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Stability of the perovskite structure and possibility of the transition to the post-perovskite structure in $CaSiO_3$, $FeSiO_3$, $MnSiO_3$ and $CoSiO_3$

Kiyoshi Fujino[a,b,*], Daisuke Nishio-Hamane[a,c], Keisuke Suzuki[a], Hiroyuki Izumi[a], Yusuke Seto[a,d], Takaya Nagai[a]

[a] *Department of Natural History Sciences, Hokkaido University, Sapporo 060-0810, Japan*
[b] *Geodynamics Research Center, Ehime University, Matsuyama 790-8577, Japan*
[c] *Institute for Solid State Physics, The University of Tokyo, Kashiwa 277-8581, Japan*
[d] *Department of Earth and Planetary Sciences, Kobe University, Kobe 657-8501, Japan*

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A B S T R A C T

High pressure and high temperature experiments on $CaSiO_3$, $FeSiO_3$, $MnSiO_3$ and $CoSiO_3$ using a laser-heated diamond anvil cell combined with synchrotron X-ray diffraction were conducted to explore the perovskite structure of these compounds and the transition to the post-perovskite structure. The experimental results revealed that $MnSiO_3$ has a perovskite structure from relatively low pressure (ca. 20 GPa) similarly to $CaSiO_3$, while the stable forms of $FeSiO_3$ and $CoSiO_3$ are mixtures of mono-oxide (NaCl structure) + high pressure polymorph of SiO_2 even at very high pressure and temperature (149 GPa and 1800 K for $FeSiO_3$ and 79 GPa and 2000 K for $CoSiO_3$). This strongly suggests that the crystal field stabilization energy (CFSE) of Fe^{2+} with six 3d electrons and Co^{2+} with seven 3d electrons at the octahedral site of mono-oxides favors a mixture of mono-oxide + SiO_2 over perovskite where Fe^{2+} and Co^{2+} would occupy the distorted dodecahedral sites having a smaller CFSE (Mn^{2+} has five 3d electrons and has no CFSE). The structural characteristics that the orthorhombic distortion of $MnSiO_3$ perovskite decreases with pressure and the tolerance factor of $CaSiO_3$ perovskite (0.99) is far from the orthorhombic range suggest that both $MnSiO_3$ and $CaSiO_3$ perovskites will not transform to the $CaIrO_3$-type post-perovskite structure even at the Earth's core–mantle boundary conditions, although $CaSiO_3$ perovskite has a potentiality to transform to the $CaIrO_3$-type post-perovskite structure at still higher pressure as long as another type of transformation does not occur.

1. Introduction

In the series of silicate compounds, $MgSiO_3$, $CoSiO_3$, $FeSiO_3$, $MnSiO_3$ and $CaSiO_3$, it had been known that only $MgSiO_3$ and $CaSiO_3$ have a perovskite structure at high pressure and high temperature, and very recently, $MnSiO_3$ was also found to have a perovskite structure (Fujino et al., 2008). However, there has been no report that $CoSiO_3$ and $FeSiO_3$ compounds have a perovskite structure at high pressure, although the tolerance factors of these compounds (0.904 for $CoSiO_3$ and 0.912 for $FeSiO_3$) are between those of $MgSiO_3$ (0.900) and $CaSiO_3$ (0.990), where the tolerance factor $t=(r_A+r_O)/\left(\sqrt{2}\,(r_B+r_O)\right)$ and r_A, r_B and r_O are the ionic radii of eightfold A cation, sixfold B cation and oxygen, respectively, in ABO_3 compounds (Goldschmidt, 1926) (here the ionic radii were taken from Shannon, 1976).

The stable form of $FeSiO_3$ at ambient pressure, Fe_2SiO_4 (olivine) + SiO_2 (quartz), transforms to $FeSiO_3$ (orthopyroxene) and to $FeSiO_3$ (clinopyroxene) with increasing pressure (Akimoto et al., 1965). $FeSiO_3$ (clinopyroxene) decomposes into Fe_2SiO_4 (γ-spinel) + SiO_2 (stishovite) at 9 GPa and 1200 K (Akimoto, 1970), and it further transforms to FeO with a rock salt structure (B1 structure) + SiO_2 (stishovite) at 20 GPa and 1800 K (Ming and Bassett, 1975). However, the further phase transformation of $FeSiO_3$ at still higher pressure has not been reported except for the rhombohedral distortion of FeO and the polymorphic phase transition of SiO_2.

$CoSiO_3$ does not exist as a stable single compound at ambient pressure. The stable assemblage of Co_2SiO_4 (olivine) + SiO_2 (quartz) at ambient pressure transforms to $CoSiO_3$ (orthopyroxene) and to $CoSiO_3$ (clinopyroxene) with increasing pressure (Akimoto et al., 1965). It decomposes into Co_2SiO_4 (γ-spinel) + SiO_2 (stishovite) at 10 GPa and 1273 K (Ringwood, 1970), and further decomposes into CoO (B1) + SiO_2 (stishovite) at 17 GPa and 2000 K (Ito, 1975). So far, the phase transformation at still higher pressure has not been reported.

Meanwhile, $MnSiO_3$ has many high pressure polymorphs at pressures up to around 20 GPa, starting from rhodonite to

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[*] Corresponding author at: Geodynamics Research Center, Ehime University, 2-5 Bunkyo-cho, Matsuyama 790-8577, Japan. Tel.: +81 89 927 8150; fax: +81 89 927 8167.
E-mail address: fujino@sci.ehime-u.ac.jp (K. Fujino).

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pyroxmangite, to clinopyroxene, and to tetragonal garnet (Akimoto and Syono, 1972; Fujino et al., 1986). Regarding the stable form of $MnSiO_3$ at higher pressures, Liu (1976) reported that $MnSiO_3$ garnet decomposes into MnO (B1) + SiO_2 (stishovite) at 26 GPa and from 1673 to 2073 K, and Ito and Matsui (1977) also reported the stable assemblage of the same oxide mixture at 22 GPa and 1273 K. However, our recent study showed that $MnSiO_3$ has also a perovskite structure similar to $MgSiO_3$ and $CaSiO_3$, at the lower temperature side of MnO (B1) + SiO_2 (stishovite) (Fujino et al., 2008).

If $FeSiO_3$ and $CoSiO_3$ do not have a perovskite structure even at higher pressure, then, the other factor than the tolerance factor would control the stability of the perovskite structure of $FeSiO_3$ and $CoSiO_3$. One of the possible candidates will be the crystal field stabilization energy (CFSE) of Fe^{2+} and Co^{2+} with unfilled 3d electrons (six 3d electrons for Fe^{2+} and seven 3d electrons for Co^{2+}), because Mn^{2+} has five 3d electrons and has no CFSE. CFSE of the octahedral site of mono-oxides is large compared to that of the dodecahedral site of perovskites (Burns, 1993), and would favor a mixture of mono-oxide + SiO_2 over a perovskite structure.

Another interesting point in the above series of silicate compounds is that $MgSiO_3$ perovskite further transforms to the $CaIrO_3$-type post-perovskite structure at around 125 GPa and 2500 K (Murakami et al., 2004; Oganov and Ono, 2004), while there has been no report of the phase transition of the other silicate perovskites to the $CaIrO_3$-type post-perovskite structure at very high pressure. Then, what factors control the phase transition of the perovskite structure to the $CaIrO_3$-type post-perovskite structure? Are there any other silicate perovskites that transform to the $CaIrO_3$-type post-perovskite structure?

To clarify the above problems, we have examined the high pressure phase relations of $CaSiO_3$, $FeSiO_3$, $MnSiO_3$ and $CoSiO_3$ using a laser-heated diamond anvil cell combined with synchrotron X-ray diffraction. Here, the focus is laid on what factors control the stability of perovskite structure and the phase transition to the $CaIrO_3$-type post-perovskite structure in $CaSiO_3$, $MnSiO_3$, $FeSiO_3$ and $CoSiO_3$.

2. Experimental

2.1. Laser-heated diamond anvil cell experiments

The high pressure and high temperature experiments to synthesize the high pressure forms of respective compounds were carried out using an YLF or YAG laser-heated diamond anvil cell (LHDAC). The synthesis conditions were 30–149 GPa and 1600–2100 K for $CaSiO_3$–$FeSiO_3$, 15–85 GPa and 1200–2600 K for $MnSiO_3$ and 50, 79 GPa and 2000 K for Co_2SiO_4. The starting materials for the LHDAC experiments were gel (+crystal) for $CaSiO_3$–$FeSiO_3$, synthetic $MnSiO_3$ rhodonite for $MnSiO_3$, and synthetic Co_2SiO_4 olivine for $CoSiO_3$. The reason why Co_2SiO_4 olivine was used as a starting material for $CoSiO_3$ is because the $CoSiO_3$ compound is not stable as a single phase at ambient pressure. A small amount of Au or Pt was added to some samples to determine pressure in high pressure and high temperature X-ray diffraction experiments by the equation of state (Anderson et al., 1989 for Au and Holmes et al., 1989 for Pt). Diamond anvils with a 300 or 200 μm culet were used for pressures less than 100 GPa, while beveled diamonds with an inner culet of 150 μm and an outer culet of 450 μm were used for pressures higher than 100 GPa. The samples were loaded into the hole of 50–100 μm diameter in a Re gasket (the original thickness was 0.25 mm) and sandwiched by NaCl pellets in a DAC. Samples in a DAC were heated from both sides with an YLF or YAG laser. Temperature was measured by the spectroradiometric method (Watanuki et al., 2001). Pressure at room temperature was measured by the ruby fluorescence technique (Mao et al., 1986), by the Raman spectral shift of diamond (Akahama and Kawamura, 2005) or by the equation of state of NaCl (Sata et al., 2002). Further details for $MnSiO_3$ are described in Fujino et al. (2008), and those for $CaSiO_3$–$FeSiO_3$ will be described elsewhere (Fujino et al., in preparation).

2.2. Synchrotron X-ray diffraction experiments

Angle-dispersive X-ray diffraction experiments of $CaSiO_3$–$FeSiO_3$, $MnSiO_3$ and Co_2SiO_4 at room temperature were performed at BL-13A (wave length of 0.42–0.43 Å) and BL-18C (wave length of ~0.61 Å) of Photon Factory, KEK, and those at high pressure and high temperature were carried out at BL-10XU (wave length of 0.41–0.42 Å) of SPring-8 of the Japan Synchrotron Radiation Research Institute. Monochromatic X-ray incident beams were collimated to 15–20 μm (BL-13A and BL-18C), and to 20–30 μm (BL-10XU). Diffraction patterns were recorded on an imaging plate (3000 × 3000 pixels for BL-13A and BL-10XU and 2000 × 2500 pixels for BL-18C with a pixel size of 100 μm × 100 μm) at all the beam lines. The exposure times were 10–60 min at BL-13A, 30–120 min at BL-18C and ~5 min at BL-10XU. Two-dimensional X-ray diffraction images on the imaging plates were integrated as a function of 2θ in order to obtain the conventional one-dimensional diffraction profiles and analyzed using the software PIP (Fujisawa and Aoki, 1998) or IPA and PDI (Y. Seto, available from http://www2.kobe-u.ac.jp/~seto/). The typical diffraction patterns obtained for the compounds $FeSiO_3$, $CaFeSi_2O_6$, $MnSiO_3$ and Co_2SiO_4 at high pressure and high temperature or high pressure and room temperature quenched from high temperature are presented in Fig. 1.

3. High pressure phase relations

3.1. $CaSiO_3$ and $FeSiO_3$

In the system $CaSiO_3$–$FeSiO_3$ at 30–149 GPa and 1600–2100 K (Fujino et al., in preparation), the stable assemblage of the end member $FeSiO_3$ was a mixture of FeO (B1 structure) + high pressure polymorph of SiO_2 (stishovite, $CaCl_2$-type or α-PbO_2-type with increasing pressure) up to 117 GPa and 2100 K (Fig. 1(a)). Further, the stable assemblage of the intermediate composition $CaFeSi_2O_6$ was a mixture of Fe-bearing $CaSiO_3$ perovskite + FeO (B1 structure) + high-pressure polymorph of SiO_2 (stishovite, $CaCl_2$-type or α-PbO_2-type with increasing pressure) up to 149 GPa and 1800 K (Fig. 1(b)). These results indicate that $CaSiO_3$ has a perovskite structure up to 149 GPa and it does not transform to the post-perovskite structure even at this pressure, while the high pressure form of $FeSiO_3$ is a mixture of FeO (B1) + high pressure polymorph of SiO_2 and $FeSiO_3$ perovskite does not become stable up to 149 GPa. All the Fe-bearing $CaSiO_3$ perovskite phases showed cubic symmetry (space group *Pm*3*m*) at high pressure and high temperature, but showed tetragonal symmetry (exact space group could not be determined) at high pressure and room temperature. The c/a ratio (<1) of the refined cell parameters of present Fe-bearing $CaSiO_3$ perovskite at high pressure and room temperature decreases with pressure (Fujino et al., in preparation) in the same way as pure $CaSiO_3$ perovskite (Ono et al., 2004). These results indicate that the tetragonal distortion of $CaSiO_3$ perovskite increases with pressure.

3.2. $MnSiO_3$

Our recent X-ray diffraction experiments at high pressure and high temperature up to 85 GPa and 2600 K (Fujino et al., 2008) revealed that at the higher temperature region $MnSiO_3$ garnet decomposes into an assemblage of MnO (B1) + SiO_2 (stishovite), while at the lower temperature region $MnSiO_3$ garnet directly