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Article

High-Pressure Synthesis and Transport Properties of a New Binary Germanide, $SrGe_{6-\delta}$ ($\delta \cong 0.5$), with a Cagelike Structure

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A new germanide, $SrGe_{6-\delta}$ ($\delta \cong 0.5$), was synthesized by the reaction of Sr and Ge mixtures under a pressure of 5 GPa at 1200 °C. It crystallized in the orthorhombic space group *Cmcm* (No. 63) with $a = 4.0981(6)$ Å, $b = 11.159(1)$ Å, $c = 12.6825(8)$ Å, $V = 580.0(1)$ Å^3, and $Z = 4$. $SrGe_{6-\delta}$ is composed of a Ge covalent network having a cagelike structure and Sr atoms situated in the cages. Each Ge atom is coordinated by four neighboring Ge atoms. The coordination polyhedra are fairly distorted from an ideal tetrahedron, and the Ge network contains vacancies and disordering. The resistivity shows metallic behavior down to 2 K, and the positive thermoelectric power indicates the dominant carriers to be holes.

Introduction

For the purpose of synthesizing new types of intermetallic compounds having interesting structural and/or physical properties, the use of high-pressure and high-temperature reactions is a promising choice. New materials with unexpected features are often obtained in such extreme conditions. For example, a new germanide, $LaGe_5$, has been discovered by the reaction of constituent elements under 5 GPa and 1200 °C.[1] It has a novel germanium network composed of buckled sp^3 Ge layers. The layers are connected through further Ge atoms between the layers, and form tunnels, where La atoms are situated. It showed superconductivity with a critical temperature $T_c = 7.0$ K.

In the binary Ba−Si system, a new trigonal $BaSi_2$ phase was synthesized at 5.5 GPa and 400 °C.[2,3] It showed superconductivity with a T_c of 6.8 K.[4] Furthermore, high-pressure reactions produced two new silicon-rich phases, $Ba_{24}Si_{100}$ and $Ba_{8-x}Si_{46}$, which were obtained by reactions of $BaSi_2$ and Si at 800 °C under pressures of 1.5 and 3 GPa, respectively.[5−8] Their host networks are composed of large Si cages, and called clathrate compounds. $Ba_{8-x}Si_{46}$ is isotypic with well-known gas hydrates with the type I structure,[9,10] in which large Si_{20} and Si_{24} cages constitute the framework by sharing all faces, and contain Ba ions at their centers. It should be noted that $Ba_{8-x}Si_{46}$ is the first superconducting silicide having a Si sp^3 network with a T_c of 6−8 K.[6−8] Compounds having large cages filled with heavy atoms have recently been considered to be good candidates of new thermoelectric materials. This idea is known as the rattling mechanism proposed by Slack, Nolas, et al.[11,12] Some germanides having the type I clathrate structure have attracted much attention in light of this idea.[11,13]

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The results of the La−Ge and Ba−Si systems suggested that the high-pressure synthesis was useful for the preparation of Si/Ge-rich phases. As a matter of fact, no silicide with an atomic ratio of Si to Ba >2 was obtained by simple melting methods at ambient pressure. $BaSi_2$ had been the Si-richest compound in the binary Ba−Si system before the clathrate compounds were discovered. Similarly, only La-rich phases such as La_3Ge, La_5Ge_3, La_4Ge_3, La_5Ge_4, LaGe, and $LaGe_2$ had been reported before $LaGe_5$ was obtained.[14−18]

In the present work, we have studied the binary Sr−Ge system. So far, six Sr-rich compounds, Sr_2Ge, Sr_5Ge_3, SrGe, $Sr_{0.76}Ge$, $SrGe_2$ (trigonal), and $SrGe_2$ (orthorhombic), have been found in this system.[19−24] To prepare new Ge-rich phases, we have performed high-pressure and high-temperature reactions using arc-melted samples with Ge:Sr > 5.

Experimental Section

Synthesis. Mixtures of flakes of strontium metal (Katayama Chemical, 99.9%) and germanium (Katayama Chemical, 99.999%) with different molar ratios of Sr to Ge from 1:5 to 1:6 were subjected to reaction in an Ar-filled arc furnace. The silver metallic products obtained were ground in an Ar-filled glovebox, and then placed into h-BN cells (5 mm inner diameter and 5 mm depth). Each cell was put in a carbon tube heater, and was placed in a pyrophyllite cube as a pressure medium ($20 \times 20 \times 20$ mm^3). The details of the cell assembly were described elsewhere.[7] The cube was pressed at 5 GPa in a multianvil assembly and heated at 1200 °C for 30 min, followed by quenching to room temperature.

Characterization. X-ray powder diffraction (XRD) patterns were measured using a MacScience M18XHF diffractometer with graphite-monochromated Cu Kα radiation. The composition of the obtained germanide was determined on 12 single crystals with an electron probe microanalyzer, EPMA (JEOL JCMA-733II). A single crystal suitable for X-ray single-crystal structure analysis with dimensions of $0.08 \times 0.12 \times 0.04$ mm^3 was selected, and its intensity data were collected with a Rigaku R-AXIS imaging plate area detector using graphite-monochromated Mo Kα radiation. The structure was solved using the CrystalStructure crystallographic software package.[25]

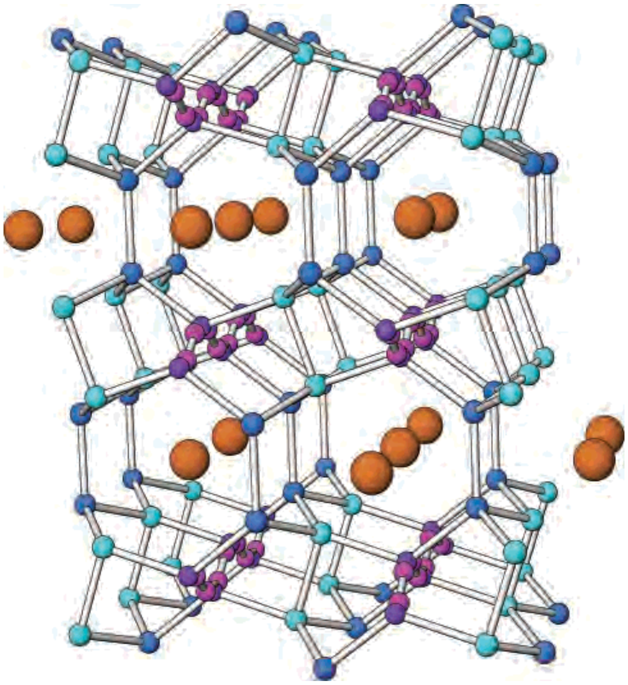

Figure 1. A crystal structure of $SrGe_{6-\delta}$ projected along the *a* axis. Sr atoms are shown as large orange balls. The Ge1, Ge2, Ge3a, and Ge3b sites are shown as blue, light blue, purple, and light purple balls, respectively.

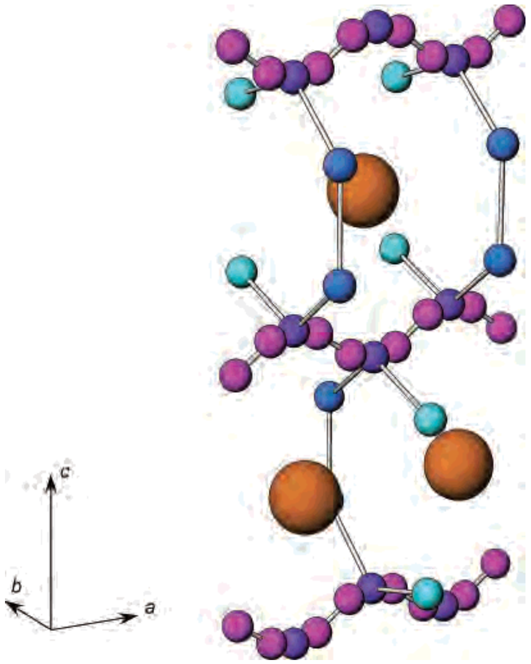

Figure 2. A partial structure of $SrGe_{6-\delta}$ showing the disorder of the Ge3 site. The Ge1, Ge2, Ge3a, and 3b sites are shown as blue, light blue, purple, and light purple balls, respectively. The Ge3a and 3b sites are dispersed on lines waving along the *a* axis.

Physical Properties Measurements. The temperature dependence of the electrical conductivity was measured by the van der Pauw method in a temperature range from room temperature to 2 K on a disk with 8 mm diameter and 1 mm thickness. The disk was sliced from the cylindrical product obtained from the starting mixture with the atomic ratio Sr:Ge = 1:5.5. The thermoelectric power measurement was performed on a bar-shaped sample of $1 \times 1 \times 5$ mm^3 by using the MMR Seebeck effect measurement system, with a temperature gradient of 2−5 K.

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Table 1. Crystallographic Data and Atomic Parameters of $\mathrm{SrGe}_{6-\delta}$[a]

atom	Wyckoff notation	x	y	z	B_{eq}	ocp	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr	4*c*	0	0.29364(9)	0.25	1.34(3)	1.0	0.0096(8)	0.0117(6)	0.0296(5)	0	0	0
Ge1	8*f*	0.5	0.07654(7)	0.15081(5)	0.94(2)	1.0	0.0103(6)	0.0143(5)	0.0109(3)	0	0	−0.0023(4)
Ge2	8*f*	0.5	0.46412(6)	0.09340(5)	1.01(2)	1.0	0.0109(3)	0.0162(5)	0.0114(3)	0	0	−0.0026(4)
Ge3a	8*f*	0.5	0.2517(3)	0.0351(3)	0.2(1)	0.29(1)						
Ge3b	16*h*	0.356(1)	0.2502(3)	0.0242(2)	1.36(9)	0.246(5)						

[a] Space group *Cmcm* (No. 63). Lattice constants $a = 4.0981$ (6) Å, $b = 11.159$ (1) Å, $c = 12.6825$ (8) Å, $V = 580.0($ 1) Å^3, and $Z = 4$. R/R_w ($I > 3\sigma(I)$) = 0.019/0.010 for 7127 reflections (396 unique peaks).

Table 2. Selected Interatomic Distances (Å) and Bond Angles (deg) in $\mathrm{SrGe}_{6-\delta}$

Ge1−Ge1	2.516(1)	Ge1−Ge2	2.510(1)	Ge1−Ge3a	2.444(4)	Ge1−Ge3b	2.585(3)
Ge2−Ge2	2.501(1)	Ge2−Ge3a	2.483(4)	Ge2−Ge3b	2.611(3)		
Ge1−Ge1−Ge2	106.86(2)	Ge2−Ge1−Ge2	109.41(4)				
Ge1−Ge2−Ge2	96.6(6)	Ge3a−Ge2−Ge2	91.4(9)				

Band Structure Calculation. Band calculations of SrGe_6 were performed using the WIEN2k package with a general potential LAPW code.[26] We used for all calculations $r_{\mathrm{MT}}k_{\max} = 7$, $l_{\max} = 10$, and $G_{\max}= 14$; r_{MT} of Sr and Ge is 2.0.

Results and Discussion

Synthesis and Structure of $\mathrm{SrGe}_{6-\delta}$. The arc-melted products were found to be mixtures of orthorhombic SrGe_2 and Ge. The mixtures changed into a new germanide by the high-pressure treatment of 5 GPa at 1200 °C. We obtained ingots of the new germanide which contained a small amount of Ge because of the Ge defect structure of this compound as discussed below. Single crystals of the new germanide with silver metallic luster were obtained from a crashed ingot prepared from the mixture of Sr:Ge = 1:5.5. The new germanide crystallized in the orthorhombic space group *Cmcm* (No. 63) with $a = 4.0981(6)$ Å, $b = 11.159(1)$ Å, $c = 12.6825(8)$ Å, $V = 580.0(1)$ Å^3, and $Z = 4$. The composition of the germanide determined on 12 single crystals by EPMA ranged from 5.43 to 5.86. This finding suggested that the germanide was a nonstoichiometric compound having Ge vacancies. The formula of this compound is, therefore, described as $\mathrm{SrGe}_{6-\delta}$ in this Article.

We can easily keep compositions of reaction systems by the high-pressure technique. The technique is, therefore, good for the preparation of compounds containing highly volatile components such as alkali, alkaline-earth, and rare-earth elements, sulfur, and bromine. In our previous studies, new compounds were obtained by this technique in silicide, sulfide, and halide systems. Some of them are polymorphs having denser structure than known compounds (SrS_3, HfNBr),[27,28] and some have new compositions quite different from those of the known phases; CeGe_3, LaGe_5, and $\mathrm{Ba}_{8-x}\mathrm{Si}_{46}$ are tetrel element rich phases.[1,6,7,29] $\mathrm{SrGe}_{6-\delta}$ is the Ge-richest phase in the binary Sr−Ge system, and high-pressure and high-temperature conditions successfully produced the Ge-rich phase as in the La−Ge and Ba−Si systems.

The structure of $\mathrm{SrGe}_{6-\delta}$ is shown in Figure 1. It has a cage structure composed of a Ge covalent framework. Sr atoms are situated in open spaces running parallel to the *a* axis. Each Sr atom is surrounded by 14 Ge atoms. $\mathrm{SrGe}_{6-\delta}$ is isotypic with a europium compound, $\mathrm{EuGa}_2\mathrm{Ge}_4$, having a gallium−germanium covalent network.[30,31] In the Eu compound the framework is composed of tetrahedrally coordinated Ga/Ge atoms, while the framework of $\mathrm{SrGe}_{6-\delta}$ is composed of Ge atoms only.

The crystallographic data and atomic parameters of $\mathrm{SrGe}_{6-\delta}$ are listed in Tables 1 and 2. There are four Ge sites, Ge1, Ge2, Ge3a, and Ge3b, which are assigned in Figure 1. In the structure of $\mathrm{EuGa}_2\mathrm{Ge}_4$, Ga and Ge atoms are not distributed in different sites, but occupy three sites, Ga/Ge1, Ga/Ge2, and Ga/Ge3, together. The Ga/Ge3 site in the Eu compound corresponds to the Ge3a site in $\mathrm{SrGe}_{6-\delta}$. The Ge3b site of $\mathrm{SrGe}_{6-\delta}$ is split off from the Ge3a site, and yields a disordered structure. The thermal vibrational parameters for these two disordering sites were refined isotropically in the structure refinement. A local structure of $\mathrm{SrGe}_{6-\delta}$ is shown in Figure 2 to show the disordering. The Ge3a and 3b sites are arranged in waves running along the *a* axis. Hereafter, we use the term “Ge3 sites/atoms” to designate the Ge3a and 3b sites/atoms together.

The Ge3a and 3b sites are too close to each other as shown in Figure 2 to be occupied at the same time. If the occupational parameters of these sites fulfill the condition of ocp(Ge3a) + 2(ocp(Ge3b)) = 1.0, the Ge3 site is fully occupied. We refined these occupational parameters without using any constraint, and obtained results showing about 70% and 75% of Ge atoms on the Ge3a and 3b sites were vacant, respectively. Therefore, the Ge host network includes Ge vacancies. The value of δ in $\mathrm{SrGe}_{6-\delta}$ was calculated to be 0.44 from the refined occupational parameters. This composition is in good agreement with the result of EPMA.

Structural Comparison with Other Binary Germanides. The structure of $\mathrm{SrGe}_{6-\delta}$ is compared with those of LaGe_5 and SrGe_2 in Figure 3. The three structures are

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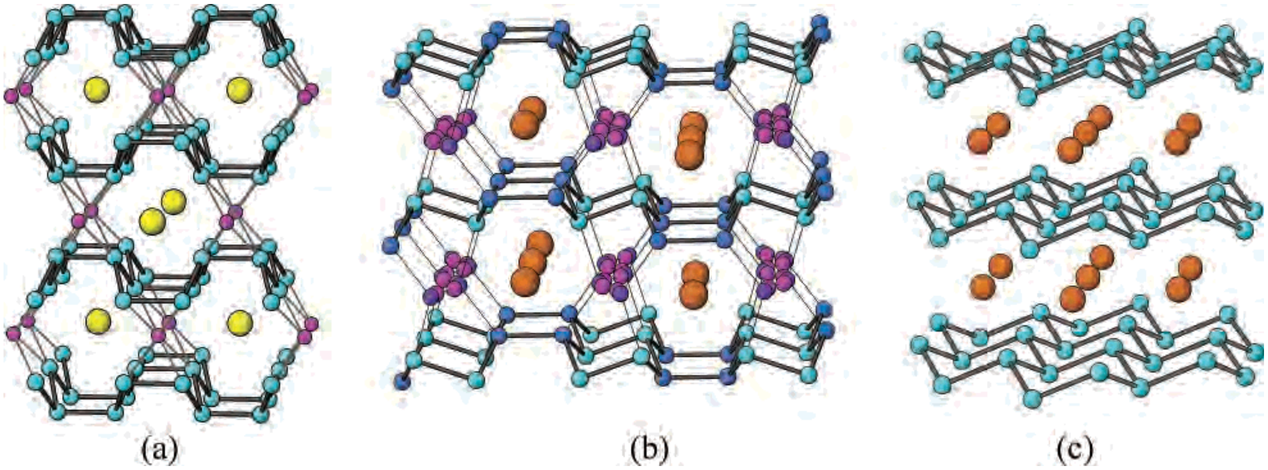

Figure 3. Comparison of the structures of Ge layers in three germanides, (a) $LaGe_5$, (b) $SrGe_{6-\delta}$, and (c) $SrGe_2$. Yellow and orange balls show La and Sr atoms, respectively. The rest are Ge atoms. The layer of $LaGe_5$ is composed of six-membered Ge rings with boat-type style only. The layer in $SrGe_2$ is composed of the rings with a chair-type conformation. The $SrGe_{6-\delta}$ layers have a mediated structure including boat- and chair-type Ge_6 rings.

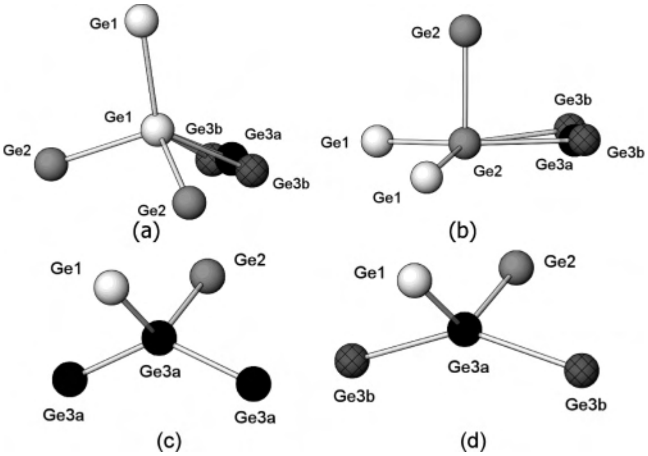

Figure 4. Local structures around the three Ge sites. Those of the Ge1 and Ge2 sites are presented in (a) and (b), respectively. For the Ge3a site, two extreme cases of coordinations are shown in (c) and (d) due to the disorder.

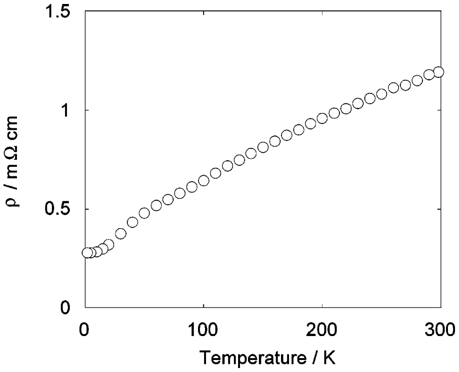

Figure 5. Temperature dependence of the electrical resistivity of $SrGe_{5.6}$.

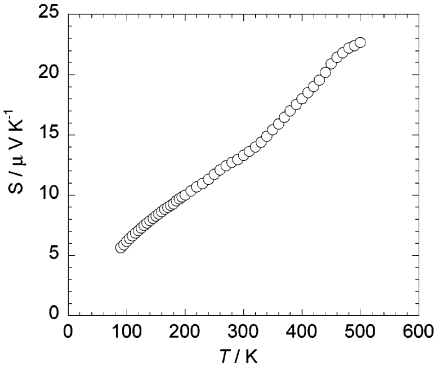

Figure 6. Temperature dependence of the thermoelectric power of $SrGe_{5.6}$ measured from 500 to 90 K.

closely related to each other because all the structures can be characterized by Ge sublayers composed of Ge six-membered rings with large cations sandwiched between the layers. It should be noted that these structures are different in the conformation of the rings. In Figure 3 intra- and interlayer Ge−Ge bonds are drawn as thick and thin bonds, respectively. The Ge sublayers in $LaGe_5$ are composed of six-membered rings in the boat conformation. In contrast, the rings of $SrGe_2$ have the chair conformation. The Ge sublayer of $SrGe_{6-\delta}$ is an intermediate one; six-membered rings in chair and boat conformations are alternately connected in the layer.

The Ge sublayers of $LaGe_5$ and $SrGe_{6-\delta}$ are connected via further Ge atoms and form three-dimensional Ge networks with large open spaces, in which large La^{3+}/Sr^{2+} cations reside. The interlayer Ge atoms in both structures seem to have special structural features. In $SrGe_{6-\delta}$, the Ge vacancies and disorder are observed only for the interlayer Ge sites. In $LaGe_5$ the interlayer Ge atoms have a higher coordination number of 8 and much longer Ge−Ge bond distances than the Ge atoms in the layers. These observations probably suggest that the interlayer Ge sites are relatively unstable, and feel more structural stress than the intralayer Ge sites.

Local Structure of $SrGe_{6-\delta}$. Figure 4 shows the local structures around the three different Ge sites. The Ge1 atom is bonded with one Ge1 atom, two Ge2 atoms, and one disordered Ge3 atom as shown in Figure 4a. Bond distances of 2.516 and 2.510 Å are observed for Ge1−Ge1 and Ge1−Ge2 bonds, respectively. These are comparable to the Ge−Ge distances of 2.477−2.591 Å observed in $Ba_{24}Ge_{100}$ clathrate compound, which is composed of sp^3 Ge.[20−22] The

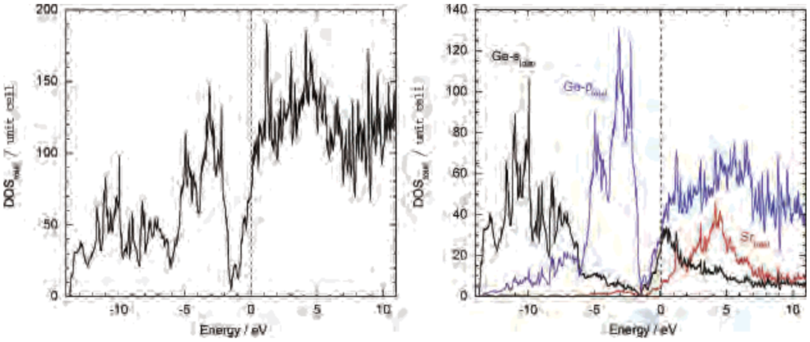

Figure 7. Total (a) and partial (b) DOS of $SrGe_6$. The Fermi level (0 eV) is shown by broken lines. In the partial DOS, Sr_{total}, Ge-s_{total}, and Ge-p_{total} are presented as red, black, and blue lines, respectively.

Ge−Ge distances in germanides are usually longer than those of the diamond Ge, because Ge becomes somehow negative due to electron donation from its countercations. Since the value of the Ge−Ge distance in the diamond Ge is 2.44 Å, the bond distance of 2.444 Å for Ge1−Ge3a is quite short for germanides. In contrast, the distance of 2.585 Å for the Ge1−Ge3b bond is a typical value in germanides. The fact that the Ge3a site is too close to the Ge1 site is possibly one reason the Ge3 site shows disorder.

The Ge2 atom is bonded with two Ge1 atoms, one Ge2 atom, and one Ge3 atom as shown in Figure 4b. The coordination polyhedron around the Ge2 site is not a tetrahedron but almost a trigonal pyramid. Bond angles of Ge1−Ge2−Ge2 and Ge3a−Ge2−Ge2 are 96.6° and 91.4°, respectively. The Ge2 atom is situated almost on the plane defined by the Ge1−Ge1−Ge3 atoms. The bond distances around the Ge2 atom are in the range 2.483−2.611 Å.

The Ge3a atom is tetrahedrally coordinated with one Ge1 atom, one Ge2 atom, and two Ge3 atoms. Two typical cases of local coordination structures around the Ge3a sites are shown in Figure 4c,d. The Ge3a−Ge3a bond distance of 2.235 Å is too short for the Ge−Ge bonding. The displacement of some Ge atoms from the Ge3a site to the Ge3b site yields longer Ge3a−Ge3b bonds with a distance of 2.746 Å. The structural tension around the Ge3a site is, therefore, relieved by this displacement. This structural misfit of the Ge3a site is probably a main cause of the Ge disordering.

Transport and Thermoelectric Properties of $SrGe_{5.6}$. The electrical resistivity of $SrGe_{5.6}$ decreased with decreasing temperature as shown in Figure 5. The residual resistivity was 0.28 mΩ cm, and the resistivity ratio $\rho(300\ K):\rho(2\ K)$ was approximately 4. The resistivity curve of $SrGe_{5.6}$ was quite similar to that of isotypic $EuGa_2Ge_4$.[30] The Eu compound showed resistivities of 0.7 and 0.25 mΩ cm at 300 and 2 K, respectively.

The positive thermoelectric power shown in Figure 6 indicates that the charge carriers are primarily holes. The thermoelectric power of 13 μV/K at room temperature is much smaller than that of 40 μV/K for $EuGa_2Ge_4$.[30] According to the rattling mechanism or the concept known as "phonon glass electron crystals" by Slack et al., compounds having large cages filled with heavy atoms can be promising candidates for new types of thermoelectric materials. Although $SrGe_{6-\delta}$ has such a cage structure, its thermoelectric power is not high enough for thermoelectric applications.

To examine the electrical structure of this compound, we performed the band structure calculation. Though the compound is nonstoichiometric, calculations of the density of state (DOS) were performed on the stoichiometric $SrGe_6$ having no Ge disorder. The Sr, Ge1, Ge2, and Ge3a sites were used in the calculation. The resulting DOS diagrams are presented in Figure 7.

In the model structure, all Ge atoms fulfill the octet rule even if no electrons are doped by Sr atoms, because each Ge atom has four covalent bonds with neighboring Ge atoms. The total DOS diagram in Figure 7 shows that $SrGe_6$ is a metal. A region where the density of state is low can be seen at around −1.5 eV in the diagram, which corresponds to the top of the valence band composed predominantly of Ge 3p orbitals. When the composition of the sample is $SrGe_{5.6}$, which was the composition determined by the single-crystal X-ray analysis, the electron counting for this compound is approximately in the following manner. Each Sr atom donates two electrons to the Ge network, whereas one Ge vacancy consumes four electrons to form four lone pairs of neighboring four Ge atoms. Hence, almost all the electrons from Sr atoms are consumed by the 0.5 Ge vacancy per Sr atom. If the rigid band model is assumed, the Fermi level of $SrGe_{5.6}$ would be actually close to the position at −1.5 eV. This is possibly a reason $SrGe_{5.6}$ did not show good conductivity.

Concluding Remarks

High-pressure and high-temperature reactions of $SrGe_2$ and Ge yielded a new binary germanide, $SrGe_{6-\delta}$, which is the Ge-richest phase in the Sr−Ge system. It is composed of a Ge covalent network having a cagelike structure. Sr ions are situated in the cages. The network has a Ge sublayers composed of six-membered rings with chair and boat conformations, and is composed of four-bonded Ge atoms with Ge−Ge−Ge angles fairly distorted from the ideal tetrahedral one. Probably due to the strain by the distortion, the germanide was nonstoichiometric, and contained Ge vacancies. $SrGe_{6-\delta}$ showed a metallic behavior from room temperature to 2 K as predicted by the band calculation. The positive thermoelectric power indicates that charge carriers are predominantly holes in this compound.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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