Cubic perovskite polymorph of strontium metasilicate at high pressures

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ABSTRACT

By using a diamond anvil cell (DAC) with laser heating technology, a cubic perovskite polymorph of SrSiO₃ has been synthesized at ~38 GPa and 1500-2000 K at the first time. The P, V data of this new phase yield its lattice volume and bulk modulus at ambient conditions of V₀ = 49.18(5) Å³, K₀ = 211(3) GPa, respectively, when they are fitted against the Birch-Murnaghan equation of state with a fixed K₀' at 4. On decompression, the SrSiO₃ cubic perovskite phase becomes unstable at ~6.2 GPa and disappears completely at ~4.7 GPa. The transformed product can be considered as an amorphous phase with a minor amount of small size crystals in the amorphous matrix when the pressure is released to ambient conditions. The first principle calculations predicted the structural properties of both the cubic and the six-layer-repeated hexagonal perovskite polymorphs of SrSiO₃ and the pressure-induced phase transition very well with the experimental results. At high pressures, the experimental and theoretical results indicate that the larger Sr²⁺ cation can substitute the Ca²⁺ cation and enter into the lattice of CaSiO₃ cubic perovskite in the lower mantle conditions with a small lattice strain. It is a good illustration that the Sr atom prefers entering the CaSiO₃ cubic perovskite and higher amount of Sr in the inclusion minerals of CaSiO₃ perovskite and its related modifications in diamonds originating from the lower mantle.
INTRODUCTION

The chemical and structural models of the Earth suggest that the Earth’s lower mantle is composed of three major mineral phases of (Mg,Fe)SiO$_3$-perovskite (MgPv), CaSiO$_3$-perovskite (CaPv) and (Mg, Fe)O-magnesiowustite (Mw), and two kinds of silicate perovskite constitute more than 80% of its volume (Irifune 1994; Kesson et al. 1998; Wood 2000). The other elements occurring in the lower mantle are considered to be either dissolved into the three main minerals (Irifune 1994; Taura et al. 2001; Corgne et al. 2005) or forming accessory minerals such as aluminosilicate hollandites (Gillet et al. 2000; Hirao et al. 2008). Partitioning experiments indicate that the geochemically important trace elements such as strontium (Sr), lead (Pb), and the rare earth elements (REE) enter preferentially into CaPv, and that CaPv can accommodate a significant amount of Sr (up to 2 wt%) (Kato et al. 1988). In addition, CaSiO$_3$ inclusions in diamonds that are believed to be CaPv originating from the lower mantle also show a strong enrichment in Sr (up to 0.85 wt%) (Stachel et al. 2000). Therefore, it is a scientific topic to confirm experimentally the substitution of Sr in CaPv by either occupying the crystallographic A-site or by generating a lattice defect in the perovskite structure. According to the size of Sr$^{2+}$ cation and the lattice strain model (Shannon 1976; Blundy and Wood 1994), it is reasonable to assume that the Sr$^{2+}$ cation may substitute Ca$^{2+}$ entering the CaSiO$_3$ perovskite. Additional indication and first hand information on the atomic volume of Sr in silicate perovskite can be obtained by synthesizing SrSiO$_3$ perovskite at high pressure and temperature. As yet, SrSiO$_3$ in the cubic perovskite structure has not been synthesized in experiments (Komabayashi et al. 2007). It is still unknown whether the corner-sharing perovskite-structured silicates could provide a lattice site large enough to accommodate the Sr$^{2+}$ cation.
SrSiO$_3$ crystallizes in a monoclinic structure ($C2/c$, $Z=12$) at ambient conditions (Nishi 1997a) isotypic to the high-temperature modification of CaSiO$_3$ (pseudowollastonite) (Yang and Prewitt 1999) and SrGeO$_3$ (Nishi 1997b). The typical features of the pseudowollastonite-type SrSiO$_3$ are alternate layers of ternary (Si$_3$O$_9$) tetrahedral rings and close-packed Sr atoms stacked along the [001] direction forming a six-layer-repeated structure (Nishi, 1997a). The high-pressure phase relations of SrSiO$_3$ were reported to be somewhat similar to that of CaSiO$_3$ (Shimizu et al. 1970; Machida et al. 1982; Fleischer and DeVries 1988; Kojitani et al. 2005; Swamy and Dubrovinsky 1997; Barkley et al. 2011). The results of high-pressure and high-temperature experiments up to 12 GPa and 1600°C suggest that the pseudowollastonite-type SrSiO$_3$ (SrSiO$_3$ I) transforms to SrSiO$_3$ II at about 3.5 GPa and then to SrSiO$_3$ III at about 6 GPa (Shimizu et al. 1970; Fleischer and DeVries 1988). The structure of SrSiO$_3$ II has been determined to be isotypic to walstromite ($\delta$-SrSiO$_3$, $P-\overline{1}$, $Z=6$), and the SrSiO$_3$ III has been determined to be a monoclinic structure in which four-membered (Si$_4$O$_{12}$) tetrahedral rings are contained ($\delta'$-SrSiO$_3$, $P2_1/c$, $Z=8$) (Machida et al. 1982). The further high-pressure and high-temperature experiments indicate that the SrSiO$_3$ III decomposes to SrSi$_2$O$_5$ plus Sr$_2$SiO$_4$ at about 11 GPa and 1000°C, which is similar to that of CaSiO$_3$ (Kojitani et al. 2005). At much higher pressures of above about 20 GPa, the thermodynamic stable phase of SrSiO$_3$ is identified as a six-layer-repeated hexagonal perovskite (6H-type, $P6_3/mmc$, $Z=6$) (Yusa et al. 2005; Akaogi et al. 2005). It is the same structure as the hexagonal BaTiO$_3$ perovskite.

The perovskite structures of ABO$_3$-type oxides can be considered as derived from the close packing of AO$_3$ layers (Katz and Ward 1964). If all of the stacking of AO$_3$ layers is either cubic (c) or hexagonal (h) (Katz and Ward 1964), the structure will be referred to as 3C or 2H, which corresponds to the corner- or face-sharing arrangement of BO$_6$ octahedra, respectively (Cheng et al. 2009). Mixed cubic and hexagonal stacking with different ratios can also occur as hexagonal perovskite polytypes, such as 9R (hhchhhchhc), 4H (hchc), and 6H (hcchcc). The tolerance factor,
89 \[ t = \left( \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \right), \]
90 where \( r_A, r_B, \) and \( r_O \) are the ionic radii of 12-fold
91 coordinated A cation, 6-fold coordinated B cation, and oxygen anion, respectively, is
92 often used to estimate the possible perovskite polymorphs adopted by the ABO_3-type
93 oxides. Generally, if the tolerance factor \( t \) equals unity, the ideal perovskite structure
94 \((Pm\bar{3}m)\) is stabilized, which can be regarded as a three-dimensional framework built
95 up by the corner-sharing BO_6 octahedra with a large A cation in the 12-coordinated
96 cavities of the framework, as shown in Figure 1a. The hexagonal perovskite polytypes
97 are usually formed in the ABO_3 compounds having a tolerance factor \( t > 1 \). The
98 hexagonal perovskite polytypes, as indicated by a value of polyhedral volume ratio
99 \((V_{AO12}/V_{BO6})\), larger than 5, the value of that in an ideal cubic perovskite structure,
100 provide the 12-coordinated cavities larger than that of the 3C perovskite polymorphs
101 to accommodate a larger A cation (Thomas 1991). The strontium metasilicate \((SrSiO_3)\)
102 with a tolerance factor \( t \) of 1.12 (calculated by using the 12-fold coordinated Sr cation
103 radius of 1.44 Å) or 1.04 (calculated by using the 8-fold coordinated Sr cation radius
104 of 1.26 Å (Shannon 1976)), crystallizes into a 6H-type hexagonal perovskite to
105 contain the large \( Sr^{2+} \) cation at high pressures of 25-35 GPa (Yusa et al. 2005), as
106 shown in Figure 1b. This kind of the hexagonal perovskite structure of \( SrSiO_3 \),
107 however, cannot explain why \( Sr^{2+} \) partitions preferentially into the 3C-type \( CaSiO_3 \)
108 perovskite in the lower mantle.
109
110 Since the A-O bond is generally more compressible than the B-O bond in ABO_3
111 perovskites, the A-O bond length decreases more rapidly with pressures leading to a
112 reduced tolerance factor, and the 3C-type perovskite can be transformed from the
113 hexagonal perovskite polytypes at high pressures and high temperatures. For example,
114 the 9R-BaRuO_3, stable at ambient conditions, transforms to a 4H phase at 3 GPa, a 6H
115 phase at 5 GPa, and finally a 3C phase at 18 GPa (Jin et al. 2008). We consider that,
116 as suggested by Yusa et al. (2005), a 3C-type perovskite polymorph of \( SrSiO_3 \) appears
117 at a pressure higher than 25-35 GPa. Here we report a cubic perovskite of \( SrSiO_3 \)
118 which was observed at high pressures in our experiment. This new high pressure
119 \( SrSiO_3 \) cubic perovskite becomes unstable and starts a phase transition when the
pressure is released to about 6 GPa, and the transition is totally completed when the pressure is released lower than 4.7 GPa. The transformed product can be considered as an amorphous phase with a minor amount of small size crystals or pre-nucleated centers in the amorphous matrix upon release of the pressure to ambient conditions. Furthermore, the theoretical calculations indicate that the cubic perovskite of SrSiO$_3$ is the stable phase compared to the other possible 3C-type perovskites in the pressure range of 0-40 GPa, and predict that the phase transition from the 6H-type perovskite to the cubic perovskite occurs at 32 GPa.

**EXPERIMENTAL AND THEORETICAL METHODS**

The raw material of monoclinic SrSiO$_3$ used as the high pressure experimental sample was prepared by the conventional solid-state reaction method (Yamaguchi et al. 1979). Analytical grade SrCO$_3$ (99.9%) and SiO$_2$ (99.99%) in stoichiometric amounts were weighed and mixed. The grounded mixture was sintered within a platinum crucible at 1350°C for 10 hrs in a furnace in air. The quenched crystalline sample has been confirmed to be the pure monoclinic SrSiO$_3$ by X-ray powder diffraction with its lattice parameters of $a = 12.345(5)$ Å, $b = 7.131(2)$ Å, $c = 10.924(5)$ Å, $\beta = 112.00(6)^\circ$, and $V = 891.6(4)$ Å$^3$, respectively. It is in good agreement with the single crystal X-ray diffraction results of the pseudowollastonite-type SrSiO$_3$ (Nishi 1997a).

The high-pressure experiments were carried out by using a symmetric Mao-Bell type of DAC. A pair of 300 µm culet-size diamond anvils was used in our experiments. A gasket was prepared by indenting a piece of T301 stainless steel foil to a thickness of about 40 µm and then drilled a 100 µm hole serving as the sample chamber. The monoclinic SrSiO$_3$ powder mixed with 1 wt% platinum powder was pressed to a pellet with a thickness of about 15 µm, and a piece of sample about 60 µm in diameter was loaded into the sample chamber. Argon was used as a pressure-transmitting medium. Besides absorbing the heating laser power, the mixed 1 wt% platinum powder in the sample was also used as standard for *in situ*
measurement of the sample pressure (Holmes et al. 1989). The sample in the DAC was pressurized up to about 38 GPa and then heated by a YAG laser to temperatures of around 1500 to 2000 K.

*In-situ* high pressure angle-dispersive X-ray diffraction (ADXD) experiments were performed at the 4W2 beam line of Beijing synchrotron radiation facility (BSRF). An image plate detector (MAR-345) was used to collect diffraction patterns. The wavelength of the monochromatic X-ray beam is 0.6199 Å calibrated by scanning through the Mo metal $K$-absorption edge. The X-ray beam was focused to a beam size of 20 (vertical) × 30 (horizontal) $\mu$m$^2$ full width at half maximum by a pair of Kirkpatrick-Baez mirrors. The distance between the sample and the detector was calibrated to be 350.54 mm by using CeO$_2$ as a standard. All of the ADXD patterns were collected in the decompressed process from 37.8 GPa to 0.1 MPa at room temperature without further annealing. The collected diffraction patterns were analyzed by integrating images as a function of $2\theta$ using the program Fit2D (Hammersley et al. 1996) to obtain a conventional, one dimensional diffraction profile. In addition, the 14.3 GPa and 37.8 GPa patterns were further analyzed by Rietveld refinements using the GSAS software (Toby 2001).

The first-principles calculations were performed using the CASTEP code (Clark et al. 2005) based on density functional theory (DFT) with Vanderbilt-type ultrasoft pseudopotentials and a plane-wave expansion of the wavefunctions. An energy cutoff of 750 eV was used for all calculations. The exchange-correlation potential was treated within the generalized gradient approximation (GGA) in the PBE scheme. Pseudo-atomic calculations were performed for Sr$4s^24p^65s^2$, Si$3s^23p^2$ and O$2s^22p^4$. As for the Brillouin zone k-point sampling, we used the 6×6×6 Monkhorst-Pack scheme. Geometry optimizations were performed to fully relax the atomic internal coordinates and the lattice parameters within the BFGS minimization algorithm. The self-convergence thresholds for energy change, maximum force, maximum stress, and maximum displacement between optimization cycles were 5×10$^{-6}$ eV/atom, 0.01 eVÅ$^{-1}$, 0.02 GPa and 5×10$^{-4}$ Å, respectively. In the process, the optimized lattice
parameters and energy values are obtained at various pressures.

RESULTS

Experimental results

Figure 2 exhibits two representative X-ray diffraction (XRD) patterns of the sample which has been produced at ~38 GPa with laser-heating. Two patterns were collected at the pressure of either 14.3 GPa or 37.8 GPa, respectively, in which the scatter background were subtracted. Other XRD patterns collected at pressures between 9 GPa and 37.8 GPa are similar to the displayed patterns in Figure 2. They indicate that no phase transition in the sample has been occurred in this pressure range, however, the diffraction patterns are different from that of the 6H-type hexagonal perovskite of SrSiO$_3$ and only much less reflection peaks can be observed (Yusa et al. 2005), thus it should be a new phase of SrSiO$_3$ with a higher symmetric structure which has not been reported previously. Because there are SrSiO$_3$, argon medium and platinum powder only in the sample chamber, we consider the peaks in the XRD patterns are composed of the diffracted signals of these three kinds of materials mentioned. Diffraction peaks belonging to argon and platinum with the face center cubic structure (fcc, $Fm\overline{3}m$) are easily indexed in the patterns, as shown in Figure 2. At the same time, the other six reflection peaks in the patterns can be indexed into a simple cubic structure with smaller estimated standard deviations of the lattice parameters by using the DICVOL04 code (Boultif and Louër 2004). The tentative tetragonal and hexagonal structures converge to the cubic structure with a negligible discrepancy. The lattice volumes are 43.00(2) Å$^3$ at 37.8 GPa and 46.35(5) Å$^3$ at 14.3 GPa, as shown in Figure 2. The cell volumes indicate that there is only one chemical formula of SrSiO$_3$ in each unit cell, and the simple cubic phase of SrSiO$_3$ is possibly a cubic perovskite structure ($Pm\overline{3}m$). The cubic perovskite model of SrSiO$_3$ accompanying with the face center cubic structures ($Fm\overline{3}m$) of argon and platinum has been used to fit the observed XRD patterns collected at 14.3 GPa and 37.8 GPa, respectively. The Rietveld refinements, as shown in Figure 2, gave good agreement between the observed and calculated synchrotron XRD patterns. The final
discrepancy indices are $R_{wp}=1.16\%$, $R_p=0.91\%$, $R(F^2)=0.0819$, reduced $\chi^2=0.1087$

for the 37.8 GPa pattern, and $R_{wp}=2.27\%$, $R_p=1.39\%$, $R(F^2)=0.3141$, reduced $\chi^2=0.0871$ for the 14.3 GPa pattern. The small reduced $\chi^2$ values are caused primarily by the high scattering background. Even though, the distortion from the cubic to a lower symmetrical perovskite polymorph may be subtle and leads to unnoticeable difference in the XRD pattern. In the 14.3 GPa pattern, the refined curve deviates slightly from experimental data at several peak positions (especially the (100) and (110) peaks) leading to asymmetric residuals. The refined (200) peak of argon also deviates a little from its observed position in this pattern. The slight deviation could be attributed to the differential stress in the sample system, or insufficient sample statistics. Thus, we consider that, based on the powder XRD resolution, the cubic symmetry could be a reasonable explanation for our experimental data, and therefore, a cubic perovskite polymorph of SrSiO$_3$ is obtained at high pressures in our experiments. For comparison, we also refined the 37.8 GPa pattern with the 6H-type model as shown in Figure 2.

Figure 3 shows several low-pressure XRD patterns of the sample collected from 9 GPa down to atmospheric pressure, which describes the phase transition of the SrSiO$_3$ cubic perovskite as the pressure releasing. When the pressure is unloaded from 9 GPa to 6.2 GPa, the intensity of the reflection peaks of the SrSiO$_3$ cubic perovskite decreases markedly leading to the increasing scattering background and the lowering signal to noise ratio; at the same time, two weak peaks appear at $\sim 2.85\ \text{Å}$ and $\sim 4.67\ \text{Å}$. The original diffraction peaks from the SrSiO$_3$ cubic perovskite almost completely disappear at 4.7 GPa. At atmospheric pressure, besides the (111) and (200) diffraction peaks of platinum, there are some weak peaks observed at 5.04 Å, 3.68 Å, 3.38 Å, 3.31 Å, 2.96 Å, and 2.86 Å superimposing on the intense background, as shown in Figure 3. These broad weak diffraction reflections, denoting a very bad crystallinity in the transformed production, cannot be assigned to any known structure of the SrSiO$_3$ compound and its decomposed oxide assemblage of SrO (ICDD 06-0520) and SiO$_2$ (ICDD 46-1045). The hexagonal perovskite of SrSiO$_3$, a low-pressure polymorph of
its cubic perovskite, transforms to an amorphous phase upon release to ambient conditions (Yusa et al. 2005). The CaSiO$_3$ cubic perovskite, which has a smaller lattice volume than the SrSiO$_3$ cubic perovskite, also transforms to the amorphous state at the zero-pressure (Mao et al. 1989, Wang et al. 1996). The PbGeO$_3$ cubic perovskite transforms to an amorphous phase on decompression, in which a few weak diffraction peaks also appear in the XRD patterns and is considered as a small amount of nano-sized crystals or pre-nucleated centers in the amorphous matrix (Xiao et al. 2012). Here, we propose the transformed production of the SrSiO$_3$ cubic perovskite is an amorphous phase, with a minor amount of small size crystals or pre-nucleated centers embedded in the amorphous matrix. Nevertheless, more experimental evidences are provided to clarify the nature of the transformed product of the SrSiO$_3$ cubic perovskite.

Table 1 lists the unit cell data of the SrSiO$_3$ cubic perovskite obtained at different pressures in this study, and those pressure-volume data are plotted in Figure 4. In this diagram, the unit formula volume of the SrSiO$_3$ hexagonal perovskite (6H-type) at 25 GPa determined by Yusa et al. (2005) is also plotted for comparison. From the P-V data in Figure 4, we can find that the 6.2 GPa volume deviated from the experimental P-V trend shows a smaller volume. The SrSiO$_3$ cubic perovskite becomes unstable and begins its phase transition (amorphization) at ~6.2 GPa, thus the anomalous volume is probably associated with this process. This kind of volume reduction (induced by the phase transition, i.e. amorphization) has been also observed in both CaSiO$_3$ and PbGeO$_3$ perovskites (Wang et al. 1996; Xiao et al. 2012). Therefore, the volume at 6.2 GPa has not been used in our equation of state analysis. The remaining 16 P-V data of the SrSiO$_3$ cubic perovskite have been fitted into the Birch-Murnaghan equation of state,

$$F = \frac{3}{2} K_0 \left[\left(\frac{V}{V_0}\right)^{7/3} - \left(\frac{V}{V_0}\right)^{5/3}\right] \left[1 + \frac{3}{2}\left(\frac{V}{V_0}\right) - 4\left(\frac{V}{V_0}\right)^2\right]$$

Where $V_0$, $K_0$ and $K_0'$ are the volume, the isothermal bulk modulus, and its pressure derivative at the room pressure, respectively. With fixed $K_0'$ as 4, the fitting results
yield \( K_0 = 211(3) \) GPa and \( V_0 = 49.18(5) \) Å\(^3\), respectively. The fitted zero-pressure lattice constant (\( a = 3.6638 \) Å) of the SrSiO\(_3\) cubic perovskite agrees well with that of the value of 3.6588 Å (with a deviation of 0.14%) given by the empirical relationship between the lattice constant and the composition ion radii in cubic perovskites (Ubic 2007; Shannon 1976).

**Theoretical results**

Several possible 3C-type perovskites of SrSiO\(_3\) with space groups \( R-3c, I4/mcm, I4/mmm, P4/mmb, Imma \) and \( Pnma \) as the superstructures of the ideal cubic perovskite \( (Pm3m) \) were constructed. The initial atomic coordinates adopted the corresponding values as the LaAlO\(_3\) perovskite for the \( R-3c \) structure (Howard et al. 2000) and the CaSiO\(_3\) perovskite for the \( I4/mcm, I4/mmm, P4/mmb, Imma \) and \( Pnma \) structures (Caracas and Wentzcovitch 2006). These superlattices as well as the cubic perovskite were performed the geometrical optimization in the total energy framework with variables of the lattice parameters and the atomic coordinates at 0 GPa and 40 GPa, respectively. The geometrical optimization of these superstructures moves the atoms at the ordinary coordinates initially to the special values and produces the peculiar geometrical relationships of lattice parameters (i.e., a 2 or a square root of 2 times the cubic perovskite lattice constant), and thus all of the six kinds of superstructures are converted to a cubic perovskite structure. Moreover, the total energies of the different superstructures have a same value as the cubic perovskite within a calculated accuracy (the discrepancies are less than 1 meV per formula). The calculated results indicate that these superstructures converge to the ideal cubic perovskite, and the SrSiO\(_3\) cubic perovskite is more stable than other possible 3C-type perovskite polymorphs in the experimental pressure range of 0-40 GPa in this study.

Geometrical optimization of the cubic and 6H-type perovskite polymorphs of SrSiO\(_3\) in the pressure range of 0-40 GPa with a 5 GPa pressure interval were performed. The initial atomic positions of the 6H-type perovskite \( (P6_3/mmc, Z=6) \) of SrSiO\(_3\) employed the corresponding values of the BaTiO\(_3\) hexagonal perovskite (Akimoto et al. 1994). The lattice constants, unit-cell volumes and enthalpies were
obtained in the total energy minimum scheme at various pressures. The results are shown in Figure 5, in which the c/a ratio change of the 6H-type perovskite with the pressure is also depicted in the lower left inserted plot, and the 6H-type perovskite unit-cell volumes are shown as V/Z (Z=6) in comparison with the cubic perovskite conveniently. The volume-pressure data of both polymorphs were fitted to a Birch-Murnaghan equation of state, resulting in a zero-pressure bulk modulus \( K_0 = 207.7(4) \text{ GPa} \) and unit-cell volume \( V_0 = 49.97(1) \text{ Å}^3 \) for the cubic perovskite, and \( K_0 = 183.8(6) \text{ GPa} \) and \( V_0 = 311.23(10) \text{ Å}^3 \) for the 6H-type perovskite, when \( K_0' \) is fixed at 4. The theoretical zero pressure volume of the cubic perovskite is about 1.6\% larger than that of the experimental values. The calculated unit-cell volume of the 6H-type perovskite at 25 GPa is also about 1\% larger than the experimental value (Yusa et al. 2005), as shown in Figure 5. Generally, the GGA method underestimates the binding energy and induces a large unit-cell volume. Nevertheless, the theoretical predictions of the lattice parameters of both cubic and 6H-type perovskites agree well with the experimental results. In addition, the theoretical zero pressure bulk modulus of the cubic perovskite is very close to the experimental result of 211(3)GPa in this study.

The phase transition pressure of SrSiO\(_3\) from the low-pressure 6H-type perovskite to the high-pressure cubic perovskite is predicted by comparing the enthalpies of both polymorphs. The enthalpy differences at various pressures are plotted as the upper right inserted graph in Figure 5. From the illustration, we can see that the phase transition occurs at 32GPa, a pressure consistent with the experimental result of between 25GPa and 38GPa. The phase transition induces a 2.5\% volume collapse, as shown in Figure 5.

DISCUSSION

The SrSiO\(_3\) cubic perovskite has been observed at high pressures in this study for the first time. It has the largest tolerance factor \((t = 1.12)\) for SrSiO\(_3\) in the ABO\(_3\)-type oxides in the cubic perovskite structure found up to now. Normally, ABO\(_3\)-type oxides with such a large tolerance factor form various hexagonal perovskite polytypes with a different AO\(_3\) layers stacking sequence. These kinds of hexagonal perovskite
structures are common in the transition metal oxides (Akimoto et al. 1994; Jin et al. 2008; Cheng et al. 2009; Belik et al. 2011). As the pressure increases, the hexagonal perovskite polytypes show a transformation sequence of 2H→9R→4H→6H, and finally transform to 3C polymorphs (Cheng et al. 2009). This kind of phase transformation sequences exhibits an increased ratio of the cubic to the hexagonal layers stacking. The existence of both polymorphs of 6H-type (Yusa et al. 2005) and 3C-type perovskite of SrSiO$_3$ at different pressures indicate that the metasilicate containing a large A cation, thus with a large tolerance factor, also shows a same phase transformation sequence as the transition metal oxides. The experimental observation of the 9R and 6H perovskite polytypes of BaSiO$_3$ at various high pressures also agrees with the phase transformation tendency (Yusa et al. 2007). In addition, the unit formula volume of the cubic perovskite of SrSiO$_3$ is about 3.1% or 2.5% smaller than that of its 6H-type perovskite polymorph at about 25 GPa (experimental) or 32GPa (theoretical), respectively, as shown in Figure 4 and Figure 5. The volume difference between the 3C and the 6H perovskite polymorphs of SrSiO$_3$ is also in the good accordance with that of the transition metal oxides such as BaRuO$_3$ (~2.9%; Zhao et al. 2007; Jin et al. 2008), BaTiO$_3$ (~2.8%; Edwards et al. 1951; Akimoto et al. 1994), and SrMnO$_3$ (~3.5%; Kriegel and Preuß 1996; Belik et al. 2011). It proposes that, if they have a larger tolerance factor than unity, both of the main group oxides and the transition metal oxides comply with the similar crystal chemistry criteria, and show the similar phase transformation sequence from the face-sharing hexagonal perovskite polytypes to the corner-sharing 3C-type perovskite polymorph under high pressures. It would be interesting to verify whether the SrSrO$_3$ compound crystallizes in the other hexagonal perovskite polytypes at pressures lower than 25 GPa or not.

Yusa et al. (2005) gave the lattice plane distances and the lattice constants of the 6H-type perovskite of SrSiO$_3$ at 25 GPa in Table 1 in their paper. The c/a ratio of 2.4498 is nearly equal to $\sqrt{6}$, and is well consistent with the theoretical result, as shown in Figure 5. Moreover, it is interesting that some lattice distances of (102), (104), (006), (204), (116) and (108) can be indexed into a cubic structure with the
lattice constant of $a_c=3.5844(2)$ Å, a same value as the cubic perovskite polymorph of SrSiO$_3$ at 16GPa in our experiments. We also refined the 37.8 GPa pattern of our data with the 6H model, as shown in Figure 2. All of the six diffracted peaks belonging to the SrSiO$_3$ compound can be indexed to the 6H structure; however, the refinement results show remarkable residual and excess important strong peaks in the refined curve. Although the same AO$_3$ atomic layers stacking of hccchcc along the c-axis in the 6H structure contrasting to ccc along the [111] direction in the 3C structure induces the lattice parameters relationship of $a_h\approx\sqrt{2}a_c$ and $c_h\approx2\sqrt{3}a_c$, and accordingly, some nearly identical diffracted signal positions, the distinctively different atomic arrangement between the two structures leads to significant difference in diffraction intensity and extinction rules. It is exactly the reason that the 6H symmetry is unsuitable to model our observed data.

Table 2 lists the available bulk moduli ($K_0$) and unit formula volumes ($V_0$) of the alkaline earth silicate, germanate, and titanate perovskites which are being concerned in the mantle mineralogy. These $K_0$-$V_0$ data are also plotted in Figure 6. The inverse relationship between bulk modulus $K_0$ and unit formula volume $V_0$ has been widely used for predicting bulk moduli of mantle minerals crystallizing in the similar structures (Anderson and Anderson 1970). It can be expressed as $K_0V_0 = \text{constant}$. According to the data of CaSiO$_3$ and MgSiO$_3$ perovskites and the inverse relationship above mentioned, the predicted bulk modulus of the SrSiO$_3$ cubic perovskite is either 215 or 214 GPa, respectively. It is well consistent with the experimental value of 211(3) GPa obtained in this study. In addition, as can be seen in the inset in Figure 6, the three alkaline earth silicate perovskites also exhibit an excellent linear relationship between their unit formula volumes and bulk moduli. The linear fitting gives a formula as $K_0(GPa) = 491(3)-5.69(7)\times V_0(Å^3)$ with a coefficient of determination ($R^2$) of 0.999. Furthermore, the $K_0$-$V_0$ data of all of the nine perovskites listed in Table 2 also are fitted a good lineal relationship of $K_0(GPa)=464(12)-5.1(2)\times V_0(Å^3)$ with $R^2 = 0.986$, as shown in Figure 6. Obviously, the $K_0$-$V_0$ linear function is better than the inverse relationship to predict the bulk modulus of the alkaline earth oxide perovskites.
in a wide volume and component range. It indicates that there are similar factors to
govern the compression behaviors in these alkaline earth oxide perovskites.

Strontium (Sr) is one of such elements of geochemical importance (Sobolev et al.
2011). The identification of the SrSiO₃ cubic perovskite at high pressures provides the
experimental evidences to understand the occurrence of Sr atom in the Earth’s lower
mantle. The existence of the SrSiO₃ cubic perovskite demonstrates that the
crystallographic A-site of the silicate cubic perovskite is large enough to
accommodate the large Sr²⁺ cation on the conditions of the lower mantle. The recent
experimental results indicate that CaSiO₃ is stable with the cubic perovskite structure
in the high pressure and high temperature environments inside the lower mantle
(Komabayashi et al. 2007). In addition, both silicates of SrSiO₃ and CaSiO₃ show
similar phase transition sequence under high pressures, as discussed above. It reveals
that the two kinds of silicate compounds have similar physical and chemical
properties in the Earth’s crust and mantle. Therefore, the P-V equations of state of
both the SrSiO₃ and CaSiO₃ cubic perovskites, as shown in the inset in Figure 4, can
be used to estimate the lattice strain generated by the introduction of large Sr²⁺ cation
into the smaller A-site in the CaSiO₃ cubic perovskite structure. The difference of the
lattice constant \[ (a_{SrPv} - a_{CaPv}) / a_{CaPv} \] between the SrSiO₃ and CaSiO₃ cubic perovskites
is about 2% at 24 GPa, the pressure of the upper-lower mantle boundary, and 0.8% at
136 GPa, the pressure of the core-mantle boundary. The small lattice constant
difference implies that the substitution of Ca atom by Sr atom in the lower mantle
mineral of CaSiO₃ cubic perovskite generates a small lattice strain; and therefore, the
CaSiO₃-SrSiO₃ system could possibly form the complete cubic perovskite solid
solution in the lower mantle. It can explain the facts, from the view of crystal
chemistry, that the Sr atom enters preferentially into the CaSiO₃ cubic perovskite
other than the MgSiO₃ orthorhombic perovskite in the partitioning experiments (Kato
et al. 1988), and the inclusion minerals of CaSiO₃ perovskite and its variants in
mantle-derived diamonds have a high Sr abundance (Joswig et al. 1999; Stachel et al.
2000).
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Thermoelastic properties and crystal structure of MgSiO$_3$ perovskite at lower mantle


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diffraction study of rhombohedral rare-earth aluminates and the rhombohedral to


Captions

FIGURE 1. (color online) Polyhedral SiO$_6$ presentation of the SrSiO$_3$ perovskite structures. (a) the cubic perovskite of 3C-SrSiO$_3$ with all corner-sharing SiO$_6$ octahedra, (b) the hexagonal perovskite of 6H-SrSiO$_3$ with mixing face-sharing and corner-sharing SiO$_6$ octahedra. Sr, Si and O atoms are shown as big green, middle blue and small red spheres, respectively.

FIGURE 2. (color online) Rietveld refinement analyses of the powder XRD patterns collected at 37.8 GPa and 14.3 GPa, respectively, and room temperature. SrSiO$_3$ was refined in the the 6H-type (P6$_3$/mmc) and cubic (Pm3m) perovskite structures. The observed (crosses), calculated (red solid line), and the difference (black solid line) curves were shown on the same scale. Background was subtracted. The vertical bars below the diffraction profiles represent the calculated positions of the diffraction peaks of the SrSiO$_3$ hexagonal or cubic perovskites, argon medium, and platinum standard, respectively. The final discrepancy indices are $R_{wp}$=3.47%, $R_p$=1.77%, $R(F^2)$=0.5497, reduced $\chi^2$=1.809 for the 37.8 GPa pattern modeling by the 6H symmetry; $R_{wp}$=1.16%, $R_p$=0.91%, $R(F^2)$=0.0819, reduced $\chi^2$=0.1087 for the 37.8 GPa pattern, and $R_{wp}$=2.27%, $R_p$=1.39%, $R(F^2)$=0.3141, reduced $\chi^2$=0.0871 for the 14.3 GPa pattern modeling by the cubic symmetry.

FIGURE 3. X-ray powder diffraction patterns at pressures between 0-9 GPa showing the pressure-released transition process of the SrSiO$_3$ cubic perovskite. The remarkable reduction of the diffraction intensity of the SrSiO$_3$ cubic perovskite and the appearance of the weak and broad 2.85 and 4.67 Å peaks reveal the occurrence of the phase transition at 6.2 GPa. The complete disappearance of the diffraction lines of the SrSiO$_3$ cubic perovskite at 4.7 GPa indicates the phase transition was completed. The broad weak peaks superimposing on the intense background, as labeled in the 0.1
MPa pattern, may represent that the transformed product of the SrSiO$_3$ cubic perovskite is an amorphous phase with a minor amount of small size crystal in the amorphous matrix.

**FIGURE 4.** Pressure-Volume relationship of the SrSiO$_3$ perovskites. The solid cycles represent the observed data of the SrSiO$_3$ cubic perovskite, and the solid square indicates the unit formula volume of the 6H-type SrSiO$_3$ perovskite at 25GPa (Yusa et al. 2005). The solid curve is the Birch-Muraghan equation of state fit with the listed parameters. Notice that at 6.2 GPa, the unit cell volume deviates from the experimental P-V tendency showing a reduced volume, which is associated with the phase transition occurring on decompression. The estimated standard deviations of the unit cell volume (see Table 2) are smaller than the size of the symbols. The error bars of pressure show the uncertainties estimated by the reading uncertainties of the reflection peaks of platinum standard and the pressure differences calculated by the (111) peak and (200) peak of the platinum standard. The inset shows the equations of state of the SrSiO$_3$ cubic perovskite (solid line) and the CaSiO$_3$ cubic perovskite (dotted line) in the pressure range of the whole mantle.

**FIGURE 5.** The theoretical pressure-volume relationship of the SrSiO$_3$ perovskites. The solid triangle and diamond symbols represent the calculated P-V data of the cubic and 6H-type perovskite polymorphs, respectively. The curves stated by the legends indicate the theoretical Birch-Muraghan equation of states of the cubic and 6H-type perovskites and the experimental equation of state of the cubic perovskite. The upper right inset depicts the calculated enthalpy differences between the cubic and 6H-type perovskites at various pressures, and the phase transition pressure of the two polymorphs is determined at 32GPa. The lower left inset shows the calculated c/a ratio changing of the 6H-type perovskite with pressure. The experimental c/a ratio at 25GPa (Yusa et al. 2005) is shown as solid triangle. The dotted line indicates the special value of $\sqrt{6}$. 

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FIGURE 6. The unit formula volume ($V_0$) - bulk modulus ($K_0$) relationship of the perovskite-structured alkaline earth silicates, germanates, and titanates (see Table 3). The $K_0$-$V_0$ data of the all nine perovskites can fit a good linear function as shown in the plot. The inset emphasizes the excellent $K_0$-$V_0$ linear relationship of the three kinds of silicate perovskites of MgSiO$_3$, CaSiO$_3$ and SrSiO$_3$. The vertical error bars show the estimated standard deviations of the zero-pressure bulk modulus (see Table 3). The uncertainties of the unit formula volume are smaller than the size of the symbols.

TABLE 1. Experimental pressure-volume data of SrSiO$_3$ cubic perovskite. The estimated standard deviations of the fitted unit cell volume are given in parentheses. The uncertainties of pressure given in parentheses are estimated by the reading uncertainties of the reflection peaks of platinum standard and the pressure differences calculated by the (111) peak and (200) peak of the platinum standard.

TABLE 2. Comparison of zero-pressure bulk modulus ($K_0$) and unit formula volume ($V_0$) of SrSiO$_3$ cubic perovskite with that of relative perovskite-structural alkaline earth silicate, germanate, and titanate compounds. These $K_0$-$V_0$ data show a good linear relationship in a wide volume and component range. The uncertainties of both unit formula volume and zero-pressure bulk modulus are given in parentheses.
**FIGURE 1**

(a) 3C  
(b) 6H
FIGURE 2

37.8 GPa
6H-type

\[
a=4.9673(12)\,\text{Å} \\
c=12.133(7)\,\text{Å} \\
V=259.28(17)\,\text{Å}^3
\]

37.8 GPa
Cubic

\[
a=3.5034(7)\,\text{Å} \\
V=43.00(2)\,\text{Å}^3
\]

14.3 GPa
Cubic

\[
a=3.5920(14)\,\text{Å} \\
V=46.35(5)\,\text{Å}^3
\]

Two theta (degree)

Intensity (arb. unit)

SrSiO$_2$-cPv
Ar
Pt

SrSiO$_2$-cPv
Ar
Pt
FIGURE 4

- This study
- Yusa et al. (2005)
- Fitted EOS

Volume (Å$^3$)

$V_0 = 49.18(5) \, \text{Å}^3$

$K_0 = 211(3) \, \text{GPa}$

$K_0' = 4$ (assumed)

Pressure (GPa)

EOS of SrSiO$_4$-Pv
EOS of CaSiO$_3$-Pv

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FIGURE 5

[Graph showing volume (Å^3/formula unit) versus pressure (GPa) for different phases of PV with experimental and calculated EOS, and inset showing change in volume difference (Å^3/formula unit) with pressure.]
FIGURE 6

Bulk modulus (GPa) vs. Unit formula Volume (Å³)

\[ K_s (\text{GPa}) = 464(12) - 5.1(2) \times V_0 (\text{Å}^3) \]

\[ R^2 = 0.986 \]
### TABLE 1

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<th>Pressure (GPa)</th>
<th>Volume (Å³)</th>
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### TABLE 2

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<th>Structure</th>
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<td>Wang et al. (1996)</td>
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