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Bonding nature between atoms in ABX₃ perovskites is considered to be closely related to their phase instability [1]. The bond length would have primary importance to bonding nature. The bond length can be easily controlled by applying pressure onto the materials. In this study, bonding nature of KMnF₃ is investigated by visualizing the charge density distributions under high-pressure.

The synchrotron-radiation powder diffraction experiment was carried out at Spring-8 BL10XU up to 5 GPa under ambient temperature. The pressure-induced phase-transition from cubic to tetragonal phase was confirmed by observing superlattice-reflections at R points, such as (3/2 1/2 1/2), at the vicinity of 3.2 GPa.

The charge-density distributions of the both phases were obtained by the MEM/Rietveld analysis. From the MEM charge densities of the cubic phase, it was revealed that the covalency of Mn-F bond is weakened as the pressure increases. This shows high contrast to the fact that the bond length is shortened as the pressure increases, which is very normal behavior under high pressure. Accompanying these changes under high pressure, the atomic vibration of F atoms perpendicular to the Mn-F bond became greater, which should be related to the softening of rotational mode of the Mn-F₆ octahedron.

[1] Aoyagi S., et al., *J. Phys. Soc. Jpn.*, 2002, **71**, 2353.

Keywords: perovskites, powder diffraction under non-ambient condition, charge density studies

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High Pressure X-ray Diffraction Studies Of Purely Siliceous Zeolites

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High pressure synchrotron X-ray powder diffraction measurements of purely siliceous zeolites were performed using a diamond anvil cell. The behaviour under pressure is partly driven by the ability of the pressure transmitting fluid to enter the neutral SiO₂ framework.

Measurements of purely siliceous zeolite Y (Sil-FAU) using silicone oil as the pressure transmitting medium show compression of the zeolite followed by a loss of long range ordering at 2.2 GPa. When using a methanol:ethanol:water mixture (16:3:1) as the pressure transmitting medium, two distinct compressibility regions are observed with a dramatic change in the compression mechanism at 4 GPa. Rietveld refinement analysis of the powder patterns explains the different regions as sequential pore filling being the main response to pressure up to 4 GPa and distortion of the framework involving the sodalite and double 6 ring (D6R) units at higher pressures.

Purely siliceous chabazite (Sil-CHA) was measured to 5.5 GPa using an alcohols/water mixture, previously described, as the pressure transmitting fluid. As with Sil-FAU, two distinct regions of compressibility were observed. Rietveld refinements indicated initial pore filling occurs upon application of pressure to ~3 GPa in the case of Sil-CHA. This is followed by framework distortion as a response to increased pressure. Further experiments on these and related systems will be performed in April, and results presented.

Keywords: synchrotron X-ray diffraction, zeolite, diamond anvil cell

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High Pressure High Temperature Carbon Dioxide

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Carbon dioxide is widely studied molecular compound because of

its importance in life and geological sciences. Despite the simplicity of the molecule, the solid shows several high-pressure polymorphs quenchable at room temperature and its phase diagram isn't still fully characterized [1,2,3]. In particular the structure of the high temperature phases II and IV have not been well established and the claimed molecule pairing in phase II [4] and bent molecular geometry in phase IV [5] have been recently questioned [6].

I present here a FTIR and Raman study of high pressure high temperature CO₂ phases up to 30 GPa performed between 80 and 650 K by using a resistively heated diamond anvils cell and an N₂ flux cryostat. The complete vibrational information gives some constraints on the crystal symmetry, allowing to choose the crystal structures of phases II and IV among those proposed in the literature.

Moreover we have determined the melting curve and the transition lines for high temperature phases, between 300 and 800 K, and found them quite different from published results.

[1] Iota V., Yoo C.S., *Phys. Rev. Lett.*, 2001, **86**, 5922. [2] Santoro M., et al., *J. Chem. Phys.*, 2004, **121**, 2780. [3] Gorelli F.A., Giordano V.M., et al., *Phys. Rev. Lett.*, 2004, **93**, 205503. [4] Yoo C.S., et al., *T. Phys. Rev.*, 2002, **B65**, 104103. [5] Park J.H., et al., *Phys. Rev. B*, 2003, **68**, 014107. [6] Bonev S.A., et al., *G. Phys. Rev. Lett.*, 2001, **91**, 065501-1.

Keywords: high-pressure phase transformations, spectroscopy and molecular structure, crystal symmetry

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High P-T phase Diagram of Solid Benzene, and Transformation to an Extended Amorphous State

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The high pressure structural properties of solid benzene have been investigated in the P-T range where the chemical reaction does occur, e.g. above 15-40 GPa depending on temperature, by x-ray diffraction and infrared absorption techniques. Sample annealing above 500 K produces pure phase II crystals (monoclinic P2₁/c). X-ray diffraction patterns collected at 540 K on these crystals allowed the equation of state of benzene to be obtained. These results indicate the stability of phase II up the pressure where benzene reacts and no evidences of the III and III' crystal structures is gained. On these bases the existing thermodynamic phase diagram of benzene was reinterpreted and a simplified new one is proposed [1]. Unique features of the high pressure transformation to the extended amorphous state of this important model system were unveiled by observing, *in situ*, the pressure evolution of the Bragg peaks. Indeed the crystalline pattern merges, at high pressure, into a broad amorphous-like diffraction profile related to the static structure factor S(Q) of the final product.

[1] Ciabini L., Gorelli F.A., Santoro M., Bini R., Schettino V., Mezouar M., *High temperature equation of state and phase diagram of solid benzene, submitted to PRB.*

Keywords: high pressure, benzene, amorphization

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Molecular Dynamics Simulations of Cubic CaSiO₃ at Lower Mantle Conditions

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First-principles projector-augmented wave (PAW) molecular dynamics was used to investigate structure and properties of what is thought to be the third most abundant phase in the Earth's lower mantle,

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.

[1] Ono S., Ohishi Y., Mibe K., *Am. Mineral.*, 2004, **89**, 1480-1485. [2] Shim S.-H., Duffy T.S., Shen G., *Phys. Earth Planet. Int.*, 2000, **120**, 4, 327-338. [3] Shim S.-H., Duffy T.S., *J. of Geophys. Res.*, 2000, **105**, B11, 25955-25968. [4] Shim S.-H., Jeanloz R., Duffy T.S., *Geophys. Res. Lett.*, 2002, **29**, No.24, 2166. [5] Nosé S., Klein M., *J. Chem. Phys.*, 1984, **78**, No. 11.

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. 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.

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