Unquenchable hexagonal perovskite in high-pressure polymorphs of strontium silicates

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ABSTRACT

The presence of hexagonal silicate perovskite (6H-BaTiO3 type) was confirmed in the SrSiO3 compound by in-situ angle dispersive X-ray diffraction at high pressure. The perovskite was crystallized from pressure-induced amorphous SrSiO3 in a diamond anvil cell by laser heating at 35 GPa. On releasing the pressure, the perovskite also changed into an amorphous state as does CaSiO3 perovskite. This SrSiO3 perovskite, with a tolerance factor greater than unity, forms a face-sharing SiO6 octahedron, which leads to a structure with hexagonal symmetry. Incorporation of Sr into CaSiO3 perovskite in the early stage of the differentiation in the Earth’s mantle might have influenced the symmetry of CaSiO3 perovskite in the present lower mantle. As far as we know, this is the first report suggesting the existence of hexagonal perovskite in silicates.

INTRODUCTION

It is known that certain high-pressure minerals exhibit unquenchability at atmospheric pressure, in which the minerals turn into an amorphous state even at room temperature. In the silicate minerals, the CaSiO3 perovskite is known to be a typical unquenchable phase. In-situ X-ray measurements have confirmed it to be the cubic perovskite structure (Pm3m) in the Earth’s lower mantle (Mao et al. 1989; Shim et al. 2000). The symmetry of silicate perovskites is closely correlated with the ionic radii of eightfold-coordinated cations. In the case of Mg2+, which is smaller than Ca2+, the MgSiO3 perovskite takes on an orthorhombic symmetry (Pnma), which is distorted from cubic symmetry (Horiuchi et al. 1987). Until now, silicate perovskites consisting of eightfold-coordinate cations larger than Ca2+ have not been investigated. Sr and Ba, which are related to Mg and Ca in the periodic table, would be candidates to occupy the octahedral or dodecahedral site in silicate perovskite.

In recent experiments on a SrSiO3 composition, using a large volume high-pressure apparatus, we found an amorphous state in the recovered products after exposure to 20 GPa and 1500 °C. Mixed crystalline phases of SrSiO3 (larnite type) + Sr2Si2O5 (BaGe2O5 III type) could be recovered at pressures as low as 13 GPa (Kojitani et al. 2005, in preparation). For the CaSiO3 composition, mixed phases of CaSi2O5 (larnite) + CaSi2O5 (titantite) recombine into the unquenchable perovskite structure at about 12 GPa (Gasparik et al. 1994; Akaogi et al. 2004). In addition, these ambient phases of SrSiO3 (pseudowollastonite type) and CaSiO3 (wollastonite) make a transition to a walstromite type structure at about 3 GPa (Gasparik et al. 1994; Akaogi et al. 2004). The similar phase sequences of SrSiO3 and CaSiO3 under pressure give us a hint at the possibility that the recovered amorphous SrSiO3 could have been a perovskite structure at high pressure. Therefore, to illuminate the structure of the unquenchable phase of SrSiO3, we have conducted an in-situ X-ray diffraction study at high pressure.

EXPERIMENTAL PROCEDURES

The starting sample of pseudowollastonite-type SrSiO3 was prepared from a powder mixture of reagent grade strontium carbonate (SrCO3) and silicic acid (SiO2·11/2H2O). The mixture was ground in a mortar and heated in a platinum crucible at 1200°C for 60 hrs. The synthesized sample was confirmed to be a single phase of pseudowollastonite by X-ray diffraction analysis (JCPDS 36-0018). The powder was mixed with a small amount of platinum powder (0.1 wt%) for effective heating using an infrared laser beam. The sample was put in a hole (0.15 mm in diam.) drilled in a rhodium gasket (0.06 mm in thickness) in a diamond-anvil cell (DAC) together with a few grains of ruby for pressure measurements. No pressure medium was used in this experiment to avoid unexpected chemical reactions with the sample.

The experiments were done using the synchrotron radiation facility at SPring-8. The Nd:YLF laser heating system installed on the beam line (BL-10XU) was used in the high P-T experiments (Watanuki et al. 2001). The angle dispersive X-ray diffraction rings detected by the area detector of an imaging plate (IP) provided highly precise d-values as well as intensity data. The high energy of the incident beam (30 keV) and the wide conical aperture of the tungsten carbide seating the diamond anvil made it possible to collect full Debye rings up to 18 degrees two theta. Double-sided heating helped to make the temperature gradient in the depth direction of the sample as low as possible. The temperature was determined by fitting the emitted light to a gray body radiation function. The heated area was exposed with a collimated X-ray beam (40 µm in diam.).

RESULTS AND DISCUSSION

We recorded the diffraction pattern before the heating experiments and after the compression up to 35 GPa. The diffraction pattern was an amorphous halo (Fig. 1a) except for diffraction lines of platinum and thus can be explained by pressure-induced