Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

SMP42-01 Room:102A Time:May 26 14:15-14:30

High-pressure phase transitions of Zn_2SiO_4: In-situ Raman spectroscopic study

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Zn and Mg have similar ionic radii, but their crystal chemical behaviors in silicates are quite different. In phase relation of Zn_2SiO_4 system, I (willemite), II, III, IV, V (modified spinel) phases are known (Syono et al., 1971), but only V has common structure with Mg_2SiO_4 system. Neither olivine nor spinel structures exist in Zn_2SiO_4. There difference is quite interesting in term of crystal chemistry. Recently, we have determined crystal structures of phases III and IV, and suggested that these phases are retrograde phases (Liu et al., 2013). In order to check this possibility, first-principles DFT calculations were conducted, and pressure-induced transitions for III and IV were discovered (Kanzaki, JpGU meeting 2014). In the present study, these transitions were checked experimentally using in-situ Raman spectroscopy. Phase II was also studied, since this phase is found to transform to (metastable) spinel structure by first-principles calculations.

For observation of phase transitions, in-situ Raman spectroscopy of samples in diamond anvil cell (DAC) was conducted. Symmetric DAC was used with low-fluorescence diamond (500 micron culet). Samples of phases II, III and IV were fragments made by multi-anvil press quench experiments (Liu et al., 2013). Gasket was made of SUS301H with 250 micron thick, and 200 micron hole after indentation was made. Pressure medium was alcohol mixture for phases III and IV, and KBr for phase II. Pressure was determined by Ruby fluorescence technique. All experiments were done at room temperature.

For phase III, Raman spectrum at 5.5 GPa gradually changed to new spectrum during compression process. During decompression, back transformation was observed at 1.5 GPa, and original spectrum of phase III was observed again. For phase IV, a transition was found at 2.5 GPa for both compression and decompression processes. For phase II, new spectrum appeared at about 13 GPa during compression process, but peaks were broad, possibly due to non-hydrostatic condition. Change of Raman spectrum at each transition was discontinuous, so these transitions should be 1st order in nature.

Present in-situ Raman spectroscopic studies confirmed that phases III and IV are indeed retrograde phases. Observed transition pressures were lower than their supposed stable pressure region, consistent with previous quench experiments (Syono et al., 1971). These results were consistent with our first-principles study too. However, for phase transition of III, octahedral Si is expected for high-pressure phase. Rather low observed transition pressure (5.5 GPa) suggests that the transition is not same as that observed by first-principles calculation.

Curretly, structural identification of high-pressure phases is underway by calculation of Raman spectra of candidate phases from first-principles.

Reference:

Liu, X., Kanzaki, M., Xue, X.(2013) Crystal structures of Zn_2SiO_4 III and IV synthesized at 6.5-8 GPa and 1,273 K, *Phys. Chem. Minerals*, **40**, 467-478.

Syono, Y., Akimoto, S., Matsui, M. (1971) High pressure transformations in zinc silicates, *J. Solid State Chem.*, **3**, 369-380.

Keywords: Zn2SiO4, phase transition, Raman spectroscopy, high pressure, crystal chemistry, crystal structure

SMP42-02 Room:102A Time:May 26 14:30-14:45

OH defects in hydrothermally synthesized monazite (LaPO4) and xenotime (YPO4) single crystals

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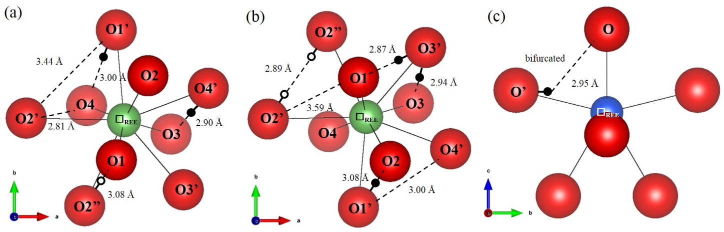
Monazite and xenotime are common REE (rare earth elements: here considered as Y and lanthanoid) minerals in crustal metamorphic and granitic rocks (e.g. Spear and Pyle 2002). These minerals are widely used in petrologic studies as a U-Th-Pb geochronometer (e.g. Parrish 1990, Suzuki et al. 1991) and a geothermometer (e.g. Gratz and Heinrich 1997, Pyle et al. 2001 and Viskupic and Hodges 2001). Furthermore, these minerals have been focused on as a functional material owing to their several exceptional physical and chemical properties such as the high fusion temperature, high chemical durability and wide stability fields, etc. (see also reviewed papers: e.g. Boatner 2002, Kolitsch and Holstam 2004, Clavier et al. 2011).

The X-ray analyses for these minerals has been conducted by Ni et al. (1995). Monazite has monoclinic symmetry with space group $P2_1/n$, and preferentially incorporates LREE (light rare earth elements, here La˜Gd). On the other hand, xenotime has tetragonal symmetry with space group $I4_1/amd$ (isostructure with zircon), and preferentially incorporates HREE (heavy rare earth elements, here Tb˜Lu + Y). Monazite and xenotime can contain trace amount of hydrogen as nominally anhydrous minerals (NAMs). However, only few studies have been reported on infrared spectroscopic measurements of monazite and xenotime. In this study, we conducted polarized infrared spectroscopic observation on hydrothermally synthesized monazite ($LaPO_4$) and xenotime (YPO_4) single crystals.

The single crystals of monazite and xenotime, synthesized with a piston-cylinder apparatus under a pressure of 1.0 GPa and cut perpendicular and parallel to the elongated direction, are mounted and doubly polished (i.e., monazite: $\boldsymbol{E}$ is nealy perpendicular to Y or Z, xenotime: $\boldsymbol{E} \perp c$ or a). The polarized infrared spectra of monazite and xenotime single crystals were measured in the transmission mode by Nicolet iN10 (Thermo Scientific Inc.).

Monazite crystals show two pleochroic absorption bands at 3164 cm^{-1} (FWHM = ca. 50 cm^{-1}) and around 3330 cm^{-1} (FWHM = ca. 140 cm^{-1}). On the other hand, xenotime crystals show a pleochroic absorption band at 3302 cm^{-1} (FWHM = ca. 10 cm^{-1}). According to obtained absorption figures, the OH dipole in monazite is weakly oriented to [110], while in xenotime, it is strongly oriented perpendicular to c-axis. Based on these results, we suggest the OH incorporation models as shown in Figure 1. Two incorporation models must be considered on monazite due to the n glide symmetric element. The charge balancing mechanism in monazite is expressed as $REE^{3+} \leftrightarrow \square_{REE} + 3H^{+}$. In contrast, the charge balance in xenotime is maintained by the reaction of $REE^{3+} + O^{2-} \leftrightarrow \square_{REE} + \square_{O} + H^{+}$. When the Libowitzky (1999) correlation is applied to the obtained band positions (monazite: 3164 cm^{-1} and 3330 cm^{-1}, xenotime: 3302 cm^{-1}), the O-O distance of 2.69, 2.76 and 2.74 Å is estimated, respectively. Considering the estimated inter-atomic distance and our OH incorporation models, we could suggest the formation of vacant REE site cause the slight deformation of monazite and xenotime crystal lattices.

Keywords: Monazite, Xenotime, Hydrothermal syntheses, Nominally Anhydrous Minerals, Polarized infrared spectroscopy



donor - acceptor : O1'- O4, O2'' - O1, O4' - O3

donor - acceptor : O1'- O2, O2'- O2'' or O2'' - O2', O3' - O1 or O3' - O3

●	Hydrogen atom bonded to the donor oxygen with 'two'-fold coordination
○	Hydrogen atom bonded to the donor oxygen with 'three'-fold coordination
$\square_{REE}$	Vacant REE site

The structural models are drawn using VESTA (Momma and Izumi 2011)

Figure 1. OH incorporation models of monazite (a), (b) and xenotime (c).
(a), (b) Two types of hydrogen sites, which corresponding to the coordination number of the donor oxygen, are considered. The two band positions at 3164 cm^{-1} and 3330 cm^{-1} would be brought by the coordination number difference of the donor oxygen.
(c) The hydrogen position would demand a bifurcated hydrogen bonding. This incorporation model is also proposed by Talla et al. (2011). Additionally in zircon (isostructural with xenotime), the same incorporation model is proposed by Nasdala et al. (2001).

The site and coordination number of oxygen atom in monazite and xenotime can be summarized as below. The oxygen atom in monazite occupies the four general positions (from O1 to O4). O1, O3 and O4 bond with two REE atoms and one P atom. Only O2 bonds with three REE atoms and one P atom. On the other hand, the oxygen atom in xenotime has only one site placed in a mirror plane, and bonds with two REE atoms and one P atom. For more details, see also Ni et al. (1995).

SMP42-03 Room:102A Time:May 26 14:45-15:00

X-ray and neutron diffraction experiments on hydrous silica glass under pressure

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We have studied structure of hydrous silica glass by using X-ray and Neutron diffraction experiments up to 10 GPa at ambient temperature. Hydrous silica glass was synthesized by quenching from melts under pressure, which contains 13 wt % of D_2O. X-ray diffraction experiments were conducted at BL04B2 of SPring-8 and AR-NE5 of Photon Factory. Neutron diffraction experiments were carried out at BL11 of MLF, J-PARC. Both X-ray and neutron diffractions show the shift of the FSDP of structure factor toward higher Q with increasing pressure, indicating the shrinkage of the intermediate range order with pressure. The radial distribution functions shows that the SiO_4 unit does not change up to 10 GPa but the Si-Si distance decrease with pressure. These also indicate the change of the intermediate range order. D-O distance in the hydrous silica glass is nearly constant, 0.92 Å. The changes of silica framework with pressure in hydrous silica glass are similar to those in dry silica glass.

Keywords: silicate glass, magma, neutron

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SMP42-04 Room:102A Time:May 26 15:00-15:15

Structural change of hauyne with increasing temperature

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Hauyne, $Na_3CaSi_3Al_3O_{12}SO_4$, belongs to the sodalite group. Most of nature hauynes have modulated structure. Previous researchers (e.g. Saalfeld, 1961; Tsuchiya and Takeuchi, 1985) studied the modulated structure of hauynes from some localities by X-ray and electron diffraction methods. The results from heating experiments showed there is a discontinuity of thermal expansion between 550 ℃ and 700 ℃, and the themal expansion coefficient of hauyne changed to small value above 700 ℃ (e.g. Taylor, 1968). Disappearance of satellite reflections, which indicated the phase transition, was observed between 390 ℃ and 407 ℃ by high temperature in situ synchrotron X-ray powder diffraction experiment (Hassan *et al*., 2004). The relationship between the structural change and the discontinuity of thermal expansion is unclear. High temperature in situ single crystal X-ray diffraction experiments was conducted to investigate relationship between structural charge and discontinuity of thermal expansion.

Hauyne from eifel, German was used to our experiments. The backscattered electron images showed the chemical composition of the crystal was homogenerous, and its chemical formula was determined as $Na_{2.83}Ca_{0.95}K_{0.21}Si_{3.06}Al_{2.93}O_{12}(SO_4)_{0.95}Cl_{0.03}$ by using an energy dispersive X-ray spectrometer (JEOL, JSM-7001F). High temperature in situ single crystal X-ray diffraction experiments were examined by using an imaging plate type X-ray diffractmeter (Rigaku, R-AXIS IV++) with a horseshoe-shaped Pt heater (Huber). Observation of the satellite peaks and determination of cell parameter were performed at eight points between 20 ℃ and 700 ℃. Crystal Clear-SM 1.4.0 (Rigaku) was used for data analysis.

The lattice parameter of the modulated structure of the sample was approximately eight times long as the basic structure. Satellite reflections were disappeared around 700 ℃ although they were observed until 600 ℃, therefore, structural change was indicated in the temperature range. Also, the axial length of a-axis increased monotonously with increasing temperature, and the thermal expansion coefficient between 600 ℃ and 700 ℃ have smaller value. The results suggested structural change of hauyne would affect the discontinuity of thermal expansion.

Keywords: hauyne, modulated structure, single-crystal X-ray diffraction, high temperature, in situ observation

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SMP42-05 Room:102A Time:May 26 15:15-15:30

Application of free volume theory to the model of thermal pressure for NaCl

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Mie-Gruneisen type equation is frequently used for the Temperature-Pressure-Volume equation of state (EoS) for pressure standard materials and minerals in the Earth's interior. Mie-Gruneisen type equation consists of the isothermal compression term and the thermal pressure term. In the thermal pressure term, Gruneisen parameter (γ) is very important thermodynamic parameter. It is known that γ relates to the property of isothermal compression as Slater's equation [1]. From the studies of molecular dynamics and potential theory, Barton and Stacey [2] advanced the free volume theory [3], and then derived the equation (called as "modified free volume formula" or "Barton-Stacey formula"), which can calculate practical γ values from the parameters of an isothermal compression curve. It is important that this formula gives theoretically support for volume dependence of γ, and moreover reduces the parameters of total EoS in number.

In this study, we apply Barton-Stacey formula to NaCl-B1 phase. We use the CT-EoS data as experimental reference, and the thermal pressure model, which include effect of intrinsic anharmonicity, as base model [4]. The power law γ at zero temperature in the base model is replaced by Barton-Stacey formula with the parameters of the isothermal EoS at zero temperature [5,6]. The value of f, which is the parameter relating to the randomness of thermal motion of atoms in Barton-Stacey formula, is estimated from using the free volume γ [3]. The present model reproduce successfully values of γ and specific heats without sacrificing accuracy, in spite of reducing one parameter of the EoS.

References

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[4] T. Sumita, A. Yoneda: Phys. Chem. Minerals, 41, 91 (2014)
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[6] A. Keane: Australian J. Phys., 7, 323 (1954)

Keywords: equation of state, thermal pressure, free volume theory, Gruneisen parameter, thermodynamics, NaCl-B1 phase

SMP42-06 Room:102A Time:May 26 15:30-15:45

Pressure measurements using diamond and cubic boron nitride

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Experiments using diamond anvil cells have been important in many studies of crystals and liquids at high pressure and temperature because these cells permit not only optical observation of the sample but also in situ measurement of the sample's physical and chemical properties. The pressure in the sample chamber of such cells is often determined by the shift in the wavenumber of a fluorescence line of ruby inside the sample chamber. However, the intensity of the ruby fluorescence decreases rapidly with increasing temperature. It is known that the first-order Raman mode of diamond anvil has been considered as a strong candidate of pressure marker because its Raman signal is intense and the diamond is always used as the anvil material in the DAC experiments. Cubic boron nitride (c-BN) is also a candidate of pressure marker because of chemical inertness and high temperature stability. It is the purpose of this study to present the dependences of pressure and temperature in the Raman lines of diamond and c-BN, using techniques combining synchrotron X-ray diffraction measurement with the Raman spectroscopic measurement.

The first-order Raman line at the culet face of the diamond anvil was investigated because the high-frequency edge of the Raman mode was correlated with the normal stress at the culet face of the diamond anvil. Thus, the edge frequency is a function of pressure and temperature in the sample chamber of the DAC experiment. Raman spectrum of c-BN exhibits two intense lines at 1054 and 1305 cm^{-1} under ambient conditions, corresponding to the Brillouin zone center transverse optical (TO) and longitudinal optical (LO) modes, respectively. The Raman line of the LO mode overlaps an intense Raman line of diamond at pressures higher than 3 GPa. Therefore, it is difficult to observe the LO line in high-pressure experiments using the diamond anvil cell. In contrast, the TO mode could be used as the pressure calibrant in diamond anvil cells under high pressure and temperature conditions.

High-pressure X-ray diffraction experiments were carried out in an external heated diamond anvil cell. The small sample sandwiched between pellets of NaCl powder was loaded into a hole that had predrilled into a rhenium gasket. The heating temperature was up to 1000 K, and was recorded using the K-type of thermocouples. The sample was probed using angle-dispersive X-ray diffraction, located on the synchrotron beam line, at BL10XU of the Spring-8. The angle-dispersive X-ray diffraction patterns were obtained on the X-ray CCD collection system. The pressure was calculated from the MgO unit cell volume using the equation of state (EOS) for MgO.

Experimental runs were carried out at pressures of up to 110 GPa. In each run, the sample was compressed to the desired pressure, and then heated to measure the shift of the Raman spectra of diamond [1] and c-BN [2] at high pressure and temperature. At each pressure increment, the cell was screwed to hold the sample pressure and the Raman spectra were acquired at 300-1000 K with decreasing temperature. Two peaks, which corresponded to the TO mode of c-BN and the LTO mode of diamond, were identified at high pressures and temperatures. At pressures higher than 90 GPa, the TO mode of c-BN overlapped with the intense Raman peak of diamond. This indicated that c-BN can be used as the pressure calibrant at pressures below 90 GPa in diamond anvil cell experiments [2].

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[2] Ono et al., *In situ* Raman spectroscopy of cubic boron nitride to 90 GPa and 800 K, J. Phys. Chem. Solid, 76, 120-124 (2014).

Keywords: Diamond, Cubic boron nitride, High pressure and high temperature

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SMP42-07 Room:102A Time:May 26 15:45-16:00

Diamond formation from magnesite in the presence of C-H-O fluid under high pressure and temperature

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Diamond formation in the Earth's mantle is believed to be a metasomatic process by fluid/melt with peridotitic and/or eclogitic rocks (e.g. Shirey et al., 2013). The ubiquitous occurrence of nano- to micro fluid inclusions in natural diamond and the result of recent experimental studies (e.g. Sokol et al., 2009) suggest that the presence of C-H-O fluid, which consist of a mixture of H_2O, CO_2, CH_4, etc. plays an important role in diamond forming reaction. The composition of C-H-O fluid depends largely on the surrounding oxygen fugacity. Taking into an account the oxygen fugacity values estimated from diamond-bearing xenoliths, the most major components of such fluids at the depth of 150-200 km are likely H_2O and CH_4 (Shirey et al., 2013). In the deeper mantle, the relative proportion of CH_4 is expected to increase with depth (Frost and McCammon, 2008). In the present work, we studied the diamond formation through the reaction between magnesite and reduced C-H-O fluid at high pressure and high temperature.

A series of high-pressure and high-temperature experiments (up to 30 GPa, 2000K) were performed by using laser-heated diamond anvil cell (LH-DAC). A small fragment of natural pure magnesite (either polycrystalline aggregate or single crystal) is loaded together with stearic acid ($C_{18}H_{36}O_2$) or pure CH4 in a sample chamber drilled in a pre-indented rhenium gasket. Upon laser-heating, the stearic acid is expected to produce CH4-rich fluid as a result of decomposition reaction ($C_{18}H_{36}O_2 \rightarrow 8CH_4 + 2H_2O + 10C$). A dual-beam CO_2 laser system (at Ehime Univ.) or a dual-beam fiber laser system (at SPring-8) was used for the heating. In-situ XRD observation at high pressure and high temperature was conducted in BL10XU of SPring-8. The samples after recovery were examined by XRD, Raman spectroscopy and scanning and transmission electron microscopies.

In-situ XRD observation showed that magnesite, $MgCO_3$ decomposes into periclase, MgO, brucite, $Mg(OH)_2$) and diamond in the presence of CH_4-rich fluid at pressures above 18 GPa and at ~2000K. Brucite is likely to be a metastable product, because the formation is usually observed at the beginning of the reaction and its relative proportion decreases with time by being taken over by the formation of periclase. The formation of nanocrystalline diamond was also observed in the samples recovered from the experiments. Although diamond was produced by the decomposition reaction of stearic acid through the equation described above, the reduction of magnesite by CH4-rich fluid must also have resulted in diamond formation. Inclusion studies of super-deep (lower-mantle derived) diamonds reported that the most dominant mineral phase found in such diamonds is periclase (up to 60%). However, this is not consistent with the result of high-pressure experimental studies using pyrolitic composition, where Mg-perovskite (bridgmanite) is the most dominant. Our result implies that some of the periclase inclusions solely found in those diamonds might have formed as a result of the reaction of Mg-rich carbonate with reduced C-H-O fluid. This means that the information obtained from diamond inclusion does not necessarily reflect the balk composition of the lower mantle. Furthermore, the formation of periclase at shallower condition (at 18 GPa) suggests that such formed periclase inclusions in diamond may not be used as indicator of lower-mantle origin.

Keywords: Diamond, Magnesite, C-H-O fluid, High pressure and high temperature

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SMP42-08 Room:102A Time:May 26 16:15-16:30

High-pressure behavior of cuprospinel $CuFe_2O_4$: the Jahn-Teller effect of Cu^{2+} on the spinel structure

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The Jahn-Teller-effect at Cu^{2+} in cuprospinel $CuFe_2O_4$ was investigated using high-pressure single-crystal synchrotron x-ray diffraction (XRD) techniques at beamline BL10A at the Photon Factory, KEK, Japan. Six data sets were collected in the pressure range from ambient to 5.9 GPa at room temperature. Structural refinements based on the data were performed at 0.0, 1.8, 2.7, and 4.6 GPa. The unit cell volume of cuprospinel decreases continuously from 590.8 (6) Å^3 to 579.5 (8) Å^3 up to 3.8 GPa. Least-squares fitting to a third-order Birch-Murnaghan equation of state yields zero-pressure volume V_0 = 590.7 (1) Å^3 and bulk modulus K_0 = 188.1 (4.4) GPa with K' fixed at 4.0. The crystal chemical composition determined by electron-probe analysis and site-occupancy refinement is represented as $^{[4]}[\mathrm{Fe}_{0.901}\mathrm{Cu}_{0.099}]^{[6]}[\mathrm{Fe}_{1.500}\mathrm{Cu}_{0.500}]\mathrm{O}_4$. Most of the Cu^{2+} are preferentially distributed onto the octahedral (M) site of the spinel structure. At 4.6 GPa, a cubic-tetragonal phase transition is indicated by a splitting of the ***a*** axis of the cubic structure into a smaller ***a*** axis and a longer ***c*** axis, with unit cell parameters ***a*** = 5.882 (1) Å and ***c*** = 8.337 (1) Å. The tetragonal crystal structure with space group $I4_1/amd$ was refined to $R1$ = 0.0332 and $wR2$ = 0.0703 using observed 39 x-ray reflections. The M-O bond distances along the ***c***-axis direction of the unit cell are elongated, whereas those parallel to the ***a***-***b*** plane are compressed. At the T site, on the other hand, the tetrahedral O-T-O bond angles along the ***c***-axis direction of the unit cell increases from 109.47 ^{o} to 111.7 (6) ^{o}, which generates a compressed tetrahedral geometry along the ***c***-axis. The cubic-to-tetragonal transition induced by the Jahn-Teller effect at Cu^{2+} is attributable to the elongation at the M site. The Jahn-Teller distortion by the Cu 3d orbital at the M site is confirmed by *ab-initio* quantum chemical calculations. With the competing distortions between the elongated octahedron and the compressed tetrahedron along the ***c***-axis, the ***a*** unit cell parameter is shortened with respect to the ***c*** unit cell parameter, giving a ***c***/***a*** ratio slightly greater than unity as referred to cubic lattice (***c***/***a*** = 1.002). The ***c***/***a*** value increases to 1.007 with pressure, suggesting a further variation of the elongated octahedron and the compressed tetrahedron. The variation of ***c***/***a*** ratio of the cuprospinel is similar to that observed in the tetragonally distorted cuprospinel with Cu^{2+} fully occupying the octahedral site of the structure.

Keywords: cuprospinel $CuFe_2O_4$, high-pressure, single-crystal synchrotron x-ray diffraction method, Jahn-Teller effect

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SMP42-09 Room:102A Time:May 26 16:30-16:45

Crystal growth textures developed in rapid cooling of olivine fine particles

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Olivine is one of the most common mineral in the solid Earth and chondritic meteorites. Olivine crystals show characteristic textures in chondrules depending on heating and cooling histories in chondrule formation processes at the early solar system. In this study, quick heating and cooling experiments of mixed olivine particles were carried out with a fine particles free falling apparatus with controlled gas flow (Isobe and Gondo, 2013). In the run products, characteristic melting and crystal growth textures controlled by phase relations, diffusion, and nucleation and growth behavior of olivine can be seen depending on maximum temperatures and cooling rates.

Starting material is mixed powder of natural olivine (Fo90), fayalite and an artificial olivine (Fo57). The typical diameter of the starting material particles is approximately 100 micron meters. Each particle is single crystal of olivine or mixture of two or three kinds of raw materials. Heating and cooling experiments are carried out in a high temperature furnace with mass flow controllers to regulate oxygen fugacity and total gas flow rate. Oxygen fugacity is controlled to average of FMQ and IW buffer curves in log unit. In the each run, maximum temperature of particles is just above 1500 degree C or 1400 degree C. Gas flow rates are 2.6, 1.3 or 0.65 l/min@RT. Particles can be heated to the maximum temperature within two seconds, are kept approximately one second and quenched within a second. Maximum temperature has negative correlation to diameter of the particles, and cooling rate has positive correlation to the diameter depending on the falling velocity of the particles. Run products show spherical shape when the particles mostly melted, and are crystal fragments when the particles did not melt. The outside shape of the retrieved run products are observed with a scanning electron microscope. Inner textures of the particles are observed on polished section of the particles. Chemical compositions are also analyzed on the sections.

Fayalite grains are completely melted and Fo90 olivine grains are not melted by themselves concordantly with the phase relation of olivine. Internal textures of Fo57 olivine crystals show quick partial melting when the temperature reach solidus temperature. Then, compositional ranges of quench crystals developed in fractional crystallization show negative correlation to cooling rates. Growth rate of quench growth olivine may be much higher than homogenization in heterogeneous silicate melt.

In the mixed olivine particles, relict crystals of Fo90 and Fo57 olivines dissolve to iron-rich melt derived from melting of fayalite. The dissolution of relict crystals produce steep chemical gradient at interface between crystals and melt. Melting kinetics of Fo90 olivine produces quite characteristic projections from the surface of spherules.

Textures of quench growth olivine on relict crystals resemble to hourglass shape. Compositions of the quench crystals range between Fo50 and Fo20. Solidus temperatures of olivine in this compositional range may keep supercooling in quenching processes.

Keywords: Olivine, melting textures, nucleation, crystal growth, dendrites, quench textures

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SMP42-10 Room:102A Time:May 26 16:45-17:00

Molecular dynamics simulations of oil wettability of muscovite-NaCl solution interface

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The investigations of the properties of mineral-electrolyte solution-oil interface are of importance for developments of resources and underground disposals of toxic wastes. The behavior of electrolytes at mineral-electrolyte solutions (e.g. formation of electric double layer) changes their properties. It is known that the wettability of mineral surface by oil in aqueous solutions depends on the concentration of the electrolytes. However, the fundamental relationship between the change in wettability and the behavior of electrolytes has not been revealed. Therefore, we applied molecular dynamics simulation, which provides nano-scale interfacial structure and dynamics of molecules, in order to investigate the mineral-electrolyte solution-oil interfacial structure and wettability. The muscovite, 3.0 mol/kg NaCl aqueous solution, and heptane or toluene were used as mineral, electrolyte solution, and oil, respectively. The simulations revealed that the adsorption of Na^+ at negatively charged muscovite surface decreases the interfacial tension at mineral-aqueous solution interface whereas negative adsorption of electrolytes increases the interfacial tension at oil-electrolyte solution interface for both the oil molecules. The changes in the two interfacial tensions alter the wettability of oil droplets. This research provides the fundamental knowledge for applications to enhanced oil recovery.

Keywords: Muscovite, Mineral-underground fluid interface, Wettability, Molecular dynamics

SMP42-11 Room:102A Time:May 26 17:00-17:15

High-pressure Raman spectroscopic studies of hydrogarnet, katoite Ca3Al2(O4H4)3

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Because garnet is capable of incorporating small concentrations, a lot of attention has been devoted to the hydrogarnet known as nominally anhydrous minerals (NAMs). The calcium garnet exhibits the complete solid solution between grossular Ca3Al2(SiO4)3 and Si-free katoite, hydrogarnet Ca3Al2(O4H4)3. Lager et al. (2002) suggested that in the katoite a phase transition occurred from space group Ia3d to I-43d which is a non-centric subgroup of Ia3d with increasing inter-tetrahedral H H repulsion.

We report in situ Raman spectroscopic studies of katoite in a diamond-anvil cell under hydrostatic conditions up to 10 GPa at room temperature. The vibration modes observed in the study were analyzed theoretically by factor group analysis. Three bands near 332 and 537, 3652 cm-1 were observed clearly at 1.0 GPa. In the wavenumber region of lattice modes, the lower frequency peak was assigned to a mode of Eg + F2g symmetry and the higher frequency peak was assigned to a mode of A1g + F2g symmetry. In the OH stretching vibration region, the peak was assigned to A1g + 2Eg + 3F2g symmetry. The peak positions and shapes in the Raman spectra agree well with those measured under ambient conditions. The pressure dependences of the lattice modes and the OH stretching vibration mode show a positive and negative pressure shifts, respectively. A shorter (and so stronger) hydrogen bond is well known to have lower frequencies than a weaker hydrogen bond (Nakamoto et al., 1955), therefore the negative pressure shift observed in the study indicated that the hydrogen bonding strength in katoite was increased as a function of pressure. Peak shift of the OH stretching vibration mode showed defferent trends at pressure above 5 GPa. Increasing rate of full width half maximum (FWHM) for lattice mode was varied at 6 GPa.

When the phase transition in katoite occurs from space group Ia3d (point group Oh) to I-43d (Td) at about 5 GPa (Lager et al., 2002), the vibration modes are never splitted with the phase transition. On the other hand, when the symmetry changes from Oh (cubic) to D4h (tetragonal), the Eg and F2g modes split to A1g + B1g and B2g + Eg, respectively. Therefore the expansion of FWHM above 6 GPa is interpretable as the cubic-tetragonal transition. The results in the study indicate that in katoite structural phase transition occurs from cubic to tetragonal at about 6 GPa.

Keywords: katoite, high-pressure Raman spectroscory, phase transition

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Physical properties of methane hydrate under low temperature and high pressure

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Methane hydrate, called fiery ice, has the potential to become an important energy resource in the future. It is also thought to be an important constituent of icy planets like Neptune and satellites such as Titan, thus making it an important part of planetary science. Methane hydrate is known to exhibit an sI structure at low pressures and room temperature, and transforms to an sH cage structure at approximately 0.8 to 1.0 GPa. A further transformation to a filled-ice Ih structure (FIIhS) occurs at approximately 1.8 to 2.0 GPa, with this structure consisting of an ice framework similar to ice Ih that contains voids filled with methane molecules The guest methane molecules are rotation freely in the ice framework. The FIIhS has been reported to survive up to 86 GPa at room temperature with two phase change. However, phase changes and properties at low temperatures and high pressures have not been studied so far. This study intended to clarify the changes in phase and properties of FIIhS of methane hydrate.

High pressure and low temperature experiments were performed using clamp-type diamond anvil cells and a helium-refrigeration cryostat. The pressure and temperature conditions were 2.0 to 77.0 GPa and 30 to 300 K, respectively. As the initial materials light-water host sample and deuterated-water one were used.

In situ X-ray diffractometry and Raman spectroscopy revealed existence of three phases and the phase boundaries between them. The first phase is guest orientationaly disordered phase, i.e. well-known FIIhS, which exists below 20 GPa, the second one is guest orentaional ordering phase above 20 GPa, and the third one is another guest ordering phase with different ordering manner. The results demonstrate that phase changes of methane hydrate proceed via proceeding of guest orientational ordering. However, it seemed a quite peculiar that the slopes of phase boundary are negative. Another low temperature experiments performed revealed the volume expansion at low temperature below 150- 100 K. The expansion was confirmed not due to non-hydrostatic effect but to be intrinsic by annealing treatment. The peculiar phenomenon were examined considering to host proton ordering.

Keywords: Methane hydrate, Low temperature and high pressure, Guest orientational ordering, Volume change