

Crystal Chemistry of SrGeO₃ at High Pressure

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Introduction

It is now generally accepted that the orthorhombic, *Pbnm* phase of MgSiO₃ perovskite remains the stable phase throughout the Earth's lower mantle [1]. On the other hand, experimental studies have failed to detect any deviation in cubic symmetry for CaSiO₃ above 10 GPa [2, 3], where it transforms from a pseudowollastonite-type phase to the ideal perovskite structure [4]. The prediction of a lower mantle phase transition in CaSiO₃ from the ideal cubic perovskite to a tetragonal phase [5] has therefore been of considerable interest recently. It may be that the phase transition takes place at such a high pressure it has simply not yet been observed in CaSiO₃. It is also possible that the splittings of the diffraction peaks that would accompany such a transition are not observable at the resolution of the diffraction experiment.

Understanding the crystal chemistry of these silicate phases is an important prerequisite for constructing mineralogical models of the Earth's mantle. Also, the crystal-chemical framework provides a qualitative and useful picture of the phase transitions that take place at high pressure. One of the more successful approaches in developing crystal-chemical systematics is to investigate homologous series as a means toward understanding why certain phases may or may not be stable in a given pressure-temperature (P-T) régime. To this end, the germanate phases SrGeO₃ and CaGeO₃ have become important not only as analogues for silicate phases but also as interesting structural problems in themselves.

It has been well known for some time that SrGeO₃ adopts the pseudowollastonite structure at ambient pressure [6], although recent evidence supports the existence of several polytypes of this structure [7]. On the basis of the traditional tolerance factor systematics that have been used for many years to describe the deviation of the perovskite structure from the ideal cubic arrangement, SrGeO₃ should provide a good model for CaSiO₃, since both A- and B-site cations are uniformly larger in SrGeO₃ than in CaSiO₃. On the basis of these considerations, phase transitions that ultimately would occur in CaSiO₃ should take place at a significantly lower pressure in SrGeO₃ (as has already been observed in the pseudowollastonite-perovskite transformations: 5 GPa for SrGeO₃ compared with 10 GPa for CaSiO₃), making them easier to observe in diamond anvil cell experiments.

Methods and Materials

Polycrystalline SrGeO₃ was synthesized through the solid-state reaction of SrCO₃ and GeO₂ in air at 1200°C. The product was a single-phase material (the hexagonal 6H polytype of the SrGeO₃ structure [8]) as verified by powder x-ray diffraction. A portion of this material was pressed between two 800- μ m diamonds and then cut to create a cube of material with an edge length of approximately 30 μ m. A Merrill-Bassett diamond anvil cell was then fit with 250- μ m diamonds and a rhenium gasket that had been preindented to 45 μ m. A 150- μ m hole was drilled in the gasket by spark erosion, and the gasket was replaced in the cell. The SrGeO₃ cube was then loaded into the gasket hole, and the cell was closed to a pressure of 30 GPa in an atmosphere of Ar gas, which was used as the pressure-transmitting medium and pressure calibrant.

Polycrystalline, angle-dispersive x-ray diffraction experiments were carried out at the GeoSoilEnviro Consortium for Advanced Radiation Sources (GSECARS) beamline 13-ID-D of the APS, with a wavelength of 0.4246 Å. With increasing pressure from 22 to 55 GPa, diffraction patterns were collected on a Bruker SMART charge-coupled device (CCD) detector, and at each pressure, the sample was heated to approximately 1000K with a Nd:YAG laser by using the double-sided laser heating technique [9]. Diffraction data were then processed using the FIT 2-D routines. Analysis of the diffraction patterns, including the application of a background correction, was performed with the JADE program for powder pattern manipulation.

Results

At the lowest pressure of the experiment, 22 GPa, SrGeO₃ has the cubic perovskite structure. And, despite the crystal-chemical rationale behind the prediction of a phase transition at approximately this pressure to an orthorhombic or tetragonal structure at low pressure, no evidence of any such transition was evident up to 55 GPa. The diffraction peaks remained very sharp throughout this pressure range as a result of the laser heating at low power. Figure 1 shows the variation of the volume with pressure for the sample. A fit of this diffraction data with the second-order Birch-Murnaghan equation of state gives $K_0 = 203$ GPa with an equilibrium volume of 54.41 Å³ per

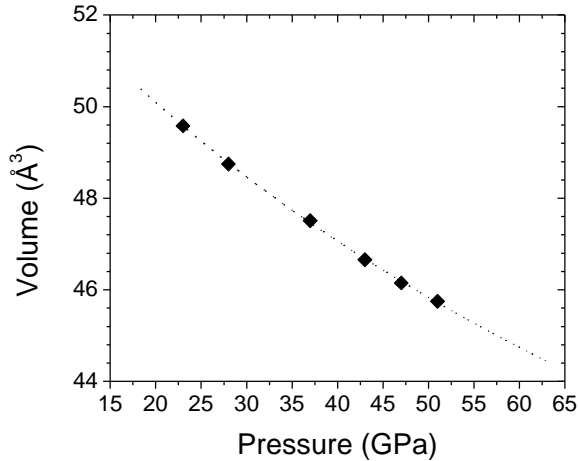


FIG. 1. Pressure-volume data at room temperature for SrGeO_3 in the ideal perovskite structure.

formula unit, which is 5% smaller than the volume of the zero-pressure perovskite predicted on the basis of crystal ionic radii, and a dramatic 32% smaller than the volume of the ambient-pressure pseudowollastonite phase.

Discussion

On the basis of the fact that the ideal perovskite SrTiO_3 transforms to the tetragonally distorted modification at only 6 GPa, the expectation was that SrGeO_3 would transform to a distorted phase at a similarly low pressure, perhaps no higher than about 20 GPa. It is certainly possible that the splittings of the diffraction peaks that would be indicative of a transformation to a lower-symmetry variant could not be observed within the resolution of the diffraction experiment. Subsequently, however, extensive Raman spectroscopy of the SrGeO_3 sample at pressures to 75 GPa, did not reveal any indication of a phase transition [10]. It then became important to understand why SrTiO_3 and SrGeO_3 were so different.

A simple model can help to explain the very interesting results of the diffraction and spectroscopy experiments. The ideal perovskite framework of SrTiO_3 and SrGeO_3 may be represented by a 1-D chain of vertex-sharing octahedra. In this model, the potential for bending the TiO_6 or GeO_6 octahedra should exhibit the same easy tendency as that with which the respective perovskite frameworks may distort with pressure. Of course, it must be pointed out that in the real perovskite structures, a combination of twisting and tilting motions is responsible for the distortion of the parent structure to the tetragonal or orthorhombic forms [11]. In the full 3-D structures, however, these effects will simply be multiplied threefold, so the 1-D chain is expected to illustrate the important features of the twisting and tilting potential. The results of a series of semiempirical molecular orbital calculations

carried out with the extended Hückel method [12, 13] is illustrated in Fig. 2. For each chain, the crystal ionic radii [14] for Ti^{4+} , Ge^{4+} (both six-coordinate) and O^{2-} (two-coordinate) were used to define the interatomic distances in the vertex-sharing TiO_6 and GeO_6 chains. It is quite clear from Fig. 2 that the most important contribution to the much lower potential for the bending of the GeO_6 chain (much stiffer) than for the TiO_6 chain at the vertex-linking oxygen atom comes from the inclusion of empty 4d-orbitals on the Ge atom into the basis. The 3d orbitals on Ti, while energetically accessible, do not provide for effective overlap with the O 2p orbitals, thus making titanate compounds essentially ionic in nature and making the Ti-O-Ti linkage flexible and therefore susceptible to distortion. On the other hand, the empty 4d orbitals on Ge are larger and more diffuse than the 3d orbitals of Ti, making the overlap of Ge and O more covalent and making the Ge-O-Ge linkage more rigid and less susceptible to distortion.

SrGeO_3 perovskite, like CaSiO_3 perovskite, forms at high pressure from a framework structure composed of vertex-sharing tetrahedra. It appears that when these frameworks condense with dramatic decreases in volume to form perovskite structures, the phase that is formed has quite a different nature than an ambient-pressure ideal perovskite such as SrTiO_3 . Among the most important differences is the wide disparity in the covalency of the Ge-O and Ti-O bonds. While the octahedra themselves remain essentially intact and undistorted through the tilting and twisting motions required to form the distorted perovskite structures, the vertex-linking topology of the perovskite provides a flexible linkage whose resistance to bending varies widely with its covalency. In the silicate and germanate perovskites, high-pressure transformations to lower-symmetry structures must overcome the significantly enhanced covalency of the vertex-linked octahedral chain, a process that makes observable phase

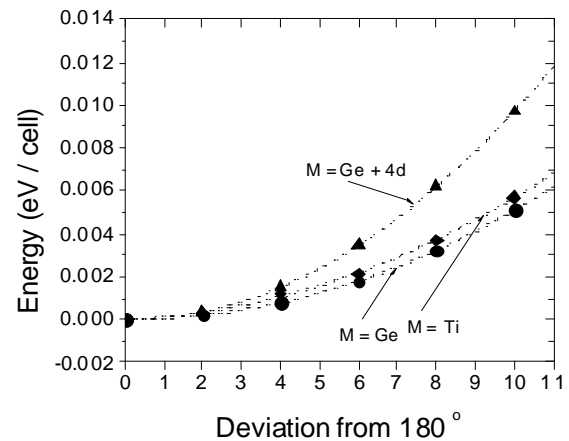


FIG. 2. Potential energy for bending the 1-D chain of MO_6 octahedra.

transformations unlikely. While the present results concern only the bending of the octahedral chain, similar overlap considerations will apply to the twisting motions as well.

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