

CaSiO₃ perovskite. The commonly assumed cubic structure was found to be stable at high temperatures and unstable at low temperatures at all pressures. On the basis of these results, we predict that the low temperature structure of CaSiO₃ perovskite is tetragonal space group *I4/mcm*. This phase would transform into an orthorhombic *Imma* structure under non-hydrostatic conditions. It is also obtained by fast quenching of cubic CaSiO₃ perovskite. This *Imma* structure explains hitherto puzzling experimental X-ray powder diffraction patterns.

CaSiO₃ perovskite is thought to comprise between 6 and 12 wt% of the lower half of the Earth's transition zone and lower mantle. Its structure throughout this regime is generally assumed to be cubic [1,2] because temperature generally increases symmetry. At lower temperature deviations towards a tetragonal structure were found [1,4].

Using VASP code in the PAW frame the CaSiO₃ cubic structures were first optimized at 0 K for pressures of 0, 50, 100, 150 GPa. For MD simulations we used an *N-V-T*-ensemble with Nosé thermostat [5]. Temperatures of 500, 1500, 2500 and 3500 K were simulated. The lattice parameters were not relaxed but on the difference of stress in the three spacial directions we could observe a phase transition from the cubic phase at high temperatures to a tetragonal phase at low temperatures. As we observe a significant difference in stress components, we predict that transition takes place between 1500K and 500K.

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Keywords: ab-initio calculations, high-pressure phase transitions, theory of kinetics of silicate minerals

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First-principles Simulations of LiH: Towards the B2 Phase

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Recent progress in high-pressure experiments has greatly expanded the accessible pressure and temperature conditions, and has proven to be a powerful approach for materials design. However, the characterization of new high-pressure phases is still challenging especially at elevated temperatures. For example, compressing hydrogen to the megabar pressure range is already accessible with laser heated Diamond Anvil Cell (DAC) techniques, yet, it has proven extremely difficult to measure the structural changes upon melting. On the other hand, ab-initio calculation methods, in principle, do not have limitations on the investigation of structural properties under high pressure and temperature conditions. To date, lithium hydride is only the alkali hydride, for which a B2 phase has not yet been found experimentally. The B1-B2 phase boundary at 0 K suggested by previous ab-initio calculations are around 4 megabar, which is still out of reach for DAC experiments, however, the temperature axis has not yet been explored. We demonstrate, by using an ab-initio two-phase simulation method, that the B1-B2 phase boundary near the melting line is as low as 1.5 megabar, which is within the reach of the laser heated DAC technique.

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Keywords: ab initio structural determination, high pressure structure, electronic structure

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Pressure-induced Structure Change of Ferroelectric KNbO₃ using SR

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KNbO₃ is a perovskite-type ferroelectrics. It exhibits three structural transitions with increasing temperature at ambient pressure:

rhombohedral -to- orthorhombic -to- tetragonal -to- cubic phase. The cubic phase is paraelectric, and the other three phases are all ferroelectric. The polymorphic structure transitions of KNbO₃ were studied under high pressure using synchrotron radiation at BL-18C, KEK with diamond anvil cell (DAC). These transition pressures were determined by profile analyses of powder diffraction data using a long wavelength, $\lambda=0.92$ Å and long film distance 500 mm. The orthorhombic -to- tetragonal transition takes place at about 6.0 GPa and the tetragonal-to- cubic transition causes at about 9.0 GPa. These transition pressures are consistent with the result of our previous dielectric measurement under compression[1]

Single crystal diffraction studies under various pressures using a new DAC [2] installed in four-circle diffractometer at BL-10A, KEK at ambient temperature: orthorhombic (Cm2m, z=2) at 0.0001, 1.6, 4.8, 5.7GPa; tetragonal (P4mm, z=1) at 6.5, 7.9GPa; cubic (Pm3m, z=1) at 9.4, 12GPa. Diffraction intensities were measured using wavelength $\lambda=0.7004$ Å, collimator 100 µm and Φ -fix mode. Reliabilities of all structure refinements including isotropic temperature factors are within R=0.04. Deformation and volume compressibility of polyhedra in each perovskite-type structure are finely analyzed in order to comprehend the dielectric property. Anisotropy in their ferroelectric property is clarified and an increase in the ferroelectricity with pressure is also elucidated.

[1] Kobayashi Y., et al., *Phys. Rev.*, 2000, **B61**, 5819. [2] Yamanaka T., et al., *Rev. Sci. Instr.*, 2001, **72**, 1458.

Keywords: KNbO₃, high pressure, ferroelectrics

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High Pressure Study of Co₂(CO)₆(XPh₃)₂ (X=As,P) Phase Transitions via SXRD

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High Pressure (HP) is a powerful tool to induce structural modifications and phase transition in crystals. Molecular crystals, in particular, may show large variations both in intermolecular and intramolecular geometrical parameters but, up to now, have been subject to few studies.

The M₂(CO)₁₀ (M=Mn,Re) dimers have been suggested to undergo a staggered to eclipsed conformational rearrangement of the equatorial carbonyls, but their crystals do not survive this phase transition. With the aim of elucidating this behaviour we report the structural characterisations of the related Co₂(CO)₆(XPh₃)₂ (X=As,P) species, which are known to undergo a second order phase transition at low T[1], at different pressures (up to 46 kbar).

We confirm that a staggered to almost eclipsed conformational rearrangement takes place in both cases. This is accompanied by significant variations of most inter and intramolecular parameters. The HP behaviour is similar but larger than that observed on cooling, allowing to observe previously undetected variations of the intramolecular parameters.

[1] Macchi P., Garlaschelli L., Martinengo S., Sironi A., *Inorg. Chem.*, 1998, **37**, 6263.

Keywords: high pressure structure determination, phase transitions crystals characterization, molecular structure

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Incommensurate Structures in the Group VIa Elements above 100Gpa

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The high-pressure behaviour of sulfur has long been known to be extremely complex, and it is only recently that it has begun to be simplified [1, 2]. The stable crystal structure at ambient conditions, S-I, comprises covalently-bonded S8-rings arranged in an orthorhombic

structure [3]. Although S-I has been reported to undergo a gradual transition to an amorphous form on compression at room temperature [4-6], we observe S-I to transform directly to tetragonal S-II [7] at 38 GPa with no evidence of any intermediate amorphous phase. Single-phase diffraction profiles of S-III were observed above 95 GPa, and these revealed that S-III adopts the same incommensurately modulated monoclinic structure as Se-IV and Te-III. Sulfur is thus the first element observed to have an incommensurately modulated structure above 100 GPa. On pressure decrease a previously unreported phase of sulfur can be assigned to the triclinic structure of Se-III and Te-II. In this contribution we describe our most recent results on S-III and Se-II.

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Keywords: high-pressure crystallography, sulfur, phase transition

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Charge-density Wave in the Incommensurate Phase of Metallic Sulfur at Megabar Pressure

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Recent discoveries of incommensurate (IC) host-guest and/or modulated phases in elemental metals at high pressure suggest that aperiodic structures are a common phenomenon among the elements under pressure. However, the driving force for development of the incommensurability and structural modulations in these elemental systems is poorly understood.

Using synchrotron x-ray diffraction and diamond anvil cells, we show that the metallic phase of sulfur stable above 83 GPa, has an IC modulated crystal structure with a monoclinic average cell and a modulation wavevector $q = \langle 0 \ 0.281 \ 0 \rangle$ at 100 GPa. We observe a strong pressure dependence of the modulation up to 135 GPa, where the modulation disappears.

We perform first-principles calculations using the density-functional theory to analyze the average structure of the IC phase. We obtain a simple Fermi surface (FS) that exhibits parallel zones, indicating a nesting, characterized by a wavevector close to the experimental modulation. The phonon dispersion shows a softening with a minimum at the same wavevector as the FS nesting vector. These indicate that the IC structure in metallic sulfur at megabar pressures is due to a charge-density wave.

Keywords: high pressure, incommensurate modulated structures, electronic band structure calculations

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Phase Transitions in the O₂ – H₂O System at High Pressures

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Pressure and temperature induced phase transformations in the O₂ – H₂O system were studied by means of Raman spectroscopy, X-ray powder diffraction and visual observations in diamond anvil cell at high pressure. Ice and liquid oxygen were loaded in high pressure cell simultaneously. Several clathrate hydrate phases in a pressure range 0.5 – 2.8 GPa were detected and assigned to known clathrate hydrate structural types including high-pressure structures recently found for methane and argon clathrate hydrates [1, 2].

Reaction of hydrogen peroxide formation from water and liquid oxygen was found at pressures lower than 1 GPa and room temperature. Brake down reaction of H₂O₂ to H₂O and O₂ was also

studied, for this purpose 30% solution of H₂O₂ was loaded in the diamond anvil cell. Influence of pressure and temperature on the chemical equilibrium $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{O}_2$ will be discussed.

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Keywords: clathrate hydrates, high-pressure phase transitions, high-pressure X-ray diffraction

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Hexagonal Diamond from Highly Crystalline Graphite Film

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While a compressed graphite transforms to a cubic diamond under high-temperature condition, a high crystalline graphite transforms to a hexagonal diamond under ambient temperature condition. The transition pressure is much affected by the nature of the sample and the compression procedure [1].

We investigated the transition pressure with a highly crystalline graphite film made from a heat-treated poly-imide by Raman spectroscopy and X-ray diffractometry. High pressure was generated by a diamond-anvil cell and Daphne7373 oil was used as a pressure transmitting medium. In Raman spectroscopy, the peaks associate with the hexagonal diamond appeared at 6 GPa and the graphite peaks vanished at 9 GPa. The transition pressure is found to be much lower than that of the previous report. On the other hand, in X-ray diffraction experiment, the transition was detected not at 6 GPa but at 19 GPa same as the previous report [2]. We propose that the transition firstly occurs on the surface at much low pressure with highly crystalline graphite film.

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Keywords: graphite, hexagonal diamond, high-pressure phase transition

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Chain Melting at HT/HP in Incommensurate Rb-IV

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Rb-IV is the stable high-pressure phase of rubidium between 16 and 21 GPa. The structure of Rb-IV has long been known to be complex, but it is only recently that it has been solved as being an incommensurate host-guest composite structure [1], comprising a tetragonal host framework containing chains of "guest" atoms that form structures incommensurate with the host. While we have observed similar composite structures in a number of other elemental metals [2], these structures all have an 8-atom host framework, while the host structure in Rb-IV contains 16-atoms. Rb-IV is also unique in that on pressure decrease below 16.3 GPa at 300K, the chains of guest atoms become disordered and liquid-like [3]. We have recently investigated the P-T dependence of this "melting" transition, and in this poster we will present the stability field of the disorderd chain phase, combining it with previous data on the P-T phase diagram of Rb up to 14 GPa.

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