Variable-temperature single-crystal X-ray diffraction study of SrGeO₃ high-pressure perovskite phase

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Single-crystal X-ray diffraction analysis of a high-pressure cubic perovskite SrGeO₃ was conducted for a temperature range of 100 to 473 K. The crystal structure begins to deteriorate at a temperature higher than 323 K and completely amorphizes by 448 K. Structure refinements in a range of 100 to 323 K show that the displacement ellipsoid of the O atom is considerably suppressed in the direction of the Ge–O bond and that its mean square displacement (MSD) in this direction is almost temperature-independent. In contrast, that in the direction perpendicular to the bond largely increases with the temperature. The Debye temperatures for each constituent atom were determined by applying the Debye model to the temperature dependence of its MSDs. The one-particle potential (OPP) coefficient evaluated from the resulting Debye temperature of the Ge atom is significantly larger than those of the Sr and O atoms. Moreover, the OPP coefficients of the O atom are significantly larger in the direction of the Ge–O bond than in the directions perpendicular to the bond. These results are concordant with our previous finding that the Ge–O bond is largely covalent. The high covalency can have a large influence on the temperature dependence of the thermal vibration of the O atom.

Keywords: SrGeO₃ perovskite, High-pressure phase, Single-crystal X-ray diffraction, Debye temperature, One-particle potential

INTRODUCTION

Perovskite-type compounds ABO₃ and their derivatives, including ferroelectric substances such as BaTiO₃ (Nakatani et al., 2016) and PbTiO₃ (Yoshiasa et al., 2016), are one of the most widely used materials for technological applications owing to their functional properties. In particular, the high-pressure perovskite phase of SrGeO₃ has attracted significant attention in materials science as a novel transparent electronic conductor (Mizoguchi et al., 2011). SrGeO₃ undergoes a sequence of phase transitions under high pressure and temperature: pyroxenoid (pseudowollastonite) type → walstromite type → perovskite type (Shimizu et al., 1970; Akaogi et al., 2005). The perovskite phase crystallizes in a cubic structure with a space group of Pm̅3m (Fig. 1) and is important in earth science as a potentially good low-pressure analog of the CaSiO₃ cubic perovskite, a constituent mineral in the Earth’s lower mantle. Recently, we successfully synthesized single-crystals of the SrGeO₃ perovskite phase at high-pressure and temperature conditions and carried out single-crystal X-ray diffraction (XRD) analyses at 296 K (Nakatsuka et al., 2015a) and 100 K (Nakatsuka et al., 2017). A comparison of the structure-refinement results between the two temperatures showed that the high covalency of the Ge–O bond largely restricts the thermal vibration of the O atom and can have a large influence on its temperature dependence. However, an atomic thermal motion analysis at a larger number of temperature points is necessary for a better quantitative estimation of the correlation between the bonding nature and thermal vibration. The analysis enables to evaluate the one particle potentials (OPP) for each constituent atom, which are an indicator of the interatomic interaction with neighboring atoms. For this purpose, in the present study, we perform variable-temperature single-crystal XRD of SrGeO₃ perovskite.

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EXPERIMENTS AND ANALYSIS

Single crystals of SrGeO₃ perovskite grown at 6 GPa and 1223 K using a 700-ton cubic anvil-type press in our previous study (Nakatsuka et al., 2015a) were employed in the present study. The detailed procedure of the high-pressure experiment is presented in Nakatsuka et al. (2015a). A single-crystal with dimensions of 0.10 × 0.09 × 0.09 mm³, different from that reported in Nakatsuka et al. (2015a), was placed into a silica-glass capillary for the XRD experiments. The experiments were carried out in the range of 100 to 473 K using a four-circle diffractometer (Rigaku AFC-7R) with a graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å) at operating conditions of 60 kV and 250 mA. The experiments below room temperature were carried out by directly cooling the crystal through a continuous cold-N₂ gas flow generated by a low-temperature apparatus (Rigaku GN2). In the experiments above room temperature, the crystal was directly heated by a continuous flow of N₂ gas heated by an electric resistance heater. Prior to the data collections, the sample temperatures were calibrated using a K-type thermocouple set exactly at the sample position. The fluctuation of the sample temperature was maintained within ±0.2 K during the data collection. XRD intensity data within 2° ≤ 2θ ≤ 120° were collected at 7 temperature-points in the range up to 323 K, in which the crystallinity was preserved, using the continuous ω-2θ scan mode. A total of 521 reflections were measured at each temperature. The unit-cell parameters were determined by the least-squares method from a set of 25 reflections within a range of 43° ≤ 2θ ≤ 50°. The intensity data were corrected for Lorentz-polarization factors and absorption effects (ψ-scan method). After these corrections, the intensity data were averaged in Laue symmetry m3̅m to provide 116 independent reflections at each temperature. Among them, the independent reflections with F₀ ≤ 3σ(F₀) were eliminated. Even if independent reflections had intensities of F₀ > 3σ(F₀) after averaging, those averaged from the dataset of equivalent reflections including reflection(s) with F₀ ≤ 3σ(F₀) were also discarded as these reflections were potentially affected by multiple scattering. Moreover, independent reflections with (sinθ)/λ < 0.229 Å⁻¹ were eliminated to reduce secondary extinction effects and to avoid dependence on atomic charge as far as possible in the choice of atomic scattering factors. Finally, 60–63 independent reflections were used in the refinements at each temperature. The internal residuals of the equivalent reflections (Rᵢ) varied between 0.0237 and 0.0277 at each temperature.

The structure refinements were carried out by minimizing the function ∑ w(|F₀| - |Fₐ|)² using the full-matrix least-squares program RADY (Sasaki, 1987). The scattering factors of Sr²⁺, Ge⁴⁺ (International Tables for Crystallography Volume C, 1992), and O²⁻ (Tokonami, 1965) were used. Anomalous dispersion coefficients for
Table 1. Summary of data collection and refinement parameters

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<thead>
<tr>
<th>Temperature (K)</th>
<th>100</th>
<th>123</th>
<th>173</th>
<th>223</th>
<th>273</th>
<th>298</th>
<th>323</th>
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<td>Cubic</td>
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<tr>
<td>Space group</td>
<td>Pm3m</td>
<td>Pm3m</td>
<td>Pm3m</td>
<td>Pm3m</td>
<td>Pm3m</td>
<td>Pm3m</td>
<td>Pm3m</td>
</tr>
<tr>
<td>(a (\text{Å}))</td>
<td>3.7921(6)</td>
<td>3.7922(5)</td>
<td>3.7930(4)</td>
<td>3.7946(3)</td>
<td>3.7963(3)</td>
<td>3.7974(3)</td>
<td>3.7988(4)</td>
</tr>
<tr>
<td>(V (\text{Å}^3))</td>
<td>54.53(1)</td>
<td>54.53(1)</td>
<td>54.57(1)</td>
<td>54.64(1)</td>
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<td>2(\theta_{\text{max}}) (°)</td>
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<td>120</td>
<td>120</td>
<td>120</td>
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<td>120</td>
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<tr>
<td>No. of measured reflections</td>
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<td>521</td>
<td>521</td>
<td>521</td>
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<td>No. of independent reflections</td>
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<td>116</td>
<td>116</td>
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<tr>
<td>No. of observed independent reflections ([F_o &gt; 3\sigma(F_o)])</td>
<td>64</td>
<td>65</td>
<td>64</td>
<td>66</td>
<td>63</td>
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<td>63</td>
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<tr>
<td>(R_{\text{int}})</td>
<td>0.0277</td>
<td>0.0276</td>
<td>0.0245</td>
<td>0.0237</td>
<td>0.0270</td>
<td>0.0250</td>
<td>0.0262</td>
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<tr>
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<td>61</td>
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<td>61</td>
<td>63</td>
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<tr>
<td>No. of parameters</td>
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<td>6</td>
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<tr>
<td>(R)</td>
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<td>0.0086</td>
<td>0.0135</td>
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<tr>
<td>(wR)</td>
<td>0.0053</td>
<td>0.0055</td>
<td>0.0083</td>
<td>0.0078</td>
<td>0.0093</td>
<td>0.0059</td>
<td>0.0093</td>
</tr>
</tbody>
</table>

Table 2. Refined equivalent isotropic displacement parameters \(U_{eq} (\text{Å}^2)\) and anisotropic displacement parameters \(U_{ij} (\text{Å}^2)\)

| Positional parameters: (0, 0, 0) for Sr, (0.5, 0.5, 0.5) for Ge, (0, 0.5, 0.5) for O. Constraints for anisotropic atomic displacement parameters: \(U_{12} = U_{13} = U_{23} = 0\) for O. |
|---|---|---|---|---|---|---|---|
| \(T (\text{K})\) | 100 | 123 | 173 | 223 | 273 | 298 | 323 |
| Sr (1a) \(U_{eq}\) | 0.00204(6) | 0.00236(6) | 0.00286(10) | 0.00360(9) | 0.00490(15) | 0.00487(8) | 0.00505(15) |
| Ge (1b) \(U_{eq}\) | 0.00103(6) | 0.00116(6) | 0.00166(10) | 0.00203(9) | 0.00237(13) | 0.00243(8) | 0.00268(13) |
| O (3c) \(U_{33}\) | 0.0021(5) | 0.0019(5) | 0.0020(8) | 0.0026(7) | 0.0023(9) | 0.0021(6) | 0.0036(9) |
| \(U_{22}\) | 0.0038(3) | 0.0042(3) | 0.0050(5) | 0.0056(5) | 0.0070(7) | 0.0078(4) | 0.0077(7) |
| \(U_{eq}\) | 0.0033(4) | 0.0034(4) | 0.0040(6) | 0.0046(6) | 0.0054(7) | 0.0059(5) | 0.0064(7) |

RESULTS AND DISCUSSION

Thermal expansion and thermal stability

Figure 2 shows the temperature dependence of the obtained unit-cell parameter \(a\) and unit-cell volume \(V\). The \(a\) and \(V\) monotonously increase with the temperature up to 323 K. The volumetric thermal expansion coefficient \(\langle aV\rangle\) was calculated from the fits to the linear equation: \(V(T) = V_r(1 + \langle aV\rangle(T - T_r))\), where \(V_r\) is the unit-cell volume at a reference temperature \(T_r\) (298 K in the present study). The obtained value is \(\langle aV\rangle = 2.4(1) \times 10^{-5} \text{K}^{-1}\), which is comparable to those of other cubic perovskites [e.g., \(2.59 \times 10^{-5} \text{K}^{-1}\) (Itoh et al., 1994) and \(3.23(2) \times 10^{-5} \text{K}^{-1}\) (Ligny and Richet, 1996) for SrTiO3].

On the other hand, Figure 3 shows that the diffraction peaks begin to broaden at a temperature higher than 323 K and completely disappear by 448 K. This observation agrees well with the results of Andrault et al. (1996), who reported that the SrGeO3 perovskite, metastable at ambient pressure, amorphized near 500 K and that the amorphous phase began to recrystallize to the thermodynamically stable pseudowollastonite phase at a higher temperature. A similar observation was reported for the CaGeO3 orthorhombic perovskite, which amorphizes near 923 K (Durben et al., 1991; Nakatsuka et al., 2015b).

Temperature dependence of mean-square displacements (MSDs) of atoms

The site-symmetry constraints require that the displace-
ment ellipsoids of the Sr and Ge atoms are spherical, whereas that of the O atom is a uniaxial ellipsoid with one determinable ellipsoid axis in the direction of the Ge–O bond and two undeterminable axes in the directions perpendicular to the bond. Figures 4 and 5 show the temperature dependence of the equivalent isotropic displacement parameter $U_{eq}$ for each atom and MSD$_j$ of the O atom, respectively, where $U_{eq}$ corresponds to the MSD of the atom averaged over all directions. MSD$_j$ is the MSD in the direction of the displacement–ellipsoid axis $j$ for the O atom ($j = 1, 2, 3$); axis 1 is in the direction of the Ge–O bond, whereas axes 2 and 3 are in the directions perpendicular to the bond. The MSD determined by the diffraction method includes the contributions of both static and dynamic disorders, and can be described based on the Debye model (Willis and Pryor, 1975):

$$\text{MSD} = \langle u^2 \rangle_s + \langle u^2 \rangle_d$$

$$= \langle u^2 \rangle_s + \frac{3h^2T}{mk_B\Theta_D^2} \int_0^{\Theta_D} \frac{x}{\exp(x) - 1} dx + \Theta_D$$

$$= \langle u^2 \rangle_s + \frac{3h^2T}{mk_B\Theta_D^2} \int_0^{\Theta_D} \frac{x}{\exp(x) - 1} dx + \Theta_D$$

(1),

where $\langle u^2 \rangle_s$, the temperature–independent static disorder component; $\langle u^2 \rangle_d$, the temperature–dependent dynamic disorder component; $m$, the mass of the atom; $k_B$, the Boltzmann constant; $h$, the reduced Planck constant; $\Theta_D$, the Debye temperature; $T$, the absolute temperature.

A nonlinear least-squares fitting of the $U_{eq}$ or MSD$_j$ data to Equation (1) (Debye model fitting) enables to evaluate $\langle u^2_{eq} \rangle_s$ and $\Theta_D$, or $\langle u^2_j \rangle_s$ and $\Theta_D$, where $\langle u^2_{eq} \rangle_s$ and $\Theta_D$, determined from the $U_{eq}$ data, are the static disorder component and Debye temperature averaged over all directions, respectively, $\langle u^2_j \rangle_s$ and $\Theta_D$, determined from the MSD$_j$ data, are the static disorder component and Debye temperature in the direction of the displacement–ellipsoid axis $j$, respectively.

The temperature dependence of $U_{eq}$ for each atom (Fig. 4) and MSD$_j$ for the O atom (Fig. 5) is well represented by the Debye model in the investigated temperature range. The resulting $\langle u^2_{eq} \rangle_s$ values are: $0.6(8) \times 10^{-4}$ Å$^2$ for Sr, $-3(1) \times 10^{-4}$ Å$^2$ for Ge, and $-5(5) \times 10^{-4}$ Å$^2$ for O, which can be regarded as zero within an error of 3σ. Therefore, we can consider that the static disorder is not present in each atom. The Debye model fitting
was performed by fixing \( \langle u_{eq}^2 \rangle_s = 0 \) or \( \langle u_i^2 \rangle_s = 0 \). The final \( \Theta_D \) values are presented in Table 3.

Assuming a harmonic OPP, \( V_{\text{OPP}}(u) = (q/2)\langle u^2 \rangle_d \) (Willis and Pryor, 1975), the OPP coefficient \( q \), corresponding to the force constant, is related to the Debye temperature \( \Theta_D \) (Nakatsuka et al., 2015b):

\[
q = -\frac{mk_D^2 \Theta_D^2}{3h^2} \tag{2}
\]

The increment in \( q \) indicates an enhancement in bonding stiffness. Upon substitution of \( \Theta_{D,eq} \) for \( \Theta_D \) in Equation (2), we can obtain the OPP coefficient, \( q_{eq} \), averaged over all directions. The calculated \( q_{eq} \) values are: 5.4(1) eV·Å\(^{-2} \) for Sr, 11.2(2) eV·Å\(^{-2} \) for Ge, and 5.2(1) eV·Å\(^{-2} \) for O. These values increase in the order of: O < Sr < Ge, which shows that the OPP of Ge is significantly narrower than that of Sr. Our previous study (Nakatsuka et al., 2015a) indicated that in the SrGeO\(_3\) perovskite, the 12-fold coordinated Sr-O bond and sixfold coordinated Ge-O bond have covalencies of 20.4 and 48.9%, respectively. Therefore, the magnitude relation of the \( q_{eq} \) values between Sr and Ge is reasonably consistent with that between the bonding stiffnesses of the Sr-O and Ge-O bonds expected from their bonding nature.

Figure 5 indicates that in the investigated temperature range, the displacement ellipsoid of the O atom is remarkably anisotropic and considerably suppressed in the direction of the Ge-O bond. As an example, the displacement ellipsoids at 298 K are shown in Figure 6. The MSD of the O atom in the direction of the Ge-O bond is almost temperature-independent, whereas that in the direction perpendicular to the bond largely increases with the temperature (Fig. 5). This result confirms the prediction of Nakatsuka et al. (2017), who inferred the temperature dependence of the MSD of the O atom by comparison between previously reported refinement results at 296 and 100 K. Such peculiar temperature dependence of the O atom will originate in strong interactions with

### Table 3. Debye temperatures (K) determined from the Debye model fitting

<table>
<thead>
<tr>
<th></th>
<th>Sr</th>
<th>Ge</th>
<th>O</th>
</tr>
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<tbody>
<tr>
<td>( \Theta_{D,eq} )</td>
<td>324(3)</td>
<td>511(6)</td>
<td>738(6)</td>
</tr>
<tr>
<td>( \Theta_{D,1} )</td>
<td>—</td>
<td>—</td>
<td>1175(61)</td>
</tr>
<tr>
<td>( \Theta_{D,2} )</td>
<td>—</td>
<td>—</td>
<td>644(7)</td>
</tr>
<tr>
<td>( \Theta_{D,3} )</td>
<td>—</td>
<td>—</td>
<td>644*</td>
</tr>
</tbody>
</table>

* \( \Theta_{D,1} = \Theta_{D,3} \)

Figure 4. Temperature dependence of \( U_{eq} \). The solid curves represent the Debye model fitting.

Figure 5. Temperature dependence of the MSD for the O atom. The solid curves represent the Debye model fitting.

Figure 6. Unit cell of the SrGeO\(_3\) perovskite at 298 K with displacement ellipsoids drawn at a probability level of 80%.
adjacent Ge atoms, forming rigid bonds with the O atom. For a better estimation of the bonding stiffness, we evaluate the anisotropic OPP coefficients $q_i$ of the O atom by substituting its $\Theta_D$ for $\Theta_0$ in Equation (2), where $q_i$ is the OPP coefficient of the O atom in the direction of its displacement-ellipsoid axis $i$. The obtained OPP coefficients of the O atom are: $q_1 = 13(1) \text{ eV} \cdot \text{Å}^{-2}$ in the direction of the Ge–O bond and $q_2 = 3.9(1) \text{ eV} \cdot \text{Å}^{-2}$ in the directions perpendicular to the bond. The former value is significantly larger than the latter value, which indicates that the Ge–O bond is largely rigid.

As reported in our previous study (Nakatsuka et al., 2015a), the sixfold-coordinated Ge–O bond in the SrGeO$_3$ perovskite has a high covalency comparable to those of the fourfold-coordinated Si–O bonds in silicates of approximately 50%. As a supportive observation, in our recent study (Nakatsuka et al., 2017), we successfully detected the residual electron density peaks originating in the bonding electrons of the Ge–O bonds in the difference Fourier map at 100 K. The peculiar temperature dependence of the thermal vibration of the O atom observed in Figure 5 can be attributed to the high covalency of the Ge–O bond.

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REFERENCES


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