

Single-crystal structure analyses of $(\text{Ca}_{1-x}\text{Sr}_x)\text{TiO}_3$ perovskite solid solution under high pressure

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CaSiO_3 perovskite has been interested as Ca reservoir of the lower mantle. The detailed structure has not been studied because of the non-quenchable ion radius ratios of A and B cations are very similar between $(\text{Mg}_{1-x}\text{Fe}_x)\text{SiO}_3$ perovskite solid solution and $(\text{Ca}_{1-x}\text{Sr}_x)\text{TiO}_3$. The solid solutions change their structure from orthorhombic CaTiO_3 to cubic SrTiO_3 . The structure changes with the cation ratio (x) were investigated by single-crystal structure analyses. Diffraction intensity measurements of CaTiO_3 ($x=0.0$) and $(\text{Ca}_{0.4}\text{Sr}_{0.6})\text{TiO}_3$ ($x=0.6$) under high pressure were also carried out using single crystals through synchrotron radiation at SPring-8. The variation of site volume, bulk volume and t with pressure were also clarified in the present high-pressure diffraction study.

Introduction

Since it was discussed the silicate perovskites are dominant silicate phases in mineral assemblages of the Earth's lower mantle, many X-ray diffraction studies on $(\text{Mg,Fe})\text{SiO}_3$ perovskite have been reported because of one of the most abundant minerals in the lower mantle. Calcium plays an important role for the phase relations and elasticity of the lower mantle. The detailed structure of CaSiO_3 has not been studied because of the non-quenchable phase.

No phase transition was found from single crystal diffraction study up to 10GPa at room temperature (Ross and Angle, 1999) but it is assumed that orthorhombic CaGeO_3 possibly transforms into higher symmetry form.

Ion radius ratios of A and B cations and tolerance factors are very similar between $(\text{Mg}_{1-x}\text{Fe}_x)\text{SiO}_3$ perovskite solid solution and $(\text{Ca}_{1-x}\text{Sr}_x)\text{TiO}_3$.

It has been known that SrTiO_3 has a cubic perovskite structure. Hence the solid solutions of $(\text{Ca}_{1-x}\text{Sr}_x)\text{TiO}_3$ change their structure from orthorhombic to cubic. In the present experiment, structure variation with the cation ratio (x) at the A site and high-pressure structure change were investigated by single-crystal structure analyses.

Experiment

X-ray diffraction study

Single crystals of the solid solutions of $(\text{Ca}_{1-x}\text{Sr}_x)\text{TiO}_3$ ($x=0.0, 0.2, 0.5, 0.6$ and 1.0) were synthesized for X-ray structure analyses. Intensity measurements were made by a four-circle diffractometer using MoK α radiation ($\lambda=0.71069\text{nm}$) emitted from a rotating anode X-ray generator with 50kV and 180mA. The incident beam was monochromated by pyrolytic graphite. Reflections with $F(hkl) > 3\sigma F(hkl)$ were used for the refinement. The diffraction intensities were corrected for X-ray absorption, Lorentz and polarization factors. The full matrix least-squares refinement has been carried out.

High-pressure diffraction study

Diffraction intensity measurements under high pressure were also carried out by using single crystals. Present structure analyses of CaTiO_3 ($x=0.0$) and $(\text{Ca}_{0.4}\text{Sr}_{0.6})\text{TiO}_3$ ($x=0.6$) were carried out at 2.5GPa and 4.1GPa and at 3.5GPa and 6GPa using synchrotron radiation at SPring-8. Using DAC the single cube crystal of 20micron was placed in the gasket hole of 200micron in diameter. Pressure measurement was made by the ruby fluorescence system. Diffraction intensity data were collected by the ϕ -fixed mode and ω -scan mode, scan speed of 1deg/min, scan width of 2deg in ω , step interval of 0.01deg/step.

Result

Structure refinements of $(\text{Ca}_{1-x}\text{Sr}_x)\text{TiO}_3$ solid solutions by full-matrix least-squares method provide reliable parameters R factor within $R=0.03$. $(\text{Ca}_{0.4}\text{Sr}_{0.6})\text{TiO}_3$ ($x=0.6$) is very close to cubic symmetry. In $x > 0.6$, tetragonal phase is possible. Tilting angle of octahedron becomes smaller with increasing Sr in A site. But the site volume is gradually increased.

The tolerance factor, $t = (A-X)/\sqrt{2(B-X)}$, becomes unit with increasing X, and finally SrTiO_3 is an ideal cubic perovskite. $\text{Ca}(\text{Ti}_{1-x}\text{Si}_x)\text{O}_3$ shows the cation-ordered arrangement in the B site (Leinenweber et al., 1997). However, we did not find any evidence the cation ordering Ca and Sr in the A site of $(\text{Ca}_{1-x}\text{Sr}_x)\text{TiO}_3$. Neither superstructure nor diffuse spot was found in the diffraction patterns.

Structure analyses of CaTiO_3 ($x=0.0$) and $(\text{Ca}_{0.6}\text{Sr}_{0.4})\text{TiO}_3$ ($x=0.6$) under pressure show a tendency towards orthorhombic symmetry resulted from anisotropic compression of Ti-O bonds. B-site volume is less compressible than that of A-site. The variation of site volume, bulk volume and t with pressure were also clarified in the present high-pressure diffraction study.