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Bonding nature between atoms in ABX_3 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 $KMnF_3$ 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 $Mn\text{-}F_6$ 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 SiO_2 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 CO_2 phases up to 30 GPa performed between 80 and 650 K by using a resistively heated diamond anvils cell and an N_2 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 $P2_1/c$). 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 $CaSiO_3$ 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,