

mantle. Here we report equation of state (EoS) and Rietveld refinement data of MgGeO₃-ppv phase (CaIrO₃-type, Cmc₂) together with EoS data of silicate-ppv phase experimentally determined for the first time.

Germanate and silicate ppv phases were synthesized from MgGeO₃ and Mg_{0.9}Fe_{0.1}SiO₃ orthopyroxene at 86 GPa, ~1600 K and 103 GPa, ~1900 K, respectively, using laser-heated diamond cells with Ar or NaCl pressure medium. Angle-dispersive X-ray diffraction experiments were conducted at 13-ID-D, Advanced Photon Source. EoS data (bulk modulus, its pressure derivative, and room pressure unit cell volume) were obtained using Birch-Murnaghan EoS to be 203(6) GPa, 4.4, 179.7(9) Å³ for MgGeO₃-ppv and 219(5) GPa, 4.4, 164.9(6) Å³ for silicate-ppv. Rietveld refinement of MgGeO₃-ppv was performed using GSAS/EXPGUI. A change in compression mechanism was found at ~45 GPa. Although b-axis is the most compressible axis in the pressure range investigated, it is significantly more compressible at the lower pressure range. The reason is explained by decrease of distortion of GeO₆ octahedron in the lower pressure range, and by both increase of distortion of GeO₆ octahedron and shortening of Mg-O distances in the higher pressure range.

Keywords: high-pressure phases, X-ray powder diffraction, Rietveld refinement

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Refinement of High Pressure Metrology to 150 GPa

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In static high pressure experiments, the pressure cannot be directly measured. Therefore, secondary pressure scales must be used, such as luminescence gauges (like ruby) and x-ray gauges (gold, platinum, MgO, etc.). The calibration of these gauges is a critical issue: for instance, geophysical studies of the Earth's mantle transition zone minerals under high pressure and temperature have revealed to be inconsistent because of the use of incompatible pressure gauges [1]. We have measured ambient temperature equations of state of 13 metals (Be, Al, Fe, Co, Ni, Cu, Zn, Mo, Ag, Ta, W, Pt, Au) under quasi-hydrostatic conditions in a diamond anvil cell, up to at least 65 GPa and at a maximum pressure of 153 GPa. The use of state of the art pressurizing and x-ray diffraction techniques [2] allowed us to obtain standard synchrotron x-ray diffraction accuracy in the volume determination to the maximum pressure. This data set can be used to re-calibrate the static pressure scale based on the ruby luminescence wavelength measurement [3]. The accuracy of various forms of luminescence wavelength vs. pressure in different pressure ranges will be discussed. In particular, this recalibration confirms recent suggestions of an underestimation of pressure by [3] at ultra-high pressure.

[1] Bina C.R., *Nature*, 2001, **411**, 536. [2] Dewaele A., et al., *Phys. Rev. B*, 2004, **70**, 94112. [3] Mao H.K., et al., *J. Geophys. Res.*, 1986, **91**, 4673.

Keywords: diamond anvil cells, high-pressure physics, X-ray diffraction

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Shock-Induced Superheating-Melting and Geophysical Implications

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Superheating is a metastable state with the long-range order of a solid sustained above the equilibrium melting temperature, and a rare phenomenon. The limit of superheating was attempted realistically by assuming an arbitrary critical nucleation rate [1]. Based on classical nucleation theory and supercooling experiments, we developed the systematics relating materials properties to the maximum superheating (supercooling) and heating (cooling) rates, consistent with shock wave experiments, molecular dynamics simulations and Landau-type models [2-5]. Superheating is more achievable under ultrafast heating rate. There are strong indications of superheating in shock

experiments on translucent solids using optical pyrometry [6-8] and on single crystal Al during dynamic spallation [9].

High strain- and heating-rates experiments such as shock wave loading are an essential complement to diamond-anvil cell techniques for investigating translucent minerals and opaque metals [10]. We present an exhaustive survey on superheating-melting behavior of alkali halides, silicates and metals, and their geophysical implications.

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Keywords: superheating-melting, shock, molecular dynamics

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Predicting Crystal Structures of New High-pressure Mineral Phases

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We approached the problem of predicting crystal structures using three different methods: CMAES [1], Metadynamics [2,3] and Evolutionary Algorithms [4].

The different methods and their results for the high-pressure structures of MgSiO₃ and MgCO₃ will be presented and discussed. On the methodological side, we will focus on our implementation of an Evolutionary Algorithm based on spatial heredity and combined with local optimization. This algorithm proved to be an efficient way to tackle high dimensional problems such as crystal structure prediction and hence has a promising future in predicting, on a fully theoretical basis, new crystal structures under pressure.

[1] Hansen N., Ostermeier A., *Evol. Comp.*, 2001, **9**, 159. [2] Martonak R., Laio A., Parrinello M., *Phys. Rev. Lett.*, 2003, **90**, 075503. [3] Oganov A.R., Martonak R., Laio A., Raiteri P., Parrinello M., 2005, *in preparation*. [4] Michalewicz Z., Fogel D.B., *How to Solve It: Modern Heuristics.*, Springer, Berlin, 2004.

Keywords: structure prediction, global optimization, evolutionary algorithm

MS55 TIME RESOLVED DIFFRACTION

Chairpersons: Jianming Cao, Hervé Cailleau

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Laser-Plasma X-ray Sources and Their Applications

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A single atomic vibrational motion is on the order of 100 fs (1 fs=10⁻¹⁵ s), which sets the fundamental timescale of material in response to an external excitation. Using pump-probe approach and initiating the dynamics with an ultra-short laser pulse, the new tool of femtosecond X-ray diffraction provides a direct means of monitoring the atomic positions during photo-induced transition in materials on this fundamental timescale and with sufficient spatial resolution.

In this talk we will show on one side the first type of femtosecond X-ray source, based on the laser-plasma interaction on solid target [1], together with its applications in the study of non-thermal melting in semiconductor [2] and the direct measurement of coherent optical phonons [3].

The second part of this talk concerns a new type of X-ray source, *betatron*, based on the relativistic laser-plasma interaction in gas. This source produces a polychromatic and highly collimated X-ray beam with duration about 25 fs. Its applications in time-resolved EXAFS and Laue diffraction, together with its comparison with other existing pulsed X-ray sources, will be presented.

[1] Rischel C., Rousse A., et al., 1997, *Nature*, **390**, 490-492. [2] Rousse A., Rischel C., et al., *Nature*, 2001, **410**, 65-68. [3] Sokolowski-Tinten K., et al., *Nature*, 2003, **422**, 287.

Keywords: time-resolved X-ray diffraction, phase transitions and structure, laser plasmas

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How do Signaling Photoreceptors Respond to Light?

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Signaling photoreceptors harness the energy derived from the absorption of a photon to generate a structural signal which is then transmitted to downstream partners and ultimately modulates a biological process such as phototropism in plants or swimming behavior of bacteria. To accomplish this with high efficiency, competing de-excitation pathways such as fluorescence and vibration have to be shut down (or greatly minimized). How are structural signals generated at the atomic level, by processes such as light-driven isomerization, bond breaking and bond making? We address these questions by nanosecond time-resolved crystallography, in which molecules in a single crystal of a photoreceptor are stimulated by a brief laser pulse and the subsequent structural changes probed by a synchrotron-derived, polychromatic, intense X-ray pulse. These time-dependent changes are revealed over the time range from nsec to sec: molecular movies. We illustrate these experiments by considering the fully-reversible photocycles of the bacterial blue light photoreceptor, photoactive yellow protein, and the heme domain of the O₂/CO sensor, fixLH. We extract by singular value decomposition the number of structurally-distinct components, identify whether a chemical kinetic mechanism characterized by a small number of distinct states exists and if so, determine the structures of these time-independent, intermediate, short-lived states.

Keywords: time-resolved crystallography, Laue diffraction, signal transduction

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Femtosecond Electron Diffraction: Making the “Molecular Movie”

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Femtosecond electron diffraction (FED) harbours great potential for providing atomic resolution of structural changes as they occur. This ability to watch atoms move in real time—to directly observe transition states—has been referred to as making the molecular movie. Many-body simulations of ultrashort electron pulse propagation [1] enabled the recent development of sources for femtosecond electron pulses with sufficient number density to execute near single shot structure determinations. This is a necessary requirement to allow studies of irreversible processes. With the realisation of joint femtosecond temporal resolution and sub-Angstrom structural resolution, an atomic level view of melting of a thin film of Al under strongly driven conditions [2] has been obtained in which the process can be described as a thermally driven phase transition that takes place in ~3.5 picoseconds. Subsequent studies of the slower melting of Au have further elucidated the mechanism for melt zone propagation.

Ongoing development in electron gun design has further improved the temporal resolution of FED for the observation of transition states

in molecular systems. The camera for “making the molecular movie” is in hand.

[1] Siwick B.J., Dwyer J.R., Jordan R.E., Miller R.J.D., *J. Appl. Phys.*, 2002, **92**, 1643. [2] Siwick B.J., Dwyer J.R., Jordan R.E., Miller R.J.D., *Science*, 2003, **302**, 1382.

Keywords: ultrafast electron diffraction, electron pulse propagation dynamics, ultrafast melting

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The Mechanism of Coherent Phonon Generation

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Coherent acoustic phonons in solids can be generated by impulsive optical excitation through ultrafast heating of lattice and electrons. The former is the thermal lattice expansion related to anharmonicity of ion-ion interaction. The latter is the thermal pressure of free electrons. Previous studies using fs optical probes indicate that both driving forces contribute the phonon generation. However, these optical measurements are indirect probes of lattice motions. Here, we report the study of coherent acoustic phonon generation mechanism by directly measuring the associated structural dynamics with femtosecond electron diffraction (FED). FED provides a quantitative measurement of the temporal evolution of both coherent and thermal lattice motions with sub milli-ångström spatial resolution and on the sub-ps timescale. The damped single-mode breathing motion of 20-nm-thick Al film along the surface normal was recorded as the coherent oscillation of Bragg peak position with a period 6.4 ps, as determined by the 1-D standing wave condition. The lattice temperature (thermal motion) evolution with a time constant of 600 fs was measured by following the associated Bragg peak intensity attenuation. By fitting these data with the differential equation of a harmonic oscillator using a driving term including both lattice and electron heating, we find that the electron pressure contributes more significantly than the lattice heating for the first half cycle of the lattice vibration. These results provide a direct and clear evidence of the non-thermal generation mechanism of coherent acoustic phonons.

Keywords: lattice dynamics, time-resolved diffraction, electron phonon coupling

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Time-resolved Diffraction Studies of the Combustion Synthesis of NiAl/TiC Composite

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Combustion synthesis is a cheap and easy technique to fabricate a large range of materials, including ceramics and composites. It is possible to synthesize a compound by exploiting the exothermic properties of the chemical reaction. Two combustion modes exist depending on whether the synthesis occurs in the form of a wave traveling through the sample (Self-propagating High-Temperature Synthesis SHS) or if it occurs simultaneously in the whole sample (Explosive mode). Despite a lot of advantages, combustion synthesis is barely used in industry due to a lack of understanding of the synthesis mechanisms.

In this work, in-situ time-resolved diffraction using synchrotron radiation has been applied to determine the crystallographic changes occurring during the SHS in air of a mixture of Al, Ni, Ti and C. Time-resolved diffraction is the only in-situ technique able to provide information about the synthesis mechanisms without influencing the propagation of the combustion front. The experiments were performed in transmission using a small X-ray beam of 200x200 μm (E=45keV). During the reaction, 2D diffraction patterns were acquired with a