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Perovskite phase relations
in the system of MgSiO_3 - MnSiO_3 - CaSiO_3
at the Earth's lower mantle conditions

(下部マントル条件下における MgSiO_3 - MnSiO_3 - CaSiO_3 系ペロブスカイトの相関係)

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Abstract

Silicate perovskites of MgSiO_3 and CaSiO_3 are considered to be major constituent minerals in the earth's lower mantle. These silicate perovskites are not chemically pure phases and should form a certain range of solid solutions with other cations. In this study, I investigated perovskite phase relations in the system of MgSiO_3 - MnSiO_3 - CaSiO_3 at the lower mantle conditions. Experimental synthesis of perovskite phases in this ternary system was performed at high pressure and high temperature, by using laser heated diamond anvil cell. Product phases were identified by in-situ synchrotron X-ray diffraction measurements and their chemical compositions were quantitatively analyzed by analytical transmission electron microscopy (ATEM) and field emission-scanning electron microscopy (FE-SEM) with energy dispersive X-ray spectrometer.

At first, perovskite phase relations on the MgSiO_3 - MnSiO_3 join were investigated. The existence of a complete solid solution was confirmed on the join. The $(\text{Mg,Mn})\text{SiO}_3$ perovskite produced is orthorhombic and changes of the unit cell parameters of this perovskite as the proportion of Mn incorporated in the mineral lattice changes seems to obey Vegard's rule at 50 GPa. The orthorhombic distortion, judged from the axial ratios of a/b and $\sqrt{2} a/c$, monotonically decreases from MgSiO_3 to MnSiO_3 perovskite at 50 GPa. The orthorhombic distortion in $(\text{Mg}_{0.5},\text{Mn}_{0.5})\text{SiO}_3$ perovskite is almost unchanged with increasing pressure from 30 to 50 GPa. MnSiO_3 is the first chemical component confirmed to form a complete solid solution with MgSiO_3 perovskite at the P-T conditions of the lower mantle.

As for perovskite phase relations on the CaSiO_3 - MnSiO_3 join, quite wide range of solid solution was confirmed at 40-60 GPa. However, quantitative chemical analyses by ATEM indicated that there is an immiscibility gap in a compositional range from $(\text{Ca}_{0.45},\text{Mn}_{0.55})\text{SiO}_3$ to $(\text{Ca}_{0.2},\text{Mn}_{0.8})\text{SiO}_3$, unlike the case of the MgSiO_3 - MnSiO_3 join. Judging from the extinction of specific reflections in the X-ray diffraction patterns, it was suggested that $(\text{Ca,Mn})\text{SiO}_3$ perovskite on the CaSiO_3 side of the immiscibility gap

is cubic, but on the other hand $(\text{Ca,Mn})\text{SiO}_3$ perovskite on the MnSiO_3 side is orthorhombic. It is important evident that MnSiO_3 is the first chemical component confirmed to form a wide compositional range of solid solution with CaSiO_3 perovskite at the P-T conditions corresponding to the lower mantle, because it has been known that CaSiO_3 perovskite is difficult to form solid solutions with other cations.

Finally, perovskite phase relations in the ternary system of MgSiO_3 - MnSiO_3 - CaSiO_3 were investigated. It was confirmed that the addition of MnSiO_3 strongly affects the mutual solubility between MgSiO_3 and CaSiO_3 . There are two perovskite regions with an immiscibility gap between them in the ternary system. Crystal structure of Ca-bearing $(\text{Mg,Mn})\text{SiO}_3$ perovskite is orthorhombic, and that of Mg-bearing $(\text{Ca,Mn})\text{SiO}_3$ perovskite is cubic. The compositional range of Mg-bearing $(\text{Ca,Mn})\text{SiO}_3$ perovskite in the ternary system expands dramatically to the Mg-rich side with increasing MnSiO_3 component.

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1. General Introduction

What is perovskite?

“Perovskite” is a mineral name of Calcium Titanate (CaTiO_3), which occurs as an accessory mineral in silica depleted rocks, such as nepheline syenites, alkaline pyroxenites and nepheline-bearing pegmatite.

It was named after Lev Aleksevich von Perovski who was a famous Russian mineralogist. However, because its similar structure occurs very common in ABO_3 compounds in materials science, materials with the perovskite structure are often called as perovskite. Nowadays, perovskite becomes a world famous mineral name not only in the geoscience community but also in the materials science community. The ABO_3 perovskite show interesting and useful physic-chemical characteristics such as superconductivity, magneto resistance, ionic conductivity, dielectric property (Lemmens and Millet, 2004; Lu et al., 2011; Viana et al., 1994) and so on.

Perovskite in the earth's interior

As shown in Figure 1-1, it is well known that the earth can be divided into three main layers which are the crust, the mantle and the core, based on the seismic discontinuities related to their physical properties and compositions. The mantle is also divided into three layers, which corresponds to the upper mantle, the transition zone and the lower mantle from the shallow part to deep part sequentially. Each layer consists of different minerals. Because earth's interior is characterized by a gradual increase in temperature (geotherm) and pressure with depth, the inner earth will consist of thermodynamically stable mineral phases at the high pressure and high temperature. For example, the pressure and temperature conditions at the top of the lower mantle are estimated at about 24 GPa and 2000 K, and those at the bottom of the lower mantle are about 135 GPa and 3000 K.

The main constituent mineral phases in the mantle can be estimated, when the chemical composition is determined for the mantle. Pyrolite is the name of a model

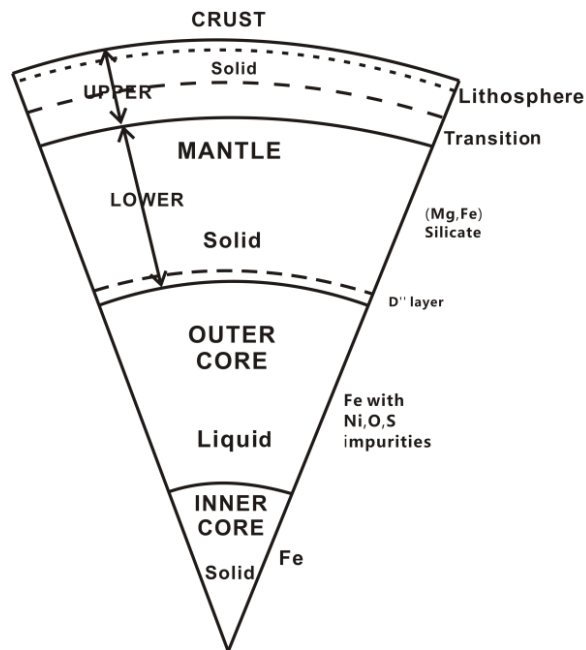


Figure 1-1. Layered structure of the earth.

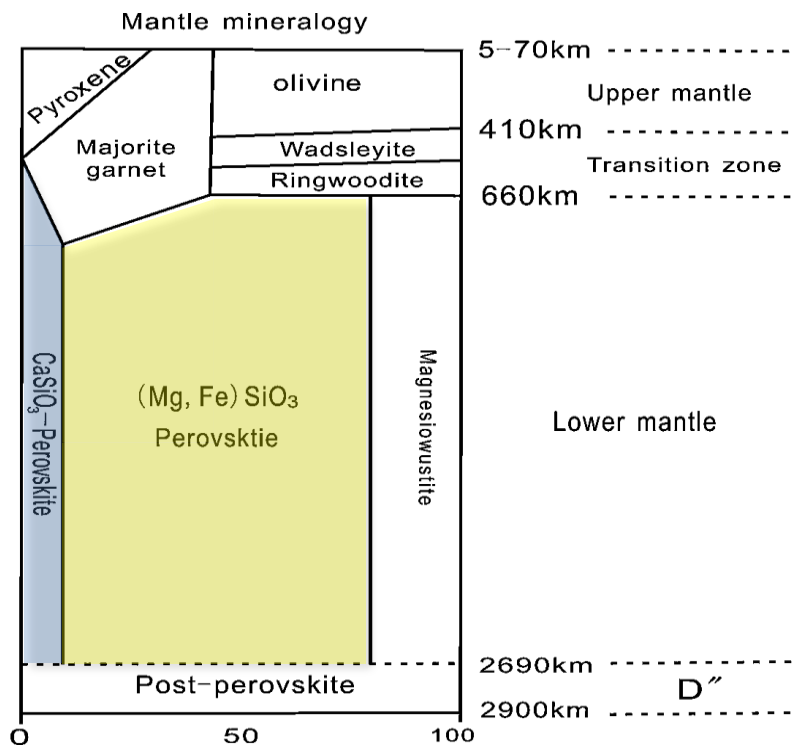


Figure 1-2. Mineralogical structure of earth's mantle based on the Pyrolite model.

chemical composition for the earth's mantle, which was proposed by Ringwood (1962). In pyrolite, as shown in Figure 1-2, the upper mantle consists of 57 % olivine, 29% pyroxene, and 14% garnet. In the transition zone, olivine sequentially transforms into wadsleyite and then ringwoodite. Pyroxene composition gradually dissolves into garnet and changes to so-called majorite garnet. The lower mantle continues from 660 km down to the core-mantle boundary, located at approximately 2890 km depth. The major constituent mineral in the lower mantle is believed as two silicate perovskites (MgSiO_3 and CaSiO_3) and ferropericlase. The pyrolite composition consists of 78 % MgSiO_3 perovskite, 6 % CaSiO_3 perovskite and 16 % ferropericlase (e.g., Hirose et al., 2004). The lower mantle occupies the largest part of the earth volumetrically. Thus, it should be very critical and important to investigate the physical and chemical characteristics of silicate perovskites in order to understand the nature and dynamics of the deep earth's interior.

Crystal structure of perovskite

As mentioned above, the perovskite structure is often adopted by many ABO_3 compounds. The ideal perovskite structure crystallographically belongs to the cubic system as it shown in Figure 1-3. In ABO_3 perovskite structure, BO_6 forms a B-centered octahedron and its corner-sharing connection forms the 3D framework. The cavities of the 3D framework are called as A-site. The A-site is coordinated to 12 oxygen atoms. It is interesting that original perovskite “ CaTiO_3 ” does not adopt the cubic structure. As shown in Figure 1-4, the crystallographic symmetry of CaTiO_3 is orthorhombic ($Pbnm$, $Z=4$) by a cooperative tilting of the TiO_6 octahedra. (Sasaki et al., 1987). The distortion from cubic to orthorhombic is caused by the mismatch between the size of A-site and ionic radius of Ca^{2+} . In CaTiO_3 , because the size of Ca^{2+} is a little smaller than the size of A-site, the distortion of octahedral tilting lowers the coordination of Ca^{2+} from 12 to 8 and decreases a strain of A-site. Such structural mechanism for reducing a structural strain in the perovskite structure produces the structural flexibility and that is one of

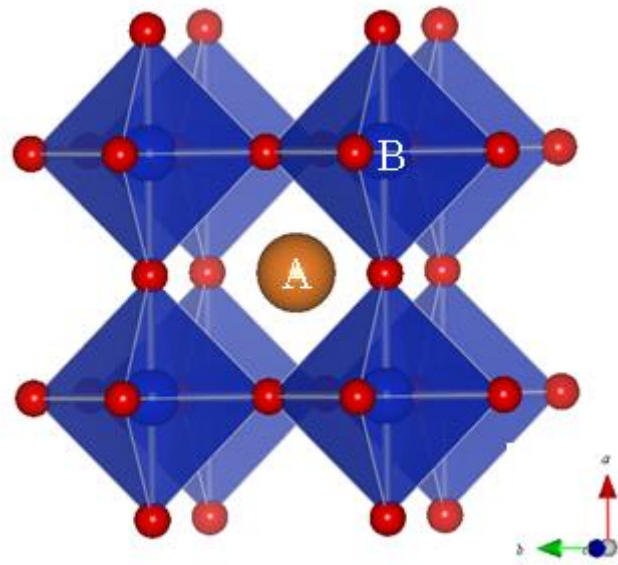


Figure 1-3. The ideal cubic perovskite structure

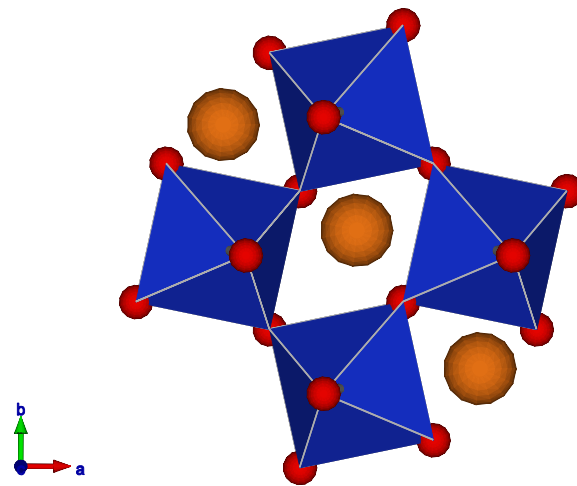


Figure 1-4. An example of octahedral operate, due to Orthorhombic distortion.

major reason that many compounds with the chemical formula ABO_3 can adapt the perovskite structure.

In silicate perovskites, $MgSiO_3$ also belongs to orthorhombic ($Pbnm$, $Z=4$) (Horiuchi et al., 1987). On the other hand, the crystal structure of $CaSiO_3$ perovskite was initially considered to adopt the cubic symmetry with the space group $Pm\bar{3}m$ (e.g., Yagi et al., 1989). However, there has been a lot of discussion about the real symmetry of $CaSiO_3$ perovskite so far. Although many experimental and theoretical studies suggested tetragonal (e.g., Shim et al., 2002) or orthorhombic (e.g., Uchida et al., 2009) depending on pressure and temperature conditions, it is hard to identify the symmetry of $CaSiO_3$ perovskite, because the distortion from the cubic may be quite small compared with experimental resolution.

The Goldschmidt tolerance factor is a kind of scale how much the A-site cation fits to the octahedral 3D framework (Goldschmidt, 1926). In an ideal cubic perovskite, the A cation is sitting at an atomic coordinate of $1/2, 1/2, 1/2$, the B cation is at $0, 0, 0$, and the oxygen is at $0, 0, 1/2$. Thus, the ratio of the A-O to the B-O bond lengths must be equal to $\sqrt{2}$. The tolerance factor can be defined as the equation [1].

$$t = \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)} \quad [1]$$

The t is the tolerance factor, r_A , r_B and r_O mean the ionic radii of the A cation, B cation and oxygen, respectively. The 12-coordinate radii of the A cation and the 6-coordinate radii of the B cation should be used in the equation [1], but the 12-coordinate radii are not available for all A-site cations in Shannon (1976). Thus, the 8-coordinate radii of the A-site cation are often used. When the tolerance factor approaches to 1, the perovskite structure can be expected to have less structural distortions from the cubic symmetry. Indeed, the tolerance factor of $CaTiO_3$ and $MgSiO_3$ with the orthorhombic symmetry is approximately 0.89. On the other hand, the tolerance factor of $CaSiO_3$ is 0.99 and very close to 1. Although the tolerance factor is just an indicator of the fit of the A-site cation to the octahedral 3D framework, as

mentioned above, there seems to be some relationship between the enthalpy of the formation and the tolerance factor (Akaogi et al., 2005). Thus, the tolerance factor is sometime used for estimating the structural stability of ABO_3 perovskite (Leinenweber et al., 1991).

Solid solution with silicate perovskites

Solid solubility of Al_2O_3 component into $MgSiO_3$ perovskite is important, because Al is the 5th most abundant element in the earth and that should affect physical properties of the mantle, especially those of subducting slab. Indeed, Zhang and Weidner (1999) indicated that the bulk modulus for $MgSiO_3$ perovskite containing 5 mol% Al_2O_3 is significantly smaller at lower mantle conditions than for Al_2O_3 -free $MgSiO_3$ perovskite. Many researches focused on incorporation mechanism of such trivalent cations into silicate perovskite have been performed and the importance of coupled substitution mechanism between $Al^{3+}+Al^{3+}$ and $Mg^{2+}+Si^{4+}$ or between $Al^{3+}+Fe^{3+}$ and $Mg^{2+}+Si^{4+}$ has been pointed out (e.g., Kesson et al., 1995; MaCammon, 1997; Andrault et al., 1998; Stebbins et al., 2001). It is noted that unquenchable perovskite with $Ca_3Al_2Si_3O_{12}$ grossular garnet composition was synthesized at about 32 GPa and about 1500 K (Yusa et al., 1995). If this composition of silicate perovskite is thermodynamically stable phase, Al^{3+} has been the most soluble cation into $CaSiO_3$ perovskite so far.

Andrault (2003) systematically investigated cationic substitution in $MgSiO_3$ perovskite under 25 GPa and 1750 K at the near top of the lower mantle to reveal the possible mechanism of cationic substitutions. It was suggested that trivalent cations, such as Sc^{3+} , Ga^{3+} and Y^{3+} can be paired with Al^{3+} and incorporate into $MgSiO_3$ perovskite, however, the amount of $ScAlO_3$, $GaAlO_3$ and $YAlO_3$ components in $MgSiO_3$ perovskite are trace, only 0.125, 0.125 and 0.267 mol%, respectively. The crystal symmetry of $MgSiO_3$ perovskite remains orthorhombic after the incorporation of these components.

Andrault (2003) also pointed out that the presence of Na^+ possibly decrease the Al

solubility in perovskite, since the Al contents in MgSiO_3 perovskite become 2.4 %pfu much lower than 14 %pfu in Na free system.

Incorporation of divalent cations into silicate perovskite is expected to be a main substitution mechanism and that is reviewed in later chapters.

Discovery of MnSiO_3 perovskite

Fujino et al. (2008) experimentally investigated the high pressure phase relation of MnSiO_3 up to 85 GPa and 2600 K. It was confirmed that MnSiO_3 garnet decomposes into a mixture of the B1 type of MnO and stishovite at pressures higher than 20 GPa and temperatures higher than 1200 K. At further high pressure and high temperature conditions, the B1 type of MnO and stishovite recombine and form a perovskite phase. This MnSiO_3 perovskite is orthorhombic with space group $Pbnm$, which is same as MgSiO_3 perovskite. Cell parameter were reported as $a = 4.616(2) \text{ \AA}$, $b = 4.653(2) \text{ \AA}$, $c = 6.574(3) \text{ \AA}$ under 85 GPa and 2600 K. Variations of the axial ratios of MnSiO_3 perovskite with pressure suggest that the orthorhombic distortion of MnSiO_3 perovskite decreases with increasing pressure and the crystal structure seems to tend toward a tetragonal perovskite.

Fujino et al. (2009) discussed the stability of the perovskite structure in MnSiO_3 . It was argued that MnSiO_3 perovskite is stabilized at high pressure and high temperature, because no crystal field stabilized energy (CFSE) is expected for Mn^{2+} with five 3d electrons. On the other hand, the CFSEs of Fe^{2+} or Co^{2+} with unfilled 3d electron orbital favor the octahedral site of a B1 structure rather than the dodecahedral site in silicate perovskites, once a mixture of simple oxides is stabilized, then the further transformation to the perovskite structure is hard to occur.

The MnSiO_3 is quite new silicate component which exhibits the perovskite structure. Less attention has been paid to the solid solubility of MnSiO_3 component into silicate perovskites, because elemental abundance of manganese is expected to be trace in the lower mantle. However, only 5 pure silicate perovskite phases (MgSiO_3 , CaSiO_3 ,

MnSiO₃, SrSiO₃ and BaSiO₃) have been reported so far and two (SrSiO₃ and BaSiO₃) of them are hexagonal perovskite (Yusa et al., 2005, Yusa et al., 2007). Therefore, it is apparently worth investigating the solid solubility of MnSiO₃ component into MgSiO₃ and CaSiO₃ perovskites at the lower mantle conditions.

Solid solution in the MgSiO₃-MnSiO₃-CaSiO₃ system at the crustal conditions

Before starting studies of perovskite phase relations in the MgSiO₃-MnSiO₃-CaSiO₃ system, it should be useful to search phase relations in those system at the crustal conditions, because it is known that solid solubility is often controlled by the ionic radius difference between the substituting cations. Of course, phases in the ternary system are not perovskite but single chain silicates. The end member of MgSiO₃ is enstatite, CaSiO₃ is wollastonite, and MnSiO₃ is rhodonite.

As shown in Figure, 1-5. Brown et al. (1980) investigated the phase relations under about P = 3~6 kbar and T = 600±100 °C. Three solid solution phases appear on the MnSiO₃ and CaSiO₃ join. A narrow wollastonite solid solution occurs near CaSiO₃ composition and about 20 mol% range of rhodonite solid solution occurs near MnSiO₃ composition. And a wide range of bustamite solid solution (about 50 mol%) forms in the middle of the MnSiO₃-CaSiO₃ join. On the MgSiO₃-MnSiO₃ join, about 10 mol% range of orthopyroxene solid solution occurs on the MgSiO₃ side and about 30 mol% range of pyroxemangite solid solution appears on the MnSiO₃ side. And in the middle of the MgSiO₃-CaSiO₃ join, relatively narrow range of clinopyroxene solid solution (about 5 mol%) can be observed. On the MgSiO₃-CaSiO₃ join, it is interesting that almost no solid solution occurs on this join and only MgCaSi₂O₆ diopside appears at the middle of this join.

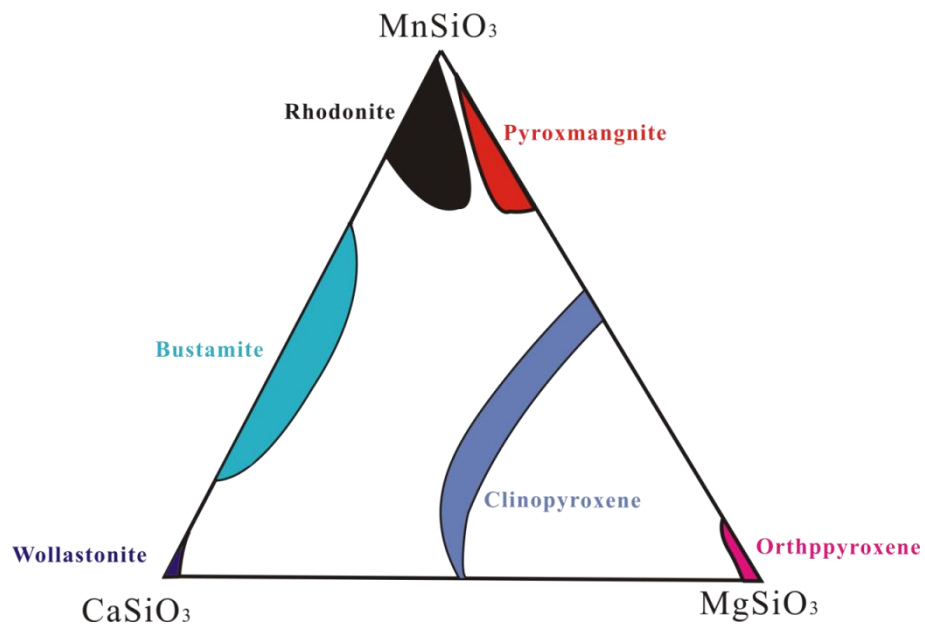


Figure 1-5. MgSiO_3 - MnSiO_3 - CaSiO_3 silicate system under crustal conditions modified from Brown et al. (1980)

2. General Experimental Procedures

This study was commonly carried out by several techniques of high pressure and high temperature synthesis using a laser heated diamond anvil cell (LHDAC), phase identification using synchrotron X-ray diffraction measurements, and chemical analysis using analytical transmission electron microscopy. Therefore, the details of the experimental procedures are described before going to the main chapters.

Preparation of starting materials

Sol-gel method

LHDAC is a very powerful tool to generate high pressure and high temperature conditions corresponding to those of the lower mantle. However, since the sample chamber is very small ($\sim 100\text{ }\mu\text{m}$ in diameter), chemical homogeneity of the starting materials is quite important to obtain reliable data. The sol-gel process is known to be a method for producing homogeneous sample at a molecular level. Therefore, the sol-gel method was used for preparing the starting materials. The detailed procedures are as follows.

- a. Sample preparation began with preparing the solutions of calcium nitrate, manganese nitrate and magnesium nitrate. These solutions were mixed at the desired molar ratios and dissolved into distilled water and almost same volume of ethanol.
- b. The solution dissolved tetraethyl orthosilicate (TEOS) into ethanol was prepared.
- c. Two solutions prepared above were mixed together at $0\text{ }^{\circ}\text{C}$ for 1 hour to make a mixed solution with the desired molar ratios of Ca, Mg, Mn and Si (the molar ratios of the total of Ca+Mg+Mn in nitrate solution to Si in TEOS solution should be 1:1). With constant stirring, an appropriate amount of 25 % ammonia was gently added into the mixed solution until a chocolate colored gel was obtained. The gel was

heated to 48 °C and kept until a shrink gel was formed. The gel was then poured into a platinum crucible and dried at 150 °C for 4 hours to transform into dried gel. Then the dried gels were calcinated at approximately 900 °C for 5 minutes to confirm there was no ammonia or nitric acid remaining in the gel.

- d. The calcinated gel was subsequently sintered for 48 hours in a high temperature furnace from 780 to 800 °C. In order to all manganese ions convert to Mn^{2+} , the oxygen partial pressure is controlled at $P_{\text{CO}_2}/P_{\text{H}_2}=2$ by $\text{CO}_2\text{-H}_2$ gas mixing in the furnace.
- e. Chemical homogeneity of gels was checked by the SEM-EDS analyses of 10-15 randomly selected points in each gel sample. These checks showed that gel compositions exhibited only small variations and were in good agreement with the intended ratios of Mg, Mn, Ca and Si.

High pressure and High temperature techniques

Preparation of Diamond Anvil Cell (DAC)

By showing in Figure 2-1, at the very beginning step, rhenium gasket of 200 μm thickness was pre-indented to 45 μm by a DAC with culet size of 200, 300 or 350 μm depending of the pressure range. Then, a hole with 60~100 μm in diameter was drilled by extra fine electric discharge machine (EEDM). One thin sample pellet and two thin NaCl pellets were prepared. The sample pellet was coated by Au on the double side of surface. Before loading samples, the prepared thin pellets were dried in a vacuum container. Here, NaCl worked as pressure transmission medium for reducing the pressure gradients in the sample chamber. NaCl also worked as a thermal insulator and protected the damage on diamonds during laser heating, because NaCl has a relatively low thermal conductivity. NaCl was sometimes used for a pressure marker. Au acted as a pressure marker and also contributed to reduce the temperature gradients of the

sample. The sample pellet was sandwiched between two NaCl pellets in a sample chamber at the center of a gasket. Then the DAC was closed and pressed gradually and check the reached pressure by Diamond Raman spectrum (Akahama and Kawamura, 2004). The DACs used in this study is a symmetrical type made by SYNTEK Co., LTD.

Laser heated diamond anvil cell (LHDAC)

When the sample can absorb infrared laser beams, the sample can be heated through diamond anvils, because almost no absorption for infrared laser beams occurs in diamond. Thus, the sample pressed at high pressure can be heated over 1000 K. The sample was heated from the both side of DAC by using a Neodymium-doped Yttrium Lithium Fluoride (Nd:YLF) laser installed in Hokkaido Univ. or a Nd-doped Yttrium Aluminum Garnet (Nd:YAG) laser, or a defocused 35 W fiber laser, which the latter two are installed at the Institute for Solid State physics (ISSP) as shown in Figure 2-2, the University of Tokyo. The laser spot size was typically 20–30 μm for the Nd:YLF laser, 50–70 μm for the Nd:YAG laser, about 30 μm for the fiber laser. All the samples were heated at the constant output power for 10~80 minutes. Generating temperature was measured by the spectroradiometric method based on the blackbody radiation theory (Boehler et al., 2000; Watanuki et al., 2001). To prevent the unexpected thermal runaway, the heating region was carefully controlled in the inner part of the sample chamber and never attach to the edge of the gasket.

The comparison of before and after heating showed in Figure 2-3.

Phase identification

Synchrotron X-ray diffraction measurements

Synchrotron X-ray beam was used for X-ray diffraction (XRD) measurements, because the strong X-ray beam was needed due to quite small amount of product phases in the DAC. Synchrotron XRD experiments under high pressure and ambient temperature conditions were performed at the beamline of NE-1 of Photon Factory,

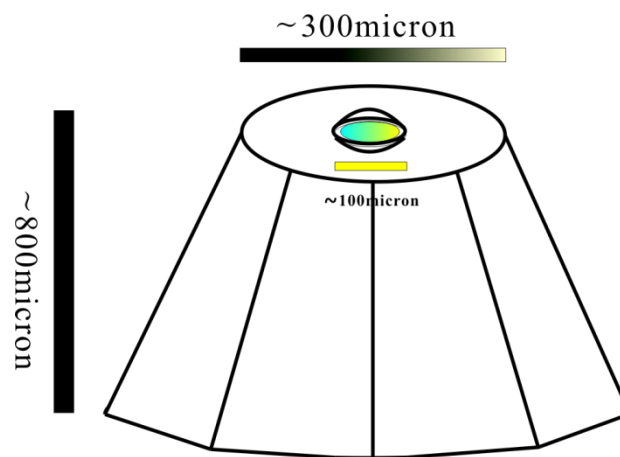


Figure 2-1. The schematic drawing of diamond anvil cell sampling assemblage.

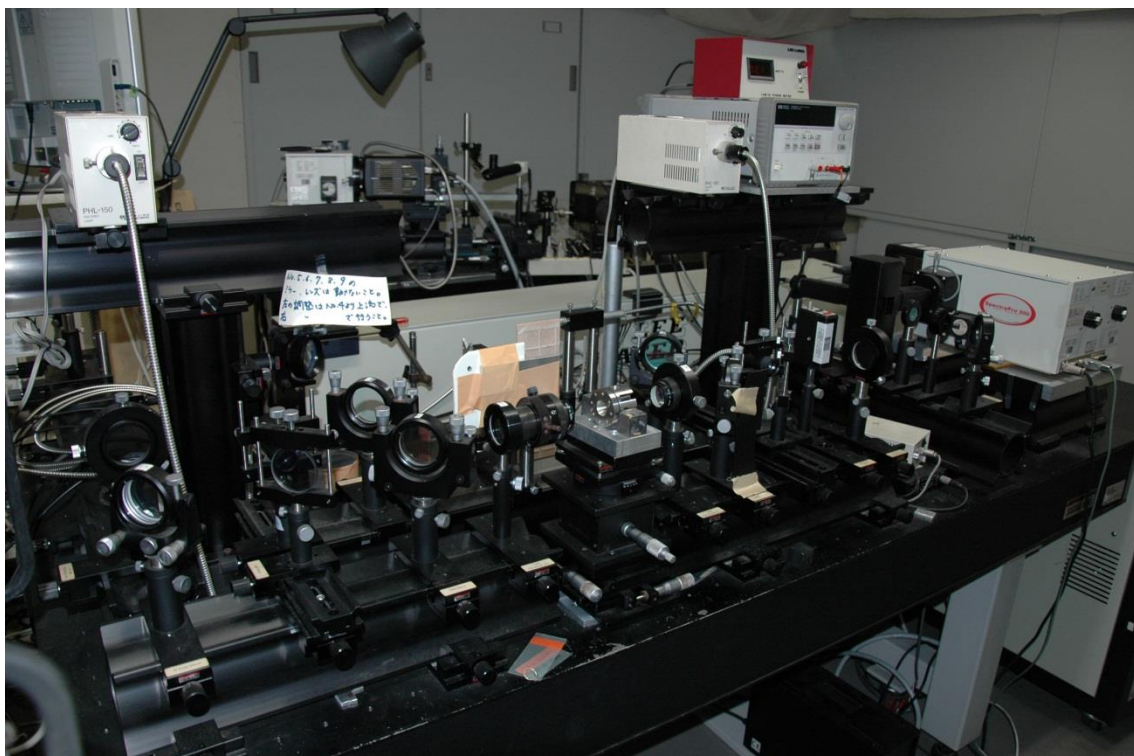
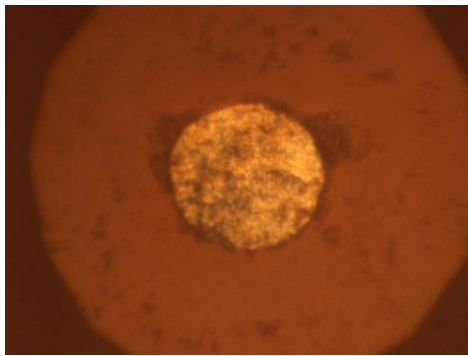


Figure 2-2. The fiber laser heating system in ISSP.



Before heating



After heating

Figure 2-3. Example of photo of LHDAC sample before and after heating. The colored area corresponds to heated area.

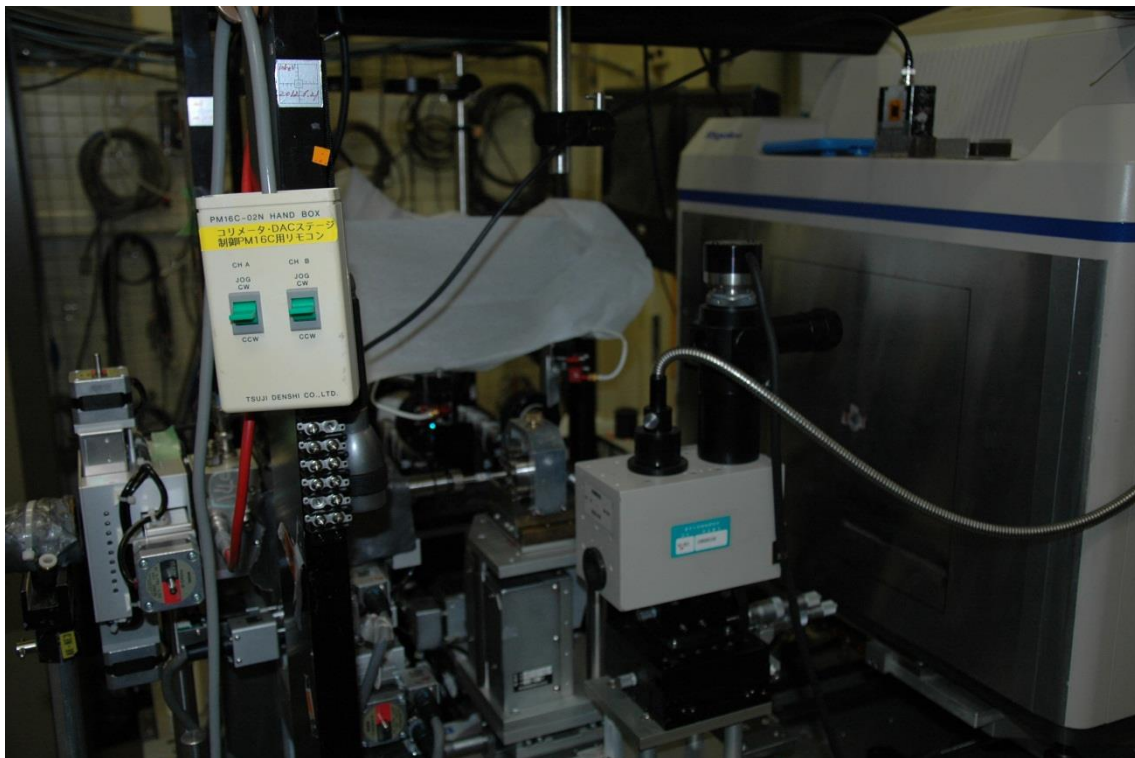


Figure 2-4. Photo of Beamline NE1 in Photon Factory, KEK.

KEK as shown in Figure 2-4. Incident X-ray beam was monochromatized at a wavelength of about 0.42 Å and then collimated to a diameter of 30 µm to avoid diffraction from the gasket. Angle dispersive X-ray diffraction patterns were recorded on an imaging plate with 3000 X 3000 pixels. Typical exposure time was for 15 minutes. Two-dimensional Debye-Scherrer rings on an imaging plate were integrated as a function of 2θ to obtain conventional one-dimensional diffraction profiles using the software of IPAnalyzer and PDIndexer (Seto et al., 2010).

Chemical analysis

Analytical transmission electron microscopy (ATEM)

After recovering the sample from high pressure and high temperature to ambient conditions, the desired area of the gasket (a little bit larger than the prepressed area) was cut by the laser processing machine (shown in Figure 2-5). Then this small piece sample was put on a single-hole mesh for a TEM sample. This mesh was set at the center of stage of Ar ion-thinning machine (Gatan DuoMill model 600 DIFF) and the sample was thinned from double side by the Ar ion beam.

TEM observation and the quantitative chemical analyses were performed by ATEM (JEOL JEM-2100) operating 200 kV with an energy distribution spectrum (EDS) analytical system (NORAN system Six, Thermo Fisher) as shown in Figure 2-6.

Before the quantitative chemical analyses of the product phases in this study, the electronic strength sensitivity adaptability test was examined using the relatively insensitive sample for electron beam, with appropriate size and thickness. Two different beam currents (10 pA/cm² and 5 pA/cm²) with a constant beam spot size of 10 nm in diameter were used for the test (the beam spot size test has been done in Table 2-1, which shows 10 nm is suitable for ATEM analysis. It shows the cation/Si ratio remain stable from 100 nm to 10 nm.), because all the grain is smaller than 1 µm in diameter. As shown in Table 2-2 found with different beam currents the cation/Si count number only have little variation. This indicates the beam currents 10 pA/cm² and spot size 10



Figure 2-5. The laser processing machine in ISSP.

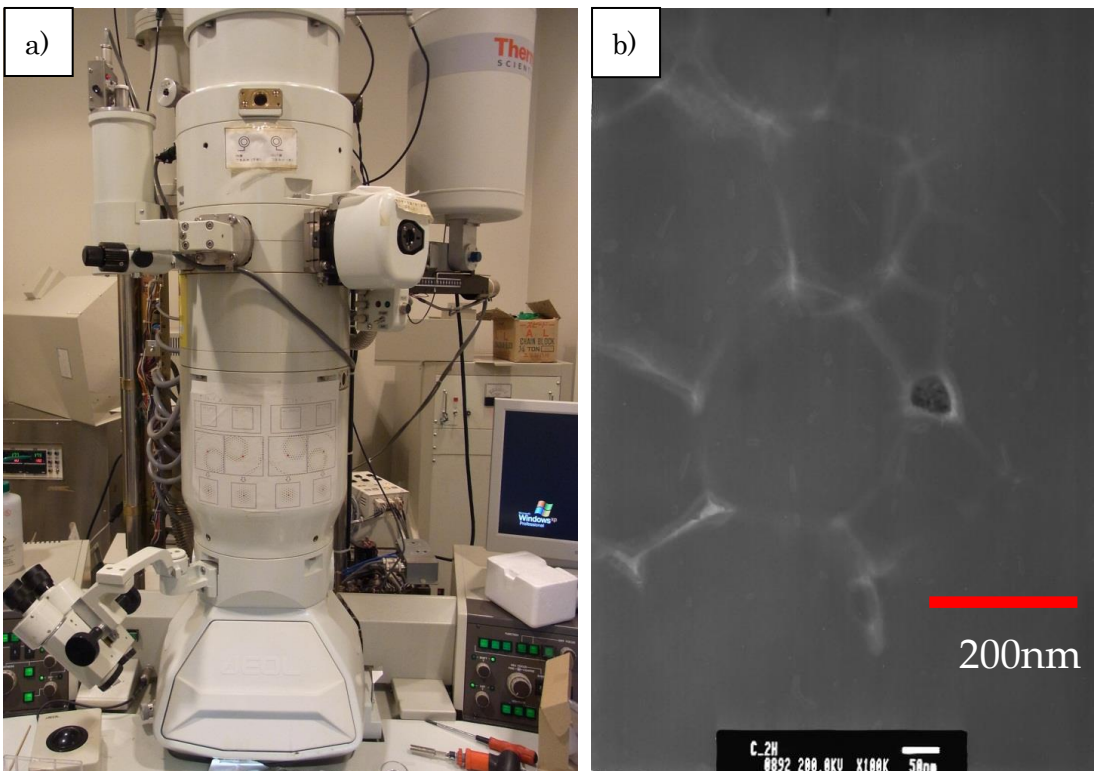


Figure 2-6. a) Analytical transmission electron microscopy (ATEM) installed in our laboratory.
b) Typical TEM image observed in this study.

Table 2-1. Beam spot size test for ATEM analysis.

Beam spot size	I(Cation)	I(Si)	I(Cation/Si)
150nm	3588	4197	0.85
125nm	3374	3993	0.84
100nm	1608	2206	0.72
75nm	2518	3208	0.78
50nm	1429	1881	0.75
10nm	1215	1664	0.73

Table 2-2. Beam current test for ATEM analysis.

Beam Current	I(Ca)	I(Mg)	I(Mn)	I(Si)	Cation/Si
10pA/cm ²	109	914	79	5128	0.21
5pA/cm ²	211	502	64	3030	0.26

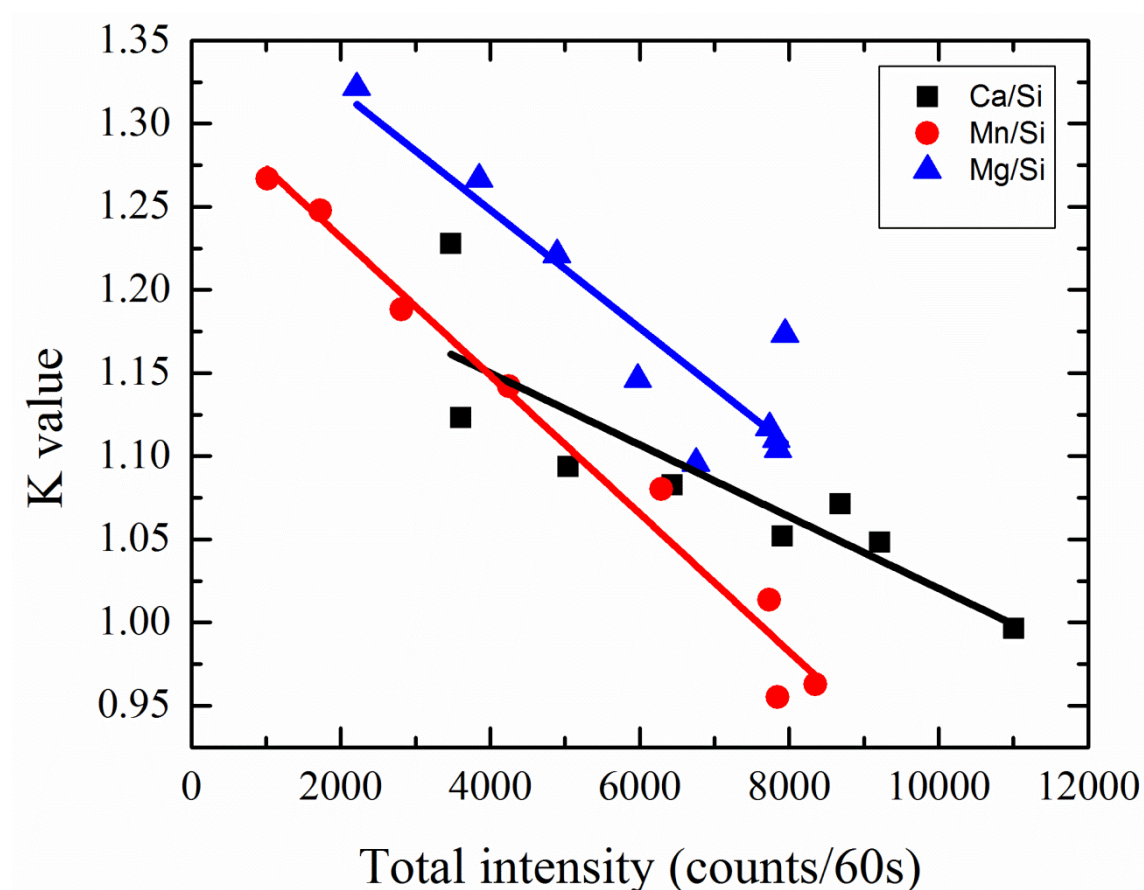


Figure 2-7. K-factor for 5pA/cm² beam condition for relative thin sample area.

nm combination can suitable for relatively thick sample area. And beam currents 5 pA/cm² and spot size 10 nm combination can suitable for the relatively thin sample area.

The quantitative chemical compositions were analyzed using experimentally obtained *k*-factors (Cliff and Lorimer, 1975). The quantitative chemical analyses were carried out following the method proposed by Fujino et al. (1998). Single crystals of a (Ca_{0.5},Mn_{0.5})SiO₃ diopside, and a pure Mg₂SiO₄ forsterite were used to calculate the corresponding *k*-factors to each elements. Generally, the *k*-factor, “*K_{ij}*” can be defined in the equation [2] as follows,

$$C_i/C_j = K_{ij}(I_i/I_j) \quad [2]$$

where *C_i* and *C_j* are the concentrations of element “*i*” and “*j*”, respectively, and *I_i* and *I_j* are X-ray intensities of element “*i*” and “*j*”, respectively. In the case of silicate minerals, the element “*j*” usually means silicon. Taking the thickness of the sample into consideration, the following advanced equation [3] was used to obtain more realistic *k*-factors.

$$C_i/C_j = (a_i T + K_{rij})(I_i/I_j) \quad [3]$$

where *a_i* is the absorption factor, which is different value depending on the HP-HT synthesis environments, the TEM beam current and TEM beam size. *T* means the detected total intensity of X-ray.

And two set of *k*-factors (for 10 pA/cm² and 5 pA/cm²) were prepared in this study and either of them was used for the quantitative chemical analysis. And for example, the *k*-factors for 5 pA/cm² series showed in Figure 2-7.

3. Perovskite Phase Relations between MgSiO_3 and MnSiO_3

3-1. Purpose

MgSiO_3 perovskite is generally acknowledged to be a major constituent mineral in the lower mantle and the most abundant silicate mineral on Earth. Because it is unlikely that MgSiO_3 perovskite exists as a chemically pure phase in the lower mantle, MgSiO_3 perovskite should form solid solutions with other elements. It is well known that the perovskite structure is tolerant of cationic substitutions and can accommodate different cations with dissimilar sizes and charges. For example, Andraut (2003) investigated various types of cationic substitutions in MgSiO_3 perovskite and discussed the possible cationic substitutions in the lower mantle.

The exchange between Mg^{2+} and other divalent cations is possibly one of the main substituting mechanisms in MgSiO_3 perovskite in the lower mantle. Because the solubility of $\text{Fe}^{2+}\text{SiO}_3$ component is important due to the elemental abundance of iron in the lower mantle, many researchers have focused on this element. Around 12 and 50 mol% ferrous iron can be incorporated into MgSiO_3 perovskite at the conditions of the top and the bottom of the lower mantle, respectively (Fei et al., 1996; Tateno et al., 2007). Conversely, it is evident that MgSiO_3 perovskite forms almost no solid solution with CaSiO_3 perovskite (e.g., Kesson et al., 1995; Jung and Schmidt, 2011). General rule of thumb is that the case which the ionic radius difference between the substituting cations is less than about 15 %, is likely to form a certain range of solid solution. According to Shannon (1976), because ionic radius of Fe^{2+} in an 8-fold site is only about 3 % larger than that of Mg^{2+} , on the other hand, Ca^{2+} is about 30 % larger than Mg^{2+} , it is understandable that Fe^{2+} can be incorporated into MgSiO_3 perovskite, but Ca^{2+} cannot be soluble in it. However, information about the solid solubility of other divalent cations in MgSiO_3 perovskite is scarce, although some partitioning studies of divalent transition elements can be found in literature (e.g., Ohtani et al., 1991; Malavergne et al., 1997).

Fujino et al. (2008) found that MnSiO_3 perovskite was stable at lower mantle

conditions. MnSiO_3 perovskite is orthorhombic; it is isomorphous with MgSiO_3 perovskite. Because the ionic radius of Mn^{2+} is between that of Mg^{2+} and Ca^{2+} , and about 8 % larger than Mg^{2+} (Shannon, 1976), it is expected that a certain range of solid solution could be formed on the MgSiO_3 - MnSiO_3 perovskite join, as mentioned above. Indeed, some solid solution phases, such as rhodonite, pyroxmangite, clinopyroxene and orthopyroxene, can be observed on the MgSiO_3 - MnSiO_3 join at atmospheric conditions (Ito, 1972). Furthermore, in terms of the Goldschmidt perovskite tolerance factor, the tolerance factor of MnSiO_3 perovskite (0.93) is much closer to that of MgSiO_3 perovskite (0.90) than that of CaSiO_3 perovskite (0.99).

Ishido (2010) performed diffraction studies at high pressures on the MgSiO_3 - MnSiO_3 join, in order to investigate the possibility of the formation of solid solutions on this join. He pointed out the possibility of formation of a complete solid solution. However, because Ishido (2010) did not analyze the chemical compositions of the product phases, the existence of a complete solid solution could not be confirmed. Therefore, in this study, some additional diffraction measurements and the quantitative chemical analyses of the product phases were performed to reveal the formation of solid solutions. In this chapter, the formation of a complete solid solution on the MgSiO_3 - MnSiO_3 join and crystal chemical consideration for this solid solution are discussed.

3-2. Experimental methods

I used gels of $(\text{Mg}_x\text{Mn}_{1-x})\text{SiO}_3$ composition with $x = 0.25, 0.5, 0.75$ as mentioned above. I used gels because we judged gels to be more chemically homogeneous than oxide mixtures.

High pressure conditions were generated using diamond anvil cells (DAC) with a 200 or 300 μm culet. A gel sample sandwiched by NaCl pellets was loaded into a 100 μm diameter hole (the sample chamber) at the center of a pre-indented rhenium gasket. A small amount of gold powder was mixed with the samples. A Neodymium-doped Yttrium Lithium Fluoride (Nd:YLF) laser or a Nd-doped Yttrium Aluminum Garnet (Nd:YAG) laser was used to heat the sample from both sides of the DAC. Gold was added to serve as a laser power absorber and also acted as a pressure marker (Anderson et al. 1989). The laser spot size was typically 20–30 μm for the Nd:YLF laser and 50–70 μm for the Nd:YAG laser. Temperature was measured by the spectroradiometric method and the temperature uncertainty was estimated to be about ± 200 K. Laser heating was carried out for between 10 and 80 minutes.

To identify the phases produced after laser heating, synchrotron X-ray diffraction patterns were measured at the NE-1 or BL13A beamlines at the Photon Factory of the High Energy Accelerator Research Organization in Japan, or the BL-10XU beamline at the SPring8 synchrotron of the Japan Synchrotron Radiation Research Institute. Diffraction patterns were recorded on an imaging plate (IP) at all beamlines. Two-dimensional X-ray diffraction images on the IP were integrated as a function of 2θ to obtain conventional one-dimensional diffraction profiles using the IPA and PDI software (Seto et al. 2010). It is noted that Debye-Scherrer rings of product phase look a little spotty, possibly due to the grain growth at high temperature. Chemical analyses for the recovered samples were done on an EDS system with a field emission-scanning electron microscope (FE-SEM; Jeol, JSM-7000F).

3-3. Results and Discussion

Formation of a complete solid solution of (Mg,Mn)SiO₃ perovskite

A summary of experimental results is shown in Table 3-1. X-ray diffraction patterns were measured at pressure after laser heating to identify the product phases. For example, Figure 3-1 shows a diffraction pattern for a run using a (Mn_{0.5}, Mg_{0.5})SiO₃ starting gel measured at 50 GPa and room temperature, after laser heating to about 1400 K.

All diffraction peaks can be indexed as either an orthorhombic phase, the B2 phase of NaCl, or gold. According to SEM-EDS analysis, the chemical composition of the product is identical to that of the starting material. This is the common case for all of the other experimental runs for all of the different gel compositions used. Table 3-2 lists the average chemical compositions and in Figure 3-2 the SEM photography for the silicate phases produced by this study and unit cell parameters for those phases are shown in Table 3-3.

The diffraction patterns from the orthorhombic phases are quite similar to those for silicate perovskites (e.g., Tateno et al., 2007). Furthermore, as shown in Figure 3-3, each unit cell parameter measured at about 50 GPa plots close to the straight line linking cell parameters for pure MnSiO₃ perovskite at 51 GPa (Fujino et al., 2008) with pure MgSiO₃ perovskites at 48 GPa (Ballaran et al., 2012). A linear relationship between crystal lattice parameters and the concentration of the constituent elements is known as the Vegard's rule and is commonly seen in solid solutions. The results from the experimental runs suggest that the phase produced in each run could have an orthorhombic perovskite structure with the same chemical composition as the starting material. It is indicated that a complete solid solution exists between Mg and Mn end members in the MgSiO₃-MnSiO₃ perovskite system at pressures from 30 to 50 GPa at high temperature.

The axial ratios of a/b and $\sqrt{2} a/c$ for the synthetic Mg-Mn perovskites are plotted as a function of composition in Figure 3-4, along with the ratios for MgSiO₃ perovskite

Table 3-1. Synthesis conditions and identified product phases.

Starting gels ^a	Pressure (GPa)	Temperature (K)	Heating Time (min)	Product phases
9:1	44	1600	60	Pv ^c
9:1	39	1500	15	Pv
9:1	34	1500	15	Pv
9:1	33	1600	15	Pv
9:1	Recovered ^b			Pv
3:1	50	1600	15	Pv
3:1	Recovered			Amorphous
1:1	48	1400	60	Pv
1:1	45	1300	10	Pv
1:1	40	1300	20	Pv
1:1	35	1500	20	Pv
1:1	Recovered			Amorphous
1:3	50	1800	80	Pv
1:3	45	1600	15	Pv
1:3	40	1600	15	Pv
1:3	Recovered			Amorphous

^aRatios represent molar ratios of MgSiO₃: MnSiO₃ components.

^bRecovered = X-ray diffraction was measured at 1 atm after recovery.

^cPv = perovskite

Table 3-2. Chemical compositions of the product phases analyzed by SEM-EDS.

Cations	3:1 ^a	1:1 ^a	1:3 ^a
Mg	0.76(1)	0.58(3)	0.26(3)
Mn	0.28(3)	0.49(4)	0.77(5)
Si	0.98(1)	0.96(3)	0.98(1)
CationsTotal	2.02(2)	2.03(3)	2.01(3)
Cation number for O $\equiv$ 3			
^a Molar ratios of MgSiO ₃ : MnSiO ₃ components in starting gels			
Standard deviations in the last digits are in parentheses			

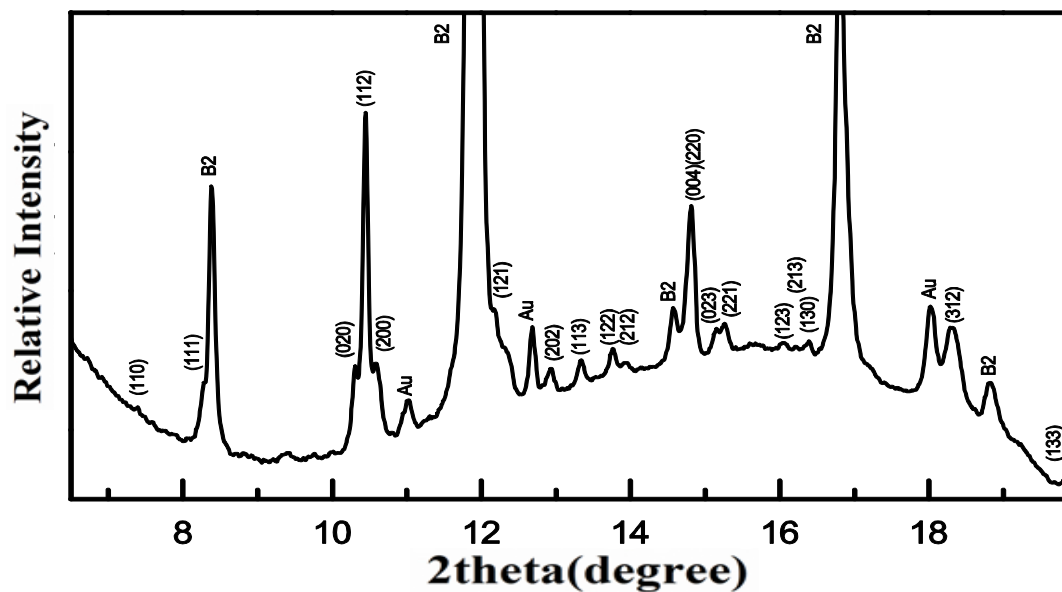


Figure 3-1. X-ray diffraction pattern of $(\text{Mg}_{0.5},\text{Mn}_{0.5})\text{SiO}_3$ perovskite at 50GPa and room temperature after laser heating to 1400 K. Monochromatized X-rays with a wavelength $\lambda = 0.4266 \text{ \AA}$ were used. Indexed peaks are from the perovskite phase. Peaks labeled Au and B2 represent peaks from gold and the B2 phase of NaCl.

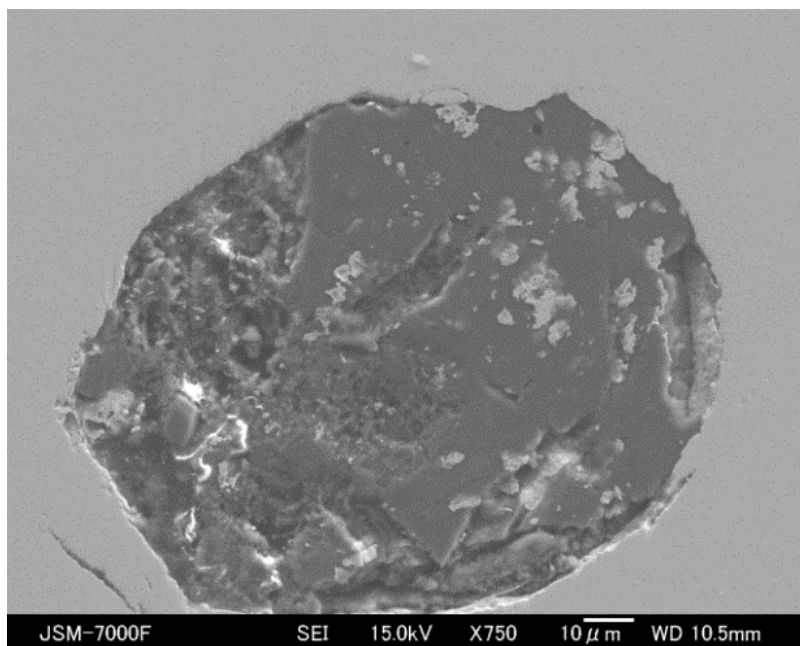


Figure 3-2. SEM image of the product of start gel with Mg:Mn=1:1. The right part is the perovskite phase.

Table 3-3. Unit cell parameters of (Mg,Mn)SiO₃ perovskite at high pressure room temperature.

Compositions ^a	Pressure(GPa)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
9:1	44	4.575(3)	4.755(3)	6.618(5)	143.9(2)
9:1	39	4.598(2)	4.768(3)	6.635(3)	145.5(1)
9:1	34	4.605(5)	4.786(5)	6.663(7)	146.8(3)
9:1	33	4.617(6)	4.785(7)	6.684(9)	147.7(4)
9:1	Recovered ^b	4.799(2)	4.938(2)	6.916(2)	163.9(1)
3:1	50	4.576(4)	4.732(2)	6.586(3)	142.6(2)
1:1	48	4.610(2)	4.734(2)	6.621(3)	144.5(1)
1:1	45	4.623(2)	4.769(3)	6.649(2)	146.6(1)
1:1	40	4.643(1)	4.783(2)	6.677(2)	148.3(1)
1:1	35	4.654(2)	4.794(2)	6.687(3)	149.2(1)
1:3	50	4.647(2)	4.747(1)	6.664(3)	147.0(1)

^a Ratios represent molar ratios of MgSiO₃: MnSiO₃ components in (Mg,Mn)SiO₃ perovskite

^b Recovered = X-ray diffraction was measured at 1 atm after recovery

Unit cell parameters were refined from *d*-values of orthorhombic indexing 10-15 reflections

Standard deviations in the last digits are in parentheses

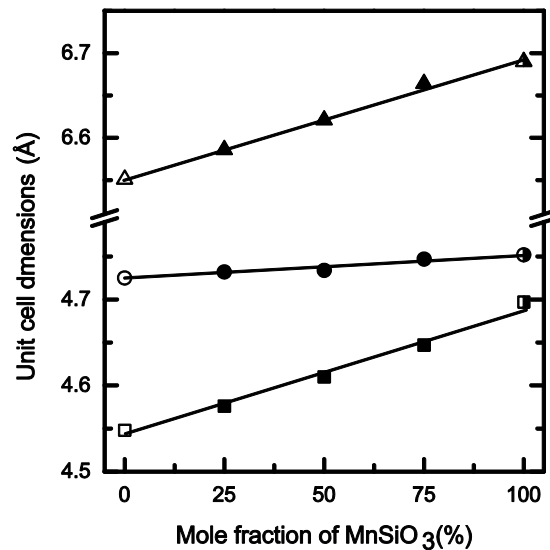


Figure 3-3. Cell parameters of perovskites in MgSiO₃–MnSiO₃ system with different Mg:Mn ratios at about 50 GPa. The unit cell dimension of *a*, *b*, and *c* corresponds to *closed squares*, *closed circles*, and *closed triangles*, respectively. The values for the pure MgSiO₃ (*open symbols*) and MnSiO₃ (*half closed symbols*) perovskites are from Ballaran et al. (2012) and Fujino et al. (2008). The errors are smaller than the symbols used.

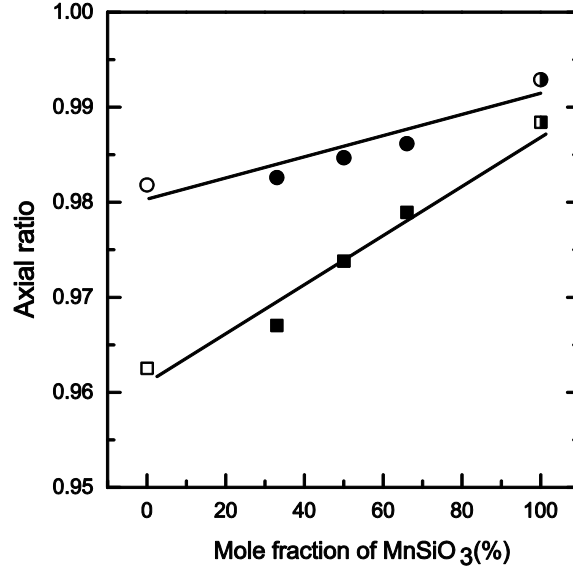


Figure 3-4. Axial ratios of a/b (closed squares) and $\sqrt{2} a/c$ (closed circles) calculated for (Mg,Mn)SiO₃ perovskites with different Mg:Mn ratios. The values on the pure MgSiO₃ (open symbols) and MnSiO₃ (half closed symbols) perovskites are from Ballaran et al. (2012) and Fujino et al. (2008).

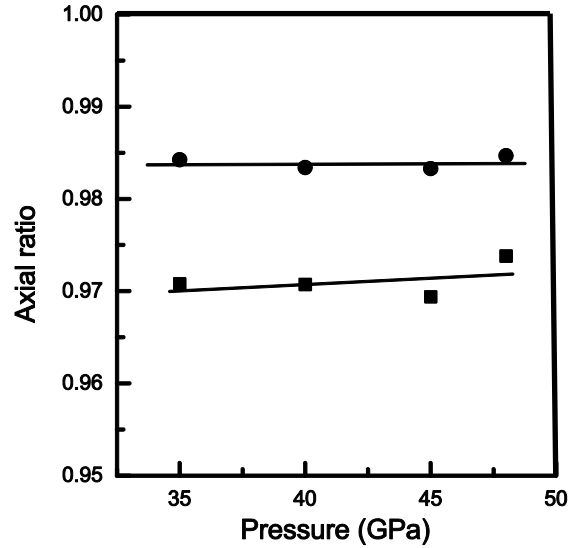


Figure 3-5. Changes in the axial ratios of a/b (closed squares) and $\sqrt{2} a/c$ (closed circles) calculated for (Mg_{0.5}, Mn_{0.5})SiO₃ perovskites at different pressures. The solid lines are just guides for the eyes. The errors are smaller than the symbols used.

and MnSiO_3 perovskite measured at about 50 GPa (Ballaran et al. 2012; Fujino et al. 2008). Both ratios increase monotonically with increasing MnSiO_3 content. These axial ratios should be exactly 1.00 for the ideal cubic perovskite structure and deviation from 1.00 corresponds to increasing orthorhombic distortion. Clearly, the orthorhombic distortion in $(\text{Mg,Mn})\text{SiO}_3$ perovskite solid solutions decreases with increasing MnSiO_3 component. This indicates that the system of $(\text{Mg,Mn})\text{SiO}_3$ perovskite forms a relatively regular solid solution and variations of the orthorhombic distortion in $(\text{Mg,Mn})\text{SiO}_3$ perovskite mainly depend on the average size of the cation occupying the A-site in the perovskite structure.

Structural variations of $(\text{Mg,Mn})\text{SiO}_3$ perovskite as a function of pressure

Figure 3-5 shows how the axial ratios of a/b and $\sqrt{2} a/c$ of $(\text{Mg}_{0.5},\text{Mn}_{0.5})\text{SiO}_3$ perovskite change with pressure. Those ratios for $(\text{Mg}_{0.5},\text{Mn}_{0.5})\text{SiO}_3$ perovskite show no significant difference with pressure. This means that its orthorhombic distortion is essentially unchanged at different pressures, although there are only a few data points confined to a relatively narrow pressure range (35 to 48 GPa). Conversely, it is known that orthorhombic distortion in MgSiO_3 perovskite increases with pressure whereas MnSiO_3 distortion decreases (Fujino et al. 2008; Ballaran et al. 2012). It is interesting that the pressure dependence of the axial ratios of $(\text{Mg}_{0.5}, \text{Mn}_{0.5})\text{SiO}_3$ perovskite shows a behavior intermediate to that of MgSiO_3 and MnSiO_3 perovskite. Because the orthorhombic distortion of $(\text{Mg}_{0.9}, \text{Mn}_{0.1})\text{SiO}_3$ perovskite increases with pressure, it seems that the compression mechanism of $(\text{Mg}, \text{Mn})\text{SiO}_3$ perovskite monotonically changes from MgSiO_3 to MnSiO_3 composition. This suggests that pressure induced changes in the orthorhombic distortion of $(\text{Mg,Mn})\text{SiO}_3$ perovskite depend on the average size of the cation occupying the A-site in the perovskite structure.

3-4. Summary

Formation of a complete perovskite solid solution is confirmed between MgSiO_3 and MnSiO_3 . It is noted that MnSiO_3 is the first chemical component confirmed to form a complete solid solution with MgSiO_3 perovskite at the P-T conditions in the earth's lower mantle.

4. Perovskite Phase Relations between CaSiO_3 and MnSiO_3

4-1. Purpose

As mentioned in general introduction, CaSiO_3 perovskite is the third most abundant mineral after MgSiO_3 perovskite and ferropericlase in the lower mantle assuming a pyrolitic composition. Thus, it is apparent that understanding of the physical and chemical behavior of CaSiO_3 perovskite at the lower mantle conditions is of great interest.

The crystal structure of CaSiO_3 perovskite was initially considered to be the cubic symmetry with the space group $Pm\bar{3}m$ (e.g., Yagi et al., 1989). In terms of the Goldschmidt tolerance factor, a value of 0.99 for CaSiO_3 perovskite indicates that the ionic radii of Ca^{2+} fits well to the A-site in the silicate perovskite structure and the cubic symmetry is likely adopted. However, since some theoretical studies have proposed that some non-cubic symmetry is suitable depending on pressure and temperature conditions, quite a few theoretical and experimental researches have discussed the crystal symmetry of CaSiO_3 perovskite (e.g., Stixrude et al., 1996; Akber-Knutson et al., 2002; Shim et al., 2002; Uchida et al., 2009). There have been a lot of arguments about the crystal symmetry of CaSiO_3 perovskite, because it undergoes the transformation to the amorphous state upon decompression, and furthermore, the distortion from the cubic symmetry is so small that experimental technique could not evaluate the symmetry due to the resolution limit.

Meanwhile, CaSiO_3 perovskite is considered to be chemically inert, because it is known that CaSiO_3 perovskite is difficult to form solid solutions with other cations, especially divalent cations (e.g., Irifune, 1994; Jung and Schmidt, 2011). Kesson et al. (1995) pointed out that the solubility of MgSiO_3 component into CaSiO_3 perovskite is extremely limited because of the ionic radius difference between Ca^{2+} and Mg^{2+} . Some theoretical studies also suggested that it is hard to expect the solid solution on the CaSiO_3 - MgSiO_3 perovskite join (e.g., Vitos et al., 2006; Jung and Schmidt, 2011). On the other hand, CaSiO_3 perovskite is considered to be a major host mineral of some rare

earth elements (e.g., Kato et al., 1996; Hirose et al., 2004). However, since those studies focused on element partitioning between CaSiO_3 perovskite and MgSiO_3 perovskite or melts, no crystal chemical consideration about the incorporation mechanism of such elements has been argued. Thus, CaSiO_3 perovskite has been often treated as a pure phase in the lower mantle.

As mentioned above, Fujino et al. (2008) found MnSiO_3 perovskite at lower mantle conditions. In terms of the ionic radius, Mn^{2+} is between Mg^{2+} and Ca^{2+} , and about 14 % smaller than Ca^{2+} (Shannon, 1976). According to a general rule of thumb, the case which the ionic radius difference between the substituting cations is less than about 15 % is expected to form a certain range of solid solution. From this rule, it is subtle whether the substitution between Mg^{2+} and Ca^{2+} occurs in a silicate perovskite. It is noted that solid solutions appear on the CaSiO_3 and MnSiO_3 join under the crustal environments (e.g., Glasser, 1962; Brown et al., 1980). Wollastonite (about 90 mol%) solid solution forms in CaSiO_3 and MnSiO_3 join. A relatively narrow rhodonite solid solution forms at the MnSiO_3 side. In terms of the Goldschmidt perovskite tolerance factor, the tolerance factors of MnSiO_3 perovskite and CaSiO_3 perovskite are 0.93 and 0.99, respectively. This difference of the tolerance factors seems to be subtle. However, although MnSiO_3 perovskite is orthorhombic and isomorphous with MgSiO_3 perovskite, Fujino et al. (2008) indicated that the orthorhombic distortion of MnSiO_3 perovskite decreases with increasing pressure and temperature. Thus, it would be expected that practical tolerance factors of MnSiO_3 perovskite and CaSiO_3 perovskite approach each other at high pressure and temperature.

I performed preliminarily X-ray diffraction measurements in order to check the solubility on CaSiO_3 - MnSiO_3 join (Li, 2010). As the result, the possibility of the formation of solid solutions was confirmed on this join and a certain range of the immiscibility gap was found. Furthermore, it was also suggested that $(\text{Ca,Mn})\text{SiO}_3$ perovskite on the CaSiO_3 side of the immiscibility gap is cubic, but on the other hand, $(\text{Ca,Mn})\text{SiO}_3$ perovskite on the MnSiO_3 side is orthorhombic. However, no data of the

quantitative chemical compositions has been available so far, because only the X-ray diffraction measurements were carried out in Li (2010). Therefore, in this study, some additional diffraction measurements and the quantitative chemical analyses by ATEM were performed to reveal the formation of solid solutions and determine the accurate range of the immiscibility gap. In this chapter, the formation of solid solutions on the $\text{CaSiO}_3\text{-MnSiO}_3$ join and crystal chemical consideration for this solid solution are discussed.

4-2. Experimental methods

The starting gelled materials with the mole ratios of Ca:Mn of 4:1, 2:3, 1:3, 1:1, 3:2, 3:1, 4:1 and 9:1 in the (Ca,Mn)SiO₃ composition were prepared by the sol-gel method. The detailed procedure is as mentioned above.

High pressure conditions were generated using diamond anvil cells (DAC) with a 200 or 300 μm culet. A gel sample sandwiched by NaCl pellets was loaded into a 100 μm diameter hole at the center of a pre-indented rhenium gasket. A small amount of gold powder was mixed with the samples and a Nd:YLF laser was used to heat the sample from both sides of the DAC. Gold was added to serve as a laser power absorber and also acted as a pressure marker (Anderson et al., 1989). The laser spot size was typically 20–30 μm . Temperature was measured by the spectroradiometric method and the temperature uncertainty was estimated to be about ± 200 K. Laser heating was carried out for between 10 and 80 minutes.

To identify the phases produced after laser heating, synchrotron X-ray diffraction patterns were measured at the NE-1 beamline at the Photon Factory of the High Energy Accelerator Research Organization in Japan. Diffraction patterns were recorded on an imaging plate (IP) at all beamlines. Two-dimensional X-ray diffraction images on the IP were integrated as a function of 2θ to obtain conventional one-dimensional diffraction profiles using the IPA and PDI software (Seto et al. 2010). The chemical compositions of the product phases were analyzed by FE-SEM (FE-SEM; Jeol, JSM-7000F) with the EDS detector, and by ATEM (JEM-2010, JEOL) with EDS.

4-3. Results and Discussion

Li (2010) preliminary pointed out the formation of solid solutions on the $\text{CaSiO}_3\text{-MnSiO}_3$ perovskite join and the possibility of a certain range of the immiscibility gap between the solid solutions. Figures 4-1a and 4-1b show examples of X-ray diffraction patterns of CaSiO_3 -rich and MnSiO_3 -rich side samples on the $\text{CaSiO}_3\text{-MnSiO}_3$ join, respectively. Chemical analyses by FE-SEM with EDS in Table 4-1, confirms that the chemical compositions of those phases are same as those of their starting gels. Thus, it is concluded that a certain range of solid solutions are formed on the $\text{CaSiO}_3\text{-MnSiO}_3$ join. Furthermore, some specific peaks in Figure 4-2a seem to disappear by comparing with X-ray diffraction peaks in Figure 4-2b. This can be explained by the extinction of diffraction peaks caused by the crystallographic symmetry. Therefore, $(\text{Ca,Mn})\text{SiO}_3$ perovskite on Ca-rich side is cubic and that on Mn-rich side is orthorhombic. These are in agreement with Li (2010).

Figure 4-3 shows X-ray diffraction pattern of product phases of the starting gel composition with $\text{CaSiO}_3\text{:MnSiO}_3 = 3\text{:}2$ obtained at 41 GPa. This pattern can be explained as coexistence of two perovskites with cubic and orthorhombic symmetry. As shown in Figure 4-4, I performed several synthesis experiments for this composition and checked the reproducibility. Therefore, the coexistence of two perovskite phases apparently indicate the existence of the immiscibility gap on the $\text{CaSiO}_3\text{-MnSiO}_3$ join. ATEM analysis of this sample can quantitatively determine the range of the immiscibility gap between 55(5) mol% and 80(5) mol% of MnSiO_3 component on the $\text{CaSiO}_3\text{-MnSiO}_3$ join as shown in Figure 4-5.

The unit cell parameters of $(\text{Ca}_{0.2},\text{Mn}_{0.8})\text{SiO}_3$ perovskite can be calculated as $a = 4.747(5) \text{ \AA}$, $b = 4.765(5) \text{ \AA}$, $c = 6.723(6) \text{ \AA}$ and $V = 152.1(3) \text{ \AA}^3$ (refined from d -values of orthorhombic indexing 12 reflections as shown in Table 4-2). The unit cell parameters of $(\text{Ca}_{0.55},\text{Mn}_{0.45})\text{SiO}_3$ perovskite are determined as $a = 3.402 \text{ \AA}$ and $V = 39.37 \text{ \AA}^3$. The unit cell volume of Mn-rich $(\text{Ca,Mn})\text{SiO}_3$ perovskite is larger than that of pure MnSiO_3 perovskite $150.1 \text{ \AA}^3$ for orthorhombic cell (this unit cell parameter been

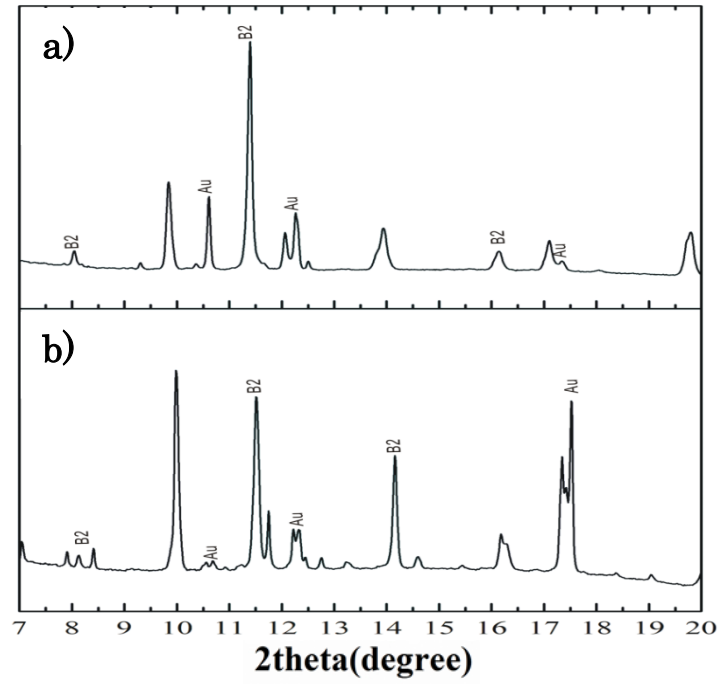


Figure 4-1. X-ray diffraction pattern the samples of starting gel composition with a) Ca:Mn = 1:1 at 45 GPa and ambient temperature, b) Ca:Mn = 1:9 at 50 GPa and ambient temperature. unmarked peaks in a) belong to Ca-rich perovskite, in b) belong to Mn-rich perovskite. Au = Gold; B2 = NaCl(B2).

Table 4-1. Chemical compositions of the product phases by SEM-EDS analysis

Cations	3:1 ^a	1:1 ^b	1:3 ^c
Si	4.0	4.1	4.0
Ca	0.9	2.0	3.0
Mn	3.1	1.8	1.0
CationsTotal	4.0	3.8	4.0

Cation number for O $\equiv$ 12

^a Molar ratios of CaSiO₃: MnSiO₃ components in starting gels recovered from 45GPa

^b Molar ratios of CaSiO₃: MnSiO₃ components in starting gels recovered from 50GPa

^c Molar ratios of CaSiO₃: MnSiO₃ components in starting gels recovered from 36GPa

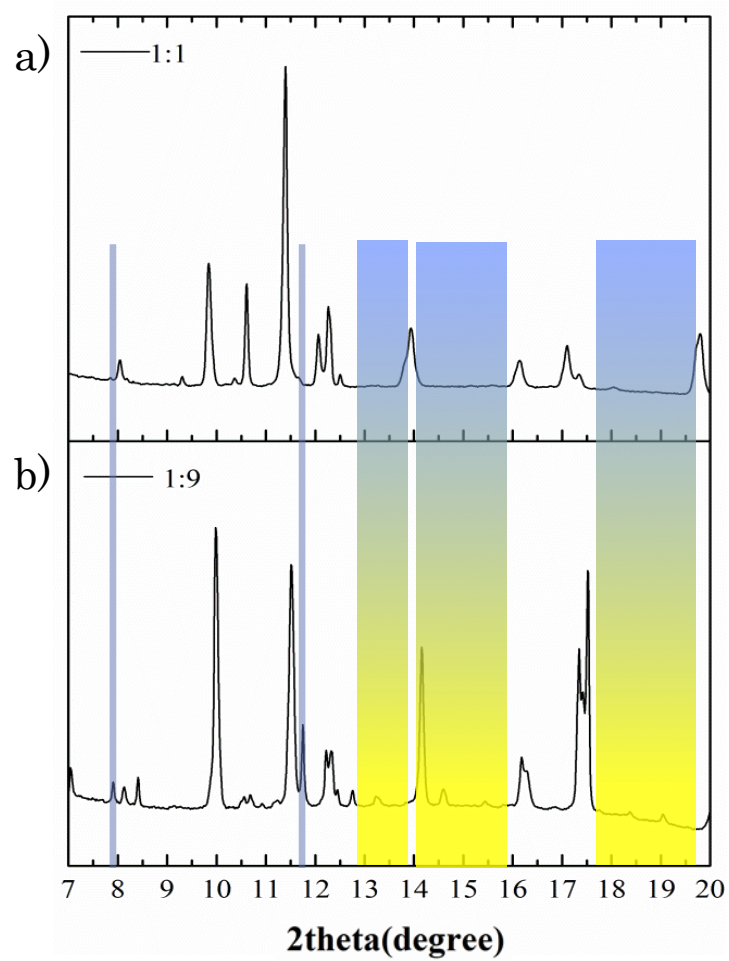


Figure 4-2. X-Ray diffraction patterns of a) Ca-rich side and b) Mn-rich side.

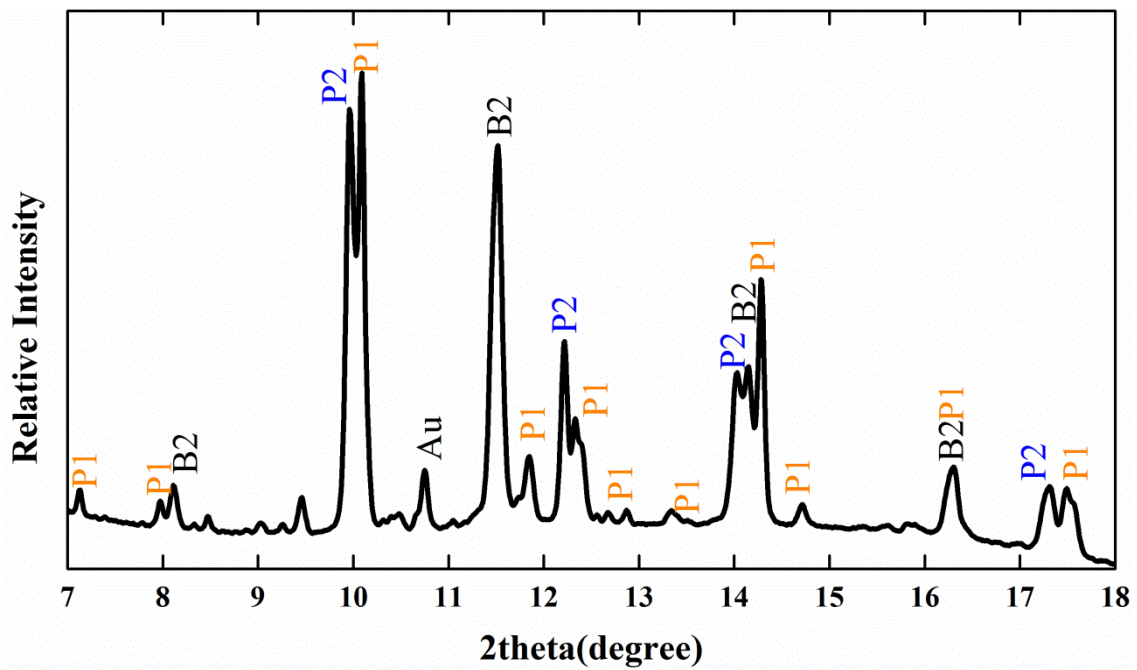


Figure 4-3. X-ray diffraction pattern of starting gel with Ca:Mn = 2:3 under 41GPa. P1 = orthorhombic perovskite; P2 = cubic perovskite; B2 = NaCl-B2 type; Au = gold. The spilt main peaks are the characteristics peak.

Table 4-2. Observed and calculated d -values of the $(\text{Ca}_{0.2}\text{Mn}_{0.8})\text{SiO}_3$ perovskite at 41 GPa and room temperature.

h	k	l	$d_{\text{obs}}(\text{\AA})$	$d_{\text{calc}}(\text{\AA})$	$d_{\text{obs}}-d_{\text{calc}}$
1	1	0	3.3616	3.3630	-0.0004
0	0	2	2.3616	2.3614	-0.0001
1	1	2	2.3762	2.3775	-0.0005
2	0	0	2.3759	2.3736	0.0010
0	2	2	1.9454	1.9438	0.0008
2	0	2	1.9351	1.9389	-0.0020
1	2	2	1.7995	1.7988	0.0004
2	1	2	1.8005	1.7959	0.0025
2	2	0	1.6804	1.6815	-0.0007
1	2	3	1.5730	1.5728	0.0002
0	2	3	1.6320	1.6323	-0.0002
2	2	1	1.6305	1.6313	0.0001
1	3	3	1.2775	1.2773	-0.0005

Note: Refined unit cell parameters are $a=4.747(5)$ $\text{\AA}$, $b=4.765(5)$ $\text{\AA}$, $c=6.722(6)$ $\text{\AA}$, $V=152.1(3)$ $\text{\AA}^3$.

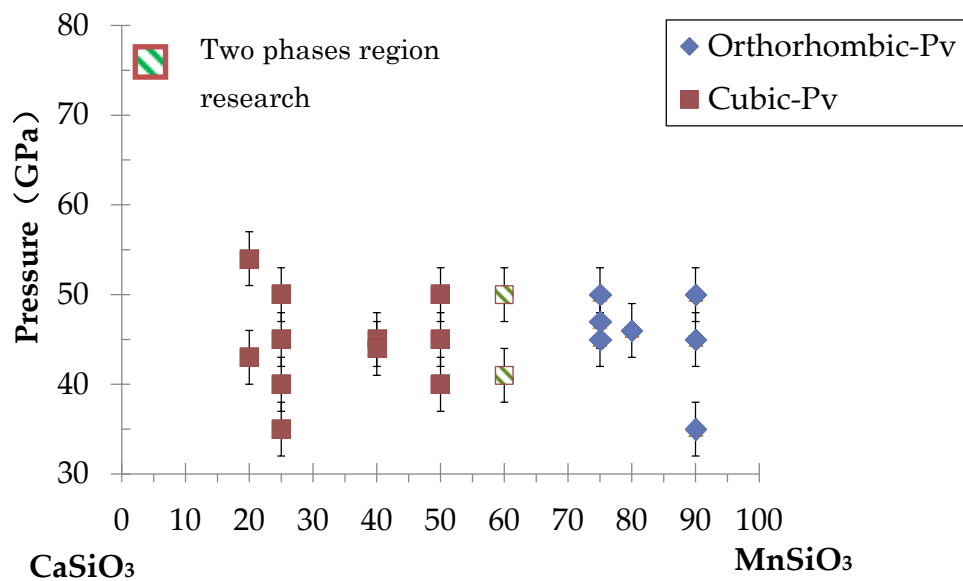


Figure 4-4. Phase diagram where the appearing phases is the plotted at each starting gel composition and experimental pressure.

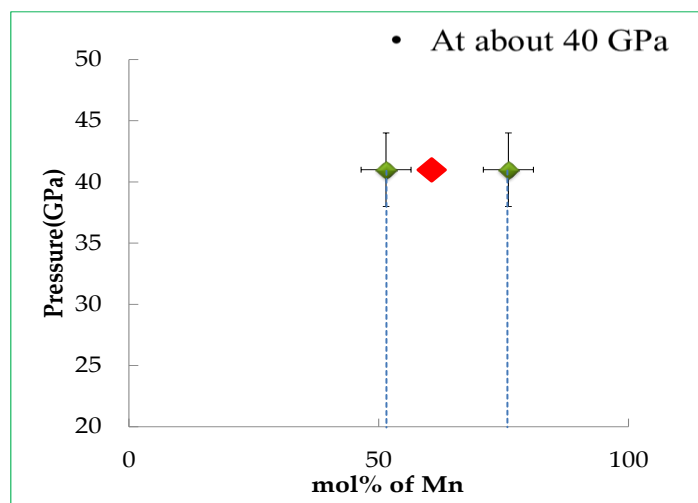


Figure 4-5. The accurate chemical compositions of the phase boundary at almost 40 GPa. The red diamond label is the starting gel composition plotted. The immiscibility gap locates at 55 mol% ~80 mol% of Manganese contents.

calculated to $37.34 \text{ \AA}^3$ for cubic perovskite cell) reported in Fujino et al. (2008). On the other hand, the unit cell volume of Ca-rich (Ca,Mn)SiO₃ perovskite is much smaller than the volume of pure CaSiO₃ perovskite $41.81 \text{ \AA}^3$ calculated from the EOS in Shim et al. (2002). These evidences are consistent with the fact that the ionic radius of Mn²⁺ is smaller than that of Ca²⁺.

4-4. Summary

Mn^{2+} can substitute Ca^{2+} in CaSiO_3 perovskite and quite wide ranges of solid solutions are formed on the CaSiO_3 - MnSiO_3 join. It is noted that CaSiO_3 perovskite has been believed as a pure phase so far. The solubility of Ca and Mn components on the CaSiO_3 - MnSiO_3 join are about 55 mol% and 20 mol%, respectively.

(Ca,Mn) SiO_3 perovskites on the CaSiO_3 side is cubic and that on the MnSiO_3 side is orthorhombic.

5. Perovskite Phase Relations in the System of MgSiO_3 - MnSiO_3 - CaSiO_3

5-1 Purpose

FeSiO_3 has been the most soluble chemical component into MgSiO_3 perovskite so far. However, only about 12 mol% of FeSiO_3 component can dissolve into MgSiO_3 perovskite at the top of the lower mantle (Fei et al., 1996) and even at the bottom of the lower mantle, at most 50 mol% can be incorporated into MgSiO_3 perovskite (Tateno et al., 2007). On the other hand, even if Al^{3+} is the most soluble cation into CaSiO_3 perovskite as mentioned above, only 25 mol% Al_2O_3 component dissolves into CaSiO_3 perovskite (Yusa et al., 1995). Of course, Al^{3+} is a trivalent cation and CaSiO_3 perovskite has been considered to be an almost pure phase for substitution of any divalent cations.

In chapter 3 and chapter 4 in this study, I described perovskite phase relations in the MgSiO_3 - MnSiO_3 system and in the CaSiO_3 - MnSiO_3 system. As described in those chapters, it is concluded that MnSiO_3 is quite unique chemical component for MgSiO_3 and CaSiO_3 perovskites. I found that MnSiO_3 component can form a complete solid solution with MgSiO_3 perovskite in this study. Furthermore, I found that quite wide range of solid solution can form on the CaSiO_3 - MnSiO_3 join, although there is an immiscibility gap in a compositional range from 55 to 80 mol% of MnSiO_3 component.

In researches of earth's interior, extending the chemical system treated from binary to ternary seems to be not so common. There have been a lot of studies dealing with phase relations in binary systems. And then people often extend the chemical system to multi-components system such as pyrolite or MORB, which are chemical models for the real mantle. Thus, when the phase relation in a binary system is somewhat different from that in a multi-component system, it seems that which element directly affects the phase relation is sometimes unclear.

In this study, synthesis experiments in the ternary system of MgSiO_3 - MnSiO_3 - CaSiO_3 perovskites at high pressure and high temperature were performed by using LHDAC. Synchrotron X-ray diffraction measurements and the quantitative chemical analyses

using ATEM were performed to identify the product phases. Then, the effects of the addition of MnSiO_3 component to the mutual solubility between MgSiO_3 and CaSiO_3 perovskite were investigated.

5-2. Experimental methods

The starting gelled materials with the mole ratios of Mg:Mn:Ca of 10:1:10, 2:1:2, 3:4:3, 1:1:2, 1:1:3, 15:15:70, 15:40:45 and 45:40:15 in the (Mg,Mn,Ca)SiO₃ composition were prepared by the sol-gel method. The detailed procedure is as mentioned above.

High pressure conditions were generated using diamond anvil cells (DAC) with a 200 or 300 μm culet. A gel sample sandwiched by NaCl pellets was loaded into a 100 μm diameter hole at the center of a pre-indented rhenium gasket. A small amount of gold powder was mixed with the samples. A fiber laser installed at the ISSP, the University of Tokyo was used to heat the sample from both sides of the DAC. Gold was added to serve as a laser power absorber and also acted as a pressure marker (Anderson et al. 1989). The laser spot size was typically 20–30 μm . Temperature was measured by the spectroradiometric method and the temperature uncertainty was estimated to be about ± 200 K. Laser heating was carried out for between 10 and 80 minutes.

To identify the phases produced after laser heating, synchrotron X-ray diffraction patterns were measured at the NE-1 beamline at the Photon Factory of the High Energy Accelerator Research Organization in Japan. Diffraction patterns were recorded on an imaging plate (IP) at all beamlines. Two-dimensional X-ray diffraction images on the IP were integrated as a function of 2θ to obtain conventional one-dimensional diffraction profiles using the IPA and PDI software (Seto et al. 2010). The chemical compositions of the product phases were analyzed by ATEM (JEM-2010, JEOL) with EDS.

5-3. Results

The experimental conditions and the product phase have been summarized in Table 5-1. All the samples were heated at about 1400~1900 K (± 200 K) depending on pressure. Since as mentioned in Fujino et al. (2008), the MnSiO_3 can be decomposed into the B1 type of MnO and stishovite at relatively higher temperature and even at high pressure, laser power was carefully controlled. When the laser heating successfully finished, a little color change to brown could be observed in the sample through the CCD unit and monitor.

Identification of the product phases and their chemical analyses

Figure 5-1 shows the synchrotron X-ray diffraction pattern of the product phases with bulk composition of $\text{Mg:Mn:Ca} = 10:1:10$ obtained at 54 GPa and room temperature after laser heating and the diffraction pattern of its recovered sample. Coexistence of two perovskite phases can be observed at high pressure with one perovskite being apparently orthorhombic and Mg-rich, and the other being cubic and Ca-rich. Peak positions of each perovskite suggest that the orthorhombic phase is Mg-rich and the cubic phase is Ca-rich, because Ca-rich perovskite should have larger unit cell than that of Mg-rich perovskite. In the diffraction pattern of the recovered sample, since reflections from the orthorhombic perovskite can be observed, the cubic perovskite phase is unquenchable. The results of ATEM chemical analyses for the product phases are summarized in Table 5-2 and the data are plotted in the ternary diagram of $\text{MgSiO}_3\text{-MnSiO}_3\text{-CaSiO}_3$ (Figure 5-2). It is clearly indicated that the product phases are Ca-bearing $(\text{Mg,Mn})\text{SiO}_3$ perovskite and Mg-bearing $(\text{Ca,Mn})\text{SiO}_3$ perovskite. And it is consistent with the results in chapter 3 and 4 that Ca-bearing $(\text{Mg,Mn})\text{SiO}_3$ perovskite is orthorhombic and quenchable, and also Mg-bearing $(\text{Ca,Mn})\text{SiO}_3$ perovskite is cubic and unquenchable.

Table 5-1. Synthesis conditions and identified product phases.

Starting gel*	Pressure ‡ (GPa)	Temperature (K)	Heating (min)	Product phase	TEM available
2:1:2	30	1500	50	2Pv	
2:1:2	40	1600	40	2Pv	
2:1:2	55	1800	30	2Pv	
2:1:2	60	1800	15	2Pv	√
2:1:2	66	1800	15	2Pv	
10:1:10	30	1400	55	2Pv	√
10:1:10	40	1600	40	2Pv	
10:1:10	53	1700	30	2Pv	√
10:1:10	57	1800	30	2Pv	
10:1:10	70	1700	40	2Pv	√
10:1:10	100	1900	20	2Pv	
3:4:3	54	1700	15	Pv	√
3:4:3	67	1800	15	Pv	√
15:40:45	40	1500	15	Pv	√
15:40:45	55	1700	15	Pv	
45:40:15	41	1600	15	2Pv	√
45:40:15	55	1800	15	2Pv	
1:2:1	45	1600	15	Pv	√
1:2:1	55	1700	15	Pv	√
1:3:1	40	1600	15	Pv	√
1:3:1	50	1700	15	Pv	√
15:70:15	40	1600	15	2Pv	√
15:70:15	45	1700	15	2Pv	√

* The mole ratio of Mg:Mn:Ca.

‡ This is the before heating pressure measured by the Diamond Raman. The accurate producing phases pressure determined by the NaCl equation of state proposed by Sata in 2002.

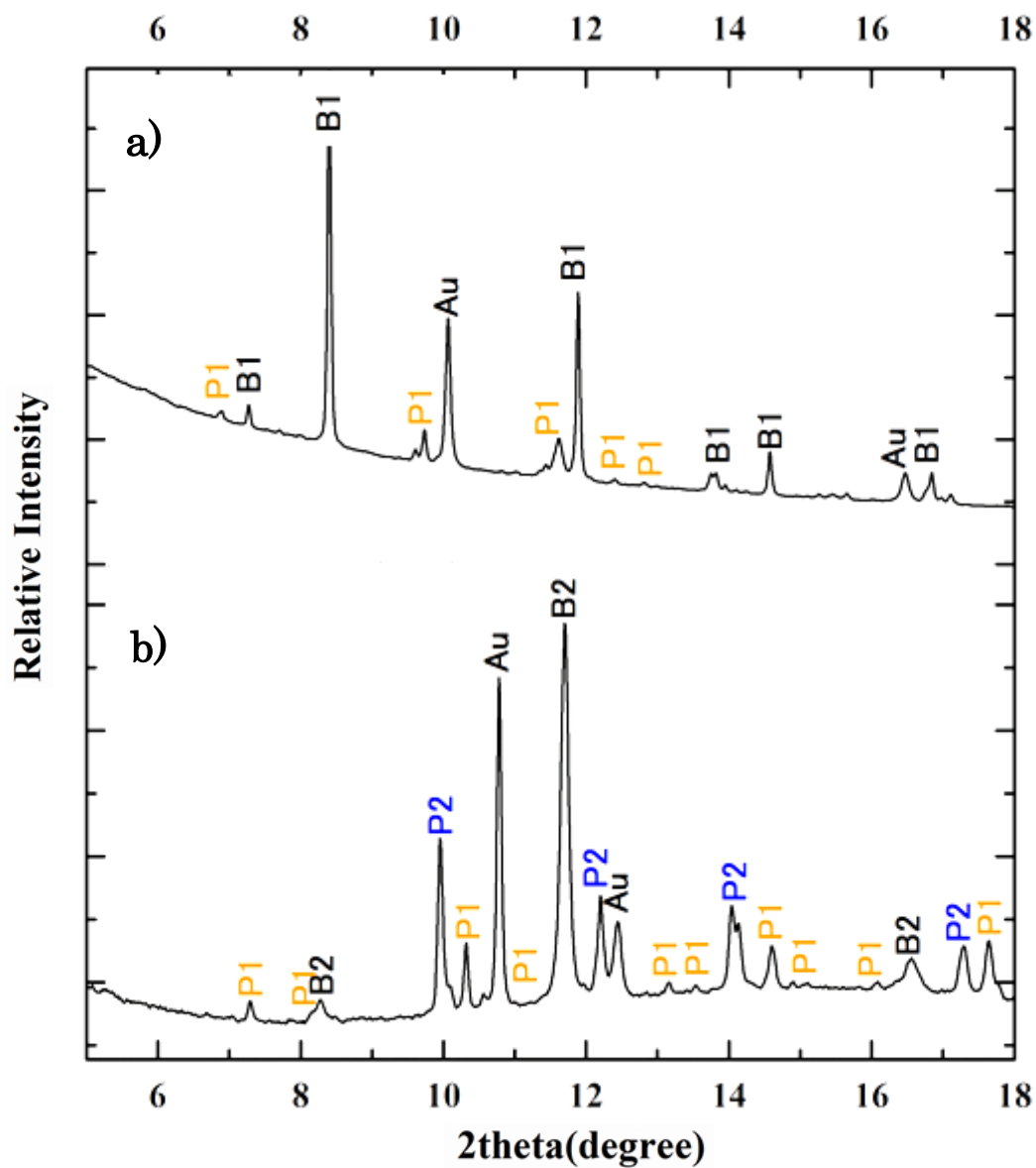


Figure 5-1. X-ray diffraction patterns of a) recovered sample from b. b) product phases with starting gel $\text{MgSiO}_3\text{:MnSiO}_3\text{:CaSiO}_3=10\text{:1:10}$ at 54 GPa and room temperature and Peaks labeled Au and B2 represent peaks from gold and the B2 phase of NaCl. P1 = orthorhombic perovskite; P2 = cubic perovskite.

Table 5-2. Chemical compositions of product phases of the starting material with the bulk composition of $\text{MgSiO}_3\text{:MnSiO}_3\text{:CaSiO}_3 = 10\text{:1:10}$.

Chemical composition in atoms per formula unit									
Number of oxygen atoms are fixed as 12.									
MP	1	2	3	4	5	6	Ave		
Mg	3.75	4.18	3.93	3.58	3.74	3.91	3.85(8)		
Ca	0.02	0.15	0.06	0.07	0.09	0.03	0.07(2)		
Mn	0.02	0.05	0.03	0.09	0.07	0.03	0.05(1)		
Si	4.20	4.05	4.06	4.03	4.01	4.05	4.07(3)		

CP	1	2	3	4	5	6	7	8	Ave
Mg	0.07	0.06	0.10	0.15	0.11	0.19	0.05	3.70	0.55(5)
Ca	3.56	3.44	3.68	3.57	3.52	3.66	3.66	0.17	3.16(4)
Mn	0.03	0.07	0.06	0.11	0.06	0.02	0.13	0.05	0.07(1)
Si	3.99	3.93	4.00	3.96	4.11	4.10	4.05	3.96	4.01(2)

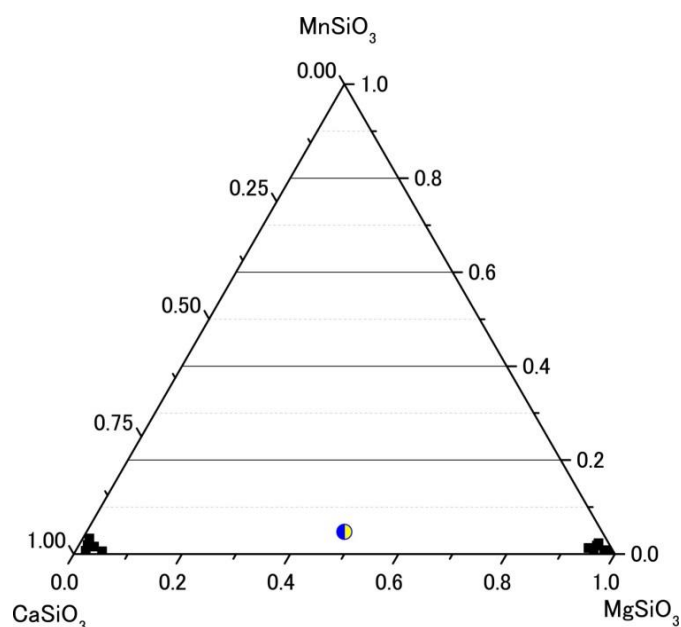


Figure 5-2. Plots of chemical compositions (mol%) of product phases in Table 5-2 in the system of $\text{MgSiO}_3\text{-MnSiO}_3\text{-CaSiO}_3$. A half shaded circle represents the composition of the starting materials. Closed squares indicate composition of product phases.

Figure 5-3 displays the synchrotron X-ray diffraction pattern of the product phases with bulk Mg:Mn:Ca composition equal to 2:1:2 obtained at 60 GPa and room temperature after laser heating. Two perovskite phases are observed at high pressure. One perovskite is orthorhombic which rich in Mg, and the other is cubic and Ca-rich. No reflections of perovskite phases are observed in the diffraction pattern of the recovered sample, therefore both the orthorhombic and cubic perovskite phases became unquenchable. The results of ATEM chemical analyses for the product phases are summarized in Table 5-3 and the data are plotted in the ternary diagram as Figure 5-4.

Figures 5-5 and 5-6 demonstrate the synchrotron X-ray diffraction pattern of the product phases with bulk composition of Mg:Mn:Ca = 3:4:3 obtained at 55 GPa and room temperature after laser heating, and the bulk composition of Mg:Mn:Ca = 15:40:45 obtained at 55 GPa and room temperature after laser heating, respectively. Under this experiment conditions, only one perovskite phase is observed at high pressure. Based on the same evidence as mentioned above, it is suggested that this perovskite is and looks like cubic. The results of ATEM chemical analyses are summarized in Table 5-4 for the product phases and the data are plotted in a ternary diagram as in Figure 5-7.

The synchrotron X-ray diffraction pattern in Figure 5-8 demonstrates the product phases with the bulk composition of Mg:Mn:Ca = 45:40:15 obtained at 55 GPa and room temperature after laser heating. Under these conditions, the coexistence of two perovskite phases is observed. The results of ATEM chemical analyses for the product phases are summarized in Table 5-5 and the data are plotted in the ternary diagram in Figure 5-9. An immiscibility gap and relatively stable solubility of CaSiO_3 component into $(\text{Mg,Mn})\text{SiO}_3$ perovskite are noticed, however, the solubility of MgSiO_3 component into $(\text{Ca,Mn})\text{SiO}_3$ perovskite increases dramatically.

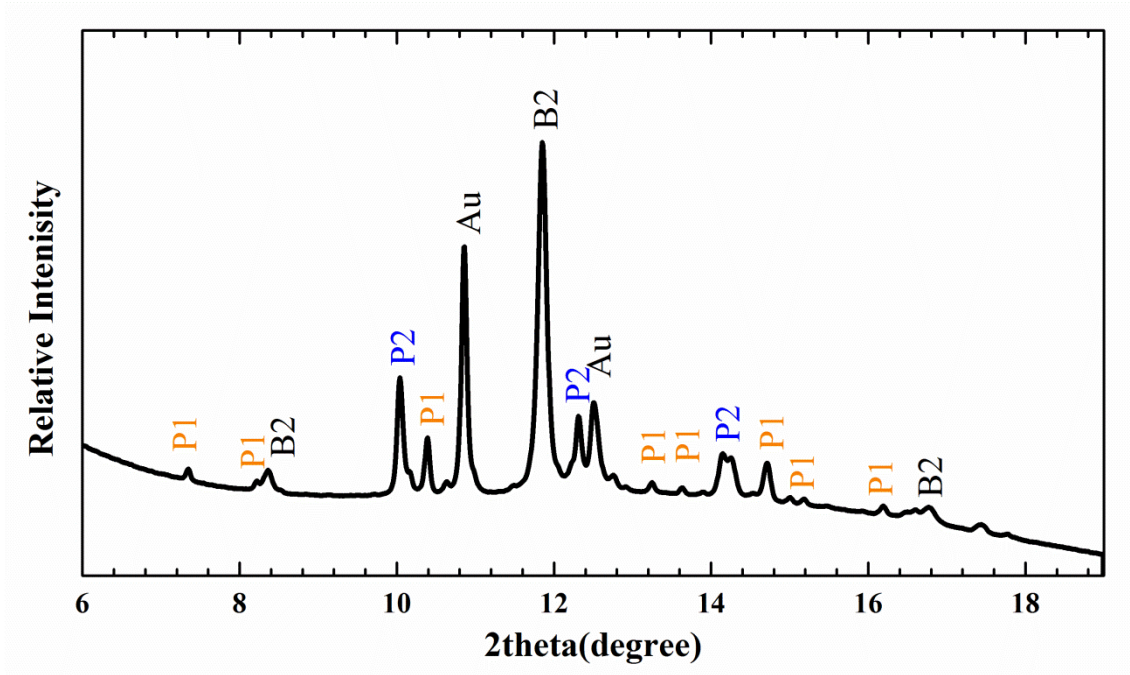


Figure5-3. X-ray diffraction pattern of $\text{MgSiO}_3\text{:MnSiO}_3\text{:CaSiO}_3=2\text{:1:2}$ perovskites at 60 GPa and room temperature. Peaks labeled Au and B2 represent peaks from gold and the B2 phase of NaCl. P1 = orthorhombic perovskite; P2 = cubic perovskite.

Table 5-3. Chemical compositions of product phases of the starting material with the bulk composition of $\text{MgSiO}_3\text{:MnSiO}_3\text{:CaSiO}_3 = 2\text{:}1\text{:}2$.

Chemical composition in atoms per formula unit										
Number of oxygen atoms are fixed as 12.										
	1	2	3	4	5	6	7	8	9	Ave
Mg	2.85	3.62	2.82	2.93	3.18	2.61	3.15	3.22	3.19	3.06(9)
Ca	0.05	n.d.	n.d.	0.16	0.18	n.d.	0.01	0.02	0.01	0.05(2)
Mn	0.92	0.39	0.80	0.90	0.82	1.36	1.00	0.82	0.87	0.88(8)
Si	4.00	3.81	3.96	4.03	4.08	3.98	3.99	3.94	3.86	3.96(3)

	1	2	3	Ave
Mg	0.53	0.60	0.73	0.62(6)
Ca	2.38	2.80	2.96	2.71(17)
Mn	0.81	0.64	0.52	0.66(8)
Si	4.07	3.83	3.92	3.94(7)

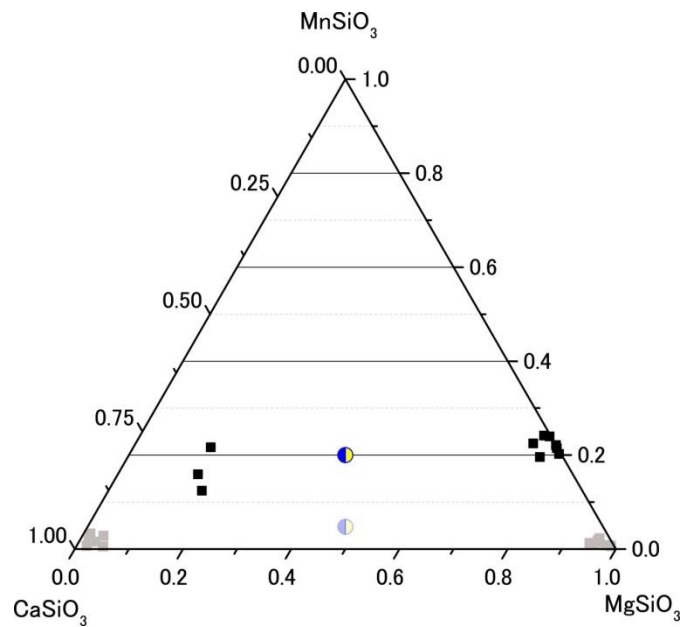


Figure 5-4. Plots of chemical compositions (mol%) of product phases in Table 5-3. in the system of $\text{MgSiO}_3\text{-MnSiO}_3\text{-CaSiO}_3$. A half shaded circle represents the composition of the starting materials. Closed squares indicate composition of product phases.

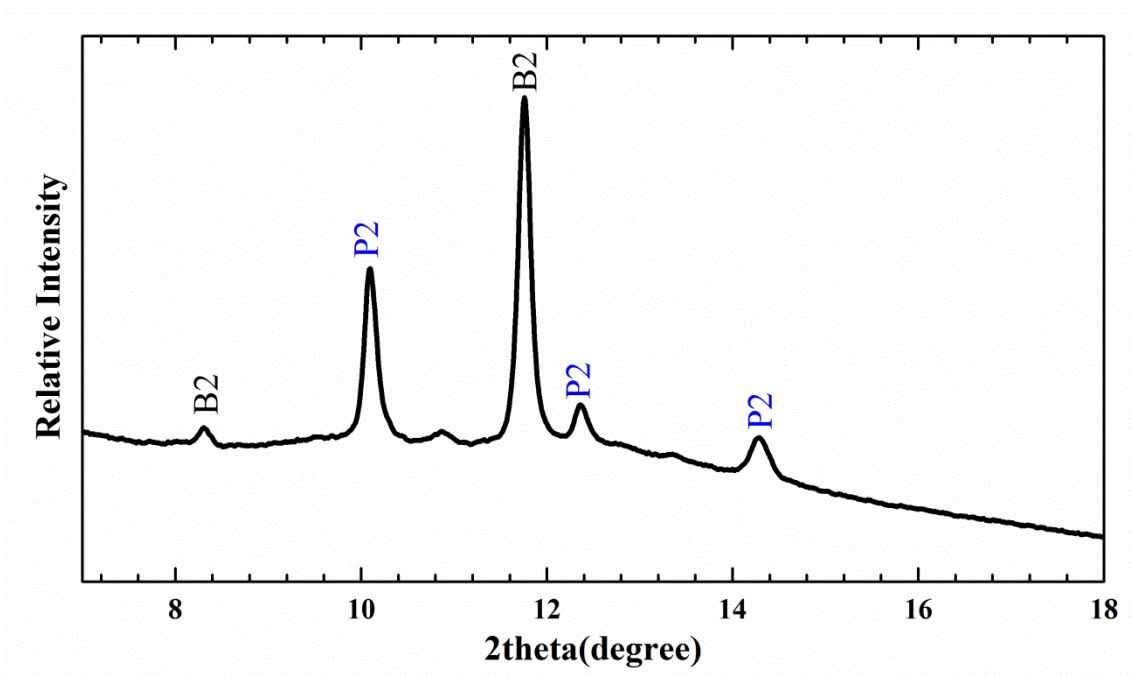


Figure 5-5. X-ray diffraction pattern of $\text{MgSiO}_3\text{:MnSiO}_3\text{:CaSiO}_3 = 3\text{:4:3}$ perovskites at 55 GPa at room temperature. Peaks labeled B2 represent peaks from B2 phase of NaCl. P2 = cubic perovskite

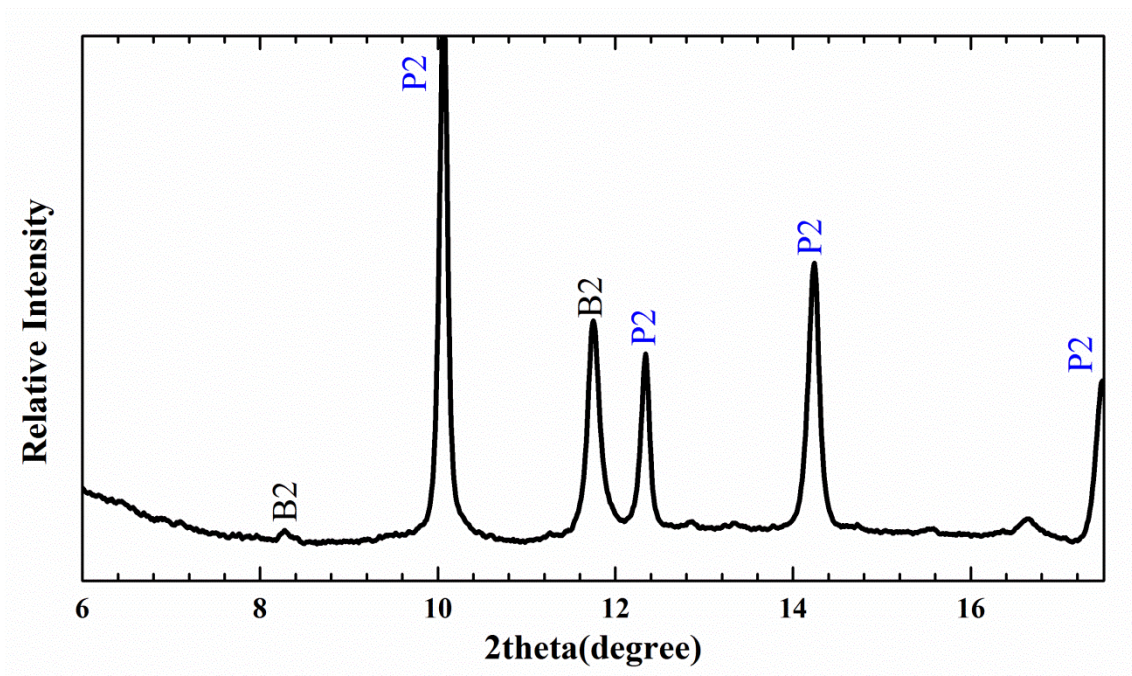


Figure 5-6. X-ray diffraction pattern of $\text{MgSiO}_3\text{:MnSiO}_3\text{:CaSiO}_3 = 15\text{:40:45}$ perovskites at 55 GPa at room temperature. Peaks labeled B2 represent peaks from B2 phase of NaCl. P2 = cubic perovskite.

Table 5-4. Chemical compositions of product phases of the starting material with the bulk composition of MgSiO_3 : MnSiO_3 : $\text{CaSiO}_3 = 3:4:3$ and $15:40:45$.

Chemical composition in atoms per formula unit						
Number of oxygen atoms are fixed as 12.						
	1	2	3	4	5	Ave
Mg	1.41	1.09	1.28	1.16	1.29	1.25(5)
Ca	0.93	1.01	1.26	1.21	1.11	1.11(6)
Mn	1.74	1.35	1.38	1.53	1.58	1.52(7)
Si	4.02	4.36	4.01	4.06	4.00	4.09(7)

	1	2	3	Ave
Mg	0.55	0.55	0.52	0.54(1)
Ca	1.69	1.83	1.82	1.78(4)
Mn	1.75	1.62	1.66	1.68(4)
Si	4.02	4.00	4.01	4.01(1)

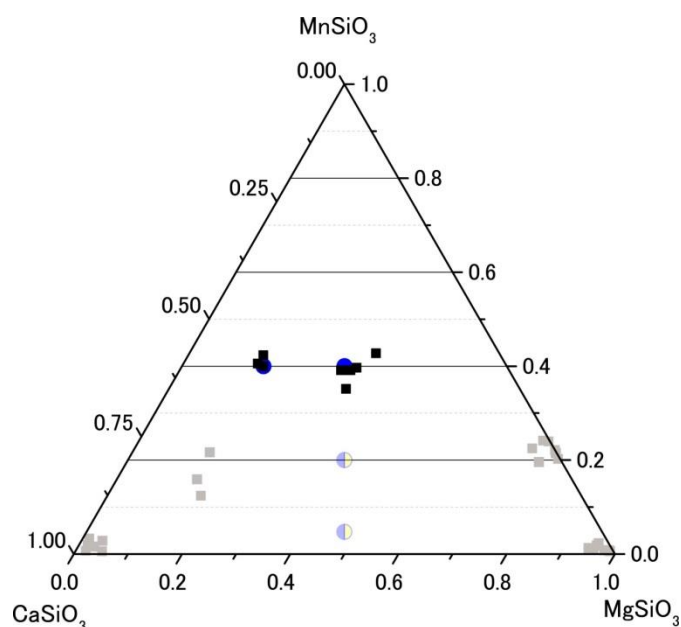


Figure5-7. Plots of chemical compositions (mol%) of product phases in Table 5-4. in the system of MgSiO_3 - MnSiO_3 - CaSiO_3 . A shaded circle represents the composition of the starting materials. Closed squares indicate composition of product phases.

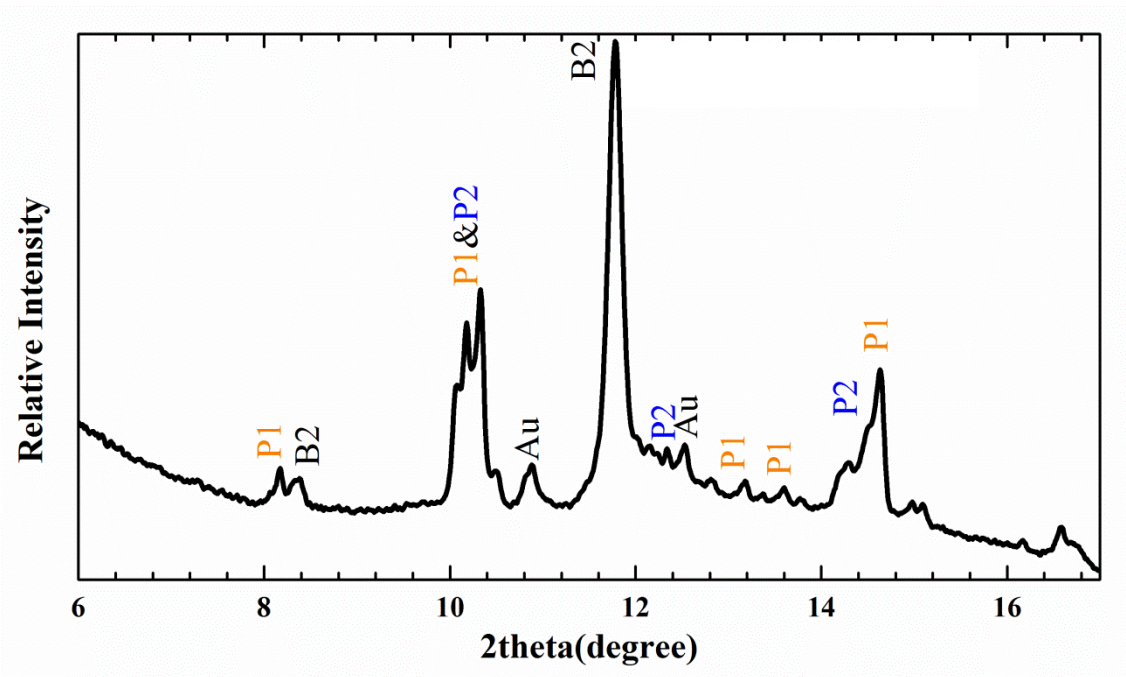


Figure 5-8. X-ray diffraction pattern of MgSiO₃:MnSiO₃:CaSiO₃ = 45:40:15 perovskites at 55 GPa at room temperature. Peaks labeled Au and B2 represent peaks from gold and the B2 phase of NaCl. P1 = orthorhombic perovskite; P2 = cubic perovskite.

Table 5-5. Chemical compositions of product phases of the starting material with the bulk composition of MgSiO_3 : MnSiO_3 : CaSiO_3 = 45:40:15.

Chemical composition in atoms per formula unit				
Number of oxygen atoms are fixed as 12.				
	1	2	3	Ave
Mg	2.23	2.36	2.66	2.42(12)
Ca	0.11	0.05	0.21	0.12(4)
Mn	1.59	1.53	1.04	1.39(17)
Si	4.05	4.04	4.17	4.09(4)

	1	2	3	Ave
Mg	1.64	1.64	1.18	1.49(15)
Ca	0.71	0.74	0.72	0.72(8)
Mn	1.58	1.62	2.01	1.74(14)
Si	4.05	3.97	4.00	4.01(2)

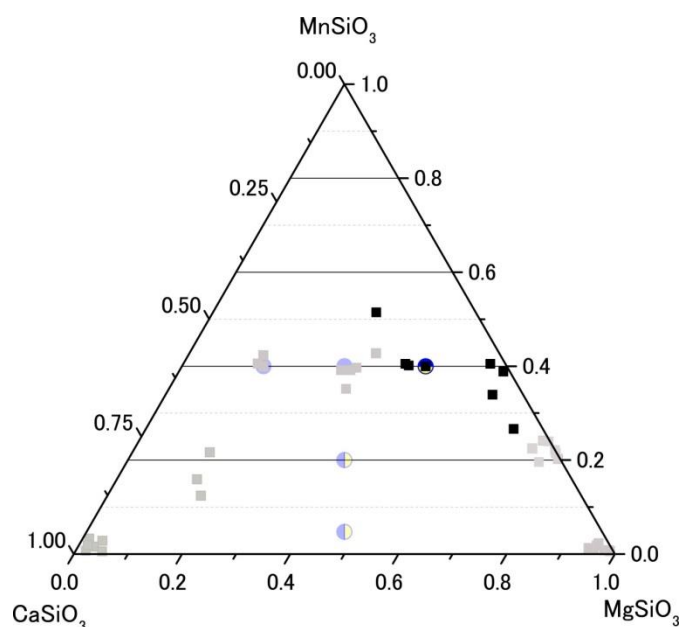


Figure 5-9. Plots of chemical compositions (mol%) of product phases in Table 5-5. in the system of MgSiO_3 - MnSiO_3 - CaSiO_3 . A half shaded circle represents the composition of the starting materials. Closed squares indicate composition of product phases.

Figure 5-10 displays the synchrotron X-ray diffraction pattern of the product phases with bulk composition of Mg:Mn:Ca = 1:2:1 at 55 GPa and room temperature after laser heating. Under this experiment conditions, only one perovskite phases can be observed and looks like cubic. The results of ATEM chemical analyses are summarized in Table 5-6 for the product phases and the data are plotted in the ternary diagram in Figure 5-11.

When the bulk composition of Mg:Mn:Ca is equal to 1:3:1, the product phases at 55 GPa and room temperature after laser heating are demonstrated by the synchrotron X-ray diffraction pattern in Figure 5-12. It is inferred from some obscure peaks in the pattern that two perovskite phases might coexist under this experiment conditions with the main one looks like cubic. The results of ATEM chemical analyses for the product phases are summarized in Table 5-7 and the data are plotted in the ternary diagram (Figure 5-13).

Our experiment with bulk composition of Mg:Mn:Ca = 15:70:15 at 45 GPa and room temperature after laser heating yield synchrotron X-ray diffraction pattern of the product phases and recovered sample as in Figure 5-14. The possibility of coexistence of two perovskite phases can be inferred from the broaden main peak. The results of ATEM chemical analyses for the product phases clearly indicate the coexistence of two perovskite phases as shown in Table 5-8 and the data are plotted in the ternary diagram (Figure 5-15).

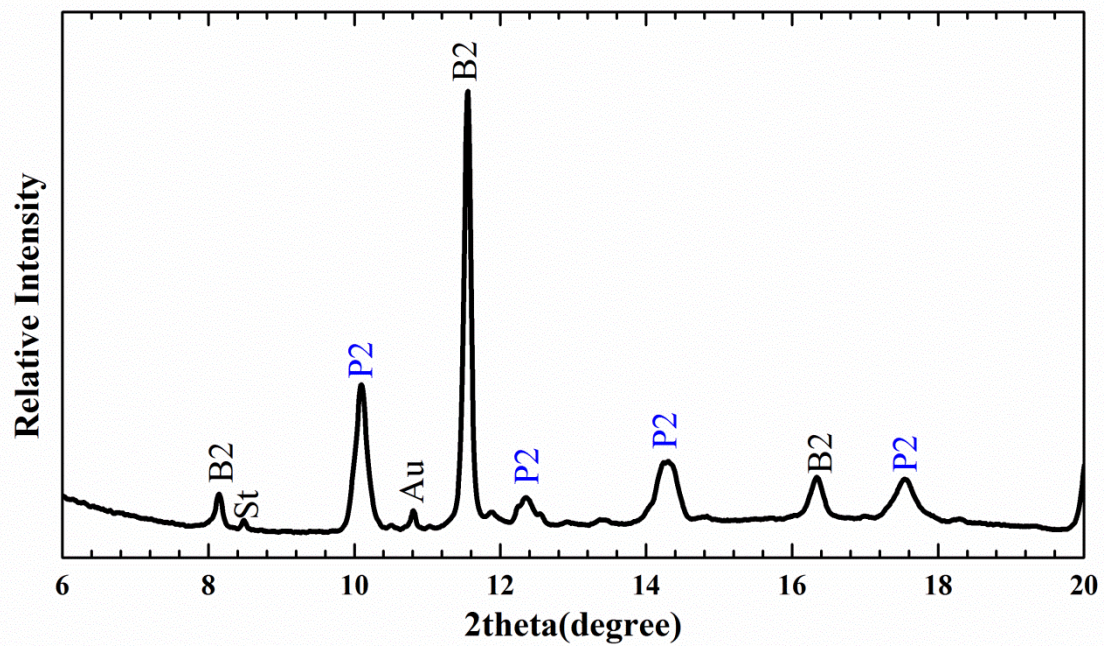


Figure 5-10. X-ray diffraction pattern of $\text{MgSiO}_3\text{:MnSiO}_3\text{:CaSiO}_3 = 1\text{:}2\text{:}1$ perovskites at 55 GPa at room temperature. Peaks labeled B2 represent peaks from B2 phase of NaCl. P2 = cubic perovskite.

Table 5-6. Chemical compositions of product phases of the starting material with the bulk composition of MgSiO_3 : MnSiO_3 : CaSiO_3 = 1:2:1.

Chemical composition in atoms per formula unit				
Number of oxygen atoms are fixed as 12.				
	1	2	3	Ave
Mg	0.95	1.05	1.02	1.00(3)
Ca	0.96	1.03	0.90	0.97(4)
Mn	2.08	1.93	2.09	2.04(5)
Si	4.00	4.02	4.02	4.01(1)

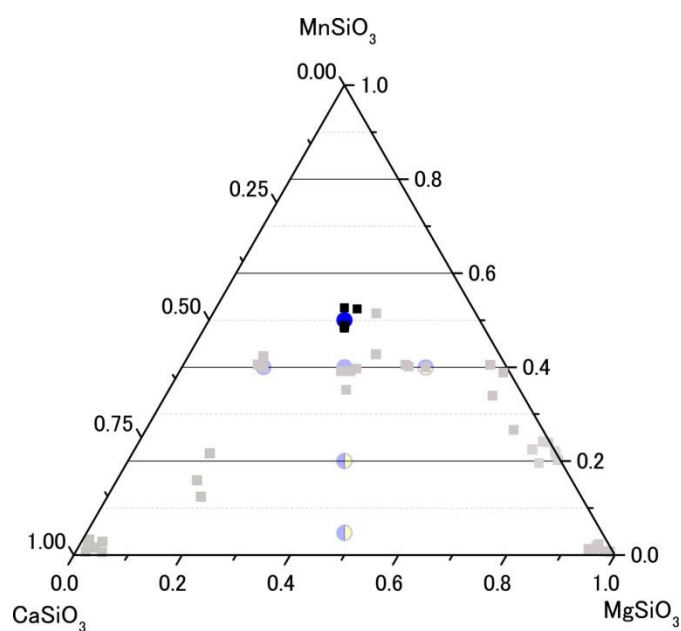


Figure 5-11. Plots of chemical compositions (mol%) of product phases in Table ## in the system of $\text{MgSiO}_3\text{-MnSiO}_3\text{-CaSiO}_3$. A shaded circle represents the composition of the starting materials. Closed squares indicate composition of product phases.

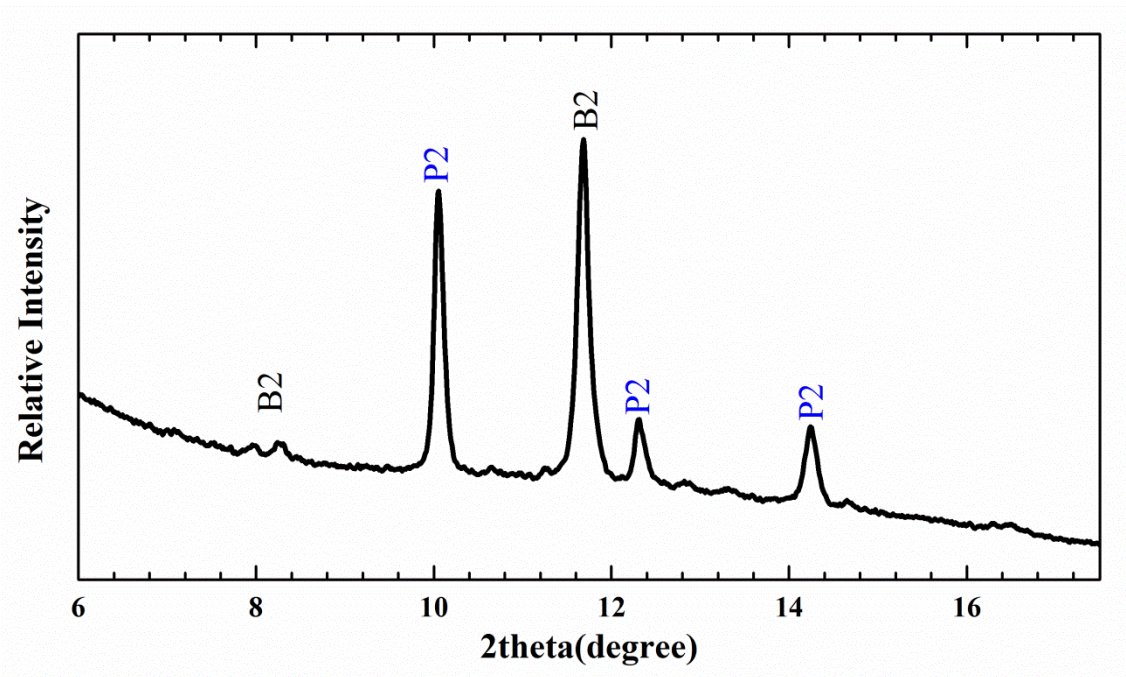


Figure 5-12. X-ray diffraction pattern of $\text{MgSiO}_3\text{:MnSiO}_3\text{:CaSiO}_3 = 1\text{:}3\text{:}1$ perovskites at 50 GPa at room temperature. Peaks labeled B2 represent peaks from B2 phase of NaCl. Trace amount of P1 perovskite peaks can be observed at around $2\Theta = 13^\circ$. P2 = cubic perovskite.

Table 5-7. Chemical compositions of product phases of the starting material with the bulk composition of MgSiO_3 : MnSiO_3 : $\text{CaSiO}_3 = 1:3:1$.

Chemical composition in atoms per formula unit						
Number of oxygen atoms are fixed as 12.						
	1	2	3	4	5	Ave
Mg	0.96	1.11	1.63	0.85	1.03	1.12(14)
Ca	0.75	0.91	0.79	0.91	0.76	0.82(4)
Mn	2.25	2.13	1.74	2.27	2.11	2.10(10)
Si	4.03	4.16	4.04	3.97	4.10	4.06(3)

	1
Mg	0.62
Ca	0.71
Mn	2.75
Si	3.92

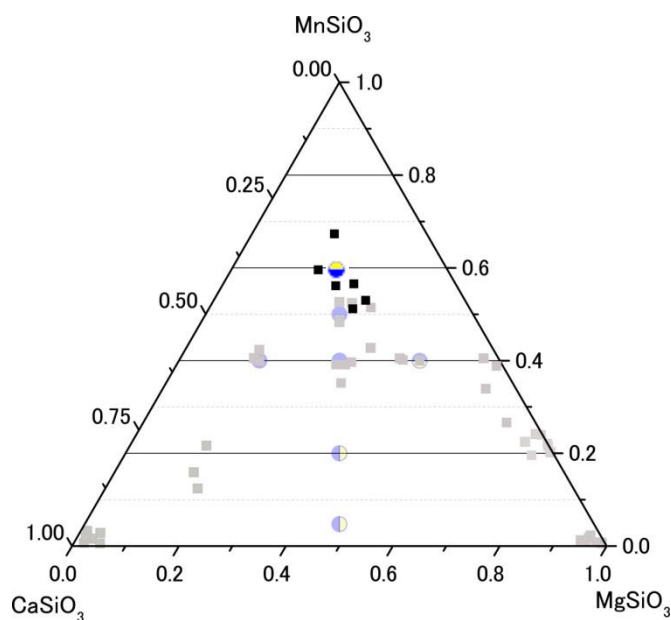


Figure 5-13. Plots of chemical compositions (mol%) of product phases in Table 5-7 in the system of MgSiO_3 - MnSiO_3 - CaSiO_3 . A half shaded circle represents the composition of the starting materials. Closed squares indicate composition of product phases.

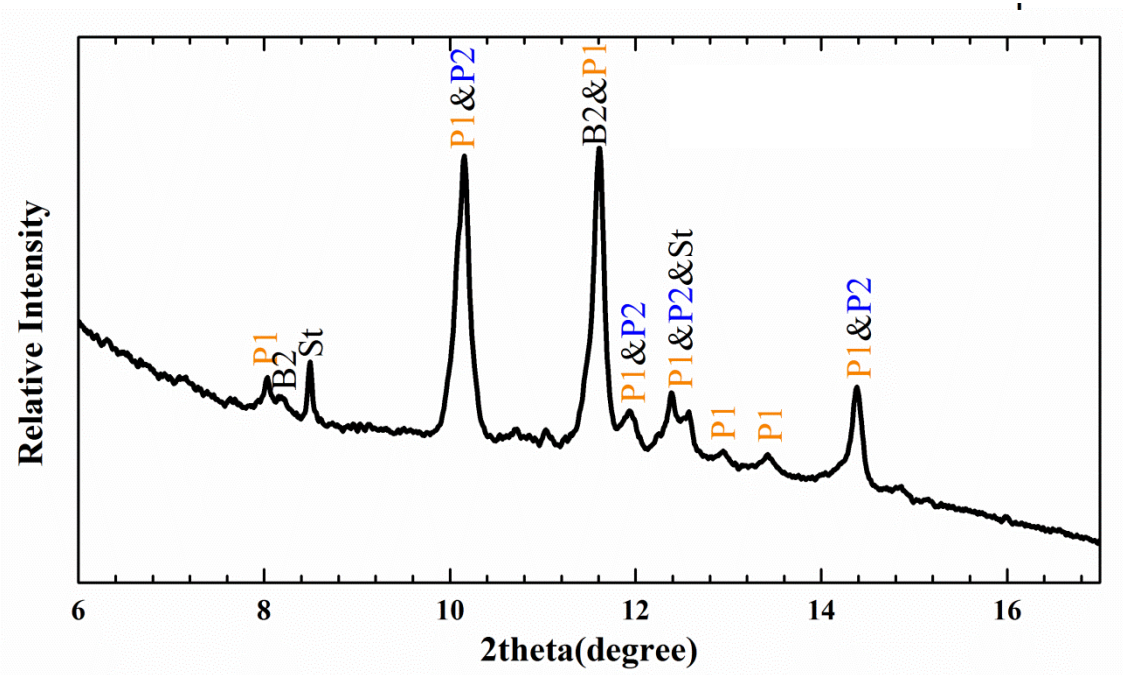


Figure 5-14. X-ray diffraction pattern of $\text{MgSiO}_3\text{:MnSiO}_3\text{:CaSiO}_3 = 15\text{:}70\text{:}15$ perovskites at 45 GPa at room temperature. Peaks labeled B2, St represent peaks from B2 phase of NaCl and Stisovite. P1 = orthorhombic perovskite; P2 = cubic perovskite.

Table 5-8. Chemical compositions of product phases of the starting material with the bulk composition of MgSiO_3 : MnSiO_3 : $\text{CaSiO}_3 = 15:70:15$.

Chemical composition in atoms per formula unit						
Number of oxygen atoms are fixed as 12.						
	1	2	3	4	5	Ave
Mg	0.97	0.64	1.02	0.95	0.87	0.89(7)
Ca	0.76	0.97	0.86	0.80	0.83	0.84(4)
Mn	2.27	2.39	2.09	2.27	2.30	2.26(5)
Si	4.20	4.00	4.00	3.95	3.90	4.01(5)

	1	2	Ave
Mg	0.41	0.61	0.51(10)
Ca	0.58	0.26	0.42(16)
Mn	3.01	3.13	3.07(6)
Si	4.00	4.00	4.00(0)

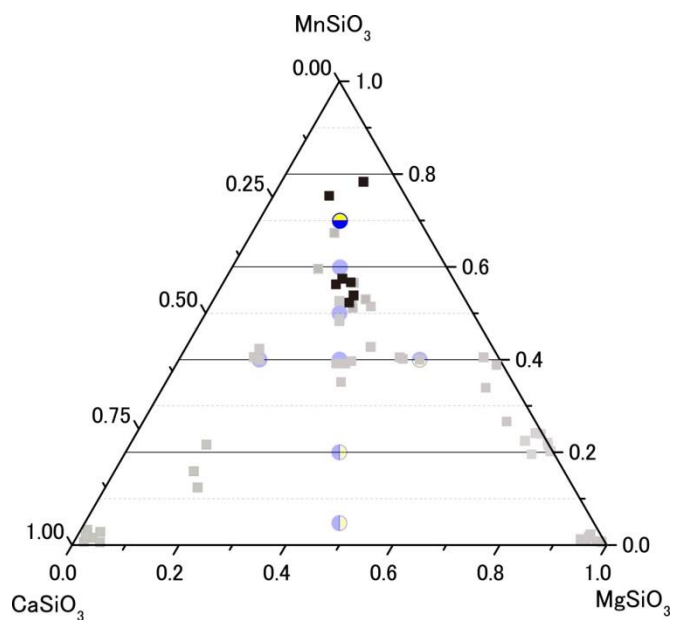


Figure5-15. Plots of chemical compositions (mol%) of product phases in Table 5-8 in the system of MgSiO_3 - MnSiO_3 - CaSiO_3 . A half shaded circle represents the composition of the starting materials. Closed squares indicate composition of product phases.

Perovskite phase relations in the system of MgSiO_3 - MnSiO_3 - CaSiO_3

All the data obtained in this study, as described above, can be put together in the ternary diagram of Figure 5-16. It is confirmed that the addition of MnSiO_3 strongly affects the mutual solubility between MgSiO_3 and CaSiO_3 . There are two perovskite solid solution regions with an immiscibility gap between them in the ternary system. The crystal structure of the Ca-bearing $(\text{Mg,Mn})\text{SiO}_3$ perovskite is orthorhombic, whereas that of the Mg-bearing $(\text{Ca,Mn})\text{SiO}_3$ perovskite is cubic. The compositional range of the Mg-bearing $(\text{Ca,Mn})\text{SiO}_3$ perovskite in the ternary system expands dramatically to the Mg-rich side with increasing MnSiO_3 component.

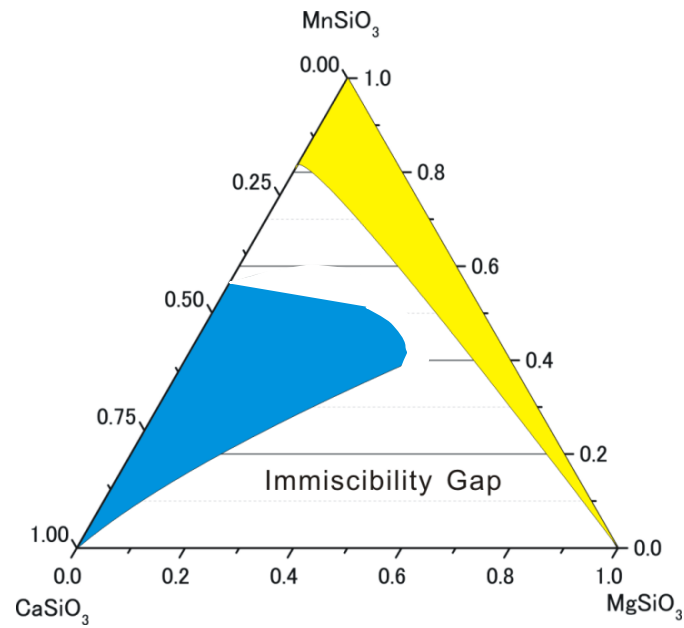


Figure 5-16. Model of MgSiO_3 - MnSiO_3 - CaSiO_3 silicate perovskite phase relations under 40~60 GPa. The blue region means cubic perovskite phase domain. The yellow region means orthorhombic perovskite phase domain.

5-4. Discussion

From the present study, it was confirmed that the addition of MnSiO_3 component to the MgSiO_3 - CaSiO_3 perovskite system strongly affects the mutual solubility between MgSiO_3 and CaSiO_3 as shown in Figure 5-16. This evidence is surprising because it has been generally considered that the solid solution of MgSiO_3 - CaSiO_3 perovskite is extremely limited (e.g., Kesseon et al., 1995; Jung and Schmidt, 2011).

As mentioned in chapter 3, variations of the axial ratios of a/b and $\sqrt{2}a/c$ for the orthorhombic perovskites on the MgSiO_3 - MnSiO_3 join at a high pressure, as shown in Figure 3-4, indicate that the orthorhombic distortion in $(\text{Mg,Mn})\text{SiO}_3$ perovskite solid solutions decreases with increasing MnSiO_3 component. On the other hand, as mentioned in chapter 4, quite wide range of solid solution was confirmed at high pressure for perovskite phase relations on the CaSiO_3 - MnSiO_3 join. And as shown in Figure 4-5, it was found that there is an immiscibility gap in a compositional range from $(\text{Ca}_{0.45},\text{Mn}_{0.55})\text{SiO}_3$ to $(\text{Ca}_{0.2},\text{Mn}_{0.8})\text{SiO}_3$, unlike the case of the MgSiO_3 - MnSiO_3 join. Furthermore, it was suggested that $(\text{Ca,Mn})\text{SiO}_3$ perovskite on the CaSiO_3 side of the immiscibility gap is cubic, but on the other hand $(\text{Ca,Mn})\text{SiO}_3$ perovskite on the MnSiO_3 side is orthorhombic.

I can summarize those evidences schematically as shown in Figure 5-17. From this schematic diagram, the formation of Ca,Mn -bearing MgSiO_3 perovskite could be explained as follows. It is apparent that the degree of the structural distortion from the ideal cubic is far different between pure MgSiO_3 and pure CaSiO_3 , because pure MgSiO_3 is orthorhombic perovskite, but pure CaSiO_3 is cubic. Thus, it is hard to imagine the formation of a wide range of solid solution between $(\text{Mg,Mn})\text{SiO}_3$ and $(\text{Ca,Mn})\text{SiO}_3$ perovskite in MnSiO_3 -poor region and indeed, there is a wide range of immiscibility gap. However, it is expected that the degree of the structural distortion of $(\text{Mg,Mn})\text{SiO}_3$ perovskite approaches to that of $(\text{Ca,Mn})\text{SiO}_3$ perovskite with increasing MnSiO_3 component, because the crystal structures of $(\text{Mg,Mn})\text{SiO}_3$ and $(\text{Ca,Mn})\text{SiO}_3$

perovskite are less distorted orthorhombic near pure MnSiO_3 perovskite, as mentioned in chapter 3 and 4.

The compositional range of Mg-bearing $(\text{Ca,Mn})\text{SiO}_3$ perovskite in the ternary system expands dramatically to the Mg-rich side by adding MnSiO_3 component. On the other hand, although the compositional range of Ca-bearing $(\text{Mg,Mn})\text{SiO}_3$ perovskite expands gradually to the Ca-rich side by adding MnSiO_3 component. These evidences are greatly interesting, however, further investigation is needed to reveal the reason of the tolerance of $(\text{Ca,Mn})\text{SiO}_3$ perovskite for substitution of Mg^{2+} .

An implication of the phase relations at higher pressure

As mentioned in chapter 3, it is suggested that the compression behavior of $(\text{Mg,Mn})\text{SiO}_3$ perovskite monotonically changes from pure MgSiO_3 to pure MnSiO_3 composition. The orthorhombic distortion in $(\text{Mg,Mn})\text{SiO}_3$ perovskite near MgSiO_3 end member increases with pressure (Ballaran et al., 2012) and that in $(\text{Mg}_{0.5},\text{Mn}_{0.5})\text{SiO}_3$ perovskite show no significant difference with pressure (this study) and then that in $(\text{Mg,Mn})\text{SiO}_3$ perovskite near MgSiO_3 end member decreases with pressure (Fujino et al., 2008). From these compression behaviors of $(\text{Mg,Mn})\text{SiO}_3$ perovskite, Figure 5-17 might be modified as shown in Figure 5-18, which shows a speculation about the perovskite phase relations in the ternary system at higher pressure. This suggests that the degree of the structural distortion of Mn-rich $(\text{Ca,Mn})\text{SiO}_3$ perovskite and Mn-rich $(\text{Mg,Mn})\text{SiO}_3$ perovskite could become more close each other at higher pressure and that could expand the range of solid solution to more Mn-poor area. And in an extreme case, the immiscibility gap may close in relatively Mn-rich area (Fig. 5-19). However, the immiscibility gap in Mn-poor area will not close, because the orthorhombic distortion in $(\text{Mg,Mn})\text{SiO}_3$ perovskite near MgSiO_3 end member increases with pressure (Ballaran et al., 2012; this study) and the structural difference to $(\text{Ca,Mn})\text{SiO}_3$ perovskite will increase at higher pressure.

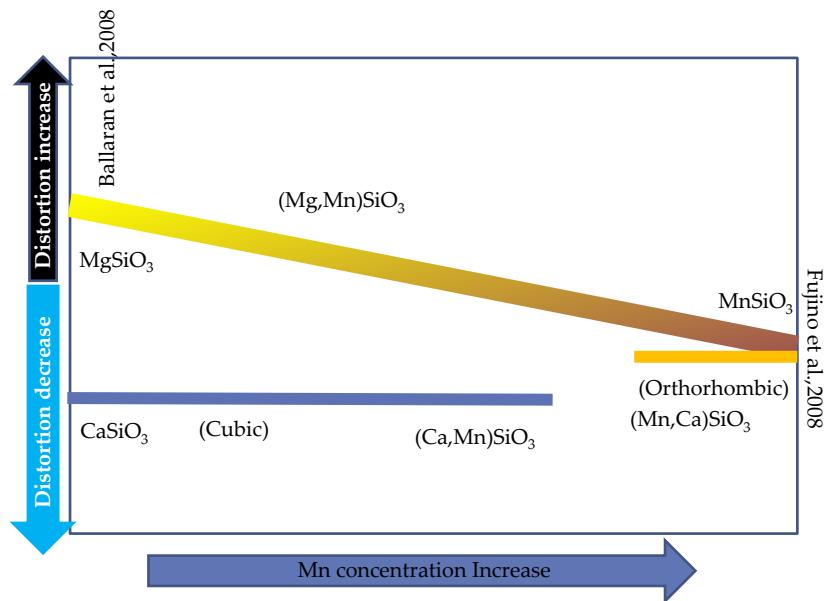


Figure 5-17. Model of distortion relationship in the MgSiO_3 - MnSiO_3 - CaSiO_3 perovskite at about 40 GPa. On vertical axis, the plus direction means perovskite distortion increases and the opposite direction means the distortion decreases. The horizontal axis is the Mn concentration. Plus direction means increases of the Mn concentration.

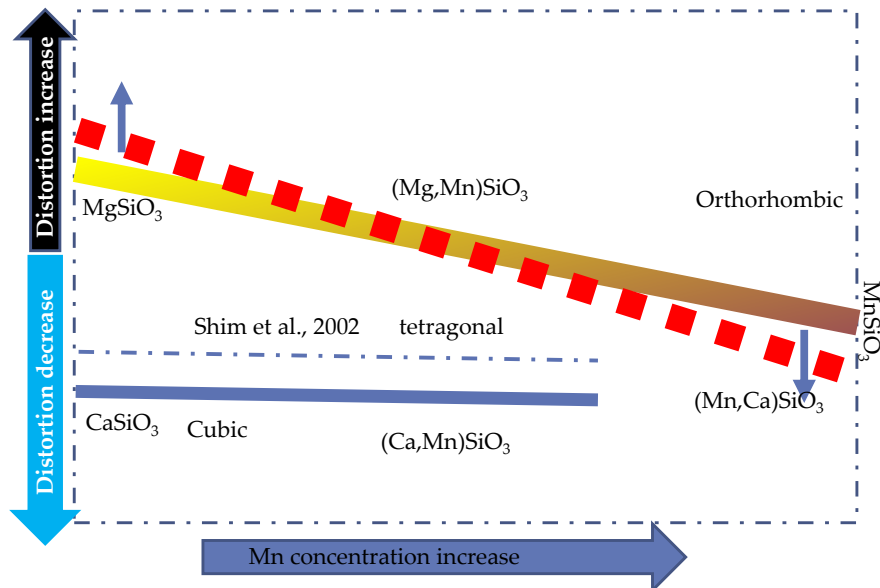


Figure 5-18. Model of distortion relationship in the MgSiO_3 - MnSiO_3 - CaSiO_3 perovskite at about 40 GPa and higher pressure. The dash line represents the distortion with higher pressure on MgSiO_3 - MnSiO_3 join.

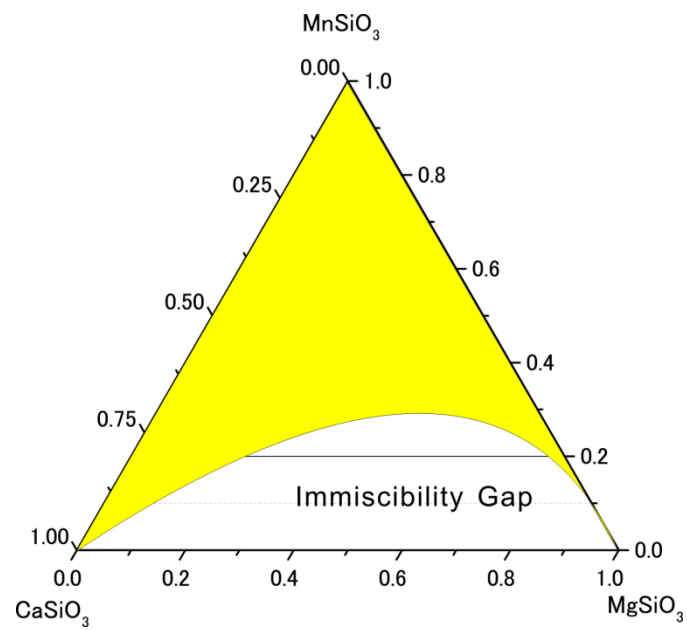


Figure 5-19. Model of MgSiO_3 - MnSiO_3 - CaSiO_3 silicate perovskite phase relations under much higher pressure.

5-4. Summary

Formation of very wide range of solid solutions are confirmed in the system of MgSiO_3 - CaSiO_3 - MnSiO_3 under 40~60GPa. It is suggested that the immiscibility gap possibly decreases with increasing pressure on the MnSiO_3 rich side from the crystal chemical consideration. On the other hand, it is hard to expect that the gap becomes narrower on the MnSiO_3 poor side.

6. Conclusions

Perovskite phase relations between MgSiO_3 and MnSiO_3

Formation of complete perovskite solid solution is confirmed between MgSiO_3 and MnSiO_3 . Diffraction peaks from perovskites in this solid solution can be indexed as orthorhombic.

Perovskite phase relations between CaSiO_3 and MnSiO_3

Mn^{2+} can substitute Ca in CaSiO_3 perovskite and quite wide range of solid solution is formed on the CaSiO_3 - MnSiO_3 join. The solubility of mutual Ca and Mn components on the CaSiO_3 - MnSiO_3 join are about 55 mol% and 20mol%, respectively. (Ca, Mn) SiO_3 perovskites on the CaSiO_3 side is cubic and that on the MnSiO_3 side is orthorhombic.

Perovskite phase relations in the system of MgSiO_3 - MnSiO_3 - CaSiO_3

It is confirmed that the addition of MnSiO_3 strongly affects the mutual solubility between MgSiO_3 and CaSiO_3 . There are two perovskite regions with an immiscibility gap between them in the ternary system. Crystal structure of Ca-bearing (Mg,Mn) SiO_3 perovskite is orthorhombic, and that of Mg-bearing (Ca,Mn) SiO_3 perovskite is cubic. The compositional range of Mg-bearing (Ca,Mn) SiO_3 perovskite in the ternary system expands dramatically to the Mg-rich side with increasing MnSiO_3 component.

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