Mineralogical/crystallographic features of polycrystalline diamond, Yakutite

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Yakutite is a type of polycrystalline diamonds occurred from alluvial deposits in Northern Yakutia of Russia. It is characterized by a massive morphology and black color and appears to be similar to carbonado, another type of polycrystalline diamond. There are only a few previous studies on Yakutite and its origin (formation process and environment) and mineralogical/crystallographic characteristic have still remained unclear. In this study, I examined the microtexture of Yakutite samples by means of electron microscopy as well as x-ray diffractometry and Raman spectroscopy to understand what actually Yakutite is in material point of view.Raman spectra collected from Yakutite show a characteristic profile in which only a small and very wide diamond Raman peak at ~1330 cm^{-1} is observed together with a significant background increase toward the higher frequency side probably due to strong fluorescence signal from sample itself. The result suggests that the constituent diamond crystals in Yakutite are extremely small like the case of synthetic nano-polycrystalline diamond (NPD). The result of micro-focus XRD revealed the presence of varying degrees of lattice preferred orientation of diamond crystals and coexistence of lonsdaleite. Most samples show the co-axial relation between lonsdaleite 100 and diamond 111, suggesting that Yakutite is a product of direct conversion (martensitic transformation) from well-crystalline graphite.TEM observation showed that Yakutite consists of extremely small diamond grains of 5-50 nm which constructs weak lineation (layered-structure) along a particular direction. Electron diffraction also showed the coexistence of lonsdaleite with the co-axial relation to diamond (lonsdaleite 100 // diamond 111). Such a microtexture is well comparable to that of impact diamond from Popigai crater that is located at Northern West of Yakutia and produces a large amount of natural poly-crystalline diamond (Ohfuji et al., 2015). The distance between the locality of Yakutite and the Popigai crater is 350-500 km, which seems to be within the outreach of the long-distance ejecta from the crater. Therefore, Yakutite is an impact diamond that is originated from the large meteoritic impact at Popigai.

Keywords: Diamond, Phase transition, Meteoritic impact

Revisit to the structure of Ice XV: a DFT study

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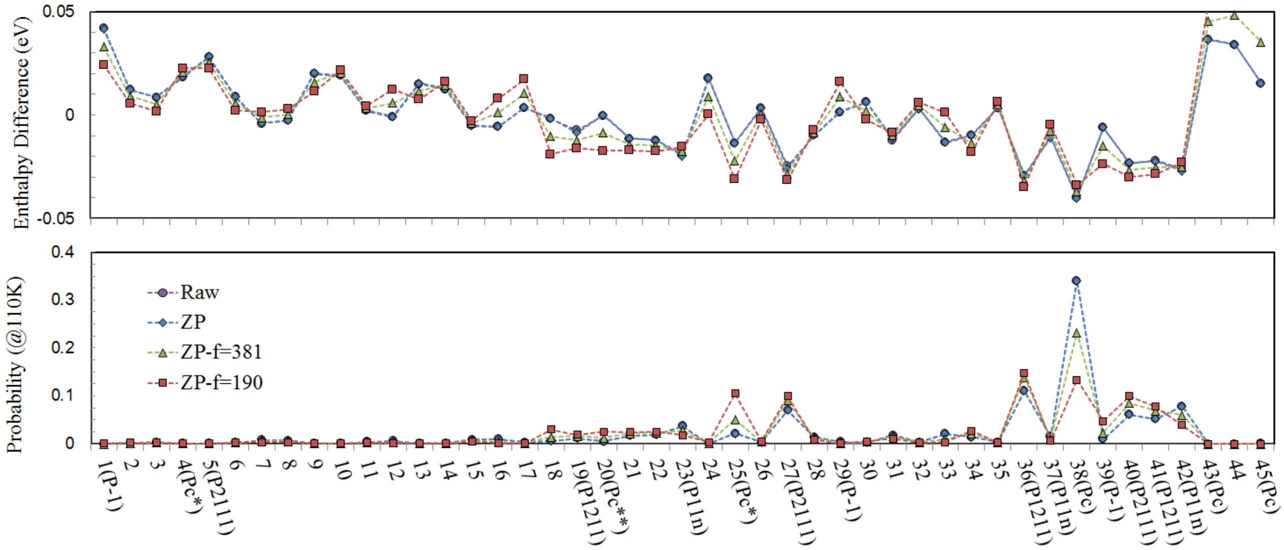
There are open questions in the study of ice XV, the ordered phase of ice VI. The previous studies give inconsistent results between permittivity measurement (Johari & Whalley, 1976), neutron diffraction study (Saltzmann et al. 2009), and theoretical studies (Kuo & Kuhs, 2006; Knight & Singer, 2005). Permittivity measurements and theoretical study suggest that ice XV is ferroelectric, whereas neutron diffraction study suggests that ice XV is anti-ferroelectric.

To obtain the consistent result, we classified 45 possible hydrogen configurations using a newly developed invariant, and then performed neutron Rietveld analyses and DFT calculations for every 45 possible configurations. The Quantum Espresso (Giannozzi et al. 2009) was used for the DFT calculations (Hohenberg and Kohn, 1964; Kohn and Sham, 1965). Quantum Espresso is a package for the calculation of electronic structure properties using a plain-wave basis set and pseudopotentials. We used Perdew-Burke-Ernzerhof type non-empirical exchange-correlation functionals (Perdew et al, 1996) for this study. PBE type Xc/Corr energy form gives similar energy tendency (del Ben et al., 2014) with approximations from wave function theory such as a MP2 (Head-Gordon et al. 1988) and RPA (Macher et al., 2014). The pseudopotentials are derived using Troullier-Martins Method (Troullier and Martins, 1991). The enthalpies of 45 possible configurations for ice XV were calculated within an unit cell with the kinetic energy cutoff of 70 Ry and the Brillouin zone k mesh of 5 x 5x 6. The cell and atomic parameters were optimized using BFGS quasi-Newton method (Broyden, 1970; Fletcher, 1970; Goldfarb, 1970; Shanno, 1970) at atmospheric pressure. The phonons were calculated using density functional perturbation theory (Baroni et al., 2001). To correct the effect of zero-point motions of atoms, we added calculated phonon energy ($=1/2\Sigma_n\omega_n$) to the enthalpies from structural optimizations for each configuration. The effect of ferro-electricity were corrected by the Ewald construction, the same as the previous work about ice XV (Del Ben et al., 2014).

A consistent result was obtained about the structure of ice XV that the experimentally obtained ice XV have *Pmmn* space group, that is, the structure of ice XV is partially ordered structure. Our DFT calculations with surface effect corrections suggest that the energy difference between 45 possible patterns is between 0.05 eV (20 K in the reduced temperature). Moreover, the energy differences among several lower energy configurations are within 0.01 eV. Such a small energy difference gives us an interpretation of our experimental result that the ice XV has a *Pmmn* space group as time-space averaged structure.

Keywords: Ice, Density Functional Theory


0.05
0
-0.05
Enthalpy Difference (eV)
0.4
0.3
0.2
0.1
0
Probability (@110K)
Raw
ZP
ZP-f=381
ZP-f=190
1(P-1)
2
3
4(Pc*)
5(P2111)
6
7
8
9
10
11
12
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19(P1211)
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23(P1n)
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27(P2111)
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36(P1211)
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39(P-1)
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41(P1211)
42(P1n)
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45(Pc)

Imaging Analysis of trace elements for high pressure minerals using LA-ICP-MS

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In order to investigate details of the Earth's deep interior, it is required to analyze the run product of high pressure experiments with highly sophisticated technique. Major and minor element concentrations of the sample are analyzed by EPMA, while trace elements are generally analyzed by using Laser Abration-Induction Coupled Plasma-Mass Spectroscopy (LA-ICP-MS), and Secondary Ion Mass Spectroscopy (SIMS). In these trace element measurements, an area with a few tens of microns in diameter is abrated by laser beam or ion beam, and quantitative analysis is performed. In recent years, two-dimensional imaging analysis has been made by LA-ICP-MS, and this technique has been used for qualitative analysis of trace element distributions in the sample. However, such data also can be used for quantitative analysis by adopting new data processing technique. In this study, the run products of high pressure melting experiments were analyzed by LA-ICP-MS imaging technique. The results are not only used for the qualitative two-dimensional distribution analysis of trace elements, but also used for estimation of the quantitative trace element concentration in high pressure minerals and silicate melts.

In this study, a peridotitic composition powder, which is doped with trace elements in approximately 200 ppm, was used for the starting material. High pressure melting experiments were performed by a Kawai-type multi anvil press installed at Tokyo Institute of Technology. In order to obtain large sized crystals of high pressure minerals, the temperature of the sample was raised above the liquidus, and then slowly cooled down to the desired temperature. Once the temperature reached the final target temperature, the sample was held for 30 to 60 minutes, and quenched isobarically. The recovered specimen was polished and their major and minor element compositions were determined by EPMA. Two-dimensional trace element analysis was performed by LA-ICP-MS at Kyoto University. This system is consisted of ArF Excimer laser and quadrupole-type ICP-mass spectrometer. The sizes of laser beam used in the present imaging analysis were 10 to 20 microns.

In the run products, garnet and wadsleyite were found as liquidus phases at 17 GPa. Under higher pressure conditions, liquidus phase changed to garnet + ferropericlase, and at above 23 GPa, they were bridgmanite + ferropericlase. The crystal sizes of these liquidus phases were larger than 50 microns except in ferropericlase. Compositional gradients of trace elements were found in large sized high pressure minerals by LA-ICP-MS imaging analysis. These compositional gradients must be originated from the slow cooling step in the present high pressure experiments. Compositionally homogeneous regions in high pressure minerals were selected from imaging analysis, and trace element concentrations were calculated. Partition coefficients between minerals and silicate melt were estimated from these quantitative results. The acquired partition coefficient values are consistent with the results which were obtained by the “normal” LA-ICP-MS analysis.

Keywords: high pressure minerals, trace elements, imaging

Density measurements of the FeS-NiS binary melts at high pressure

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Planetary cores consist mainly of iron, nickle and some light elements. Sulfur is thought to be a primary lightening element in the metallic core of the small planets, satellites and planetesimals. Planetary magnetism arises from a dynamo driven by convection in the liquid core. Physical properties of sulfur-bearing Fe liquids are, therefore, fundamental to understand the dynamics of liquid core in the planetary interior. Here we report the results of density measurements of FeS-NiS binary sulfide melts at high pressure by means of X-ray absorption technique. Experiments were conducted at BL22XU of SPring-8, at which the cubic-type multi-anvil press is equipped and highly brilliant monochromatic X-ray is available. We determined the densities and the expansivities of NiS, $(Fe_{0.3}Ni_{0.7})S$, $(Fe_{0.5}Ni_{0.5})S$ and $(Fe_{0.7}Ni_{0.3})S$ composition liquids at about 2GPa and 1273-1673 K. Density of (Fe,Ni)S liquid increases with Ni content. Compositional dependence of density allow us to evaluate the partial molar volumes of liquids FeS and NiS. The partial molar volumes of liquids FeS and NiS are consistent with those at 1 atmospheric pressure (Kress, 2008). On the other hand, the extrapolated densities of liquid FeS is 8-10% lower than the EoS determined by Nishida et al (2011). Our new data would contribute to understand compressional behavior as well as thermochemical properties of Fe-Ni-S liquid alloys under pressure.
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References

Kress,V (2008) Contrib Mineral Petrol, 156, 785-797.
Nishida, K et al (2011) Am Mineral, 96, 864-868.

Keywords: sulfide melt, density, partial molar volume, planetary core

Determination of low-temperature heat capacity and standard entropy of $Mg_{14}Si_5O_{24}$ anhydrous phase B

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It is expected that $Mg_{14}Si_5O_{24}$ anhydrous phase B (Anh-B) forms in the Earth's mantle by the reaction $5Mg_2SiO_4$ forsterite (Fo) + 4MgO = $Mg_{14}SiO_5O_{24}$ Anh-B when SiO_2 component in olivine and pyroxenes dissolves selectively into fluid and the residue is rich in MgO component. Entropy of Anh-B, which is needed to examine its thermodynamical stability, has not been determined experimentally yet. In this study, low-temperature heat capacity (Cp) was measured using PPMS equipment and standard entropy at 298 K was determined from the obtained heat capacity. The measured low-temperature Cp was also applied to modeling of a vibrational density of state used for Kieffer model calculation of the high-temperature Cp.

High-pressure synthesis of Anh-B was performed using a Kawai-type multi-anvil high-pressure apparatus. The starting material of the mixture of Fo and MgO (5:4 in mole ratio) was kept at 15 GPa and 2073-2273 K for 3 hours. After quenching, the sample was decompressed to ambient pressure. Micro-focused X-ray diffractometry and SEM-EDS analysis confirmed that the recovered samples were the single phase of Anh-B. Low-temperature Cp was measured in the temperature range of 2-307 K and with the step of about 2 K using PPMS (Quantum Design) by the thermal relaxation method. The bottom of the cylindrical samples was polished into very flat for better thermal contact with a heating stage. The total weight of the samples used for the PPMS measurement was 10.988 mg.

Low-temperature Cp was measured with the accuracy of about 0.3% at each measurement temperature. The Cp around 300 K obtained in this study is the same as that determined by our DSC measurement. This indicates the validity of the present measurement. By integrating Cp/T from 0 to 298 K using the obtained Cp, the standard entropy at 298 K was determined to be 554.17(1) J/mol.K. This value is smaller than 561.2 J/mol.K obtained by ab initio calculation of Ottonello et al. (2010) and is in good agreement with 547.3 J/mol.K estimated from entropies of the constituent oxides by Ganguly and Frost (2006). In addition, by the Kieffer model calculation using a vibrational density of state model which reproduces the low-temperature Cp measured in this study, the high-temperature Cp was extrapolated above 800 K at which Cp cannot be measured due to the collapse of the crystal structure by heating at 1atm. The Cp was obtained to be $Cp(T)=6.624\times10^2+2.123\times10^4T^{-0.5}-4.827\times10^6T^{-2}+2.221\times10^9T^{-3}-1.061\times10^{-1}T-3.643\times10^5T^{-1}$ in the range from 300 to 2000 K.

Keywords: anhydrous phase B, heat capacity, entropy, thermodynamical stability, lattice vibrational model calculation

Terahertz micro-Raman spectroscopy and its application to mineral sciences

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The terahertz (THz) region in the Raman spectroscopy refers to 200 cm^{-1} or less in the relative wave number. This region has been measured for a long time by a Raman system with triple-monochromator. However, less expensive and compact Raman systems with notch filter + single-monochromator + cooled CCD detector have been used widely recently. The filters used for these systems hardly measure the THz region. Therefore, THz region is less and less measured in recent years. Although THz region is not particularly necessary for the identification of mineral phases, boson peaks in glasses and soft modes of phase transitions are present in this region, making important region for dynamical studies. This unfortunate situation is now over, as ONDAX developed a new filter which can go down to about 5 cm^{-1} (doi: 10.1063 / 1.3520137). We adopted this filter to our home-made micro-Raman system, and the THz region can now be observed routinely. In this talk, I will present details of our system, and also demonstrate some applications.

Our original system is backscatter geometry, and use a Raman edge filter of Semrock, and can measure down to 100 cm^{-1}. When measuring the THz region, the filter is replaced with the ONDAX's filter (SureBlock, 488 mm). Since single filter is about OD4, so two filters are necessary to observe Raman peaks. They must be tilted a few degrees with respect to the optical axis, so are mounted on the kinematic mounts of Thorlab. The intensity of the Rayleigh scattering is minimized by adjusting tilting angles. Since the transmittance is about 60%, one-third sensitivity drop is expected compared to original system.

Sulfur is measured first. Sulfur is known to have a Raman peak at 27 cm^{-1}. The peak was observed in both the anti-Stokes and Stokes sides. When silica glass was measured, a boson peak was observed as expected. Then, moganite phase of $AlPO_4$, which was reported before, was measured. Two new peaks in the THz region are found. Since moganite phase has a transition at high temperature like quartz phase, these peaks might be related to soft mode.

Alanine, one of the amino acids, were also measured. Alanine molecule has the chirality, and it is impossible to distinguished D- or L-alanine molecule by Raman spectroscopy. However, situation is different, if it crystallized. The D- or L-alanine and racemized DL-alanine now have different symmetry in crystalline states, which could now be distinguished by Raman spectroscopy. Since the difference is mainly reflected in the vibrations between the molecules, the difference is expected to appear at the THz region. Therefore, D-, L-, and DL-alanine crystals were measured and compared. It was found that D-, L-alanine and DL-alanine can be distinguished by Raman peaks in THz region. This could be used to study racemization process experimentally.

Keywords: Micro-Raman spectroscopy, terahertz, mineral, alanine, racemization

High-pressure structural behavior of hydrogrossular, katoite $Ca_3Al_2(O_4H_4)_3$

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Nominally anhydrous minerals (NAMs) in the Earth's mantle are important because they may potentially introduce a large amount of water in the Earth mantle thus significantly modifying its elastic properties. Calcium aluminum garnet, grossular $Ca_3Al_2(SiO_4)_3$, with the largest divalent cation Ca^{2+} and the smallest trivalent cation Al^{3+} exhibits a complete solid solution with katoite, $Ca_3Al_2(O_4H_4)_3$, which is the Si-free end member of the hydrogrossular. Katoite is known as a typical model for the hydrogarnet substitution ($Si^{4+} \leftrightarrow 4H^+$) in garnets and other silicates. The replacement Si^{4+} by $4H^+$ results in profound changes in the physical properties and thermodynamic stability of garnet structure. We carried out high-pressure Raman spectroscopy, high-pressure single-crystal synchrotron X-ray diffraction study, and high-pressure neutron diffraction study to clarify the physical and structural properties of katoite at the mantle condition. Raman spectra collected at ambient conditions clearly showed the OH stretching vibration at 3652 cm^{-1}. Translational OH motion and mixed translational/librational motions of O_4H_4 were observed at 537 cm^{-1} and 332 cm^{-1}, respectively. It is noteworthy that with increasing pressure the OH stretching vibration mode exhibited a negative pressure shifts above 5 GPa, which is responsible for the hydrogen bonding formation in the O_4H_4 cluster. In addition, the pressure dependence of the full width half maximum (FWHM) of the OH stretching mode was also changed at the pressure, which is interpretable as a result of peak-splitting derived from cubic-tetragonal transformation. The results of high-pressure single-crystal X-ray diffraction and high-pressure neutron diffraction studies exhibited a discontinuous volume change occurs between 5 and 6 GPa, which supports the cubic (space group *Ia*-3*d*) to tetragonal (space group *I*-43*d*) phase transformation.

Keywords: hydrogrossular, katoite, high-pressure Raman spectroscopy, high-pressure single-crystal synchrotron X-ray diffraction, high-pressure neutron diffraction, structural phase transformation

Phase relations in SiC under high pressure and temperature and compression behavior in rock-salt-type phase

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Although planets in the solar system are oxygen-rich compared to the carbon, the exoplanets may have fundamentally different chemistry. For example, recently found super-Earth, 55 Cancri e is orbiting around the host star, which has particularly high C/O ratio. According to the mass-radius relations (McArthur et al., 2004; Winn et al., 2011; Demory et al., 2011), the interior of 55 Cancri e is expected to be carbon-rich similarly with the host star, and is possibly constructed from iron, silicon-carbide (SiC) and carbon (Madhusudhan et al., 2012). However, the physical property of SiC is so far poorly understood under high pressure conditions, although it is essentially important to know the internal structure of the super-Earth.

SiC is known to have polytypes such as 3C and 6H at ambient condition. It is reported that zincblende type 3C phase undergoes phase transition to rock salt type phase under high pressure. However, the phase transition pressures are inconsistent between theoretical prediction and experimental results. *Ab initio* calculation showed that the 3C phase transformed into the rock salt type phase at 66 GPa (Chang et al., 1987; Karch et al., 1996). In contrast, the previous experimental study observed the phase transition at 100 GPa or higher (Yoshida et al., 1993).

In this study, we have examined the phase relations of SiC under high pressure and temperature conditions by a combination of laser-heated diamond-anvil cell and *in-situ* X-ray diffraction (XRD) measurements at BL10XU of SPring-8. In addition to the phase relations, the compression behavior of rock salt type phase was firstly determined by means of experimental method. The XRD data were obtained up to around 100 GPa and 3500 K. The results showed that the rock salt type phase is stable above about 74 GPa and 2000 K, which is significantly lower pressure than the previous study without annealing. Obtained results showed that the rock salt type phase is 19.4 % denser than 3C phase at about 74 GPa. Such large increase of density may have a strong effect on the estimation of the internal structure of super-Earth, such as 55 Cancri e.

Keywords: silicon carbide, carbon planet, super-Earth, high-pressure phase transition, X-ray diffraction, laser-heated diamond-anvil cell

Synthesis of $LiNbO_3$-type $Mg_3Al_2Si_3O_{12}$ at 44 GPa and 2000 K using Kawai-type multianvil press with tungsten carbide anvils

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Garnet is one of the major constituent minerals of the upper mantle. In particular, pyrope is one of the most abundant components. Pyrope transforms to aluminous bridgmanite (Al-Brm) + corundum at about 25 GPa and Al_2O_3 content in Brm increases with increasing pressure (e.g. Kubo and Akaogi, 2000; Liu et al. submitted). Finally, Al-Brm with pyrope composition is synthesized over 40 GPa and 2000 K (Liu et al. submitted). Recently, Ishii et al. (2016) reported that recovered sample synthesized at 44 GPa and 2000 K has $LiNbO_3$ (LN)-type structure. Although there are synthesis reports of LN phase with $(Mg,Fe,Ca,Mn)Al_2Si_3O_{12}$ natural garnet (Funamori et al., 1997; Miyajima et al. 1999), synthesis with composition of pyrope end-member is first time and this structure refinement has never been made. Therefore, we made the Rietveld refinement of LN phase with pyrope composition. We also introduce high-pressure generation technique for synthesis over 40 GPa with a Kawai-type multianvil press (KMAP) in this study.

We used a 15-MN KMAP with DIA-type guide blocks carefully optimized to make a cubic compression space formed by first-stage anvils. WC anvils (TF05, Fujilloy Co., Ltd) of 1.5 mm truncation with 1.0 degree tapering were adopted for generating pressure over 40 GPa, combining a semi-sintered MgO + 5wt.%Cr_2O_3 octahedron as a pressure medium. Pressure at 2000 K was estimated with Al_2O_3 content in aluminous Brm by Liu et al. (submitted). Sintered ilmenite-type $Mg_3Al_2Si_3O_{12}$ (py-Ak) was synthesized as starting material at 26 GPa and 1200 K (Kubo and Akaogi, 2000) to minimize the pressure drop for volume change by phase transition. Sample was put in Re furnace surrounded by a $LaCrO_3$ thermal insulator. Al_2O_3 rods were placed at the both end of the sample in a heater and these were separated with Re disks. A microfocus X-ray diffractometer and an FE-SEM-EDS were used to analysis phase and composition of recovered sample. Synchrotron XRD data for Rietveld analysis were collected rotating sample at ambient conditions in SPring-8 (BL10XU). Rietveld refinement of recovered sample was performed using the RIETAN-FP/VENUS package (Izumi and Momma, 2007).

R factors for structure refinement were converged to reasonable values (R_{wp}, R_B and R_F<5). Lattice parameters of this phase with space group of R3c were determined as a = 4.8196(3) Å, b = 4.8195(3) Å, c = 12.6877(8) Å, V = 255.2(1) $Å^3$.

Keywords: LiNbO3 structure, Rietveld refinement, High-pressure generation technique, akimotoite, pyrope, Kawai-type multianvil press

The effect of high temperature on carbon solubility in cristobalite

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Silicates is one of the major and important components in the Earth’s crust and mantle. Because an enormous amount of carbon is stored in the Earth’s interior, it can be suggested that the silicates must be exposed to carbon under high-pressure and high temperature conditions (Sen et al. 2013). Recently, Santoro et al. (2014) demonstrated that carbon atoms can be substituted with silicon in cristobalite at $P = 16\text{-}22$ GPa and $T > 4000$K. Furthermore, the first-principles calculation showed the possibility that a continuous solid-solution can be formed between SiO_2 and CO_2 in a metastable cristobalite phase at ambient pressure (Aravindh et al. 2007). However, the effect of temperature on carbon solubility in silica has not been confirmed yet. Accurate knowledge of the carbon solubility in silica under high temperature can help us to understand the interaction between carbon and silicate minerals in the Earth’s interior. In this study, we investigated the carbon solubility and structure change of cristobalite under high temperature condition.

First, we prepared amorphous silica and graphite as starting materials. Powder amorphous silica and graphite were mixed sufficiently by an agate mortar and pestle. Second, the mixture was vacuum-enclosed in a quartz tube and heated at 1300°C for 3 days. Then, it was removed from the furnace and quenched at room temperature. The sample was carefully examined by powder XRD, EPMA, and IR spectroscopic analysis.

Regardless of the Si : C ratios of starting materials, all mixtures were crystalized into cristobalite. The result of the EPMA suggested that carbon was incorporated into cristobalite. The intensity of CKα was apparently increased with the carbon content. The amount of carbon in cristobalite was < 0.4 wt%. The powder XRD analysis revealed that all peaks corresponding to cristobalite were shifted to the lower angles, indicating the increases of unit cell and volume with the carbon content. Furthermore, cristobalite incorporating carbon in the structure was reheated in a quartz tube at 1300°C for 3days. The results of powder XRD showed that all of the peak positions came back to the original positions, which suggested that the carbon in crystobalite was resubstituted with oxygen atom. Therefore, these results support the following equation:

$SiO_2 + xC \leftrightarrow Si(C_xO_{2-x}) + (x/2)O_2$ $(0 \leq x \leq \alpha)$

Here, $\alpha$is the solubility limit.

Consequently, it can be concluded that carbon can be substituted with oxygen in cristobalite at high temperature. In addition, we will report quantitative experimental results of temperature dependence on carbon solubility in cristobalite in detail.

Keywords: carbon solubility, silicate mineral, powder XRD, EPMA

A Practical Investigation on Particle Number Dependence of Particle Size and Shape Distributions of Sand Particles by Automated Particle Image Analysis.

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[Introduction]

Particle size distribution (PSD) is one of the most important soil parameters often used in soil, mineral, geological, and geomorphological laboratories. To characterize of particles , an Image Analysis (IA) based on manual microscopic techniques is one of the effective ways to determine the morphological characteristics of particles ,such as their size and shape. However, one of the major drawbacks of manual microscopic analysis is the near impossibility of measuring a statistically significant number of particles, such as measuring tens to hundreds of thousands of particles, as recommended in ISO 13322-1,2. Recent advances in computer technology have allowed for the development of a new automated particle image analysis (APIA) approach that uses digital imaging technology to allow for the acquisition of 2D particle projection images of a statistically significant number of particles. This technique has allowed for the calculation of a wide range of morphological parameters, such as the size and shape of particles, as well as allowing for the identification and quantification of the most subtle of differences within tens to hundreds of thousands of particles. This study had suggested a practical investigation of particle number dependence of particle shape distribution of soil particle by APIA.

[Method]

APIA analyses were conducted on a Morphologi G3SE as automated image analysis system (Malvern Instruments, Worcestershire, UK). Sample was subsequently dispersed with an SDU using a short duration pulse of compressed air. Measurements were collected automatically using standard operating procedures (SOPs), which clearly define the software and hardware settings used during the measurement process. The measurement sample was dispersed on a glass plate, which was used as a sample carrier to minimize environmental exposure within the enclosed sample chamber unit.

Keywords: Particle Size and Shape, Image Analysys, Partcile Number

Magnetic and Structural transition of Fe-Si alloy under high pressure

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The Earth's core is consider to be divided into the liquid outer core and solid inner core based on seismological observations. The Earth's core is mainly composed of Fe although the density of the core is smaller than that of pure iron under the core conditions. Therefore, the core has been considered to contain light elements, such as H, S, Si, C, and O. In particular, Si is one of the most important light elements in the core. Although the phase relations and compression behaviors in the Fe-Si alloy have been studied at high pressure and temperature in order to investigate properties of the inner core, magnetic properties of the alloys have not been studied well. In order to clarify the relationship between the magnetic transition and the structural transition of the Fe-Si alloy, we made simultaneous measurements of X-ray diffraction and synchrotron Mössbauer spectroscopy the Fe-Si alloy up to 40 GPa at room and high temperature.

The starting materials of Fe-Si alloys used for the measurements had compositions of $Fe_{0.95}Si_{0.05}$ or $Fe_{0.88}Si_{0.12}$ enriched with ^{57}Fe. The mixture powder were heated in the Ar-H_2 atmosphere by a double sided laser heating system and the molten samples were quenched to room temperature by shutting the laser. Mössbauer spectra and XRD patterns were obtained at the beamlines, BL10XU and BL11XU of SPring-8 up to 40 GPa at room and high temperature. Our Mössbauer data together with X-ray diffraction data revealed that the magnetic transition started to transform from magnetic to non-magnetic phase at around 15 GPa for $Fe_{0.95}Si_{0.05}$ and 14 GPa for $Fe_{0.88}Si_{0.12}$. This transition was likely simultaneous transition with the bcc to hcp transition. The magnetic and structural transition pressures increased as increasing Si amounts in the Fe-Si alloys. In addition, Mössbauer spectra and XRD patterns were obtained from room temperature to 700 K at about 7 GPa. As the temperature raised, the internal magnetic fields became small and bcc structure started to transform to fcc structure at 870 K and 8.0 GPa and only fcc structure was observed at 920 K and 8.0 GPa.

Keywords: Fe-Si alloy, Mossbauer spectroscopy, Magnetic transition, Structral stransition

Stability of hydrogen sites and hydrogen bonding in humite group minerals

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Natural humite group minerals (norbergite, chondrodite, humite, clinohumite) generally contain both F and OH in the structures, but F-free phases (chondrodite-OH, clinohumite-OH) can be stabilized under high pressures. If these minerals contain Ti, OH content is reduced by a substitution of $TiO_2 = Mg(OH)_2$. Many structural refinements of both natural and synthetic humite group minerals are conducted to date. In term of hydrogen environments, two H sites (H1 and H2) are reported for chondrodite-OH and clinohumite-OH with 50% occupancies. If H1 site is fully occupied, short H1-H1 distance is realized in the structure, and it is generally thought that such configuration is less stable. On the other hand, in natural minerals containing F and Ti, only H1 site has been reported. Based on classical energy calculations (Abott et al., AmMin, 1989), it was suggested that H2 site is more stable, and is further stabilized in F- or Ti-containing systems. This is contrary to the observations. In order to clarify this issue, and further understand stability of H1 and H2 sites in relation with hydrogen bondings in the humite group, first-principles calculations of the humite groups are conducted. The calculations include F- and Ti-containing systems too.

For the calculations, Quantum-Espresso package is used, and PAW potentials with GGA (pbesol-kjpaw_psl) were used. First, structural models are constructed, and then the structures are optimized, and enthalpies of the systems are obtained. NMR parameters are also calculated. Chemical shift of proton provides a measure of hydrogen bonding. For all calculations, single unit cell was used, except Ti-containing system (chondrodite) where a 1x2x1 supercell was used.

For F- and Ti-free systems, when fully occupied H1 site and fully occupied H2 site are compared, H1 site was more stable energetically. This rather surprising result can be explained by elongated H1-H1 distance, whereas almost no hydrogen bonding in H2 site. When H1 and H2 sites are occupied 50% each, significant energy reduction was obtained by forming O-H1...O-H2 (... means hydrogen bonding) configuration. This configuration has lowest energy because H1-H1 repulsion no longer exists, and O-H1...O now forms straight hydrogen bonding. Therefore, for F- and Ti-free systems, the structures with both H1 and H2 sites half occupied are most stable as observed.

For natural minerals, OH contents are generally below 50%. As a result, O-H1...O configuration will not be realized in such systems. Therefore, solely occupied H1 or H2 sites should be compared. Our calculations reveal that in all humite minerals, H1 site is always more stable than H2. Note that short H1-H1 repulsion is no longer important in this system. Therefore, H1 is further stabilized. For Ti-containing systems, oxygens coordinating to Ti are underbonding state, and will behave as hydrogen acceptor. H1 site forms stronger hydrogen bonding with this hydrogen acceptor, where as H2 site can not, further stabilizing H1 site. Our calculations are fully consistent with the observed structures in F- or Ti-containing systems.

The present calculations reveals that hydrogen prefers H1 site, but when occupany exceeds 50%, H1-H1 repulsion forces hydrogen to occupy less stable H2 site. Similar situtation is know for topaz-F(OH), and can be interpreted similarly. Present study demonstrated that hydrogen bonding has strong influence on structural stability of humite group minerals.

Keywords: humite group, hydrogen bonding, First-principles calculation, crystal structure, hydrogen site, topaz-OH

Influence of framework and extra-framework cations substitutions on the zeolite structure: Single crystal X-ray diffraction analysis of analcime and wairakite solid solutions[$(Ca_{0.5x}Na_{1-x})AlSi_2O_6\cdot H_2O$]

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Zeolite is generally composed of Si/AlO_4 three-dimensional framework structure with interconnected cages and open channels. Cations and water molecules occupy the extra-framework space in the structure. Because the extra-framework cations can be substituted with different charged cations, consequently the Si/Al distribution in the framework is reordered to maintain its charge balance. The diversity of chemical composition caused by the coupled substitution gives the evidence of a effect of temperature, pressure and chemical potential on the mineral formation. Therefore, investigating the relationship between structural change and chemical composition may provide the clues to understanding the condition of rock forming processes at the near surface environment. The study aimed to clarify the structural change associated with chemical composition in a solid solution between analcime ($NaAlSi_2O_6\cdot H_2O$) and wairakite ($Ca_{0.5}AlSi_2O_6\cdot H_2O$). Single crystals with compositions between analcime and wairakite were synthesized by hydrothermal method. Aluminium sulfate, sodium metasilicate nonahydrate, and some calcium reagents gelled with distilled water were heated for 24 - 48 hours at 150 - 250 °C. The hydrothermally synthesized crystalline materials were analyzed by scanning electron microscope (SEM), electron probe micro-analyser (EPMA), and powder and single-crystal X-ray diffraction analyses. SEM images showed that the grown single crystals exhibited an euhedral trapezohedron shape ranging 100 - 200μm in size. From the EPMA analysis, we succeeded to synthesis the continuous solid solution exhibiting the chemical composition up to Ca/(Na+Ca) = 10 mol%. However, starting material with high Ca/Na ratio lead to yield fine products such as calcite and calcium sulfate. These by-productions inhibited the crystallization in the solid solution on the high Ca/Na side. Structure refinements based on the single-crystal X-ray diffraction data exhibited that crystal structures with the cubic Iad kept approximately unchanged with increase of Ca content in spite of the variation of Si/Al distribution in the framework. Lattice parameter a was monotonously increased from 13.713 (1) Åto 13.741 (1) Åas a function of Ca concentration. The contraction of the 6-membered oxygen rings was closely associated with exchanged Ca cations and reordered framework Si/Al cations. This study indicates that a geometry of micro-porous zeolite structure known as a molecular sieve is significantly influenced by the substitution of extra-framework cations followed by reordering of framework cations.

Keywords: zeolite, single crystal X-ray diffraction analysis

Mafic intrusion from Cape Nonamai,Shakotan Peninsula,Hokkaido

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Late Miocene doleritic intrusion are discussed from a petrological point of view.The intrusion consists of massive zone and layered zone.The massive zone is characterized by primitive olivine basalt,and the layered zone has more than 4 dolerite layers,which was originated by fractional crystallization from the mafic magma.

Keywords: fractional crystallization, dolerite, mafic intrusion