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The structural phase transformations in the chalcopyrite semiconductor AgInTe₂ have been studied up to 10 GPa on both pressure increase and decrease. The experiment were carried out using angle-dispersive X-ray diffraction with synchrotron radiation and an image plate. The diffraction patterns of AgInTe₂ at ambient pressure reveal two coexisting phases: the first has the chalcopyrite structure while the second has a zinc blende like structure. On pressure increase both phases transformed at 3-4 GPa to a cation-disordered structure with spacegroup Cmcm, the atomic coordinates of which $v=0.75$ for Ag or In and $v=0.25$ for Te - correspond to a NaCl-like structure. On pressure increase the Cmcm phase was stable up to at least 10.25 GPa. On pressure decrease, the chalcopyrite phase started to reappear at 0.55 GPa, and the Cmcm phase disappeared completely at ambient pressure. In addition to the experimental study, we have also performed density functional theory calculations. The calculated transition pressure from the chalcopyrite phase to the Cmcm phase is 4.08 GPa, and the calculated atomic positions in the Cmcm phase are in excellent agreement with those determined experimentally.

Keywords: diamond anvil cells, X-ray diffraction, *ab-initio* calculations

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High-pressure behavior of iron-nickel phosphides and its implications for meteorites and Earth core

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Minerals with composition (Fe,Ni)_xP, are rare, but important accessory phases present in iron, and chondrite meteorites. The occurrence of these minerals in meteoritic samples is believed to originate either from the equilibrium condensation of protoplanetary materials taking place in solar nebulae or from crystallization processes in the cores of parent bodies. Fe-Ni phosphides are considered an important candidate for a minor phase present in the Earth core, and at least partially responsible for the observed core density deficit with respect to pure Fe. We report results of high-pressure high-temperature single-crystal X-ray diffraction experiments with a range of materials belonging to the (Fe,Ni)_xP family, including Fe₃P, Fe₂P, and Ni₂P. A new phase transition to the Co₂Si-type structure (allabogdanite) has been found in Fe₂P at 8.0 GPa, upon heating. The high-pressure phase can be metastably quenched to ambient conditions at ambient temperature, and then, if heated again, transforms back to barringerite. Contrary to the recent reports, we find Fe₃P to remain stable in the schreibersite structure up to at least 60 GPa and 2000 K. Our results indicate that the presence of allabogdanite in meteoritic samples places two important constraints on the thermodynamic history of the meteorite. First, it imposes a minimum pressure and temperature for the formation of the Fe₂P, and additionally rules out any higher temperature low pressure alterations. If present in the Earth core, Fe₂P will have the allabogdanite rather, than barringerite structure. Crystal chemical

trends in the compressibility and thermal expansion of (Fe,Ni)_xP compounds, as well as polymorphic transition paths are analyzed in the context of the Earth's core composition and properties.

Keywords: Earth core, phase transitions, high pressure

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High-pressure and low-temperature charge density study of Pr_{1-x}Ca_xCoO₃ by SR powder diffraction

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The Pr_{1-x}Ca_xCoO₃ system exhibits a phase transition from a conductive to an insulating state with decreasing temperature under high pressure. The transition has found in the very narrow region of $x \sim 0.5$ at ambient pressure. Similar transition has also found in the wide x region under high pressure. No indication of this kind of transition has been observed in other species of R and A in the R_{1-x}A_xCoO₃ system (R = rare earth elements; A = Ca, Ba and Sr). The structural change through the pressure-induced phase transition under high pressure has never been determined. To investigate the structural change and the role of Pr and Ca in the pressure-induced phase transition, we carried out the high-pressure and low-temperature structural study of Pr_{0.7}Ca_{0.3}CoO₃ by the synchrotron radiation (SR) powder diffraction. The phase transition from a conductive to an insulating state has been found above 1.0 GPa for Pr_{0.7}Ca_{0.3}CoO₃ by the electrical resistivity measurement. The SR powder diffraction data of Pr_{0.7}Ca_{0.3}CoO₃ were collected at Spring-8 BL10XU beamline. The sample pressure and the temperature were controlled by the He-gas flow type cryostat combined with a He-gas driven diamond anvil cell (DAC). A change of the diffraction pattern indicating the structural phase transition was observed around 100 K at 1.3 GPa. The electron charge density distributions and the crystal structures were determined by the MEM/Rietveld analysis. It was revealed that the covalency of Pr/Ca-O bond is increased in the low-temperature phase. This fact implies that the Pr 4f-O 2p orbital hybridization contributes to the stabilization of the low-temperature insulating phase.

Keywords: high pressure, charge density, Co oxides

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Synthesis and structure of new platinum hydrides at high pressure

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High pressure can produce a very steep increase of the chemical potential of hydrogen, resulting in a drastic enhancement of the solubility in metal. A number of transition metal hydrides have been synthesized under high-pressure conditions. As far as the platinum group metals are concerned, these metals have been generally known as highly active catalysts in metal-hydrogen systems. There has been experimentally no observation of platinum metal hydrides, except for palladium and rhodium hydrides. A theoretical calculation predicts formation of platinum metal hydrides with high concentration of hydrogen at high pressure. We investigated iridium-, platinum-, and gold-hydrogen systems at high pressure to synthesize metal hydrides. In platinum-hydrogen system, a pressure-induced structural phase transition of face-center-cubic phase into hexagonal-close-packing + tetragonal phases was observed at 24-25 GPa by in situ X-ray study. The volumes of new phases are likely to propose the formation of platinum hydrides. In other systems, no formation of metal hydrides was observed up to 30 and 40 GPa, respectively.

Keywords: diamond anvil cells, high-pressure synthesis, metallic hydride

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Pressure-induced structural transition in rare-earth metal hydrides

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Pressure induced structural transitions of rare-earth metal hydrides have been investigated under hydrostatic pressure at room temperature. Tri-hydride, YH₃, exhibits a hexagonal metal lattice containing three hydrogen atoms per metal atom in the interstitial spaces: two hydrogen atoms at the tetrahedral sites and one hydrogen atom near the Y metal plane in the octahedral sites. To study high-pressure structural properties, we performed synchrotron radiation x-ray diffraction experiments by using a diffractometer for diamond anvil cells installed at the BL22XU beamline in SPring-8. We observed the pressure-induced structural transformation from the hexagonal metal lattice into a face-centered cubic (fcc) one through an intermediate state, which appears in the wide pressure span of 12-22 GPa. The obtained x-ray diffraction patterns in the intermediate state are represented by long-period rhombohedral structures, e.g. 27R, of the yttrium metal lattice. These long-period structures are interpreted in terms of the periodic arrangements of hexagonal-type (ABA or h-type) and fcc-type (ABC or k-type) stacking layers of the yttrium metals. For example, 27R structure described as (hhhk)3 by Jagodzinski notation is one of plausible models for 14.0-GPa structure. These long-period structures gradually transform toward the fcc metal lattice with successively increasing in the fcc-type component in a unit cell upon compression. Such structural transition is considered to be characteristic for rare-earth metal hydrides and should be interpreted in terms of the hydrogen-hydrogen interactions and hydrogen-metal bonding.

Keywords: high-pressure structure determination, high-pressure X-ray diffraction, hydride structure

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Toward fully automated high pressure beamlines : Recent developments at beamline ID27, ESRF

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The automatic collection of high quality X-ray diffraction data at high pressure and high or low temperatures is a new and very challenging method. Indeed, it involves the development of specific pressure and temperature devices that can easily be interfaced to the beamline control computer in order to achieve a sequential series of command at a given pressure and temperature. This sequential series includes the automatic sample alignment, pressure and temperature measurements and XRD data collection. We present a recent development at beamline ID27 which allows the fully automated collection of high pressure XRD data in a membrane type diamond anvil cell. The potential of this new development is illustrated on a school case: the equation of state of platinum.

Keywords: X-ray diffraction, high pressure, automation

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High pressure single-crystal neutron diffraction of squaric acid

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Although powerful in many cases, the 1-d character of a powder diffraction pattern inevitably leads to loss of information due to peak overlap. Hence, detailed structural studies such as measurement of anisotropic thermal motion and multi-site disorder sometimes require the full 3-d information extracted from single-crystal data. It is currently possible to determine single-crystal diffraction patterns from micron-sized samples up to a pressure of 1 Mbar using x-ray synchrotron sources. However, form-factor effects limit the resolution of the information that can be obtained by this technique on thermal motion and disorder, particularly in the lighter elements. Neutron diffraction is the technique of choice for extracting such information from light elements, although the relatively low fluxes available mean that a sample volume in excess of 1mm³ is required. As a consequence, the devices used to generate pressures typically exploit significantly different approaches from those used at synchrotrons. To this end, we have been developing new anvil geometries and cells which allow us to collect high-resolution single-crystal neutron diffraction data up to a pressure of 8GPa. We present the results of a study in which we have used these techniques to follow a proposed hydrogen-bond centring transition previously proposed in squaric acid at ~3GPa. Just beyond this pressure, we have seen no evidence for hydrogen-bond centring but observe an extended hydrogen distribution between the oxygen atoms. Neutron diffraction data have been collected using time-of-flight techniques at the ISIS Facility, and monochromatic techniques at the Institut Laue-Langevin. The results will be presented, including details of data reduction and the techniques used to collect the new data.

Keywords: high pressure, single crystal, neutron diffraction