Structural change of plagioclase glasses by mechanical milling

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Plagioclase (NaAlSi₃O₈-CaAl₂Si₂O₈) melt is important component of magma of the Earth. The information for the structure change of plagioclase glasses by milling is useful to understand earthquake and fault formation and material industry. Silicate glass changes its structure and density even milling as well as heating and compression. For example, it was reported that SiO₂ glass increase its density with Si-O-Si angle shrinkage and formation of small rings of SiO₄ tetrahedra [1]. In this study, we analyzed the structural changes with milling by X-ray diffraction and FTIR experiments and discussed the composition dependence of milling behaviors of plagioclase glasses.

We synthesized An100 and Ab50An50 composition glasses and milled up to 500 hours by ball mill technique. These milled glasses were analyzed by particle size, X-ray diffraction, and FTIR measurements. By milling about 20-80 hours, apparent average particle size decreases to about 2 micron in diameter. This data also indicate that An100 glass is easy to downsizing than the other glasses. After 20-80 hours, the size re-increased. This indicates the formation of aggregation of small milled glass particles.

The position of First Sharp Diffraction Peak (FSDP) at around 2theta=22-26 deg of XRD pattern related to the size of basic structure unit such as 4 and 6 membered rings of TO₄ (T=Al/Si) tetrahedra. This peak position shifts to high 2theta angle with increase of small ring structure of TO₄ tetrahedra. Obtained results indicate that the structure Ab100 glass change 6 membered ring of TO₄ dominant to the mixture of 4 and 6 membered ring structure. On the other hand, the shift for An100 glass is small. This may indicate that the structure of non-milled An100 glass has already 4 membered rings dominant structure [2]. Previous studies for SiO₂ glass reported the density increase by milling related with these structure changes [1]. The shift of FSDP position of Ab50An50 is larger than the others. Therefore, the structural change of Ab50An50 glass may be larger than the others. The results for FTIR also suggest these results. However, the origin of this variation is complex. A possibility may be formation of the units centered as Na⁺ and Ca²⁺ ions.

References

Keywords: plagioclase glass, ball mill, nano-structure, X-ray diffraction, IR spectroscopy
X-ray diffraction analysis of pyrope melts at high pressures

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Silicate melts play important roles in the chemical evolution of the planetary mantle and crust. Density and viscosity are important physical properties to control the migration of silicate melts, which are strongly related to structure of silicate melts. Thus the structural studies of silicate melts are fundamental to understand magma related processes in the planetary interior. Here we report the results of X-ray diffraction analysis of Mg₃Al₂Si₃O₁₂ (pyrope) melts at high pressures.

Static structure of pyrope melts has been studied by in situ x-ray diffraction experiments using synchrotron radiation at Photon Factory, KEK, Japan. X-ray diffraction patterns were acquired just above the melting temperature to about 5.5 GPa by energy-dispersive x-ray diffraction method and were analyzed by Fourier method.

The radial distribution functions show the decrease of the peak intensity that is related to the 4-fold coordinated Al-O and Si-O. This is explained by the decrease of the 4-fold coordinated Al and the increase of highly-coordinated Al with pressure. Pyrope includes large amount non-bridging oxygen and high field strength element Mg. Thus Al in the pyrope melt takes highly coordinated state at relatively low pressures.

Keywords: magma, synchrotron radiation, high pressure
Structure and properties of forsterite-MgSiO$_3$ liquid interface

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Knowledge about viscosities and permeability of partial molten rocks is important to understand the thermal history of the Earth and volcanism. For understanding those obtained by experiments and estimating the physical properties at extreme conditions that difficult to reproduce in laboratory experiments, knowledge about structure and properties of silicate crystal-liquid interfaces is necessary. In this study, structure and properties of the forsterite-MgSiO$_3$ liquid interface are investigated by using molecular dynamics simulations. It is essential to know the structure and physical properties of forsterite-MgSiO$_3$ liquid interfaces since forsterite is the liquidus mineral of primordial magmas.

Molecular dynamics simulations were performed with NPT ensemble using MXDORTO code. The interatomic potential model used in this study is same with used in Noritake et al. (2012). The initial structure is 21440 atom system in which a sheet of MgSiO$_3$ liquid consist of 8000 atoms is sandwiched between (010) surfaces of forsterite and 43440 atom system in which a sheet of MgSiO$_3$ liquid consist of 30000 atoms is sandwiched between (010) surfaces of forsterite. Structure and properties in the vicinity of interface was obtained at 0.1 MPa and various temperatures.

From simulation results, characteristic structure was observed in the forsterite-MgSiO$_3$ liquid interface. In the crystal-liquid interface, 2-30% of SiO$_4$ tetrahedra of forsterite surface bridge SiO$_4$ tetrahedra in liquid. In liquid region, SiO$_4$ tetrahedra concentrate in the vicinity of surface and form an SiO$_4$ tetrahedra rich layer of 0.4 to 0.6 nm thickness. Inner side of the first SiO$_4$ rich layer in MgSiO$_3$ sheet in liquid, the Mg rich second layer of 0.6 nm thickness is formed. Consequently, the structure of liquid is different from that of bulk liquid in 1.2 nm from crystal-liquid surface. However, the biased concentration approaches to bulk composition with the distance from the interface. In the first layer, internal energy of the system is lowered by bridging between SiO$_4$ tetrahedra at the crystal-liquid interface, and Coulombic interaction between non-bridging oxygen in liquid and magnesium at the crystal surface. In the second layer, interaction between concentrated magnesium and excess oxygen by bridging lower the internal energy.

The 2D self-diffusion coefficient oxygen in the plane in first layer is a half order lower than that of bulk liquid. However, the 2D self-diffusion coefficient of oxygen in Mg-rich second layer is a half order higher than that of bulk liquid. Existence of bridging oxygen between crystal and liquid, and concentration of SiO$_4$ tetrahedra in first layer might decrease the self-diffusion coefficient of oxygen in the first layer. Concentration of free oxygen, non-bridging oxygen and magnesium might increase the self-diffusion coefficient of oxygen in second layer.

This simulation results suggest that existence of small amount of melt might considerably decrease the viscosities of partial molten rocks and considerably increase permeability of partial molten rocks. However, it should be confirmed that this double layered structure in forsterite-MgSiO$_3$ liquid interface is equilibrium by performing of long time calculations.

Keywords: Interface, Molecular dynamics simulation, Silicates, Crystal, Liquid
Chemical heterogeneity in mantle olivine by temperature gradient

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Laser-heated diamond anvil cell (LHDAC) has been used as a major method to generate high temperature and pressure conditions of the Earth’s interior. In the laser heating experiments, only a local region can be raised to high temperature with a strong temperature gradient in the sample. The Soret effect is known as a phenomenon of chemical diffusion induced by temperature gradient, which causes a change of homogeneous material to heterogeneous chemistry. While the Soret diffusion in liquids has been popularly studied, that in solids and its pressure dependence have not been studied well because the Soret effect is relatively slow and more complex in solids than in liquids. The previous experiments using LHDAC (Heinz & Jeanloz 1987, Sinmyo & Hirose 2010, etc.) reported that a steep temperature gradient makes a large difference of element concentration between the laser-heated spot and its edge, however, the Soret effect in LHDAC have not been quantitatively analyzed.

In this study, we studied the material experienced a steep temperature gradient using LHDAC. Single-crystal or powdered San Carlos olivine with the composition of (Mg_{0.89}Fe_{0.11})_2SiO_4 was used as the starting material. The single-crystal experiments were conducted with NaCl as a pressure medium, while we loaded no pressure medium in powder experiments. Each sample was heated using a Nd:YAG laser without moving laser spot and kept the same temperature gradient. Temperature profile was measured by a spectroradiometric method. The recovered samples were analyzed using Field Emission-Scanning Electron Microscope (FE-SEM) and Electron Probe Microanalysis (EPMA). Experimental pressure and temperature were 10-30GPa and 1000-2000K, heating duration was 10-120 minutes. Various chemical heterogeneity formation was observed in different experimental conditions such as temperature gradient, heating duration and phase transition. We will report the details of these results on the Soret diffusion.

Keywords: LHDAC, Soret effect, diffusion in solid
Crystal structures of Zn$_2$GeO$_4$ spinel and Zn$_2$SiO$_4$ modified spinel phases

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High pressure phase relations of Zn$_2$GeO$_4$ and Zn$_2$SiO$_4$ were studied in 1960s to 1970s (e.g., Syono et al., 1971) in relation to high-pressure mantle minerals, but the crystal structures of high pressure phases discovered have not been determined, except for phase II of Zn$_2$SiO$_4$. In last year’s JPGU meeting, we reported the structures of phase III and IV of Zn$_2$SiO$_4$ (SIT02-24). Here, we report the crystal structures of cubic and tetragonal spinels in Zn$_2$GeO$_4$ and phase V of Zn$_2$SiO$_4$, and also present new structural insights regarding phase III and IV of Zn$_2$SiO$_4$.

All samples were synthesized using 5000ton Kawai-type multianvil press at Misasa. Starting materials were Zn$_2$GeO$_4$ and Zn$_2$SiO$_4$ phenacite phases synthesized at ambient pressure. Powder X-ray diffraction patterns were obtained at BL19B2 of SPring-8 using a large Debye-Scherrer camera. For refinement, the Rietveld method was used (RIETAN-FP). Details of the procedure are same as those of Kanzaki and Xue (2012). $^{29}$Si MAS NMR spectrum of phase V was also obtained.

Cubic and tetragonal spinels of Zn$_2$GeO$_4$ were synthesized at 3 GPa and 1600 °C, and 5 GPa and 1200 °C, respectively. As expected, these spinels have inverse-type in which the tetrahedral site is occupied by Zn. For tetragonal spinel, the symmetry is lowered as a result of ordering of Zn and Ge in the octahedral sites. The tetragonal spinel phase is isostructural to Zn$_2$TiO$_4$. Bond distances calculated by Brown’s bond valence agree well with the experimental values from the present study.

For the structures of phase III and IV of Zn$_2$SiO$_4$, after last year’s presentation (SIT02-24), we noted that phase III is isostructural to the high-temperature phase of (Zn$_{1.1}$Li$_{0.6}$Si$_{0.3}$)SiO$_4$ (Liu et al., 2013). The latter structure is related to the olivine structure in that metal cations occupy vacant tetrahedral sites, rather than octahedral sites of the olivine structure, and is referred to as “tetrahedral olivine” by Baur (1980). In phase IV, triclusters made of two ZnO$_4$ and one SiO$_4$ sharing a common oxygen form columns running along the c-direction. Similar columns also exist in phase II, which explains the similar densities of phases II and IV.

We refined crystal structure of phase V of Zn$_2$SiO$_4$, and confirmed that it has a modified spinel structure. Its structural parameters are similar to those of Mg$_2$SiO$_4$ wadsleyite. Octahedral sites are occupied by Zn only, and no Zn/Si disorder was detected. This is consistent with the $^{29}$Si MAS NMR result that revealed a single peak of tetrahedral Si for phase V.


Keywords: Zn2SiO4, Zn2GeO4, high pressure phase, crystal structure, spinel, crystal chemistry
High-Pressure Transitions of NaZnF3 and NaMnF3 Perovskites with Implication to Mg-SiO3 Postperovskite Analogues

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It is accepted that MgSiO3-rich perovskite (Pv) transforms to postperovskite (pPv) in the lowermost mantle. Investigations on MgSiO3 pPv properties are of great interest to clarify the structure and dynamics of the core-mantle boundary region. However, because of high stability pressure and temperature of MgSiO3 pPv exceeding 120 GPa and 2000 oC and amorphization of the pPv on release of pressure, ABX3 compounds that undergo the Pv-pPv transition at lower pressure and are quenchable to ambient conditions are important as analogues for MgSiO3. In recent years, we found that CaRuO3, CaRhO3, NaNiF3 and NaCoF3 undergo the Pv-pPv transition below about 20 GPa, and determined the phase relations. We also refined the pPv structures and measured some physical properties (Kojitani et al., 2007, Shirako et al., 2009, 2012, Yusa et al., 2012). In this study, we have examined high pressure transitions in NaZnF3 and NaMnF3 and determined the phase relations as well as structural refinement of the NaZnF3 pPv. Combining the previous results on NaNiF3 and NaCoF3, we discuss on A+B2+F3 fluorides as analogue compounds for the Pv-pPv transition in MgSiO3.

High pressure experiments on NaZnF3 and NaMnF3 were made at 9-24 GPa and 600-1000 oC using a multianvil apparatus. The recovered NaZnF3 samples were crushed into powder in liquid nitrogen, and examined by powder X-ray diffraction for phase identification. The run products of sintered NaMnF3 samples were examined by microfocus X-ray diffraction method. The structure of NaZnF3 pPv was refined by Rietveld analysis.

NaZnF3 Pv transforms to pPv at 10-15 GPa. The NaZnF3 pPv partially transforms back to Pv on release of pressure. The transition boundary in NaZnF3 is expressed as P(GPa) = 4.9 + 0.011T(oC), and its volume change is -1.9 %. At 8-11 GPa, NaMnF3 Pv dissociates into two phases of Na3Mn2F7 and MnF2. Although the MnF2 phase in the recovered samples has a ?PbO2-type structure, it is suggested to be an O-I type or cotunnite-type structure at high pressure. The refined structure of NaZnF3 pPv is close to that of NaNiF3 pPv. Deformation of octahedra in the two pPv structures is similar to that of MgSiO3 pPv at 120 GPa (Murakami et al., 2004), but is smaller than those in CaMO3 pPv (M = platinum group elements and Sn). The Pv-pPv transitions in NaZnF3, NaNiF3 and NaCoF3 occur at pressure below about 20 GPa. The axial compressibilities of Pvs and pPvs of the three fluorides change in the same order as those of MgSiO3 Pv and pPv. The Pv-pPv transitions in the three fluorides occur at the Pv octahedral tilt-angle of about 26o, at which the transition occurs in MgSiO3. All of the above results suggest that the fluorides are good quenchable, low-pressure analogues for the Pv-pPv transition in MgSiO3. In particular, NaNiF3 is most valuable, because the pPv phase is quenchable as the single-phase material at ambient conditions.

Keywords: perovskite, postperovskite, high-pressure transition, fluoride, lower mantle, analogue material
Ab initio computation on the Fe L-edge X-ray emission spectroscopy of Fe-bearing MgSiO3

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Behaviors of iron (Fe) in the minerals of the Earth’s lower mantle (LM), including valence state, spin state, and chemical environments, at high pressures are important for more detailed understanding the LM properties. The pressure induced spin transition of Fe-bearing MgO and MgSiO3 perovskite (Pv) were detected usually by using high-resolution K-edge X-ray emission spectroscopy (XES) [1,2,3] and confirmed by theoretical simulations [4,5]. Since the Fe K-edge XES is associated to the 3p orbital, which is far from the valence orbitals (3d and 4s), it provides no information about Fe’s coordination environments. However, Fe L-edge XES can directly determine the distribution and intensity of Fe-3d character. To identify the spin state, valence state and substitution site of Fe in Fe-bearing Pv at the LM pressure range, we systematically investigated the L-edge XES of Fe2+ and Fe3+ (Al3+)-bearing Pv under high pressure by using the first-principles method combined with the slater-transition method. Our results show that the spin transition of Fe2+ and Fe3+ can be identified easily by the L-edge XES technique. The valence state of Fe can be furthermore certified, since the shift of the first main peak of Fe3+ is about two times larger than that of Fe2+ across the spin transition. The width of the L-edge XES of Fe3+ is also sensitive to the substitution site, indicating that their coordination environments might also be distinguishable from the Fe L-edge XES spectra. These strong sensitivities to the Fe states suggest that the high-resolution Fe L-edge XES measurement would be a useful experimental technique to investigate Fe-bearing silicate minerals. Corresponding experiments are expected.

Keywords: First-principles calculation, Fe L-edge XES, Mg perovskite
Synchrotron XRD and Mossbauer spectroscopic study on Ca$_2$MgSi$_2$O$_7$-Ca$_2$Fe$^{3+}$ series melilite at high pressures

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Synthetic Ca$_2$MgSi$_2$O$_7$ (akermanite: Ak)-Ca$_2$Fe$^{3+}$+AlSiO$_7$ (ferrialuminium gehlenite: FAGeh) series melilites were investigated using synchrotron X-ray diffraction and synchrotron-radiation-based Mossbauer spectroscopic methods to determine the distribution of Fe$^{3+}$ between two structurally independent tetrahedral sites (T1 and T2), and the relationship between ionic substitution and incommensurate structure in melilite at high pressures. $^{57}$Fe-doped Ak-FAGeh melilites were synthesized from starting material with composition of Ak$_{50}$FAGeh$_{50}$ by sintering technique at 1140-1180 oC and 1 atm for high pressure experiment. The average chemical composition of the synthetic melilites was Ca$_{2.00}$Mg$_{0.56}$Fe$_{3+0.42}$Al$_{0.44}$Si$_{1.57}$O$_7$. The site populations at the T1 and T2 sites at the synthetic condition were determined by X-ray Rietveld analysis and $^{57}$Fe Mossbauer spectroscopy (340MBq $^{57}$Co source) to be [0.557Mg+0.280Fe$^{3+}$+0.237Al]$_{T1}$[0.197Fe$^{3+}$+0.176Al+1.574Si]$_{T2}$ (apfu: atoms per formula unit), which is consistent with that by Hamada and Akasaka (in press).

The experiments at high pressures were performed using a diamond anvil cell (DAC) with cuvet size of 0.3 mm. A Rhenium gasket was pre-indented to 0.06 mm in thickness, and a hole with 0.1 mm in a diameter was drilled in the gasket as the sample chamber. NaCl was used as pressure medium. In addition to the powder sample, several ruby tips (0.01-0.02 mm in diameter) were put into the chamber as a pressure marker. The pressure was estimated based on Ruby fluorescence (Mao et al., 1978). Mossbauer spectra and X-ray diffraction were taken at the beamline BL11XU of SPring-8. The energy of used gamma-ray for Mossbauer spectroscopy was 14.4125 keV. Mossbauer spectra were measured at 0.8, 1.6, 14.1, 18.7 GPa. The spectra were fitted to Lorentzians with widths and intensities constrained to be equal at each site, using synchrotron-based-Mossbauer analysis program S8QBMOSS (Hamada and Akasaka, in prep.).

At 0.8 and 1.6 GPa, Mossbauer spectra consisted of two doublets assigned to T1 and T2 sites. However, Isomer Shifts (I.S.) of T1 and T2 sites at 1.6 GPa (0.11(5) and 0.05(5) mm/s, respectively) were smaller than those at ambient condition. Area ratio of Fe$^{3+}$ (T1):Fe$^{3+}$ (T2) at ambient condition was 47(1):53(2) (Hamada and Akasaka, in press). Whereas, area ratio at 0.8 and 1.6 GPa were 52(10):48(9) and 44(9):56(8), respectively. Mossbauer spectra at 14.1 and 18.7 GPa consisted of only one doublet assigned to Fe3+ at T2 site. However, the half width was broad, suggesting that the spectrum consists of strongly superimposed doublets.

The variation of the Mossbauer hyperfine parameters (I.S. and quadrupole splitting Q.S.) suggests that covalencies of T1-O and T2-O bonds increase and difference of geometric properties (site distortion and mean T-O distance) between T1O$_4$ and T2O$_4$ tetrahedra becomes smaller with increasing pressure. Yang et al. (1997) reported the incommensurate (IC)-normal (N) phase transition at 1.7 GPa. The smaller I.S. values may be caused by IC-N phase transition.

Keywords: Synchrotron X-ray diffraction, Synchrotron Mossbauer spectroscopy, Synthetic melilite, Incommensurate structure, High pressure
Magnetic phase diagram of (Mg,Fe)O: reinvestigation

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(Mg,Fe)O shows complex magnetic behavior due to the presence of non-magnetic magnesium ion. For example, (Mg0.23Fe0.77)0.92O shows Neel transition at 128 K and spin-glass like phenomena below 76 K at ambient pressure [Abbas and Hicks, 1990]. Although we reported a magnetic phase diagram and suggested that the magnetic structure would be differ between iron-rich side and magnesium-rich side [Fujii et al. 2011], the magnetic property of (Mg,Fe)O at ambient pressure is still unclear. In this study, we reexamined the compositional dependence of magnetic ordering of (Mg,Fe)O at ambient pressure. We used Superconducting Quantum Interference Device (SQUID) magnetometer (MPMS-7 or MPMS-XL, Quantum design Inc.) to measure the temperature dependence of magnetic susceptibility by cooling sample in zero field (ZFC) and in a field (FC). The magnetic field dependent of susceptibility and the temperature dependence of AC magnetic susceptibility were newly measured. In the iron-rich (Mg,Fe)O, the ZFC curve show a peak-like cusp at relatively high temperature and a kink at low temperature. An irreversibility was observed between the ZFC curve and FC curve below the kink temperature. These behaviors are the same as those of (Mg0.23Fe0.77)0.92O observed in the previous study [Abbas and Hicks, 1990]. Therefore, the kink and the cusp would indicate a spin-glass transition and Neel transition, respectively. In the case of the magnesium-rich (Mg,Fe)O, the ZFC curve show no kink and an irreversibility below the cusp temperature. Therefore, it would show no Neel transition but spin-glass transition. We also observed a superparamagentic like phenomena in all sample. These interpretations are supported by the magnetic field dependence of susceptibility and the AC magnetic susceptibility measurement. Therefore, the magnetic ordering of magnesium-rich (Mg,Fe)O is distinctly different from iron-rich (Mg,Fe)O at ambient pressure.

Keywords: (Mg,Fe)O, magnetic ordering
Temperature quenching mechanism of cathodoluminescence in forsterite

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Recently, cathodoluminescence (CL) zoning of the forsterite in carbonaceous meteorites has been investigated to clarify the origin and thermal history of the chondrules. CL spectroscopy can detect a trace amount of impurity elements such as Mn, Cr and Ti and lattice defects, which relate to Al-O centers and primary intrinsic centers. However, a small amount of divalent Fe ions as quencher easily eliminate CL emissions caused by any luminescent centers, so only near end forsterite could emit CL. In this study CL spectroscopy of forsteric samples has been conducted to interpret emission mechanism of their luminescent centers by an SEM-CL, and quantitatively analyze a thermal effect on forsterite CL by assuming the Mott-Seitz quenching model.

Forsterite crystals (Fo: 99.1) in basalt from Mogok, Myanmar and micro-grains (Fo: 99.7-99.8) in chondrules from Allende and Kaba meteorites classified as a CV3 were prepared for CL spectral measurements. CL spectroscopy was made by a SEM-CL system, which is comprised of SEM (JEOL: JSM-5410) combined with a grating monochromator (OXFORD: Mono CL2) at accelerating voltage of 15 kV and beam current of 1.0 nA in a beam scan mode. The sample temperature was controlled by flowing liquid nitrogen and using an embedded heater in a cryostage. All spectra were corrected for total instrumental response, which was determined using a calibrated standard lamp.

At room temperature, the CL spectra show broad emission bands at around 400 nm in blue region and at around 650 nm in red region, and pronounced emissions increasing to IR region at around 720 nm. These bands can be assigned to structural defect, divalent Mn and trivalent Cr impurity centers, respectively. Their emission intensities increase with a decrease in sample temperature. In general, luminescence efficiency decreases with rising temperature due to an increase in non-radiative transitions, which has been known as temperature quenching.

CL spectral peaks in energy unit were deconvoluted by Gaussian curve fitting to determine the emission component for each emission center. The emission peak in blue region can be separated into two components centered at 3.15 and 2.99 eV, and the peaks caused by Mn and Cr impurity centers can be fixed at 1.91 and 1.74 eV, respectively. By assuming the Mott-Seitz model, activation energy in each temperature quenching process can be calculated by Arrhenius plots using integral intensity of each component. The straight-line relationships in the plots resulted in each activation energy as follows; blue emission at 3.15 eV: 0.08-0.04 eV, blue emission at 2.99 eV: 0.10-0.05 eV, red emission at 1.91 eV: 0.01-0.005 eV, red emission at 1.74 eV: 0.01-0.02 eV. The values of activation energies for blue emissions caused by structural defects correspond to the vibration energy of Si-O stretching mode in the lattice, and the values for red emissions caused by Mn and Cr impurity centers to Mg-O vibration energy. It suggests that the temperature quenching energy might be transferred as a phonon to the specific lattice vibration.

Keywords: forsterite, cathodoluminescence, temperature quenching
Measurements of elastic constants of single-crystal chromian spinel by frequency resonant ultrasound spectroscopy

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Chromian spinel grains in mantle xenoliths usually contain fluid inclusions whose residual pressure (fluid density) can provide us the origin depth of the xenoliths. Elastic properties of chromian spinel are essential for precise estimation of the origin depth. Although elastic constants of spinel (MgAl2O4) and chromite (FeCr2O4) have been already reported, few studies have been done on chromian spinel. We thus have studied elastic constants of a chromian spinel single-crystal via a resonance method.

Chromian spinel grains were collected from mantle xenoliths from Sveigain, Russia (Yamamoto et al., 2009, Island Arc). One grain was selected in terms of the uniformity of crystallographic orientation examined by SEM-EBSD. The selected grain was shaped into a rectangular parallelepiped (0.517x0.417x0.412mm3). Each face was polished flat (< 1 micrometer) in an orientation perpendicular to {100} or {110}. The crystallographic orientation of the specimen was determined by the X-ray precession method. The density is 3.83(1) x 103 kg/m3, which is calculated from the chemical composition analyzed with EPMA and the lattice parameter (a= 0.8115(1) nm) determined by XRD.

Lower 16 oscillation modes were observed in the frequency range from 4 to 9 MHz. The oscillation of a specimen is not free oscillation, because the specimen is held between two transducers. A specimen-holding force F affects resonance frequencies. In order to infer the resonance frequencies of free oscillation, resonance frequencies were measured as a function of the specimen-holding force F and then extrapolated to F=0.

Elastic constants are determined by comparing calculated and measured resonance frequencies. FEM was employed to calculate resonance frequencies. C11, C12 and C44 are 264(3), 154(3), and 142.6(2) (GPa), respectively. Compared with elastic constants of end members, spinel (Yoneda, 1990) and chromite (Hearmon, 1990), chromian spinel has the lowest C11 and intermediate C12 and C44.

Keywords: elastic constants, chromian spinel, resonance method, mantle xenoliths
Three dimensional visualization of residual pressure around inclusions in sapphire

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Mantle derived minerals can tell us much information about processes within the deep Earth. It is important to determine the original depth of these mineral samples. Kagi et al. 2009 showed that three-dimensional Raman mapping observations can be used to visualize the distribution of residual pressure around inclusions in diamond, which has provided information about the depth of diamond formation. Corundum is the second hardest mineral after diamond and is expected to also show substantial residual pressure around inclusions.

Samples were collected from New South Wales, Australia as well as Chanaburi, Thailand and are associated with alkali basalts. It is possible to distinguish between corundum crystals formed from various settings, such as metamorphic versus igneous settings, based on trace element analyses. However, distinguishing between crystals of different geographic locality and similar geologic settings is not yet possible using nondestructive methods. Based on current geochemical observations, there are two models for the formation of igneous corundum crystals. Guo et al. 1996 proposed that these crystals formed in the middle crust by a hybrid reaction between carbonatite melt and silicic magma. Alternatively, Sutherland et al. 1998 suggested that they may form directly from volatile-rich felsic melts generated at lower crustal conditions. By using 3D mapping techniques, it may be possible to evaluate the P-T history of the host rock as well as differentiate between gems from different localities.

The fluorescence spectrum of corundum has two peaks associated with the excitation of Cr\textsuperscript{3+} impurities in its structure, R1 and R2. Because the R2 line is insensitive to differential stress, the residual pressure can be calculated based on the peak shift of the R2 line using a pressure calibration curve.

The samples were excited using 514.5 nm emission of Ar-ion laser with a diameter of 2 micron. Measurements were taken every 5 to 10 micrometers around albite, zircon, and rutile inclusions using a point-by-point mapping illumination system. The R2 and R1 lines of the fluorescence spectra were fitted by Lorentzian functions after subtraction of background. In order to account for peak oscillations caused by changes in room temperature, real-time calibration of the fluorescence spectra energy axes were performed by neon emission lines as discussed in Odake et al. 2008.

Over 25 two- and three-dimensional maps of various inclusions have been created so far. The maximum residual pressure for each map ranges from 0.1 GPa to 0.51 GPa. In many of these samples, stress distribution can be explained by differences in elastic constants between the host and inclusion. For example, our results show one slice of a 3D map around a zircon inclusion. In this case, the c-axis of the corundum and the c-axis of the zircon are nearly parallel. With decreasing temperature and pressure, the c-axis is expected to have higher residual pressure due to differences in linear thermal expansion coefficients and bulk moduli between the host and inclusion. It is clear that the c-axis has the highest residual pressure, as expected. Another notable observation is that the maximum residual pressure surrounding zircons correlates with length of the crystal along the c-axis. Two distinct trends between residual pressure and length are observed. This may be due to many factors including the relative orientation of the host and inclusion or the presence of cracks surrounding the inclusion. It could also be due to the different geographic localities. However, more measurements need to be taken to confirm.

Previous methods to determine original depth, such as those used by Barron 2005 and Izraeli et al. 1999, which assume isotropic elastic properties in inclusion and diamond, cannot be used in these corundum-inclusion pairs. Our results show that relative orientation of corundum and inclusions must be accounted for in future calculations of P-T history.

Keywords: residual pressure, fluorescence spectra, ruby, sapphire, inclusions