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Unit cell angles α , β , and γ , not fixed by symmetry, give an additional degree of freedom on the stage of crystal formation. For this reason, monoclinic crystals are the most numerous ones at ambient conditions. The oblique angles play the same role in thermal expansion; in particular they permit to demonstrate sharply anisotropic thermal expansion up to contraction along some directions. In 1982 great jump of the appearance of frequency of crystals, showing negative linear thermal expansion, was discovered between orthorhombic and monoclinic crystals [1]. It occurred that at least one third of monoclinic and triclinic crystals contracts along certain directions on heating due to so-called shears [1, 2]. This fact correlates with the existence of oblique cell angles in monoclinic and triclinic crystals only. Last quarter of a century was test and development period of the thermal contraction concept. Many types of the phenomenon were considered [2, 3 etc.]: shears, hinges, rocking polyhedra and symmetry related types etc. And now we can say that both among chemical compounds and in the earth's crust, shears are the most fruitful case of linear thermal contraction of crystals. Taking into consideration anti-similarity of thermal and pressure deformations of crystals, the same situation should be expected in connection with linear elongation under pressure.

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Keywords: negative thermal expansion, high-temperature x-ray diffraction, inorganic compounds

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The structure of type I semiconducting clathrates under pressure

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Semiconductor clathrates are compounds consisting of an open framework lattice of mainly, Si, Ge and Ga, containing a second large cation (alkali or alkali-earth) trapped in its cages. In this work, *in-situ* high pressure powder diffraction was performed on two Ge clathrates: $\text{Ae}_8\text{Ga}_{16}\text{Ge}_{30}$, where Ae = Sr, Ba. The pressure was applied to the samples by means of a diamond anvil cell (DAC) to 25 GPa and powder diffraction data were collected with high energy (100 KeV) x-rays at the APS Sector 1 at Argonne National Lab. This technique allows data collection over a wide q range [0.2 \AA^{-1} - 50 \AA^{-1}]. The structure of both samples was analyzed as a function of pressure, particularly with respect to the guest atom electron density and host lattice bonding. Both clathrates show amorphization of the host lattice for pressures in excess of 20 GPa, the structural characteristics of the structure factor functions $S(Q)$ and radial distribution functions $G(r)$ will be presented, elucidating both the local environment of the guest atoms and their short range ordering. This result suggests a promising route for obtaining periodic arrangement of guest atoms embedded in an amorphous semiconductor matrix. Oak Ridge National Laboratory is supported by the Division of Materials Sciences, U.S. D.O.E. (contract DE-AC05-00OR22725 with UT-Battelle, LLC).

Keywords: semiconducting clathrates, *in-situ* high pressure diffraction, pair distribution function

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Magnetic transition and equation of state of iron carbide to 400 GPa

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It is known that the Earth's inner core is different from pure iron because the physical properties of pure iron can not explain those of the Earth's inner core estimated by seismological observations. Cosmochemical arguments imply that minor lighter elements should be present to account for the discrepancies of physical properties between pure iron and the seismological observations. C, O, S, Si, and H are considered to be the most probable candidates. Wood (1993) proposed that iron carbide might be the major phase in the inner core based on extrapolations of thermodynamic calculations and an equation of state of iron carbide. Recently, significant advances have been achieved in static high-pressure experiments. Although the P-T range of high-pressure experiments has been extended, it is difficult to achieve extreme conditions corresponding to the Earth's inner core. In contrast, recent developments of the first-principle calculations can provide independent data from high-pressure experiments. In this study, the magnetic properties and the equation of state of Fe₃C were investigated by the first-principle calculations. We performed DFT method using VASP package to calculate magnetic states and equilibrium volumes and pressures. A method of *ab initio* molecular dynamics calculation was also used at high temperatures. The magnetic phase transition was observed at a pressure of ~55 GPa. This indicates that the stable Fe₃C is a paramagnetic phase at pressures corresponding to the Earth's core. The density of Fe₃C estimated by *ab initio* molecular dynamics calculations was sufficient different from seismological data. Our results precluded Fe₃C as the major inner core-forming phase.

Keywords: *ab-initio* calculations, iron compounds, molecular dynamics

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Crystallography of intermetallic CaLi₂ at high pressure

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Lithium and calcium are usually considered as simple metals because of the simple electronic structures with one and two conduction electrons, respectively. Recent studies have indicated that both lithium and calcium have anomalous properties at high pressure. Thus, the high-pressure properties of the Laves-phase CaLi₂, the only intermetallic compound between Li and Ca at ambient conditions, would be very interesting. Recently, Feng *et al* [1] have studied the electronic structure of CaLi₂ under pressure and found the bandwidths of the valence states decrease rapidly under compression just as in Li and Ca. Moreover, they predicted CaLi₂ could be a potential

superconductor at high pressure due to the high density of states at the Fermi level. Matsuoka *et al* [2] followed Feng's work and indeed found CaLi₂ become a superconductor at 11 GPa. However, the crystal structure of CaLi₂ under pressure is still not well established. In this work, the crystallography of CaLi₂ at high pressure has been extensively investigated by the evolutionary algorithm USPEX. We explored several new phases of CaLi₂ at pressures in range 50 – 250 GPa. The chemical bonding and the electronic structures of the high pressure phases CaLi₂ are studied in detail. The high-pressure structures of CaLi₂ and the physical mechanisms of phase transitions will be discussed.

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Keywords: *ab-initio* structure determination, high pressure, electronic structure

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Effect of pressure on the crystal structure of α' -Ca_{1.5}Sr_{0.5}SiO₄

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One of the high-temperature polymorph of Ca₂SiO₄, α' phase, which is stable above 973 K [1] is known to become quenchable to room temperature with incorporation of Sr [2]. It is reported that the phase transition between α' and α'' is displacive and α' is a hettotype of α'' which is isostructural with β -K₂SO₄. In order to estimate the structural distortion of the α' phase from the α'' phase, the tolerance factor (*t*) for the β -K₂SO₄ type structure was defined in this study. For the purpose of studying the effect of pressure on *t*, the crystal structure of Ca_{1.5}Sr_{0.5}SiO₄ was analyzed at 2.9 GPa and 4.6 GPa. A synthesized single crystal of 60 × 60 × 30 μm was placed in a modified Merrill-Bassett type diamond anvil pressure cell [3]. The pressure medium was a 4:1 mixture of methanol and ethanol and a stainless steel (SUS301) plate was the gasket. Pressure was calibrated by the ruby fluorescence method [4]. X-ray intensity measurements were performed using the BL-10A beam line at the Photon Factory (High Energy Accelerator Research Organization, Tsukuba, Japan). Judging from the observed bond compressibilities, *t* decreases with pressure and the structural distortion of Ca_{1.5}Sr_{0.5}SiO₄ increases with pressure.

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Rietveld refinement of natural fluorapatite from ultrahigh pressure eclogite

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Fluorapatite (FAP), found within eclogite from ultrahigh pressure orogen of China, is attracted for their structural response to pressure. Zhang et al. (2005) estimated the formation conditions of the ultrahigh pressure eclogite as >940°C and >4.5 GPa. Additional stress on FAP was kept away from crashing eclogite with hammer and grinding with agate mortar during the course of sample preparation. Powder X-ray diffraction method was used since the FAP aggregates containing amount of exsolutions on a scale of micrometer. The Rietveld method was performed for structure refinement. Polynomial background and the Pseudo-Voigt function were used for simulating measured profile. K-alpha 2 component was stripped and no smoothing was made. The final structure of the FAP is derived under the agreement index GOF=1.19. The space group of FAP is P6₃/m, and the refined cell parameters are *c*=6.8849(7) and *a*=9.3842(2) Å. That leads to a cell volume *V*=525.08 Å³. Metaprisim twist angle ϕ , defined as the (001) projected angle of O1-Ca1-O2, is measured as 23.91° from the refined structural model. The X⁻ ionic radius is measured as 1.313 Å from tunnel Ca-F minus Ca⁺² radius. This X⁻ ionic radius is less than 1.33 Å an expected dimension of closest packing model when *c/a*=0.734. The formula of the FAP is, on averaged, derived as: (Ca_{3.98}Sr_{0.01})_{3.99}(Ca_{5.96}Na_{0.01}Sr_{0.02})_{5.99}(P_{5.98}S_{0.02})₆O₂₄F_{1.99}. As compression on flexible one-dimension tunnel in apatite leads to structurally adjustment through an increase in angle ϕ , it follows that higher pressure correlates with higher angle ϕ . The structure of the FAP from ultrahigh pressure eclogite of China possesses a small cell volume and a large twist angle and demonstrates a good record for the ultrahigh pressure processes underwent.

Keywords: apatite, Rietveld refinement, ultrahigh pressure

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Pressure-induced structural change of Ca and Mg aluminosilicate melts

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Viscosity and density are important physical properties to control the transportation of magma in the Earth's interior, which are strongly correlated to microscopic structure of magma. Magmas have been considered to be densified by changing its structure with increasing pressure. We have studied the static structure of the Ca₃Al₂Si₆O₁₈ and Mg₃Al₂Si₆O₁₈ melts up to 5 GPa by X-ray diffraction analysis, in order to clarify pressure-induced structural change in topology and aluminium coordination environment. We have found the degenerated T-O peaks splitting into two peaks up to 5 GPa, indicating the coordination change of aluminium with pressure. This observation is consistent with the results of NMR studies on the Ca₃Al₂Si₆O₁₈ glasses quenched from high-*P* melts, showing the increase of population of highly coordinated aluminium