Ce₄Ag₃Ge₄O₀.₅ – chains of oxygen-centered [OCe₂Ce₂/₂] tetrahedra embedded in a [CeAg₃Ge₄] intermetallic matrix

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The oxidation of an intermetallic phase under high-pressure/high-temperature conditions led to the synthesis of Ce₄Ag₃Ge₄O₀.₅ exhibiting [OCe₂Ce₂/₂] tetrahedral chains, in which the oxygen atoms statistically occupy the tetrahedral centres. Starting from a 1 : 1 : 1 CeAgGe precursor (NdPtSb type), a multianvil high-pressure/high-temperature experiment at 11.5 GPa and 1250–1300 °C revealed Ce₄Ag₃Ge₄O₀.₅, crystallizing in the space group Pnma with the following lattice parameters: a = 2087.3(4), b = 439.9(1), and c = 1113.8(2) pm. Magnetic measurements showed Curie–Weiss behavior above 100 K with an experimental magnetic moment of 2.42 μB per Ce atom, close to the value for the free Ce³⁺ ion, clearly indicating trivalent cerium in Ce₄Ag₃Ge₄O₀.₅. Full potential GGA+U band structure calculations resulted in metallic properties and a magnetic ground state with one unpaired 4f-electron per cerium in agreement with the experiments.

Introduction

In contrast to the large variety of intermetallic compounds prepared under ambient pressure conditions, the number of high-pressure intermetallics is very low. The investigations are mostly limited to binary systems, presenting a series of new insights into the chemical bonding and electronic effects of high-pressure application.¹ With the successful high-pressure synthesis of the stannides HP-RePTsn (RE = La, Ce, Pr, Nd, Sm) and HP-CePdSn, we recently extended the research into the area of ternary systems.²–⁵ Now, we report the first example of an oxidation of an intermetallic phase under high-pressure/high-temperature conditions, leading to a new germanide oxide with the composition Ce₄Ag₃Ge₄O₀.₅.

The oxidation of intermetallic phases to metal oxides under ambient pressure conditions is well known from the research of Hoppe, Yvon, Schuster, and Jung.⁶–¹⁴ But only a few intermetallic oxides were established, in which crystal structure considerations and chemical analysis revealed the presence of significant oxygen concentrations. For example, the phases RE₁₂Fe₃₂Oₓ with x ≤ 2 (RE = Y, Gd, Tb, Dy, Ho, and Er)¹⁵ and Zr₃NIO¹⁶ represent oxygen-stabilized transition metal intermetallic compounds with octahedrally coordinated oxygen atoms. Furthermore, several Nowotny phases of D₈₈ type structure were stabilized by the presence of small amounts of carbon, boron, oxygen, or nitrogen.¹⁷–¹⁹ While the former mentioned phases were synthesized under ambient pressure conditions, the germanide oxide Ce₄Ag₃Ge₄O₀.₅ was synthesized under high-pressure/high-temperature conditions, starting from NdPtSb type CeAgGe²⁰–²² as a precursor compound. Since elemental silver has been detected in the X-ray powder diagram of the reaction product, the following reaction scheme under the conditions of 11.5 GPa and 1300 °C can be formulated:

$$4\text{CeAgGe} + \frac{1}{4}\text{O}_2 \rightarrow \text{Ce}_4\text{Ag}_3\text{Ge}_4\text{O}_{0.5} + \text{Ag}.$$  

The amount of oxygen needed derives from diffusion, leaking out of the experimental surroundings (oxygen containing ceramics) at temperatures exceeding 1200 °C and from surface oxidation of the milled precursor.

Thus, the structure of Ce₄Ag₃Ge₄O₀.₅ nicely extends the crystal chemistry of the large family of pnictide oxides.²³,²⁴
Experimental

Synthesis

Starting materials for the synthesis of the CeAgGe precursor were ingots of the rare earth metal (Treibacher, 99.8%), silver wire (Degussa-Hüls, 99.9%), and a germanium bar (Wacker, 99.9%). Details of the precursor preparation can be found in the original work.22

The high-pressure/high-temperature synthesis of the new compound Ce₄Ag₃Ge₄O₀.₅ took place via a multianvil Walker type module. Carefully milled CeAgGe powder was filled into a boron nitride crucible of the high-pressure assembly. A precast MgO octahedron (Ceramic Substrates & Components, Isle of Wight, UK) with an edge length of 14 mm was used as a pressure medium. Eight tungsten carbide cubes (TSM 10, Ceratizit, Austria) with a truncation of 8 mm, separated by pyrophyllite gaskets, compressed the octahedron (14/8 assembly). Details of the technique for the construction of the different assemblies can be found in ref. 25.

The intermetallic precursor was compressed to a pressure of 11.5 GPa in 3.5 hours and heated to 1250–1300 °C in the following 10 min. After maintaining this temperature for 10 min, the sample was cooled down to 900 °C in 1 min. To enhance the crystallinity of the sample, an annealing period of five hours followed, accomplished by a slow decrease of the temperature from 900 to 700 °C. Afterwards, the sample was cooled down to room temperature within 1 min. After decompression (10.5 hours), the recovered experimental octahedron was broken apart and the sample was carefully separated from the surrounding boron nitride.

The polycrystalline sample of Ce₄Ag₃Ge₄O₀.₅ is silvery with metallic luster and is stable in moist air over weeks. Powdered samples are dark grey. As a by-product during the various syntheses of Ce₄Ag₃Ge₄O₀.₅ we observed a few times the phase Ce₃Ag₄Ge₄. Precise structural data of this phase derived from single crystal structure determination are also presented in this paper.

Several phases seem to be stable in a small area of the ternary phase diagram. A third compound with a 1:2:2 stoichiometric ratio appeared occasionally in this system. The intermetallic precursor was compressed to a pressure range from 7.5 GPa to 11.5 GPa and was always stoichiometric ratio appeared occasionally in this system. The formation of this phase was generally observed at lower pressures from 7.5 GPa to 11.5 GPa and was always accompanied by the formation of Ce₄Ag₃Ge₄. Experiments without annealing period revealed traces of the starting material CeAgGe. The herein presented phase Ce₄Ag₃Ge₄O₀.₅ was also synthesized at pressures up to 13.5 GPa. Synthesis temperatures may vary from 1100 to 1300 °C resulting in different degrees of crystallinity of Ce₄Ag₃Ge₄O₀.₅.

X-ray crystallography

Intensity data of suitable crystals of Ce₄Ag₃Ge₄O₀.₅ and Ce₃Ag₄Ge₄ were collected at room temperature on an Enraf–Nonius Kappa CCD diffractometer (Bruker AXS/Nonius, Karlsruhe) with MoKα-radiation (λ = 71.073 pm) equipped with a rotating anode. Structure solution and parameter refinement (full-matrix least squares against F²) were successfully performed using the SHELX-97 software suite.26–29 An absorption correction based on multi-scans29 was applied to the data set. To check for the deviations from the ideal compositions, the occupancy parameters were refined in separate series of least-squares cycles. All relevant crystallographic data and details of the data collections are listed in Tables 1–4.

Further details of the single crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany [Fax: +49-7247-808-666; E-mail: data_request@fiz-karlsruhe.de].

### Table 1 Crystallographic data and structure refinements of Ce₄Ag₃Ge₄O₀.₅ and Ce₃Ag₄Ge₄

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ce₄Ag₃Ge₄O₀.₅</th>
<th>Ce₃Ag₄Ge₄</th>
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</thead>
<tbody>
<tr>
<td>Mw</td>
<td>1182.5</td>
<td>1142.2</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pnma</td>
<td>Immm</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα</td>
<td>MoKα</td>
</tr>
<tr>
<td>a/pm</td>
<td>(λ = 71.073 pm)</td>
<td>(λ = 71.073 pm)</td>
</tr>
<tr>
<td>h/pm</td>
<td>439.9(3)</td>
<td>713.36(6)</td>
</tr>
<tr>
<td>c/pm</td>
<td>1113.8(2)</td>
<td>1464.79(9)</td>
</tr>
<tr>
<td>V/nm³</td>
<td>1.0228(3)</td>
<td>0.472(1)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>T/K</td>
<td>293(2)</td>
<td>293(2)</td>
</tr>
<tr>
<td>Dcalc/g cm⁻³</td>
<td>7.68</td>
<td>8.04</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.02 × 0.02 × 0.02</td>
<td>0.02 × 0.03 × 0.03</td>
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<td>μ/mm⁻¹</td>
<td>34.50</td>
<td>34.70</td>
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<td>3° &lt; θ &lt; 27.5°</td>
</tr>
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<td>Reflections collected</td>
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<td>527</td>
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<td>330 [0.0192]</td>
</tr>
<tr>
<td>Reflections with f &gt; 2o(f)</td>
<td>1503</td>
<td>306</td>
</tr>
<tr>
<td>Data/parameters</td>
<td>1986/75</td>
<td>330/23</td>
</tr>
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<td>Absorption correction</td>
<td>Multi-scan²₈</td>
<td>Multi-scan²₈</td>
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<td>GOF</td>
<td>1.045</td>
<td>1.149</td>
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<tr>
<td>R indices (f &gt; 2o(f))</td>
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<td>R₁ = 0.0202</td>
</tr>
<tr>
<td></td>
<td>wR₂ = 0.0430</td>
<td>wR₂ = 0.0417</td>
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<tr>
<td></td>
<td>R indices (all data)</td>
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<tr>
<td></td>
<td>wR₂ = 0.0467</td>
<td>wR₂ = 0.0430</td>
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<tr>
<td>Extinction coefficient</td>
<td>0.00012(2)</td>
<td>0.0005(1)</td>
</tr>
<tr>
<td>Larg. diff. peak and hole (e Å⁻³)</td>
<td>2.36/2.11</td>
<td>1.4/1.1</td>
</tr>
</tbody>
</table>

### Table 2 Atomic coordinates and isotropic displacement parameters (Å²) for Ce₄Ag₃Ge₄O₀.₅ and Ce₃Ag₄Ge₄. Ueq is defined as one-third of the trace of the orthogonalized Uij tensor. The 4c oxygen site is only half occupied

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Ueq</th>
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<tr>
<td>Ce₁</td>
<td>4c</td>
<td>0.21375(2)</td>
<td>1/4</td>
<td>0.45848(3)</td>
<td>0.0099(1)</td>
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<tr>
<td>Ce₂</td>
<td>4c</td>
<td>0.03195(2)</td>
<td>1/4</td>
<td>0.37003(3)</td>
<td>0.0102(1)</td>
</tr>
<tr>
<td>Ce₃</td>
<td>4c</td>
<td>0.39643(2)</td>
<td>1/4</td>
<td>0.36594(3)</td>
<td>0.0101(1)</td>
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<tr>
<td>Ce₄</td>
<td>4c</td>
<td>0.84974(2)</td>
<td>1/4</td>
<td>0.79251(3)</td>
<td>0.0115(1)</td>
</tr>
<tr>
<td>Ge₁</td>
<td>4c</td>
<td>0.71052(3)</td>
<td>1/4</td>
<td>0.70192(6)</td>
<td>0.0106(2)</td>
</tr>
<tr>
<td>Ge₂</td>
<td>4c</td>
<td>0.67748(3)</td>
<td>1/4</td>
<td>0.48522(6)</td>
<td>0.0105(2)</td>
</tr>
<tr>
<td>Ge₃</td>
<td>4c</td>
<td>0.49712(4)</td>
<td>1/4</td>
<td>0.67924(6)</td>
<td>0.0106(2)</td>
</tr>
<tr>
<td>Ge₄</td>
<td>4c</td>
<td>0.39204(4)</td>
<td>1/4</td>
<td>0.01736(7)</td>
<td>0.0144(2)</td>
</tr>
<tr>
<td>Ag₁</td>
<td>4c</td>
<td>0.59572(3)</td>
<td>1/4</td>
<td>0.84665(5)</td>
<td>0.0152(1)</td>
</tr>
<tr>
<td>Ag₂</td>
<td>4c</td>
<td>0.28068(3)</td>
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<td>0.17013(5)</td>
<td>0.0152(1)</td>
</tr>
<tr>
<td>Ag₃</td>
<td>4c</td>
<td>0.54582(3)</td>
<td>1/4</td>
<td>0.44184(5)</td>
<td>0.0142(1)</td>
</tr>
<tr>
<td>O₄</td>
<td>4c</td>
<td>0.13905(5)</td>
<td>1/4</td>
<td>0.29839(9)</td>
<td>0.024(4)</td>
</tr>
<tr>
<td>Ce₄Ag₄Ge₄</td>
<td>2d</td>
<td>1/2</td>
<td>0</td>
<td>0</td>
<td>0.0091(2)</td>
</tr>
<tr>
<td>Ce₂</td>
<td>4e</td>
<td>0.12981(4)</td>
<td>0</td>
<td>0</td>
<td>0.0094(2)</td>
</tr>
<tr>
<td>Ag₈</td>
<td>8g</td>
<td>0.33253(4)</td>
<td>0.19323(8)</td>
<td>0</td>
<td>0.0148(2)</td>
</tr>
<tr>
<td>Ge₁</td>
<td>4f</td>
<td>0.21632(7)</td>
<td>1/2</td>
<td>0</td>
<td>0.0124(3)</td>
</tr>
<tr>
<td>Ge₂</td>
<td>4h</td>
<td>0</td>
<td>0.18010(5)</td>
<td>1/2</td>
<td>0.0102(3)</td>
</tr>
</tbody>
</table>
Temperature dependent X-ray powder diffraction

The investigation was carried out on a STOE Stadi P powder diffractometer (Mo-Kα1, λ = 70.93 pm) with a computer controlled STOE furnace: the sample was enclosed in an argon filled quartz capillary and heated from room temperature to 500 °C in 100 °C steps and from 500 °C to 1100 °C in 50 °C steps. Afterwards the sample was cooled down to 500 °C in 50 °C steps, and below 500 °C in 100 °C steps. At each temperature, a diffraction pattern was recorded over the angular range 12.5° ≤ 2θ ≤ 21°.

Magnetic measurements

The magnetic susceptibility (χ = M/H, T = 5–300 K) and heat capacity (Cp, 3–100 K) were measured on a Quantum Design – PPMS using the VSM and HC options, respectively. χ(T) was measured at a field of 10 kOe, and the Curie–Weiss law was fitted in the linear region (100–300 K) of the χ−1 vs. T plot.

Elemental analysis

Semi-quantitative EDX analyses of the single crystals studied on a diffractometer were carried out in variable pressure mode using a Zeiss EVO® MA10 scanning electron microscope with CeO2, Ag, and Ge as standards. The O/N-content was analyzed by the company Pascher (Remagen, Germany). A carrier hot gas extraction method was used after the pyrolysis of the sample in a graphite crucible followed by IR/thermal conductivity detection.

Electronic structure calculations

Electronic band structure calculations were performed with the WIEN2k program package11 using density functional theory (DFT) within the full-potential LAPW+lo method and generalized gradient approximation (GGA) with 6 Ry separation energy between the core and valence states. The energy and charge convergence criteria were 10−5 Ry per cell and 10−4 e per cell, respectively. 48 Irreducible k-points were used with a plane wave cut-off of RmaxKmax = 7.0. For detailed

Table 3 Anisotropic displacement parameters for Ce3Ag4Ge4O0.5 and Ce3Ag4Ge4

<table>
<thead>
<tr>
<th>Atom</th>
<th>U_{11}</th>
<th>U_{22}</th>
<th>U_{33}</th>
<th>U_{12}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce1</td>
<td>0.0095(2)</td>
<td>0.0083(19)</td>
<td>0.0113(19)</td>
<td>−0.0001(2)</td>
</tr>
<tr>
<td>Ce2</td>
<td>0.0103(2)</td>
<td>0.0096(2)</td>
<td>0.0105(19)</td>
<td>−0.0002(2)</td>
</tr>
<tr>
<td>Ce3</td>
<td>0.0092(2)</td>
<td>0.0080(2)</td>
<td>0.0129(19)</td>
<td>0.0010(2)</td>
</tr>
<tr>
<td>Ce4</td>
<td>0.0094(2)</td>
<td>0.0141(2)</td>
<td>0.0109(19)</td>
<td>−0.0005(2)</td>
</tr>
<tr>
<td>Ge1</td>
<td>0.0111(4)</td>
<td>0.0085(4)</td>
<td>0.0121(3)</td>
<td>−0.0017(3)</td>
</tr>
<tr>
<td>Ge2</td>
<td>0.0110(4)</td>
<td>0.0094(4)</td>
<td>0.0112(3)</td>
<td>−0.0005(3)</td>
</tr>
<tr>
<td>Ge3</td>
<td>0.0111(4)</td>
<td>0.0083(4)</td>
<td>0.0123(4)</td>
<td>0.0002(3)</td>
</tr>
<tr>
<td>Ge4</td>
<td>0.0112(4)</td>
<td>0.0096(4)</td>
<td>0.0223(4)</td>
<td>−0.0011(3)</td>
</tr>
<tr>
<td>Ag1</td>
<td>0.0179(3)</td>
<td>0.0132(3)</td>
<td>0.0143(3)</td>
<td>−0.0006(2)</td>
</tr>
<tr>
<td>Ag2</td>
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<td>0.0116(3)</td>
<td>0.0131(3)</td>
<td>−0.0027(2)</td>
</tr>
<tr>
<td>Ag3</td>
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<td>0.0126(3)</td>
<td>0.0160(3)</td>
<td>−0.0028(2)</td>
</tr>
<tr>
<td>O</td>
<td>0.0236(6)</td>
<td>0.0236(6)</td>
<td>0.0286(6)</td>
<td>−0.0065(5)</td>
</tr>
</tbody>
</table>

Table 4 Interatomic distances (pm), calculated with the powder lattice parameters in Ce3Ag4Ge4O0.5 and Ce3Ag4Ge4. All distances of the first coordination spheres are listed

| Ce1–Ge4 | 318.5(1) | 2x | Ce2–Ge3 | 311.8(1) | 2x | Ce3–Ge2 | 315.7(1) | 2x | Ce4–Ge1 | 307.6(1) |
| Ce1–Ge2 | 322.3(1) | 2x | Ce2–Ge4a | 317.0(1) | 2x | Ce3–Ge3 | 316.7(1) | 2x | Ce4–Ge3 | 309.2(2) |
| Ce1–Ag2a | 326.2(1) | 2x | Ce2–Ge4b | 317.8(1) | 2x | Ce3–Ge1 | 324.2(1) | 2x | Ce4–Ge2 | 312.6(1) | 2x |
| Ce1–Ge1 | 324.5(1) | 2x | Ce2–Ag1a | 342.5(1) | 2x | Ce3–Ag3a | 323.1(1) | 2x | Ce4–Ag3 | 351.5(1) | 2x |
| Ce1–Ag1 | 328.4(1) | 2x | Ce2–Ag1b | 346.3(1) | 2x | Ce3–Ag1 | 323.6(1) | 2x | Ce4–Ag2 | 352.3(1) | 2x |
| Ce1–Ag2b | 350.2(1) | 2x | Ce2–Ag3 | 348.6(1) | Ce3–Ag2 | 325.5(1) | Ce4–Cc2 | 377(1) | 2x |
| Ce1–Cc4 | 379.6(1) | 2x | Ce2–Cc4 | 377.0(1) | 2x | Ce3–Ag3b | 329.8(1) | 2x |
| Ge1–Ge2 | 251.0(1) | 2x | Ge2–Ag2 | 276.3(1) | 2x | Ge3–Ag3a | 273.1(1) | 2x | Ge4–Ag3 | 263.8(1) | 2x |
| Ge1–Ag2 | 262.7(1) | 2x | Ge2–Ag3 | 279.0(2) | 2x | Ge3–Ag1 | 277.7(1) | 2x | Ge4–Ag2 | 288.1(1) |
| Ge1–Ag1 | 288.8(1) | 2x | Ge2–Cc4 | 312.6(1) | 2x | Ge3–Ag3b | 283.1(1) | 2x | Ge4–Cc2a | 317.0(1) | 2x |
| Ge1–Cc3 | 322.4(1) | 2x | Ge2–Cc3 | 315.7(1) | 2x | Ge3–Cc4 | 309.2(2) | 2x | Ge4–Cc2b | 317.8(1) |
| Ge1–Cc1 | 242.5(1) | 2x | Ge2–Cc1 | 322.3(1) | 2x | Ge3–Cc2 | 311.8(1) | 2x | Ge4–Cc1 | 318.5(1) | 2x |
| Ce1–Ge2 | 319.3(1) | 4x | Ce2–Ag | 317.6(1) | 4x | Ge1–Ag | 272.3(1) | 4x | Ge2–Ge2 | 257.0(2) |
| Ce1–Ge1 | 320.3(2) | 4x | Ce2–Ge1 | 319.1(1) | 2x | Ge1–Agb | 278.4(1) | 2x | Ge2–Ge2 | 263.9(1) | 2x |
| Ce1–Ag | 361.1(1) | 8x | Ce2–Ge2 | 321.5(1) | 4x | Ge1–Cc | 319.1(1) | 2x | Ge2–Ge1 | 319.3(1) | 2x |
| | | | Ce2–Agb | 330.3(2) | 2x | Ge1–Cc1 | 320.3(2) | 2x | Ge2–Cc2 | 321.5(1) | 3x |
Results and discussion

The crystal structure of Ce₄Ag₃Ge₄O₀.₅ was solved on the basis of a single crystal structure determination revealing a new structure type. Fig. 1 presents a view along the b axis. The structure can be subdivided into two substructures, i.e. linear chains of oxygen-centred [O(Ce₂₂Ce₂)] tetrahedra, which are embedded in a three-dimensional network composed of [Ce₄Ge₄].

The structure refinement clearly revealed an occupancy of 52(2)% for the oxygen position. Careful analyses of the data set did not reveal any superstructure reflections and any diffuse scattering; the oxygen atoms statistically occupy the tetrahedral sites. The structural refinement without a half occupied oxygen position at the tetrahedral site resulted in remarkably higher residuals (e.g. $R_1 = 0.0270$ with oxygen and $R_1 = 0.0340$ without oxygen ($I > 2\sigma(I)$)). The tetrahedra are made of the Ce₁, Ce₂, and Ce₄ atoms at Ce–O distances ranging from 237 to 243 pm in excellent agreement with the Ce–O distance in the tetrahedral building units of CeMnSbO (239 pm)³⁴ and Ce₂AuP₂O (238–242 pm)³⁵. The structural motif of chains of corner-sharing tetrahedra is also known from the structures of Ca₃AlAs₃,³⁶,³⁷ and Sm₃NS₃.³⁸,³⁹

The three-dimensional [Ce₄Ge₄] network has structural building units, which are well known from various rare-earth-transition metal-silicides and germanides. All three crystallographically independent silver atoms have four germanium neighbours at Ag–Ge distances ranging from 263 to 289 pm slightly longer than the sum of the covalent radii of 256 pm.⁴₀ Within this network, we observed various weak Ag–Ag contacts (319–340 pm Ag–Ag), slightly longer than the Ag–Ag distance in fcc silver (289 pm)⁴¹ as well as typical d¹₀–d¹₀ interactions.⁴²

The Ce₄Ag₃Ge₄O₀.₅ structure contains four crystallographically independent germanium sites. While the Ge₃ and Ge₄ atoms are isolated, the Ge₁ and Ge₂ atoms build Ge₂ dumbbells with a Ge₁–Ge₂ distance of 251 pm, a little bit longer than in elemental germanium (245 pm).⁴³ The substructure, built up from silver and germanium atoms, leaves slightly distorted pentagonal prismatic voids, which are filled with Ce₃ atoms (Fig. 1). These prisms are condensed via Ag₂Ge₃ rhombs, a structural motif frequently observed in related intermetallic structures. It is worthwhile to note that similar structural features with almost similar interatomic distances were recently discovered in the Gd₃Cu₄Ge₄ type structure of Ce₄Ag₃Ge₄ (Fig. 2).⁴³ Interestingly, the phase Ce₃Ag₄Ge₄ was observed several times as a by-product during the various syntheses of Ce₄Ag₃Ge₄O₀.₅. In contrast to the results of Szytula et al., who presented neutron diffraction data on polycrystalline samples, the crystallinity of Ce₄Ag₃Ge₄ prepared under HP/HT conditions, allowed us to perform a single crystal structure determination with precise structural data (Tables 1 and 2). For a more detailed crystal chemical description of that structure type, refer to a publication on isotopic Yb₃Pd₄Ge₄.⁴⁴

To examine the oxidation state of the cerium atoms in Ce₄Ag₃Ge₄O₀.₅, magnetic measurements were performed. Fig. 3 shows the inverse magnetic susceptibility of Ce₄Ag₃Ge₄O₀.₅.

We observed Curie–Weiss behavior above 100 K with an experimental magnetic moment of 2.42 $\mu_B$ per Ce atom, close to the value of 2.54 $\mu_B$ for the free Ce³⁺ ion, clearly indicating trivalent cerium in Ce₄Ag₃Ge₄O₀.₅. The negative Weiss constant of $-8.6$ K is indicative of antiferromagnetic interactions in the paramagnetic range. Magnetic ordering at 3.2 K was evident from low-temperature specific heat data (Fig. 3).

The elemental analysis of Ce₄Ag₃Ge₄O₀.₅ by EDX analysis of the elements Ce, Ag, and Ge revealed: Ce: 47% (47.4%) (theoretical values in brackets); Ag: 27% (27.4%); Ge: 26% (24.6%). To detect the small oxygen content and a possible nitrogen contamination, the O/N-content was analyzed by an IR/thermal conductivity detection. The amount of oxygen came to a value

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Fig. 1 Projection of the Ce₄Ag₃Ge₄O₀.₅ structure onto the ac plane. Cerium, silver, and germanium atoms are represented as medium grey, black filled, and open circles, respectively. The three-dimensional [Ce₄Ge₄] network and the chains of corner-sharing oxygen centered [OCe₂Ce₂] tetrahedra are emphasized.

Fig. 2 Projection of the Ce₃Ag₄Ge₄ structure onto the ab plane. Cerium, silver, and germanium atoms are drawn as medium grey, black filled, and open circles, respectively. The three-dimensional [Ag₄Ge₄] network is emphasized.
of 0.65%, which fits well to the expected theoretical value of 0.68%. Only traces of nitrogen were detected.

Considering the trivalent and monovalent oxidation states for the cerium and silver atoms, closed-shell Ge$^{4-}$ and Ge$_6^{6-}$ dumb-bells, and a half occupied oxygen site, we obtain the following ionic formula splitting: $(4\text{Ce}^{3+})^{12+}(3\text{Ag}^{+})^{3+}(2\text{Ge}_4^{4-})^{8-}\text{Ge}_2^{6-}(1/2\text{O}_2^{2-})^{-}$. Nevertheless, Ce$_4$Ag$_3$Ge$_4$O$_{0.5}$ should be regarded as a metallic compound, possessing an ionic [OCe$_2$Ce$_2$]-strand inside a metallic matrix. A similar bonding pattern occurs in a variety of subnitrides, e.g. isolated Ba$_6$N octahedra in a sodium matrix of Na$_{16}$Ba$_6$N$_4$.46,47

To substantiate the findings regarding the metallic state and the magnetic properties, we performed DFT band structure calculations of idealized Ce$_4$Ag$_3$Ge$_4$O (full occupancy of the O-site) using the full potential LAPW method.

The calculations converged in a magnetic ground state with 0.97 unpaired electrons per cerium in excellent agreement with the experimental data, and confirm the trivalent state of cerium. Since the detailed magnetic spin structure is unknown, we confined our calculations to a ferromagnetic model. The DOS shown in Fig. 4 reveals a metallic state without contributions of the Ce-$4f$ states, which are pushed away from $E_F$ by the on-site Coulomb repulsion. The 7 eV gap in the $4f$ states depends on the choice of $U_{\text{eff}}$ which has not been optimized. The states at the Fermi-energy are dominated by Ge- and to a smaller extent by Ag-contributions; thus the Ag$_4$Ge$_4$-network is the base of the metallic property. The Ag-$4d$-states are around $-5$ eV and relatively broad, probably because of the relatively short Ag–Ag distances that allow weak $d^{10}$–$d^{10}$ interactions.

Temperature dependent X-ray powder investigations under argon revealed the stability of Ce$_4$Ag$_3$Ge$_4$O$_{0.5}$ up to a temperature of 650 °C (Fig. 5). Exceeding this temperature, Ce$_4$Ag$_3$Ge$_4$O$_{0.5}$ decomposed into Ce$_3$Ag$_4$Ge$_4$. The decomposition was completed at 800 °C, remaining stable after cooling down to room temperature.

Finally we present the comparison of the Ce$_4$Ag$_3$Ge$_4$O$_{0.5}$ structure with the large family of pnictide oxide superconductors.23,24 This fascinating field of solid state chemistry is dominated by the many tetragonal phases, which are built up from polycationic and polyanionic layers. The most prominent phase is LaFeAsO$_4$ which becomes superconducting upon fluorine doping on the oxygen site. The large majority of the ZrCuSiAs type and related pnictide oxides exclusively show layers of condensed, edge-sharing ORE$_4$ tetrahedra in the polycationic part.49,50 Ce$_4$Ag$_3$Ge$_4$O$_{0.5}$ (Fig. 1) and Ce$_2$AuP$_2$O$_5$ (Fig. 6) are first examples with one-dimensional polycationic

![Fig. 3 A plot of $\chi^{-1}$ vs. $T$ is shown in (a). The $C_p$ as a function of $T$ is shown in (b). The inset shows the low temperature (<10 K) features on an expanded scale. The onset of magnetic ordering below 3.2 K is clearly visualized in the inset.](https://example.com/Fig3.png)

![Fig. 4 Spin polarized density of states of Ce$_4$Ag$_3$Ge$_4$O. Grey: total DOS, black: contributions of the Ce-$4f$ states. An effective Hubbard $U_{\text{eff}}$ of 7 eV was applied to the Ce-$4f$ shell. The Fermi level is taken at the energy of zero.](https://example.com/Fig4.png)

![Fig. 5 Temperature-programmed X-ray powder patterns following the decomposition reaction of the metastable high-pressure phase Ce$_4$Ag$_3$Ge$_4$O$_{0.5}$.](https://example.com/Fig5.png)
units. The surrounding polyanionic part is three-dimensional in Ce₄Ag₃Ge₄O₀.₅ but consists of isolated [AuP₂]₄ polyanions in Ce₂AuP₂O (Fig. 6).³⁵

Fig. 7 summarizes the polycationic substructures in Ce₄Ag₃Ge₄O₀.₅, Ce₂AuP₂O,³⁵ and CeMnSbO.³⁴ The OCe₄ tetrahedra share common corners in the structure of Ce₄Ag₃Ge₄O₀.₅. This motif is duplicated in Ce₂AuP₂O, where condensation of a second chain leads to edge-sharing tetrahedra. Both of these motifs are one-dimensional. In CeMnSbO,³⁴ we observe the layer, which results from condensation of the rows observed in Ce₂AuP₂O. Although the tetragonal phases are by far the majority in the family of pnictide oxide superconductors, we can still expect interesting new motifs in this exciting field of solids as demonstrated by the present HP–HT route.

Conclusions

We reported on the first example of the oxidation of an intermetallic phase under high-pressure/high-temperature conditions, leading to a new germanide oxide with the composition Ce₄Ag₃Ge₄O₀.₅. The structure can be subdivided into two substructures, i.e. linear chains of oxygen-centred [OCe₂Ce₂/2] tetrahedra, which are embedded in a three-dimensional network composed of [CeAg₃Ge₄]. Curie–Weiss behavior above 100 K with an experimental magnetic moment of 2.42 µB per Ce atom clearly indicated trivalent cerium. DFT band structure calculations resulted in metallic properties and in a magnetic ground state, compatible with one unpaired 4f-electron per cerium.

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Notes and references
