond anvil cell, Journal of Applied Physics (08 2011)
08/31/2012 25.00	Michael R. Armstrong, Jonathan C. Crowhurst, Sorin Bastea, William M. Howard, Joseph M. Zaug. Prospects for achieving high dynamic compression with low energy, Applied Physics Letters (accepted) (11 2011)
TOTAL:	4

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Nicholas Holtgrewe	1.00
FTE Equivalent:	1.00
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Alex Goncharov	0.25	
M.F. Mahmood	0.25	
FTE Equivalent:	0.50	
Total Number:	2	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Tuedy Wilson	0.20	Chemical Engineering
FTE Equivalent:	0.20	
Total Number:	1	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 1.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 1.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 1.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

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The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
R.S. McWilliams	0.25
FTE Equivalent:	0.25
Total Number:	1

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

See Attachment

Abstract

We report on our progress in developing new techniques and experiments for studies of fast chemical transformations in energetic materials under conditions of high pressure and temperature. We have developed a new ultrafast mid-to-near infrared (IR) system equipped with modulated and/or continuous wave laser heating, and completed an absorption system for measuring in situ materials at high pressures and temperatures. The systems utilize ultrafast pulse amplifying instrument (Coherent Legend Elite) in combination with an optical parametric amplifier (OPA) for generation of a range of short-pulsed frequencies used to study the dynamics of chemical systems, as well as the newly purchased pulsed broadband source (Leukos Pegasus).

Experimental progress has excelled in the study of high-energy density materials (HEDMs), with promising results coming from the nitrogen-hydrogen mixtures. Results conclude that at high pressures (>47 GPa) a nitrogen backbone structure is formed and stabilized by surrounding hydrogen atoms, in deep contrast to compressed pure nitrogen at these pressures. Moreover, we show through the use of photon or multi-photon absorption that we can generate similar compounds at significantly lower pressures (~ 10 GPa). The metastability of these compounds was found to be fairly large, some even recoverable at ambient pressures and colder temperatures. To enhance our understanding of $N_2:H_2$ systems, alterations in the ratio of nitrogen to hydrogen mixture have been studied, specifically on high-hydrogen mixtures. In addition to HEDMs we have also studied noble gases under extreme conditions using combined compression and short-duration laser heating to study the evolution and dynamics of planets and stars.

Summary of Scientific Progress and Accomplishments

Development of New Techniques

A) In situ Visible Absorption at High Pressure/Temperature

We have completed and tested the construction of an absorption system capable of directly measuring absorption spectra at high temperatures in situ. A pulsed broadband source (Leukos Pegasus) and 1064 nm fiber laser output are directed into the diamond anvil cell (DAC) assembly (Figure 1), with the heating laser directed into both sides of the DAC. The transmission of the broadband source is collected by a spectrometer with a gated iCCD detector (Andor iStar), wavelength range 400-850 nm. The timing of the system is important in overcoming a poor signal-to-noise ratio due to background emission from the heated sample. The 1064 nm beam is modulated for 1 second, initiating the beginning of one spectral collection. At a specified delay (~200 ms), a train of broadband pulses (each 4 ns, collected for 500 ms) is collected at the gated iCCD detector (gate width 20 ns) operating at ~40 kHz. This cycle is repeated for each grating position and these spectra are stitched together for the final spectrum. For temperature measurements we unblock the reflection leg of the system and heat with the unmodulated heating laser (without the broadband source) to collect emission spectra from both sides of the DAC. Typically 1) before heating, 2) temperature, 3) during heating, 4) temperature, and 5) quenched spectra are all collected with their appropriate backgrounds and references.

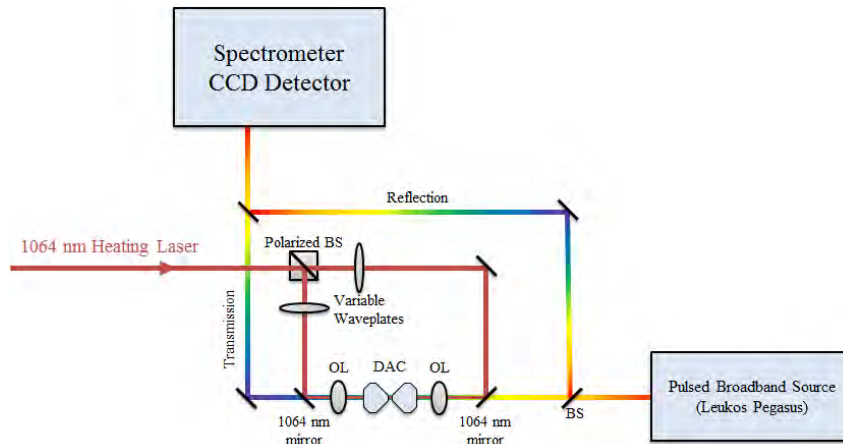


Figure 1: Schematic of high P-T absorption system with laser heating from a modulated 1064 nm fiber laser. BS: Beamsplitter, OL: Objective Lens, DAC: Diamond Anvil Cell.

Absorption spectra obtained from heating runs with ferropericlase and siderite are shown in Figure 2. Ferropericlase at 36 GPa shows a decrease in its optical absorption slope at higher temperatures (~1550K, Figure 2a), while siderite shows a clear transition from its low spin phase to its less absorbing high spin phase at high temperature (~1125K, Figure 2b). These preliminary results display the system's ability to directly measure high temperature spectra in

situ, and future improvements hold promising value for measuring chemical dynamics in these systems at high temperature.

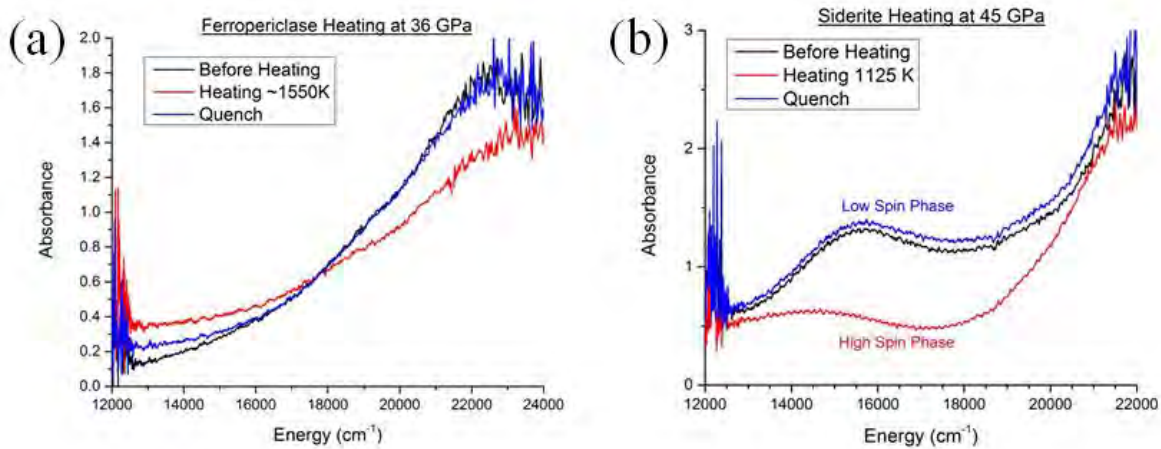


Figure 2: Direct optical absorption spectra obtained at high pressures and temperatures. (a) Ferroperricite at 36 GPa, heated to ~1550 K and (b) Siderite at 45 GPa, heated to ~1125 K.

B) Ultrafast Mid-Near Infrared (IR) Broadband Laser Heating System

We have completed the construction of an ultrafast system for near to mid IR similar to that described previously (Glascoe, E.A., et al., J. Phys. Chem. A, 2009) with the addition of either pulsed or continuous wave laser heating (Figure 3). The output from our femtosecond (fs) pulse amplifying system (Coherent Legend Elite) is split into two beams by a 50/50 800 nm beamsplitter, with one half sent to the Optical Parametric Amplifier (OPA, Coherent OPerA) for conversion into mid-near IR pulses and the other half is blocked. The IR pulses are guided through a DAC and its transmission is detected by a spectrometer coupled with a multichanneled mercury-tellurium-cadmium (MCT) detector. A modulated or continuous wave fiber laser 1064 nm beam is split by a polarized beamsplitter and sent down two paths, where there is individual control of each beam power by a pair of variable 1064 nm waveplates. Both beams are focused onto the sample in the DAC by focal lenses and small triangular 1064 nm mirrors attached to the objective lenses (OL). This work has been done in collaboration with Lawrence Livermore National Lab (LLNL), who lent us the multichanneled MCT detector with fast electronics coupled to a grating spectrograph.

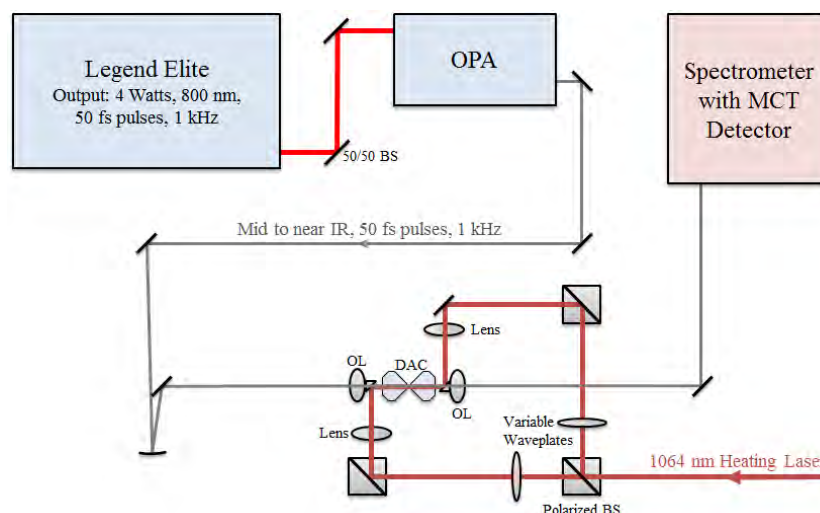


Figure 3: Schematic of ultrafast IR broadband system with laser heating from a modulated 1064 nm fiber laser. BS: Beamsplitter, OL: Objective Lens, DAC: Diamond Anvil Cell.

Preliminary results show the success of laser heating (e.g. 1,4-Decadiene - $C_{10}H_{14}$, Figure 4a), and successful detection of spectra (e.g. methane - CH_4 , Figure 4b), with an IR pulse of $\lambda=3150$ nm. Comparison with conventional Fourier-Transform-IR (FT-IR) shows that the ultrafast system is capable of collecting spectra with very few pulses ($\sim 10-100$), with the end goal of single-shot detection.

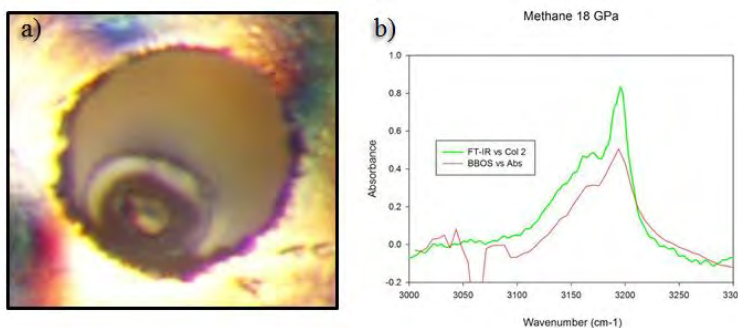


Figure 4: a) 1,4-Decadiene at 12.5 GPa after laser heating, large black area (lower left) represents area of heating and IR beam transmission. b) Comparison of methane absorption spectra with standard FT-IR (green) and the ultrafast IR system (red).

Current modifications are being made to allow for automated IR wavelength scanning with the OPA as well as development of a single shot mode with a modulated heating laser pulse.

C) Ultrafast Transient Absorption Pump-Probe System

Construction of an ultrafast transient absorption pump-probe system is currently underway in the laboratory (Figure 5), and we will be able to operate it within the same space as the ultrafast IR laser heating system mentioned in the previous section. This system will initially be used for

studying band gap dynamics in semiconductor materials (Sim et. al., 2013), but can be extended to study possible excited electronic states in energetic materials.

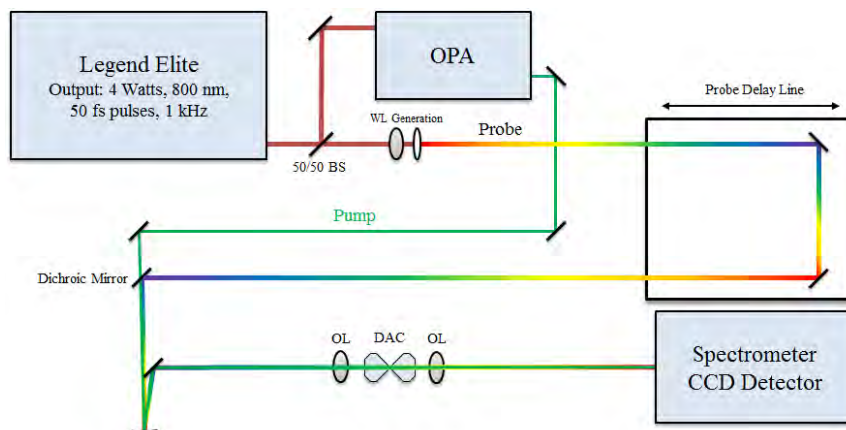


Figure 5: Schematic of ultrafast transient absorption pump-probe system. WL: White Light, OL: Objective Lens, DAC: Diamond Anvil Cell.

Similar to the previous setup, half of the amplifier output seeds the OPA for tuning of a variety of optical pump beam outputs ($\lambda = 290\text{-}10000\text{ nm}$) to match the excitation resonance. The other half of the output (probe beam) is converted into white light (WL) and sent down a delay line pathway where it then recombines with the pump beam with a dichroic mirror. Both beams are sent through the DAC and detected with a CCD detector coupled to a spectrometer. The probe delay line provides the ability to detect absorption spectra as a function of delay time between the pump and probe beams, which allows monitoring of absorption peaks as a function of time from the initial excitation pulse. We will begin testing of the system in the coming months with MoS₂ samples with an end goal of measuring time-dependent transient absorption spectra for a few-layered two-dimensional MoS₂ in collaboration with Avinash Nayak and Professor Jung-Fu Lin at the University of Texas at Austin.

Experiments and Scientific Achievements

High-pressure radiative conductivity of dense silicate glasses

The possible presence of dense magmas at Earth's core–mantle boundary is expected to substantially affect the dynamics and thermal evolution of Earth's interior. However, the thermal transport properties of silicate melts under relevant high-pressure conditions are poorly understood. Here we report in situ high-pressure optical absorption and synchrotron Mossbauer spectroscopic measurements of iron-enriched dense silicate glasses, as laboratory analogues for dense magmas, up to pressures of 85 GPa. Our results reveal a significant increase in absorption coefficients, by almost one order of magnitude with increasing pressure to ~50 GPa, most likely owing to gradual changes in electronic structure. This suggests that the radiative thermal

conductivity of dense silicate melts may decrease with pressure and so may be significantly smaller than previously expected under core–mantle boundary conditions. Such dark magmas heterogeneously distributed in the lower mantle would result in significant lateral heterogeneity of heat flux through the core–mantle boundary.

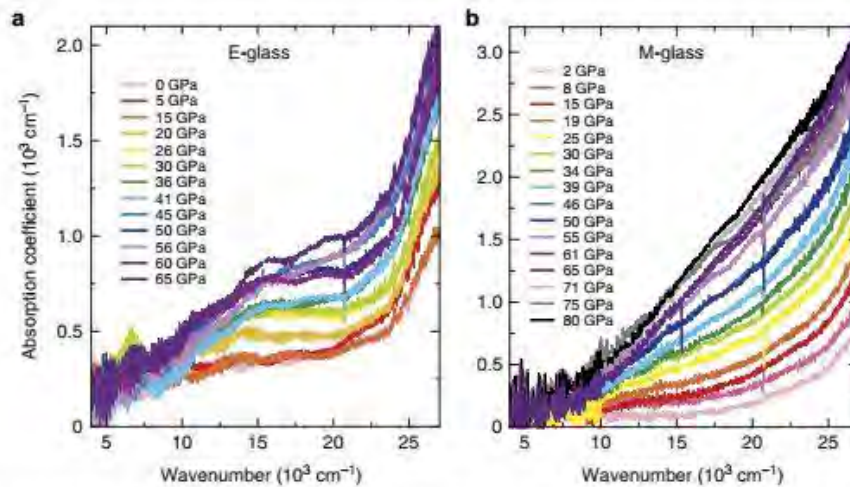


Figure 2 | Optical absorption spectra of glass samples under pressure at room temperature. (a) E-glass and (b) M-glass. The absorption coefficient was calculated using $\alpha = A \ln 10 / d$, where $A = \log_{10}(I_0/I)$; I_0 and I are the reference and sample signals, respectively; and d is the sample thickness measured using white light interferometry at ambient pressure and calculated at high pressure using an isothermal equation of state^{43,44}.

Figure from M. Murakami, A.F. Goncharov, N. Hirao, R. Masuda, T. Mitsui, S.-M. Thomas, C.R. Bina, *High-pressure radiative conductivity of dense silicate glasses with implications for dark-magmas at Earth's core-mantle boundary*, *Nature Communications*, 5 (2014) 5428.

Nitrogen/Hydrogen Mixtures

A) Backbone N_xH Compounds at High Pressures

Significant progress has been made in the study of nitrogen-hydrogen high-energy density compounds. Many simple molecular substances polymerize under pressure and these states can be conserved at ambient pressure as chemical energy storage. Moreover, these compounds can be yet unknown forms in which low-Z materials reside in giant planets. However, little is known about bound states of nitrogen and hydrogen at high pressures; ammonia is the only stable compound which is known. By combining optical and synchrotron x-ray diffraction diamond anvil cell experiments in mixed N₂ and H₂ (Figures 6 & 7) with first principles theoretical structure predictions we show the formation of oligomeric N_xH ($x \geq 1$) compounds at moderate pressure and room temperature using mechano- and photochemistry. These compounds can be recovered to ambient pressure at $T < 130$ K, whereas at room temperature, they can be metastable down to 3.5 GPa. Our results suggest new pathways for synthesis of environmentally benign high energy-density materials and alternative planetary ice. This work was a large collaboration between numerous organizations, Advanced Photon Source Argonne National Lab, DESY Photon Science Hamburg, Germany, State University of New York Stony Brook, Moscow Institute of Physics and Technology, Northwestern Polytechnical University Xi'an, China,

University College London, Institute of Geology and Mineralogy Novosibirsk Russia, and the Center for Advanced Radiation Sources, University of Chicago. (Goncharov et. al., 2014, PRL, submitted)

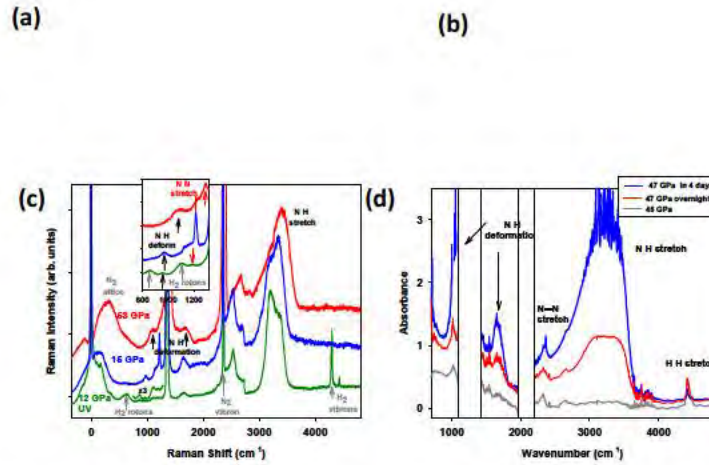


Figure 6: Transformation of the H₂-N₂ van-der-Waals crystal at P>47 GPa and 12 GPa: (a) microphotographs showing a change in color and grain structure; (b) image shows the formation of a new phase (a dark spot) after UV irradiation at 11.3 GPa (c, d) Raman and IR absorption spectra of new synthesized materials. In (c) the two top curves correspond to the material synthesized above 47 GPa (red) and unloaded down to 15 GPa (blue); the bottom curve –to UV irradiated material. In (d) the IR spectra evolution with time is shown to illustrate the reaction kinetics at 47 GPa. The inset in (c) shows the details of the N-N stretch and N-H deformation mode behavior. In (d) the spectral areas of large diamond anvil absorption are masked by boxes.

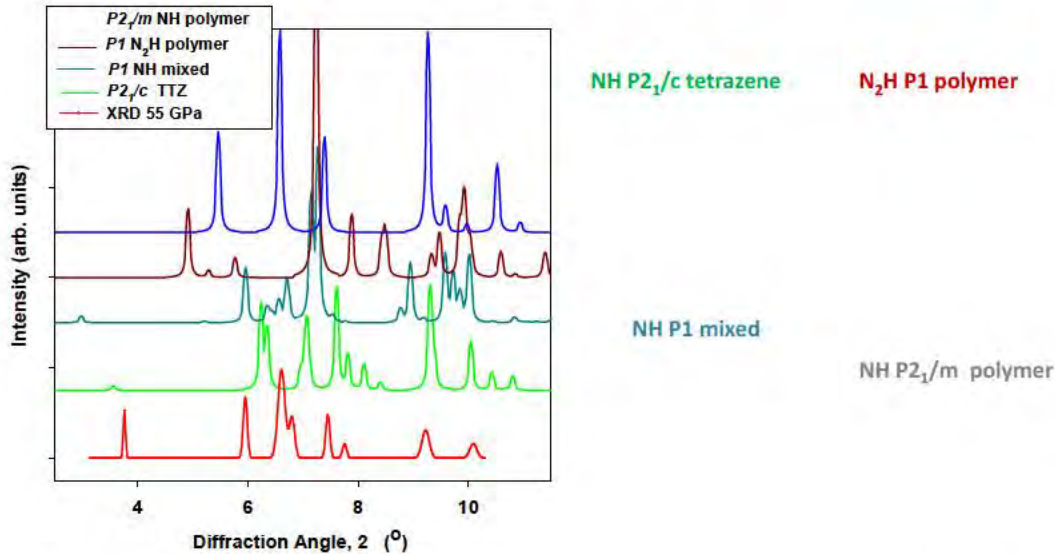


Figure 7: X-ray diffraction of a high-pressure phase at 55 GPa in comparison to the computed patterns of the theoretically predicted NH structures at 50 GPa, this work and (Hu et. al., J. Phys.: Condens. Matter, 2011). The x-ray wavelength was 0.2893 Å. The right panels show the projections of the structures illustrating the presence of molecules and/or indefinitely long N-N chains.

B) Alteration of $N_2:H_2$ ratio

High-nitrogen mixtures ($N_2:H_2$ ratio > 1) have been a popular choice for synthesis of Van der Waals complexes at lower pressures, eventually being transformed into the backbone N_xH compounds described above. In order to assess the stability of this nitrogen backbone, we have also investigated other compositions with a high in hydrogen 1:2 $N_2:H_2$ mixture. The mixture shows similar phase transformations to the high-nitrogen mixtures, implying a pure nitrogen compound is formed, but with an excess of hydrogen. However, in contrast to the previous studies of high-nitrogen mixtures, the nitrogen ν_1 vibron is completely absent and a lower frequency vibrational mode appears (Figure 8). The mode is broadened and at a lower frequency than the ν_2 mode, thus concluding it is due to N-N stretching in N_2 molecules which are either interstitials, form weak bonds to the polymer lattice, or form nanoclusters. This result suggests the lattice is void of any spherical molecular framework of the nitrogen molecules, as the ν_1 vibron is associated with this structure (Scheerboom et. al. 1992). This work was used to familiarize Howard University undergraduate Tuedy Wilson (major: chemical engineering) with both the Raman and IR spectroscopy systems in the laboratory.

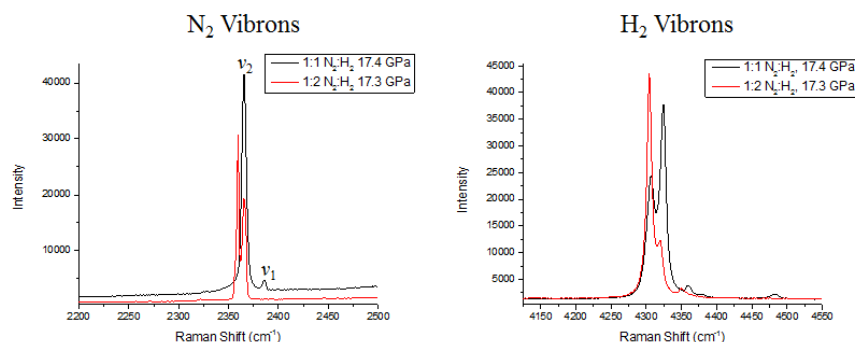


Figure 8: Comparison of the 1:1 and 1:2 ($N_2:H_2$) mixtures N_2 and H_2 vibrons.

C) Laser Assisted Chemical Reaction

Similar to the phase transition into N-H compounds at higher pressures (~ 47 GPa), a N-H compound can also be synthesized by a laser induced reaction (Bini, Acc. Chem. Res. 2004) at significantly lower pressures (~ 10 GPa), showing remarkable metastability down to 3.5 GPa at room temperatures. The result is an opaque material that has both Raman and IR features confirming N-H stretching vibrational modes. Lower synthesis pressures are a substantial advantage from a commercial perspective, due to the engineering involved for mass production purposes. Initially UV radiation from the OPA was used to initiate the chemical reaction, but it was discovered that the reaction can still be induced by much lower energy radiation near the visible/IR boundary (720 nm), indicating a much lower activation energy barrier than previously presumed. X-ray diffraction data is currently under analysis for the 1:1 $N_2:H_2$ laser irradiated samples (Figure 9).

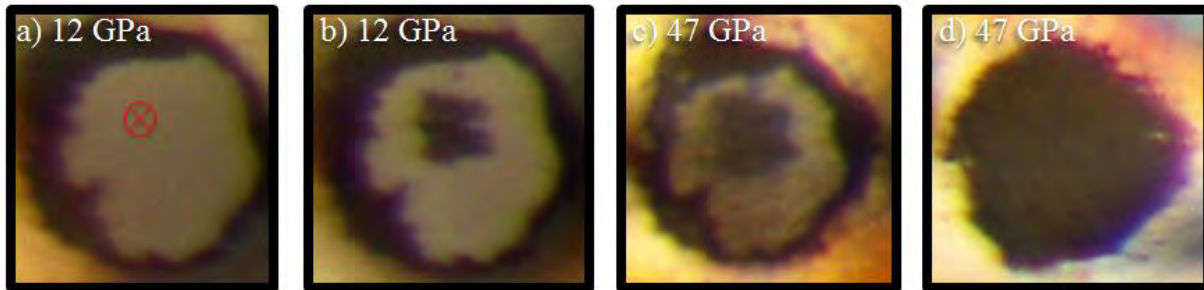


Figure 9: 1:1 N₂:H₂ mixture a) compressed to 12 GPa, red crosshair indicates UV laser irradiation target area, b) laser irradiated sample (opaque area) at 12 GPa, c) irradiated sample compressed to 47 GPa, d) opaque material spreads throughout entire sample after the sample is allowed to sit for one month at 47 GPa.

Likewise, the high-hydrogen 1:2 N₂:H₂ sample also exhibits signs of chemical reaction under laser irradiation. This sample transforms to opaque material under femtosecond pulsed irradiation as well as continuous wave 488 nm solid state lasers. The proposed method for all reactions is either single or multi-photon excitation of molecules into higher lying electronic states, whereby these states can decay into a variety of pathways including dissociation and reformation of molecular bonds. This would explain the emergence of the N-H stretching modes in all laser irradiated samples. This method will further enhance our investigations into other high-density energetic materials in future studies, as well as provide an excellent opportunity for Howard University undergraduate Tuedy Wilson to be trained in ultrafast laser systems. The results have been reported at the Gordon Research Conference (High Pressure) in June 2014 (Holtgrewe et. al., Poster, 2014)

Noble Gases

Noble gases are major and trace elements critical for understanding the evolution and dynamics of planets and stars, especially where they appear in a condensed state. In gas giant planets, helium and neon can precipitate as rain in gaseous envelopes, leading to planetary warming, and specifically the anomalously slow cooling of Saturn. In white dwarf stars cooling can be especially fast due to the predicted low opacity of dense helium atmospheres, affecting the calibration of these objects as cosmological timekeepers. Direct measurements of noble gas properties at conditions of planetary and stellar interiors have been challenging to obtain, especially at pressures and temperatures where the lightest noble gases (helium and neon) transform from electrical insulators to metals. We report new measurements on dense xenon, argon, helium, and neon using combined compression and short-duration laser heating in a diamond anvil cell that clarify the conditions where these initially-transparent insulators transform to optically-opaque conductors (Figure 10). With increasing temperature, high opacity develops at 5,000 to 15,000 K and is initially dominated by electrons of low mobility rather than free electrons. This indicates higher atmospheric opacity for helium-rich white dwarfs than

predicted by free-electron behavior, which could prolong stellar cooling and bias stellar colour through a wavelength-dependence opposite to free-electron theories. Helium is found to be insulating to conditions deep within Saturn's gaseous envelope, transforming to a poor metal or semiconductor near its core, while neon at similar conditions remains an insulator. A noble gas envelope around the core is likely for Saturn but not Jupiter, plausibly controlling Saturn's core erosion and contributing to the dichotomy in core size and thermal evolution between Saturn and Jupiter. This work was in collaboration with School of Physics and Astronomy, University of Edinburgh, Departamento de Geociencias, Universidad de Los Andes, Bogotá, Colombia, DESY Photon Science, and Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences. (McWilliams et. al., 2014, Nature, submitted)

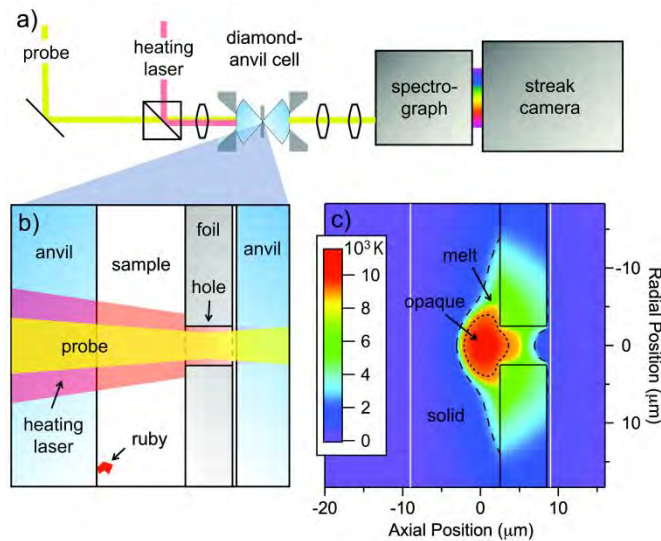


Figure 10: Creating and probing extreme states of noble gases.

a) Configuration of laser heating and transient absorption probing of the diamond anvil cell, with probe beams transmitted through the cell into a detector. b) Microscopic view of the diamond cell cavity, which contains a noble gas sample and a metal foil (Ir) which converts laser radiation to heat, and a small hole at the heated region through which probe beams are transmitted to test optical character of samples. c) Finite element model of the temperature distribution in heated Ar at 51 GPa (Fig. 2, Extended Data Fig. 3), with solid-melt and insulator-conductor ($\alpha=0.1 \mu\text{m}^{-1}$) boundaries in the sample marked dashed and dotted, respectively.

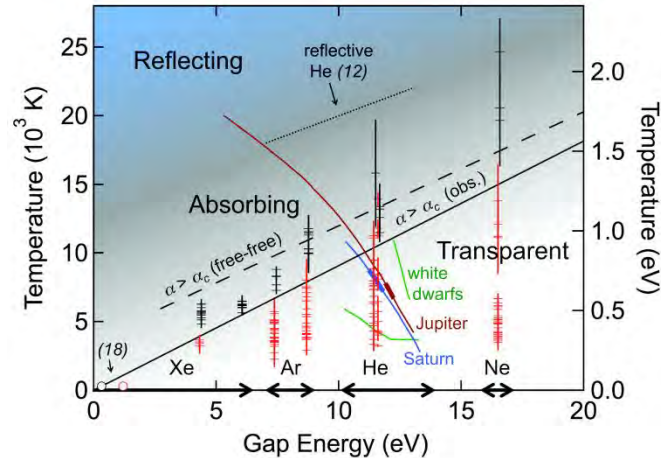


Figure 11: Optical properties of noble gases at 450 to 1075 nm as a function of band gap. Absorption coefficients α below (red) or above (black) the critical value ($\alpha_c = 0.1 \mu\text{m}^{-1}$) are from this study (horizontal dashes) on fluid Ne (15 GPa), He (22, 52 GPa), Ar (22, 51 GPa), and Xe (22, 44 GPa) and prior work (circles) on solid Xe (120 GPa), defining a boundary of linear character (black solid line) where conductivities are ~ 1 S/cm. The free-free model location of this boundary is the dashed black line. Metal-like reflectivity and conductivity (> 100 S/cm) occur above the dotted black line. Vertical bars in this study represent range of temperatures observed in each material state, plus uncertainty. High pressure and temperature band gaps are used. Coloured lines are conditions of He atmospheres of white dwarfs (green) and He rain in planets (blue, brown), with thicker areas indicating predicted onset of He-H solubility.

Summary

For the continuation of our studies we intend to employ the newly constructed ultrafast systems (IR with laser heating and transient absorption pump-probe), as well as the newly constructed high temperature broadband optical system, in studying a range of chemical materials under extreme conditions. With further automation and possible combination of these pulsed ultrafast systems we can gain further insight into fast chemical dynamics on the femto-to-picosecond timescales. Exploration of more high-energy density materials (HEDMs) will be a high priority, considering we can now utilize the ability of laser assisted chemical reactions to discover alternative methods for generation of HEDMs at significantly lower pressures.

Presentations

MR51A-02. Advanced combination of laser and synchrotron techniques to study minerals at extreme conditions in the time-domain mode (*Invited*)

Vitali Prakapenka; Pavel Zinin; Alexander Goncharov; Kirill K. Zhuravlev; Sergey N. Tkachev

AGU 2013 Fall Meeting. San-Fransisco, CA.

MR14A-02. Toward measurements of volatile behavior at realistic pressure and temperature conditions in planetary deep interiors. (*Invited*)

Ryan S. McWilliams*

AGU 2013 Fall Meeting. San-Fransisco, CA.

Nicholas Holtgrewe**, Alexander Goncharov, Mohammad F. Mahmood, Synthesis of Energetic Nitrogen and Hydrogen Compounds Using High Pressure and Multiphoton Absorption, Poster at the Gordon Research Conference on High Pressure at University of New England, Biddeford, Maine, June 22-27, 2014.

Alexander Goncharov, Invited talk: Exotic chemistry rules at high pressures, Gordon Research Conference on High Pressure at University of New England, Biddeford, Maine, June 22-27, 2014.

Alexander Goncharov, High-pressure synthesis of novel materials with new bonding patterns and unusual stoichiometries, Invited talk at 2014 IUCr Congress and General Assembly, August 2014, Montreal, Canada.

Alexander Goncharov, Elissaios Stavrou*, Sergey Lobanov, Artem R Oganov, Valery Rosen, Artem Chanyshv, Konstantin Litasov, Zuzana Konopkova, Kirill Zhuravlev, Vitali Prakapenka, Structure of methane and ethane at high pressures, 2014 IUCr Congress and General Assembly, Poster.

Papers

Elissaios Stavrou*, Muhtar Ahart, Mohammad F. Mahmood & Alexander F. Goncharov, Probing the different spatial scales of Kel F-800 polymeric glass under pressure, *SCIENTIFIC REPORTS* | 3 : 1290 | DOI: 10.1038/srep01290

Sergey S. Lobanov, Pei-Nan Chen, Xiao-Jia Chen, Chang-Sheng Zha, Konstantin D. Litasov, Ho-Kwang Mao & Alexander F. Goncharov, Carbon precipitation from heavy hydrocarbon fluid in deep planetary interiors, *NATURE COMMUNICATIONS* | 4:2446 | DOI: 10.1038/ncomms3446

W. Zhang, A. R. Oganov, A. F. Goncharov, Q. Zhu, S. E. Boulfelfel, A. O. Lyakhov, E. Stavrou, M. Somayazulu, V. B. Prakapenka, Z. Konôpková, Unexpected Stable Stoichiometries of Sodium Chlorides, *Science* 342, 1502-1505 (2013).

Yu. A. Freiman, S. M. Tretyak, Alexei Grechnev, Alexander F. Goncharov, and Russell J. Hemley, Crystal-field phenomena in hcp H₂ and D₂ at high pressures, *PHYSICAL REVIEW B* **90**, 024501 (2014)

Wei Zhou, Xiao-Jia Chen, Jian-Bo Zhang, Xin-Hua, Li, Yu-Qi Wang, and Alexander F. Goncharov, Vibrational, electronic and structural properties of wurtzite GaAs nanowires under hydrostatic pressure, *Scientific Reports*, in press (2014).

Alexander F. Goncharov, Nicholas Holtgrewe**, Guangrui Qian, Chao hao Hu, Artem R. Oganov, M. Somayazulu, E. Stavrou, Chris J. Pickard, Adam Berlie, Fei Yen, M. Mahmood, S. S. Lobanov, Z. Konôpková, V. B. Prakapenka
Backbone N_xH Compounds at High Pressures, PRL submitted (2014)

R. Stewart McWilliams*, D. Allen Dalton*, Zuzana Konôpková, Mohammad F. Mahmood, Alexander F. Goncharov
Opacity and conductivity of noble gases at conditions of planetary and stellar interiors
Nature, submitted (2014)

R.S. McWilliams*, D.A. Dalton*, M.F. Mahmood, A.F. Goncharov, Optical properties of warm dense argon in the laser-heated diamond anvil cell, *Phys Rev B*, submitted (2014).

M. Murakami, A.F. Goncharov, N. Hirao, R. Masuda, T. Mitsui, S.-M. Thomas, C.R. Bina, High-pressure radiative conductivity of dense silicate glasses with implications for dark-magmas at Earth's core-mantle boundary, *Nature Communications*, 5 (2014) 5428.

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**Current Postdoc working on current DoD funded project on energetic materials.