SMP044-01 Room:301B Time:May 25 10:00-10:15

muSR study on the behavior of trace hydrogen in silicates

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Hydrogen is the most abundant element in the solar system and the presence of water, which is formed by binding hydrogen and oxygen, makes the Earth a habitable blue planet. It is also believed that the presence of water, even if its amount is very small, alters physical and chemical properties of silicates significantly (for example, depression of melting temperature, decrease in viscosity, increase in electrical conductivity, etc.) and therefore plays an important role in geodynamics such as igneous activity and mantle convection and, what is more, in the terrestrial evolution from past to present to future.

That is why "water (hydroxyl)" in silicates has attracted a lot of interest and so far been studied by many researchers. On the other hand, "isolated hydrogen" in silicates may have been overlooked in previous studies because it is hard to probe the behavior of isolated hydrogen with ordinary techniques used in mineral physics and crystal chemistry. In the field of semiconductor science, however, it is well known that eliminating isolated-hydrogen atoms from a semiconductor is quite difficult and that their presence has remarkable effects on its physical properties. In the broad sense, silicates are classified as a semiconductor (i.e., wide-gap semiconductor) and therefore it may be possible that the same scenario takes place in them. The purpose of this study is to clarify the behavior of "isolated hydrogen" and "water" in silicates with muon spin rotation/relaxation/resonance (muSR) techniques, which have worked well in studies on "isolated hydrogen" in semiconductors.

Muon is a particle having a mass about 9 times less than that of proton and a spin of 1/2. In certain materials, a positive muon can pick up an electron to form a hydrogen-like atom called muonium. Therefore, positive muon can be considered to be a lighter version of proton. In muSR measurements, information about the site, the electronic state, and the diffusion dynamics of muon (an isotope of proton) can be obtained, by measuring the time evolution of the spin polarization of the muon implanted into a sample. Neutron diffraction is also a powerful tool to probe the behavior of hydrogen in materials. However, in neutron diffraction measurements, hydrogen should be in a framework structure of materials. muSR has the advantage of being able to probe the behavior of trace hydrogen irregularly located in interstitial sites of materials.

Japan Proton Accelerator Research Complex (J-PARC, Tokai-mura, Japan) is now successful in producing the most intense pulsed-muon beam in the world. The intense beam makes it possible to conduct muSR measurements on a relatively small sample (approximately 15 mm in diameter and 1 mm in thickness) at Materials and Life Science Experimental Facility (MLF). We applied to non-proprietary use experiments at MLF to clarify the effect of microscopic structures of silicates on the behavior of trace hydrogen and have the first beamtime in March 2011. In the first beamtime, we will conduct muSR measurements on high-pressure crystalline and glassy phases of SiO2 at ambient pressure. The samples have been prepared by using a belt-type high-pressure apparatus at National Institute for Materials Science (NIMS). In the future, we plan to develop high-pressure in-situ muSR techniques to conduct experiments at the conditions of the Earth's Interior. At the meeting, we will report about the first beamtime and discuss our plan to use muSR techniques in Earth science.

High pressure form of AlPO$_4$ with moganite structure

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We recently found three high-pressure phases of AlPO$_4$, and structural and NMR spectroscopic study of two phases (P-1, P21/c phases) are reported (Kanzaki et al., Acta Cryst. B, 2011). Third phase (synthesized at 5 GPa and 1500 ^{o}C) is later found to have moganite-type structure. Although moganite-type phase is reported for "PON" at high pressure, this is first moganite phase found in ABO$_4$ system.

AlPO$_4$ moganite was fuond in the sample recovered from 5 GPa and 1500 ^{o}C synthesized at SPring-8 using SPEED 1500 press. Micro-Raman spectroscopic inspection of the sample revealed the phase is previously unknown phase. ^{31}P MAS NMR and ^{27}Al 3Q MAS NMR indicate two tetrahedral sites for both Al and P, with intensity ratio 2:1. Powder X-ray diffraction of the sample is obtained by Rigaku's SmartLab. Since originally the structure was unknown to us, the structure was solved by FOX using XRD pattern with help of NMR information, and refined by Rietveld method (RIETAN-FP). The structure can be regarded as an ordered replacement of Si in moganite with Al and P, like berlinite. As a result, the space group of the phase is P2/c (moganite SiO$_2$ and PON are I2/a). First-principles calculation of the phase confirmed its structual stability. First-principles NMR properties calculations using GIPAW method were conducted, and the calculated parameters for moganite phase are consistent with those observed ^{31}P and ^{27}Al NMR.

The phase was also observed in in-situ high T-P powder X-ray diffraction measurements at BL04B1, SPring-8. Moganite phase stablizes at 4 GPa from berlinite. Moganite phase transforms to AlVO$_4$ (P-1) phase at 6 GPa and below 1250 ^{o}C, but at 6 GPa and above 1250 ^{o}C transforms to P21/c phase. Contrast to this, no moganite stability field was known for SiO$_2$ to date. Moganite phase was also reported in PON from high-pressure runs, but moganite phase was low pressure form of quartz phase (Chateau et al., Am. Mineral., 1999). Therefore, pressure-induced phase transformation sequence is opposite between AlPO$_4$ and PON. Differencies of enthalpy and volume of quartz and moganite is small, thus these properties might be reversed with chemistry.

Temperature-induced displacive phase transformation for SiO$_2$ moganite was reported (Heaney & Post, Am. Mineral., 2001), similar to those of quartz and cristobalite. Thus, such transition might be expected for AlPO$_4$ moganite. We are planning high-T Raman study to confirm this transition, and will report at the meeting.

To date, no synthesis condition for SiO$_2$ moganite is known, and only natural samples with low cristallinity and coexsiting other phases have been used for research. AlPO$_4$ moganite can be synthesized, and thus can be used for study to understand behavior of moganite structure.

Keywords: moganite, AlPO4, high pressure, phase transformation, crystal structure

SMP044-03 Room:301B Time:May 25 10:45-11:00

Theoretical and experimental evidence on the post-cotunnite phase transition in dioxides

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The cotunnite-type structure is identified as the highest-pressure phase in many dioxides and the post-cotunnite phase was still underdetermined. However, very recently, an *ab initio* work on silica has demonstrated a new possible phase transition to an unexpected hexagonal Fe_2P-type structure at 690 GPa with skipping the cotunnite-type stability at the static temperature (T. Tsuchiya and J. Tsuchiya, Proc. Natl. Acad. Sci. U.S.A. **108**, 1252, 2011). In this study, we systematically examined possibile post-cotunnite phase transitions in several low-pressure analogs of silica, GeO_2, SnO_2, TiO_2, and ZrO_2, with the electronic and crystallographic properties. Based on the theoretical prediction, we have performed in situ LH-DAC experiments and succeeded in experimental synthesis of the Fe_2P-type post-cotunnite phase in TiO_2.

Keywords: first principles calculation, high pressure, post-cotunnite phase transition, dioxide

SMP044-04 Room:301B Time:May 25 11:00-11:15

Development of density measurement method using X-ray micro tomography under pressure

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Density of melt is an important property for discussing melts related geodynamics processes in the deep Earth. Density measurement of melt at high-pressure is challenging because of its technical difficulties. Several methods, such as sink-float and the shock experiments have been developed to measure the densities of melts, but they are not enough. We have developed the novel X-ray absorption technique to measure the densities of melts at the desired P-T conditions using the multi-anvil press and synchrotron radiation. However, it has an intrinsic uncertainty because the length of sample is not measured directly. X-ray tomography is a breakthrough technique, which can yields the sample length as well as the sample absorption for X-ray. Thus, we are developing the new density measurement technique for melts using the high-pressure X-ray micro-tomography. Here we report the results of the reconnaissance experiments using the polycrystalline KBr up to 3 GPa.

X-ray tomography experiments were carried out using the tomography press TPH at BL20B2, SPring-8. The TPH is the 80 tons uniaxial press with two wide windows for observation and equips the toroidal type opposed-anvils. The TPH was set on the X-Y-Z-rotating stage and X-ray shadowgraphs of sample were acquired each 0.2 degree during rotation of the TPH. X-ray absorption of sample (I/I_0) was calculated from the shadowgraph image, and the sample length t was evaluated using the tomography slice image. Then, the densities of KBr at high pressures were calculated based on the Lambert-Beer law. The mass absorption coefficient of KBr was evaluated from the data acquired at 0.1 MPa, where the density is well defined.

SMP044-05 Room:301B Time:May 25 11:15-11:30

Simultaneous measurements of density and elastic wave velocities of NaCl at high pressures: absolute pressure scale

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The elastic compressional and shear wave velocities and densities of NaCl at 300 K and high pressures were measured using a combination of ultrasonic interferometry, in situ synchrotron X-ray diffraction and radiographic techniques in a large-volume Kawai-type multi-anvil apparatus. We adopted experimental data after heating the sample to 773 - 873 K under fixed press loads, to minimize nonhydrostatic components due to local deviatoric stresses, and have obtained high-quality elastic wave velocity and density data up to 12 GPa at 300 K. Both compressional and shear wave velocities are found to change linearly with density up to 12 GPa, satisfying Birch's law. Based on these measured data, we have derived the P-V equation of state (EOS) of NaCl at 300 K independent of any pressure scale. Comparison of the 300 K EOS between the present and previous studies will be presented in detail.

Keywords: pressure scale, NaCl, elastic wave velocity, high pressure

SMP044-06   Room:301B   Time:May 25 11:30-11:45

Thermodynamic properties of stishovite by heat capacity measurements and the coesite-stishovite transition boundary

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Stishovite is one of important minerals in science of the earth's mantle, and the coesite-stishovite transition boundary is widely used for pressure calibration at high temperature. The low-temperature isobaric heat capacity (Cp) of stishovite synthesized at 15.5GPa and 1400oC was measured between 2.3 and 311.4 K by thermal relaxation method using a PPMS. The measured Cp was considerably smaller than that by Holm et al. (1967) in the whole temperature range studied. The standard entropy, So298., of stishovite obtained is 24.0 J/mol.K, which is 3.8 J/molK smaller than that by Holm et al. (1967). Using the measured Cp, Debye temperature and thermal Gruneisen parameter at 298 K were calculated to be 1109 K and 1.68, respectively. The equilibrium coesite-stishovite transition boundary was calculated using the So298 of stishovite with published thermodynamic data including enthalpy of transition by Akaogi et al. (1995). The calculated boundary has a slope of 3.2?0.1 MPa/K at 1200-1600 K which is larger than the slope determined by high-pressure in situ X-ray diffraction study by Zhang et al. (1996).

Keywords: stishovite, thermodynamic property, heat capacity, coesite-stishovite transition

SMP044-07   Room:301B   Time:May 25 11:45-12:00

High-pressure Raman spectroscopy of calcium ferrite-type MgAl2O4

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A calcium ferrite phase appears as a high-pressure phase in the basalt under lower mantle conditions. Calcium ferrite-type $MgAl_2O_4$ is one of the major endmembers of the calcium ferrite phase. It is considerably difficult to synthesize a large amount of calcium ferrite-type $MgAl_2O_4$ because it is stable at pressures higher than 25 GPa. This prevents calorimetric measurements for the determination of its enthalpy, entropy and heat capacity, which are needed to discuss the thermodynamic stability. In this study, the thermal Grueneisen parameter used to calculate theoretically the isobaric heat capacity (Cp) was determined by performing high-pressure Raman spectroscopy.

A sample for the Raman spectroscopy was synthesized by keeping a starting sample of $MgAl_2O_4$ spinel at 27 GPa and 2200 C for 1 hour using a Kawai-type multi-anvil high-pressure apparatus. Micro-Raman spectroscopy was done using JASCO NRS-3100 (Nd:YAG laser with 532 nm). Observed Raman shifts were calibrated by those of trichloroethylene. A small chip of the sample was compressed using a diamond anvil cell high-pressure apparatus at ambient temperature. The pressure medium and metal gasket used were a mixture of methanol:ethanol = 4:1 (in volume) and SUS304 with 0.25 mm thickness, respectively. Pressure was determined by the ruby R_1 line.

Frequency changes for eighteen Raman-active lattice vibrational modes with increasing pressure at ambient temperature were observed in the pressure range from 1 atm to 10 GPa, at which the pressure medium is solidified. Mode Grueneisen parameters were calculated using lattice vibrational frequencies at 1 atm, pressure dependences of the frequencies, bulk modulus (K_T) of 241 GPa by Yutani et al. (1997). We obtained mode Grueneisen parameters of 1.07-2.67. The weighted average of them gave the thermal Grueneisen parameter of 1.67(4) by considering the contribution of heat capacity at constant volume (Cv) for each vibrational mode to total one, Cv_i/Cv. The Cv_i was calculated from the Einstein function. The obtained thermal Grueneisen parameter of calcium ferrite-type $MgAl_2O_4$ is slightly larger than that of calcium ferrite-type $CaAl_2O_4$ which was determined as 1.52(2) using the same method. This difference is caused by larger pressure dependencies of vibrational frequencies distributing in the range of 200-300 cm^{-1} for calcium ferrite-type $MgAl_2O_4$ than for calcium ferrite-type $CaAl_2O_4$. The vibrational modes in this region consist mainly of stretching modes of divalent cation (Mg^{2+} or Ca^{2+}). Therefore, it is implied that the lattice vibrations of divalent cations relatively affect the Grueneisen parameters in the calcium ferrite-type crystal structure.

Keywords: calcium ferrite, Raman spectroscopy, High-pressure, lattice vibration, Grueneisen parameter

SMP044-08   Room:301B   Time:May 25 12:00-12:15

## Comparison in temperature dependence of Ti K edge XAFS spectrum for PbTiO3,PZT, ATiO3 compounds (A=Mg,Ca,Sr,)

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Ti k-edge X-ray absorption near edge structure (XANES) spectra of PbTiO3 and various titanates such as ATiO3 (perovskite- and ilmenite-type structure, A=Mg,Ca,Sr,Ba,) were measured at various temperatures up to 1100 K. The composition, local structure and temperature dependence of XANES spectra was investigated especially on the phase transition. Ti atoms are located in TiO6 octahedral sites for the all samples. Ti k-edge XANES spectra change largely with different compositions, while the temperature dependence of XANES spectra is small in the each compound even if undergoing structural phase transition. Perovskite-type ATiO3 compounds reveal several phase transitions. SrTiO3 and PbTiO3 perovskite undergo structural phase transition in the temperature ranges in this study, SrTiO3; rhombohedral-tetragonal-cubic, PbTiO3; tetragonal-cubic, weak but distinct changing of the XANES spectra was observed near phase transition point. These structural transitions of perovskite are caused mainly by rotation and distortion of TiO6 octahedron. Pre-edge feature and local structure around Ti atom is little changing by rotation of octahedron. The distinct changing of pre-edge XANES spectra was observed at some transition points. Five pre-edge peaks can be identified: pp(a) 4.9667eV, pp(b) 4.9687eV, pp(c) 4.9727eV, pp(d) 4.9747eV and pp(e) 4.9796eV. The temperature dependence for each pre-edge peaks is largely different in temperature and local structure [1]. The different behaviors of the pre-edge intensity suggest that the increase and decrease of X-ray absorptivity at various temperatures is fluctuated by the hybridized orbital proportion and local symmetry.

References

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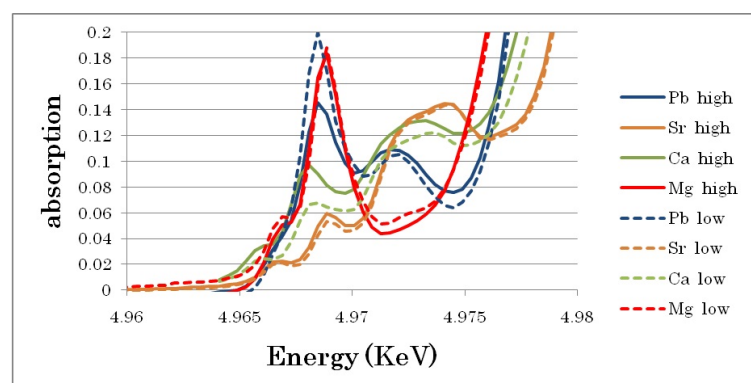
Keywords: perovskite, ferroelectric, phase transition

SMP044-09 Room:301B Time:May 25 12:15-12:30

Variety of Ti local structure in Tektite

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Tektite is formed as the meteorite impact the earth surface. Mass extinction is thought the reason of impact event, which is dated to 65 Ma. What happened at the event? According to research of tektite, speculate process of the event. Local structures of Sb, Zn in K-T clay are studied. Local structure of Ti in tektite is studied by X-ray Absorption Fine Structure (XAFS) method. XAFS is an advanced method, which can get detail information of valance state, neighboring atoms and the coordinated state. Local structures of Ti in tektites form different strewn fields are compared. The thresholds of XANES spectrum in various tektites are the same. They are also the same with nature minerals, which is Ti 4+. The intensity of pre-edge in moldavite is smaller than other tektites. But the previous studied by Farges, F. is shown the pre-edge intensity of Moldavite is strong as another tektite, and the coordination number is considered to four. According to the Fourier transformation spectrum are divided in three kinds. The Hainantite, Indochinite, Bediasite; Australite, Philippinite and the Moldavite; the Ti-O distance becomes large in proper order by each group. Coordination numbers and radial structure function determined by EXAFS analyses, we classified the tektites in three types: in Hainanite, Indochinite and Bediasite, Ti occupy 4-fold coordinated tetrahedral site and Ti-O distances are 1.84-1.79 A; in Australite and Philippinite, Ti occupy 5-fold trigonal bi-pyramidal or tetragonal pyramidal site and Ti-O distances are 1.92-1.89 A; in Moldavite, Ti occupy the 6-fold octahedral site and Ti-O distance is 2.00-1.96 A. Ti occupies the TiO6 octahedral site in many titanium minerals at ambient conditions. This study indicates that the local structure of Ti may be changed in the impact event and the following stage. Tektites splash to the space and travel in several kinds of processes and routes, which lead to different temperature and pressure history. Local structure of Ti should be related with the temperature, pressure, quenching rate, sizes of impact meteorite and size of falling melts. As a result, there are some differences in the bonding structure of Ti atoms and arrangements of neighbouring oxygen.

Keywords: local structure, titanium, tektite, XAFS

SMP044-10　　　　　　　　　　　Room:301B　　　　　　　　　　　Time:May 25 12:30-12:45

Seebeck Coefficient of Gabbro under Non-uniform Stress

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When a terminal of an air-dried igneous rock block is uniaxially loaded to form the non-uniform stress in the block at a room temperature, there appears the electromotive force that makes electric current flow from the stressed volume to the unstressed volume. Quartz-free gabbro tends to generate the stronger electromotive force than quartz-rich granite. Therefore, it is inconsistent to consider piezo-electric effect as the cause of this electromotive force. To explain this force, we have expected that positive charge carriers (holes) are generated in the stressed volume and flow into the unstressed volume. This will be the source of the electromotive force induced by non-uniform stress. However, we do not yet obtain reliable evidence for the activation/spread of positive holes. In this study, we measured thermoelectromotive force of air-dried gabbro blocks whose one terminal was uniaxially loaded/unloaded. We verified the activation/spread of positive holes from the increase/decrease of the Seebeck coefficient during loading/unloading. The hotter temperature was about 150 deg. C., the colder was about 30 deg. C., and the temperature difference was about 120 deg. C. The results indicated that the Seebeck coefficient of the gabbro without loading was about 0.8-1.2mV/K, meaning the majority of charge carriers are hole. On the other hand, the Seebeck coefficient of the volume under 60MPa of stress decreased to about 0.5-0.7mV/K, and that of the volume under stress free did not remarkably change. This meant that the concentration of holes increased in the stressed volume and such a change was little in the unstressed volume. In conclusion, it was clarified that holes were activated in the stressed volume and the distribution of the holes spreading reached only near around the stressed volume. As the source of the holes, we have focused on peroxy bonds, one of the most popular lattice defects in igneous rock-forming minerals, e.g., O_3Si-OO-SiO_3 in quartz. When this bond is deformed by mechanical force, an antibonding energy level of this bond shifts down into the Valence band and an electron can jump in this level from a neighbor oxygen site. As a result, a positive hole is activated in this neighbor site and an electron is trapped in the deformed peroxy bond. Once positive holes are activated, they can spread away through the Valence band. Provably, only a little part of the positive holes reached the unstressed edge. The slant in the distribution between these positive holes and the electrons trapped at the deformed peroxy bonds, i.e., the electric polarization in the stressed volume, is the source of the electromotive force induced by non-uniform loading.

Keywords: Igneous rock, Electromotive force, Seebeck coefficient, Lattice defect, Positive hole