**Structure change of Ca$_{1-x}$Sr$_x$TiO$_3$ perovskite with composition and pressure**

TAKAMITSU YAMANAKA,* NORIYUKI HIRAI, AND YUTAKA KOMATSU

Department of Earth and Space Science, Graduate School of Science, Osaka University, 1-1, Machikaneyama Toyonaka Osaka, 560-0043 Japan

**ABSTRACT**

Structure refinements of solid solutions of (Ca$_{1-x}$Sr$_x$)TiO$_3$ ($x = 0.0, 0.25, 0.5, 0.6, 0.65$, and $1.0$) were undertaken using single crystals at ambient conditions. Their lattice constants, $c/a$ axial ratios, and cell volumes indicate continuous changes from orthorhombic to cubic through a tetragonal phase. The orthorhombic structure is continuous between $x = 0.0$ and $x = 0.6$, and a phase at $x = 0.65$ shows a tetragonal structure with space group $I4/mcm$. With increasing Sr substitution, the symmetry changes to cubic with $Pm3m$ space group. A-O and B-O distances in ABO$_3$ perovskite were determined as a function of the composition of the A cation (Ca and Sr). Tilting and rotation angles of the TiO$_6$ octahedral linkage with $x$ of (Ca$_{1-x}$Sr$_x$)TiO$_3$ were also evaluated. Single-crystal structure refinements of Ca$_{0.35}$Sr$_{0.65}$TiO$_3$ perovskite at 3.5, 4.1, and 7.0 GPa at 300 K were carried out using a diamond anvil cell. The tetragonal phase transforms to an orthorhombic structure with space group $Pbnm$ at 3.5 GPa. The polymorphic transition of $\text{VII}^{\text{III}}\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{O}_3$ perovskites under compression is discussed.

**INTRODUCTION**

The silicate perovskites are dominant silicate phases in mineral assemblages of the Earth’s lower mantle. Numerous high-pressure experiments using diamond anvil cells or multianvil equipment have been carried out in order to understand the phase stabilities and isothermal compression of various silicates together with analogous materials such as germanate and titanate perovskites. Many X-ray diffraction studies on magnesium and iron silicate perovskites [MgFeSiO$_3$] have been reported. Calcium silicates also play an important role in phase relations and elasticity of the lower mantle, hence much attention has been paid to calcium-bearing silicate perovskites. The equation of state (EOS) of CaSiO$_3$ perovskite was determined by diamond anvil cell (DAC) experiments with YAG laser heating up to 134 GPa (Mao et al. 1989). The EOS, thermal expansion, and elastic properties of CaSiO$_3$ have also been determined with DAC or multianvil presses (Yagi et al. 1989; Wang et al. 1996; Shim et al. 2000a, 2000b).

The structure of MgSiO$_3$ perovskite has been analyzed using quenched samples (Horiiuchi et al. 1987). However, the detailed structure of CaSiO$_3$ perovskite cannot be studied because the phase is not quenchable to ambient conditions. Consequently, the precise symmetry and details of the structural transition remain undetermined.

The structures of CaTiO$_3$ and CaGeO$_3$, possible analogues of CaSiO$_3$, were studied by Sasaki et al. (1987). Structural changes in CaTiO$_3$ were intensively investigated at elevated temperature under ambient pressure (Redfern 1996; Liu and Liebermann 1993; Kennedy et al. 1999), and a series of thermal transitions [orthorhombic ($Pbnm$) $\rightarrow$ tetragonal ($I4/mcm$) $\rightarrow$ cubic ($Pm3m$)] was proposed with increasing temperature.

Bednorz and Muller (1984) measured the temperature dependence of the dielectric constant in the range $x > 0.88$ for (Ca$_{1-x}$Sr$_x$)TiO$_3$ from 4 to 300 K and found that the dielectric constant decreases rapidly with substitution of Sr$^{2+}$ by Ca$^{2+}$ because of internal lattice distortion. Ranjan et al. (1999) used neutron and X-ray powder diffraction to study (Sr$_{1-x}$Ca$_x$)TiO$_3$ with $x > 0.12$ at high temperatures and found that it was orthorhombic in addition, an intermediate phase between orthorhombic and cubic was found in the range of $0.12 < x < 0.21$. The cubic-tetragonal transition of SrTiO$_3$ was studied using Landau theory by Hayward and Salje (1999) and Salje (1998). Carpenter et al. (2001) performed a strain analysis of the phase transition in (Ca,Sr)TiO$_3$ perovskite.

Xiong et al. (1986) used X-ray powder diffraction to study high-pressure transformations in orthorhombic CaTiO$_3$. They found that orthorhombic CaTiO$_3$ (I) transforms to hexagonal perovskite (II) at about 10 GPa at room temperature and that at 1000 °C the orthorhombic phase first transforms into a tetragonal (II$'$) phase at 8.5 GPa and then to a hexagonal (II$''$) form at 15 GPa under nonhydrostatic conditions. However, Ross and Angel (1999) found no phase transition in their single-crystal diffraction study up to 10 GPa.

Structural discussions of (Ca$_{1-x}$Sr$_x$)TiO$_3$ can be applied to the crystal chemistry of the (Mg$_{1-x}$Fe$_x$)SiO$_3$ perovskite solid solution. It is known that SrTiO$_3$, an end-member of the solid solution, has the cubic perovskite structure at room condition, and that the other end-member (CaTiO$_3$) is orthorhombic. Accordingly, solid solutions of (Ca$_{1-x}$Sr$_x$)TiO$_3$ change symmetry (from orthorhombic to cubic) with increasing $x$. In the present experiment, structure change was a function of the cation ratio ($x$) at the A site and structure change at high-pressure were investigated by single-crystal structure analysis. Cation ordering in the ABO$_3$ perovskite structure was also examined at high pressure. Leinenweber et al. (1997) used electron diffraction

* E-mail: b61400@center.osaka-u.ac.jp