

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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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. Inst.*, 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.

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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