

機械的粉碎による斜長石ガラスの構造変化 Structural change of plagioclase glasses by mechanical milling

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斜長石 ($\text{NaAlSi}_3\text{O}_8$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$) 組成の融液は、マグマを構成する主要成分である。その組成のガラスの粉碎による構造変化の情報は、地震やマグマ活動に伴う斜長石組成の物質の構造や物性を考えるうえで非常に重要である。また、その構造についての詳しい情報は新しい珪酸塩ガラス粉末材料の開発のために有効である。珪酸塩ガラスは、加熱や圧縮だけでなく機械的粉碎によっても、そのナノ構造や密度が変化することが知られている。例えば、 SiO_2 ガラスは、粉碎によりその構造中の Si-O-Si 角の減少ならびに SiO_4 四面体の 4 員環や 3 員環の増加が密度増加を引き起すと報告されている^[1]。また、Albite($\text{NaAlSi}_3\text{O}_8$) 組成ガラスについても、同様の研究が行われ SiO_2 ガラスとは異なった粉碎挙動をしめすことが分かっている。本研究では、Anorthite(An100) 及び Ab50An50 組成ガラス構造の粉碎による変化を粒度分析、X 線回折及び赤外分光測定により明らかにし、既に報告されている Ab100 組成ガラスの結果を含め、斜長石ガラスの組成変化に伴う粉碎挙動の変化について考察した。

An100 及び Ab50An50 組成ガラスを溶融急冷法により作成し、ボールミルを用いて 500 時間までの粉碎実験を行った。得られたガラス試料について、粒度分析、X 線回折及び赤外分光測定を行った。約 20~80 時間までの粉碎では、ガラスの見かけの平均粒径は約 2 μm まで減少し、その後再び増加した。また、An100 ガラスが最も容易に粉碎されることを明らかにした。また、長時間の粉碎により見かけの平均粒径はすべてのガラスで増加し、これはガラス粒子の再凝集によるものと考えられ、その程度は Ab100 ガラスが最も強い。これらの結果は、Ab100 ガラスの構造単位が、An100 ガラスより大きいことと関係するものと思われる。

ガラスの XRD パターンは回折角約 22~26 °付近に First Sharp Diffraction Peak (FSDP) を示す。このピーク位置は、基本構造単位の大きさに関係し、大きな値を持つほど小さい構造単位を含むことを示す。このピークの位置は、粉碎に伴いより高角度側にシフトし、その構造単位が減少することを示す。例えば、粉碎前の Ab100 組成ガラスは、 TO_4 四面体 ($\text{T}=\text{Al/Si}$) の 6 員環を主とする構造^[2] であるが、粉碎により、より小さい 4 及び 3 員環の構造が増加したと考えられる。また、An100 ガラスの粉碎前の FSDP 位置は、Ab100 ガラスより大きい。これは、An100 ガラスの基本構造単位が 4 員環であること^[2] に関係し、その粉碎によるピークシフトが Ab100 ガラスに比べて小さいことは、粉碎による構造変化が小さいことを示している。また、 SiO_2 及び Ab100 ガラスについて粉碎による密度増加が報告されている^[2] ことから、An100 及び Ab50An50 ガラスも粉碎によりその密度が増加していると考えられる。しかし、An100 ガラスのピークシフトが Ab100 ガラスより小さいことから、粉碎による密度増加は Ab100 ガラスのほうが大きいと考えられ、これは粉碎前の構造の違いが原因と思われる。ただし、Ab50An50 ガラスの変化は三つのガラスで最も大きく、密度変化も大きいものと思われる。また、すべてのガラスで 10 時間までの粉碎では、FSDP 位置はほとんど変化しないことから、10 時間程度の粉碎では、内部構造の変化は非常に小さいものと思われる。

赤外分光測定の結果から、800 cm^{-1} 付近のバンドは、T-O-T 結合に関係している。このバンドの強度は、粉碎に伴い減少する。しかし、その減少程度は Ab100<An100<Ab50An50 の順であり、Ab50An50 ガラスで大きく減少する。このことは、粉碎により Ab50An50 ガラスが最も激しく構造を変化させることを意味し、FSDP の粉碎による変化と矛盾しない。

以上、斜長石ガラスは、粉碎によりその基本構造単位が減少し、密度が増加するものと考えられる。また、Ab50An50>Ab100>An100 の順で構造の変化が大きいことを明らかにした。この変化は、粉碎による長石ガラス中の Na^+ 及び Ca^{2+} イオンを中心としたユニットの形成に起因している可能性がある。

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キーワード: 斜長石ガラス, ボールミル, ナノ構造, X 線回折, 赤外分光

Keywords: plagioclase glass, ball mill, nano-structure, X-ray diffraction, IR spectroscopy

高压におけるパイロップメルトのAlの配位数について X-ray diffraction analysis of pyrope melts at high pressures

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固液分離は地球内部の化学進化の主要なメカニズムである。地球内部におけるメルトの移動は、その粘性と密度によってコントロールされる。これらのメルトの物性はマグマの構造と密接に関連している。そのため、高压におけるマグマの構造は地球惑星内部のマグマの関連した現象を解明する上で重要な研究課題である。珪酸塩メルトの急冷ガラスは急冷・脱圧時の構造緩和の影響を避けられないため、高压下のメルトの構造研究にはその場観察が必須である。本研究では高温高压 X 線回折からパイロップ組成メルトの構造の圧力変化について調べた。本研究で着目したパイロップは Field Strength (Z/r) が高い Mg を含むため、配位数の高い Al を含む傾向が強い。

高压実験は KEK, PF で MAX80 を用いて 5.5GPa・2300K までの条件で行った。出発試料は 1 気圧で作成した $Mg_3Al_2Si_3O_{12}$ 組成のガラスを用いて、グラファイトカプセルに封入した。メルトの回折実験は融点から 50~100K 高温側で、白色 X 線を使ったエネルギー分散法で行った。回折プロファイルから干渉関数を導き、フーリエ法で解析した。

パイロップメルトの動径分布関数 $D(r)$ の 4 配位の Al-O と Si-O に対応する第一ピーク (~1.7 Å) の圧力変化に注目すると、圧力に伴いピーク強度が減少した。一方、1.9 Å 付近では強度の増加が認められる。これは、高压ほど Al の配位数が増加して Al-O 距離が伸びていることと対応していると考えられる。 TO_4 四面体を構成する Al と Si の配位数が増加するためには非架橋酸素が存在することが要求される。NBO/T の大きいパイロップ組成 ($Mg_3Al_2Si_3O_{12}$) では非架橋酸素を多く含まれるため、配位数増加が顕著であると考えられる。

キーワード: マグマ, 放射光, 高压

Keywords: magma, synchrotron radiation, high pressure

Forsterite-MgSiO₃ 液体界面の構造と物性 Structure and properties of forsterite-MgSiO₃ 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-MgSiO₃ liquid interface are investigated by using molecular dynamics simulations. It is essential to know the structure and physical properties of forsterite-MgSiO₃ 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 MgSiO₃ liquid consist of 8000 atoms is sandwiched between (010) surfaces of forsterite and 43440 atom system in which a sheet of MgSiO₃ 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-MgSiO₃ liquid interface. In the crystal-liquid interface, 2-30% of SiO₄ tetrahedra of forsterite surface bridge SiO₄ tetrahedra in liquid. In liquid region, SiO₄ tetrahedra concentrate in the vicinity of surface and form an SiO₄ tetrahedra rich layer of 0.4 to 0.6 nm thickness. Inner side of the first SiO₄ rich layer in MgSiO₃ 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 SiO₄ 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 SiO₄ 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-MgSiO₃ liquid interface is equilibrium by performing of long time calculations.

キーワード: 界面, 分子動力学計算, 珪酸塩, 結晶, 液体

Keywords: Interface, Molecular dynamics simulation, Silicates, Crystal, Liquid

温度勾配場におけるマントルオリビンの化学的不均質形成 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 $(\text{Mg}_{0.89}, \text{Fe}_{0.11})_2\text{SiO}_4$ 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.

キーワード: レーザー加熱型ダイヤモンドアンビルセル, ソーレ効果, 固体内拡散

Keywords: LHDAC, Soret effect, diffusion in solid

Zn₂GeO₄ スピネル相と Zn₂SiO₄ 変形スピネル相の結晶構造 Crystal structures of Zn₂GeO₄ spinel and Zn₂SiO₄ modified spinel phases

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マントル高压鉱物と関連して、Zn₂GeO₄ と Zn₂SiO₄ の高压相関係について 60-70 年代に調べられたが (e.g., Syono et al., 1971)、高压相の結晶構造については Zn₂SiO₄ II 相以外は調べられていない。昨年の会議では Zn₂SiO₄ の III と IV 相の構造を報告した (SIT02-24)。本講演では、Zn₂GeO₄ の立方晶と正方晶スピネル相、Zn₂SiO₄ の V 相の結晶構造について報告し、加えて、Zn₂SiO₄ の III と IV 相について新しく分かった構造的な知見についても触れる。

試料は全て 5000 トン川井型マルチアンビル高压装置で合成し、急冷回収したものである。粉末 X 線回折パターンは SPring-8 BL19B2 にて大型デバイ・シェラーカメラで測定した。構造精密化はリートベルト法 (RIETAN-FP) で行った。解析の詳細は Kanzaki and Xue (2012) と同じである。V 相については ²⁹Si MAS NMR 測定を行った。

Zn₂GeO₄ の立方晶と正方晶スピネル相はそれぞれ 3 GPa, 1600 °C, 5 GPa, 1200 °C で合成した。両相はこれまでの予想どおり、4 配位を亜鉛が占める逆スピネル型であった。正方晶スピネルでは、Zn と Ge の八面体席での秩序化により対称性が下がっている。これは Zn₂TiO₄ と同構造である。I.D. Brown の bond valence 計算法を使った結合距離の計算は、測定結果とよく一致した。

Zn₂SiO₄ の III, IV 相の構造 (Liu et al., 2013) については昨年の要旨に出ているが (SIT02-24)、その後 III 相については構造が (Zn_{1.1}Li_{0.6}Si_{0.3})SiO₄ 高温相と同じであることが分かった。この種のオリビン構造の 6 配位を占める原子が 4 配位に移動した構造を Baur(1980) は tetrahedral olivine と呼んだ。IV 相については、2 個の ZnO₄ と 1 個の SiO₄ が 1 つの酸素を共有する tricluster が c 軸方向につながってコラムを作っている。同様なコラムは II 相にも存在し、II 相と IV 相の近い密度を説明する。

V 相が変形スピネル構造を持つことは以前から指摘されていたが (Syono et al., 1971)、今回の解析で確認された。構造は Mg₂SiO₄ wadsleyite とほぼ同じであり、Zn は八面体席のみを占めており、Zn と Si の disorder はない。これは ²⁹Si MAS NMR で 1 つの 4 配位 Si ピークが見られたことと一致する。

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ペロブスカイト型 NaZnF₃、NaMnF₃ の高圧相転移と、MgSiO₃ アナログ物質としての ポストペロブスカイト型 A+B₂+F₃ High-Pressure Transitions of NaZnF₃ and NaMnF₃ Perovskites with Implication to Mg- SiO₃ Postperovskite Analogues

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MgSiO₃ を主成分とするペロブスカイト (Pv) 相のポストペロブスカイト (pPv) への転移は下部マントル最深处で起きているとされ、pPv 型 MgSiO₃ の性質を明らかにすることはコア - マントル境界領域の構造とダイナミクスを解明するために重要である。しかしこの転移が 120GPa、2000 K を越える超高压高温下で起こることや pPv 相が常圧に戻るとアモルファス化することから、より低圧で同じ転移を起し、常温常圧に pPv 相が回収できる ABX₃ 化合物の探索とその構造、物性の研究が意義を持つと考えられる。近年、著者らは約 20GPa 以下の圧力で Pv - pPv 転移を起こす ABX₃ 化合物として、CaRuO₃、CaRhO₃、NaNiF₃、NaCoF₃ を新たに発見し、高圧相関係の決定、Pv、pPv 相の精密構造解析、物性測定などを行ってきた (Kojitani et al., 2007, Shirako et al., 2009, 2012, Yusa et al., 2012)。今回、新たに NaZnF₃、NaMnF₃ ペロブスカイトの高圧相転移を調べ、相関係の決定、NaZnF₃ Pv, pPv 相の構造精密化を行った。また NaNiF₃、NaCoF₃ の結果と合わせて、フッ化物 A+B₂+F₃ が MgSiO₃ の良いモデル物質になりうることを議論する。

マルチアンビル装置を用い 9-24 GPa、600-1100 oC において NaZnF₃、NaMnF₃ Pv の相転移実験を行った。常圧に回収された NaZnF₃ 試料は液体窒素中で粉末化した後、粉末 X 線回折装置で相の同定を行った。NaMnF₃ では高圧合成された焼結体試料を微小部 X 線回折装置で調べた。また NaZnF₃ pPv の粉末 X 線回折データを用い、リートベルト法により構造を精密化した。

NaZnF₃ Pv は約 10 - 15GPa で pPv に転移した。常圧回収された NaZnF₃ 試料は単相の pPv ではなく、一部が Pv に戻っていた。その Pv - pPv 転移の相境界線は、 $P(\text{GPa}) = 4.9 + 0.011T(\text{oC})$ と決定され、体積変化は - 1.9 % であった。NaMnF₃ Pv は約 8 - 12GPa で Na₃Mn₂F₇ 相と MnF₂ 相に分解した。その回収試料で MnF₂ 相は PbO₂ 型構造であったが、高温高压下では O-I 型またはコチュナイト型であったと考えられる。リートベルト解析により精密決定された常圧での NaZnF₃ pPv 構造は NaNiF₃ pPv 構造に近く、両者の八面体は CaMO₃ pPv (M = 白金族元素, Sn) の八面体より変形が小さく、120GPa での MgSiO₃ pPv (Murakami et al., 2004) のそれに近い。NaZnF₃、NaNiF₃、NaCoF₃ はいずれも 20GPa 以下で Pv - pPv 転移を起こし、体積変化は - 1~2 %、相境界線の勾配は 10-15MPa/ K である。またこれらのフッ化物 Pv、pPv の a, b, c 軸の圧縮率の大小関係は MgSiO₃Pv、pPv と同じであり、圧力によって Pv 八面体の回転角が 26 ° 付近まで達すると、pPv へ転移する。以上のことから、これらのフッ化物は、MgSiO₃ の Pv - pPv 転移の低圧での良いモデル物質になると考えられる。特に NaNiF₃ は pPv 相が単相で常圧回収できる点で、モデル物質として有用である。

キーワード: ペロブスカイト, ポストペロブスカイト, 高圧相転移, フッ化物, 下部マントル, アナログ物質

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 Mg-SiO₃
Ab initio computation on the Fe L-edge X-ray emission spectroscopy of Fe-bearing Mg-SiO₃

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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 of 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 3*p* orbital, which is far from the valence orbitals (3*d* and 4*s*), it provides no information about Fe's coordination environments. However, Fe *L*-edge XES can directly determine the distribution and intensity of Fe-3*d* 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.

キーワード: First-principles calculation, First-principles calculation, Fe L-edge XES, Mg perovskite
Keywords: First-principles calculation, First-principles calculation, Fe L-edge XES, Mg perovskite

Ca₂MgSi₂O₇-Ca₂Fe³⁺AlSiO₇系合成メリライトの高圧下における放射光 X 線回折及びメスbauer分光に関する研究

Synchrotron XRD and Mossbauer spectroscopic study on Ca₂MgSi₂O₇-Ca₂Fe³⁺ series melilite at high pressures

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Synthetic Ca₂MgSi₂O₇ (akermanite: Ak)-Ca₂Fe³⁺AlSiO₇ (ferrialuminium gehlenite: FAGeh) series melilites were investigated using synchrotron X-ray diffraction and synchrotron-radiation-based Mossbauer spectroscopic methods to determine the distribution of Fe³⁺ between two structurally independent tetrahedral sites (T1 and T2), and the relationship between ionic substitution and incommensurate structure in melilite at high pressures. ⁵⁷Fe-doped Ak-FAGeh melilites were synthesized from starting material with composition of Ak₅₀FAGeh₅₀ by sintering technique at 1140-1180 °C and 1 atm for high pressure experiment. The average chemical composition of the synthetic melilites was Ca_{2.00}Mg_{0.56}Fe³⁺_{0.42}Al_{0.44}Si_{1.57}O₇. The site populations at the T1 and T2 sites at the synthetic condition were determined by X-ray Rietveld analysis and ⁵⁷Fe Mossbauer spectroscopy (340MBq ⁵⁷Co source) to be [0.557Mg+0.280Fe³⁺+0.237Al]_{T1} [0.197Fe³⁺+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 culet 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 Fe³⁺(T1):Fe³⁺(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 T1O₄ and T2O₄ 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.

キーワード: 放射光 X 線回折, 放射光メスbauer分光分析, 合成メリライト, 変調構造, 高圧

Keywords: Synchrotron X-ray diffraction, Synchrotron Mossbauer spectroscopy, Synthetic melilite, Incommensurate structure, High pressure

(Mg,Fe)Oの常圧下における磁気相図の再考 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, $(\text{Mg}_{0.23}\text{Fe}_{0.77})_{0.92}\text{O}$ 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 $(\text{Mg}_{0.23}\text{Fe}_{0.77})_{0.92}\text{O}$ 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 superparamagnetic 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.

キーワード: (Mg,Fe)O, 磁気秩序

Keywords: (Mg,Fe)O, magnetic ordering

フォルステライトのカソードルミネッセンスにおける温度消光メカニズム 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. 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 forsterite 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 with small emissions at around 720 nm. These bands can be assigned to structural defect, divalent Mn and trivalent Cr impurities, 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.

キーワード: フォルステライト, カソードルミネッセンス, 温度消光

Keywords: forsterite, cathodoluminescence, temperature quenching

共振法によるクロミアンスピネルの単結晶弾性定数の測定

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 (MgAl_2O_4) and chromite (FeCr_2O_4) 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 Sveyagin, 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 ($0.517 \times 0.417 \times 0.412 \text{mm}^3$). 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 $3.83(1) \times 10^3 \text{ kg/m}^3$, which is calculated from the chemical composition analyzed with EPMA and the lattice parameter ($a = 0.8115(1) \text{ nm}$) 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. C_{11} , C_{12} and C_{44} 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 C_{11} and intermediate C_{12} and C_{44} .

キーワード: 弾性定数, クロミアンスピネル, 共振法, マントル捕獲岩

Keywords: elastic constants, chromian spinel, resonance method, mantle xenoliths

三次元顕微蛍光分光測定によって可視化されるサファイヤ中の包有物の残留圧力分布

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 Cr³⁺ 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.

キーワード: 残留圧力, 蛍光スペクトル, ルビー, サファイヤ, 包有物

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