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Extension of the Clathrate Family: The Type X Clathrate $Ge_{79}P_{29}S_{18}Te_6$**

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Clathrates present a unique class of compounds whose structures consist of a host framework and isolated guest atoms located in the large polyhedral cages formed by framework atoms.[1] The clathrates attract much interest owing to their intriguing physical properties, especially thermoelectricity and superconductivity.[2,3] To date there are only nine clathrate structure types,[1] which differ by the shape of the constituent polyhedral cages and their spatial arrangement. In contrast to clathrate gas hydrates, there is a large group of semiconducting or intermetallic clathrates, which crystallize in only four structure types.[4] The overwhelming majority of known clathrates are of type I.[4] Their frameworks are based on the Group 14 elements (Si, Ge, or Sn), and additionally contain the elements of Groups 13 and 15 (with exception of $Ge_{40.0}Te_{5.3}I_8$).[5] The peculiar exception to this rule is $Li_{17.7}Mg_{36.8}Cu_{21.5}Ga_{66}$,[6] which is a rare type IV clathrate and does not contain Group 14 elements. The framework of a typical semiconducting clathrate bares negative charge, while alkaline or alkaline earth metals occupy the guest positions. In clathrates with inverse polarity, also known as cationic clathrates, the guest atoms are usually halogen anions,[4] but several type I cationic clathrates with guest Te atoms, such as $Ge_{30}P_{16}Te_8$,[7] $Si_{46-x}P_xTe_{8-y}$,[8,2c] and $Si_{20-x}Te_{7+x}$[9] have also been reported. There is a limited variety of clathrate-forming polyhedra and restricted possibilities of their spatial arrangement, and the discovery of a new clathrate structure type opens a way for further expansion of the clathrate family,[10] probably leading to new properties. Herein we report on the synthesis and crystal structure of a novel compound $Ge_{79}P_{29}S_{18}Te_6$ belonging to the new type of clathrate structure.

The compound $Ge_{79}P_{29}S_{18}Te_6$ was obtained as a single phase from pure elements. The stoichiometric mixture of the elements was first heated at 600 °C and then annealed at 550 °C in sealed silica ampoules for 72 h. $Ge_{79}P_{29}S_{18}Te_6$ is stable in moist air at room temperature. The results of differential scanning calorimetry (DSC) show that $Ge_{79}P_{29}S_{18}Te_6$ melts incongruently above 570 °C, producing $Ge_{30}P_{16}Te_8$ and elemental sulfur. The low decomposition temperature of $Ge_{79}P_{29}S_{18}Te_6$ imposes kinetic limitations on the solid-state synthesis owing to the low reactivity of germanium. We activated elemental germanium by transforming it into the more reactive and volatile compound GeS_2. This method allows the efficient activation of elements with low reactivity, such as germanium and silicon, and provides a promising route to clathrates with poor thermal stability.

$Ge_{79}P_{29}S_{18}Te_6$ crystallizes in the rhombohedral space group $R\bar{3}m$ with unit cell parameters $a = 17.120(3)$ Å, $c = 10.608(2)$ Å, and $Z = 1$. It should be noted that the unit cell has pseudocubic metrics. To differentiate between the cubic and trigonal symmetry, an electron diffraction investigation was undertaken. The selected area electron diffraction (SAED) patterns of $Ge_{79}P_{29}S_{18}Te_6$ (Figure S1 of the Supporting Information) can be completely indexed with both trigonal and cubic unit cells. The geometry of the SAED patterns does not allow us to differentiate between these two possibilities. Convergent beam electron diffraction (CBED) clearly demonstrates the difference. The CBED patterns taken along ⟨111⟩ directions of the cubic structure should demonstrate either sixfold or threefold symmetry. In the rhombohedral structure, such symmetry is possible only for the [001] pattern, whereas it should be absent for the patterns corresponding to other ⟨111⟩ cubic directions, such as the trigonal [211] zone. CBED patterns along the [001] and [211] zone axes are shown in Figure 1. The sixfold symmetry is clearly visible on the [001] pattern, and it is definitely absent on the [211] pattern. This result rules out the cubic symmetry for $Ge_{79}P_{29}S_{18}Te_6$ and confirms the choice of the *R*-centered trigonal unit cell.

The structure was solved using the single-crystal X-ray data ($R = 0.030$, see the Supporting Information). The general view of the crystal structure is shown in Figure 2. Germanium and phosphorus atoms form the framework, whereas tellurium atoms occupy the guest positions. There is only one polyhedron type, $[5^{12}6^2]$, composed of three- and four-coordinate germanium and phosphorus atoms.[11] The unit cell contains six $[5^{12}6^2]$ tetrakaidecahedra, which are substantially distorted on account of the fact that the distances between the guest Te and framework atoms vary in a wide

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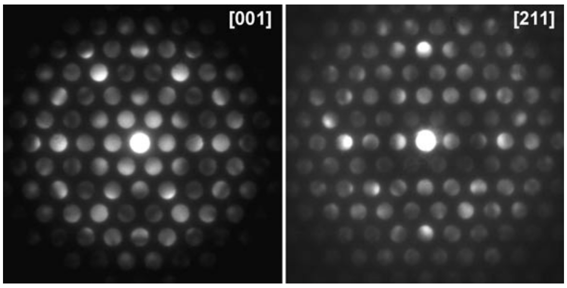

Figure 1. CBED patterns of $Ge_{79}P_{29}S_{18}Te_6$ along the [001] and [211] directions of the trigonal unit cell corresponding to the ⟨111⟩ directions of the pseudocubic unit cell. Note the presence of sixfold symmetry on the [001] CBED pattern and its absence on the [211] CBED pattern.

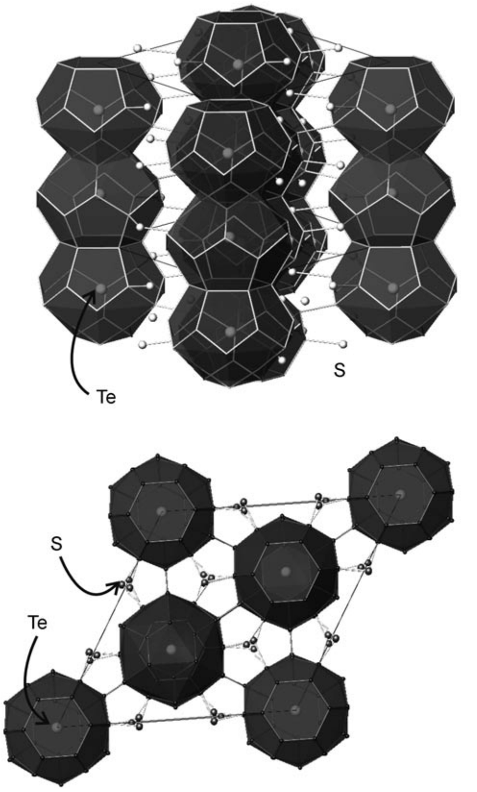

Figure 2. Crystal structure of $Ge_{79}P_{29}S_{18}Te_6$. Top: Columns of distorted [$5^{12}6^2$] polyhedra linked by sulfur atoms. Bottom: A view along the *c* axis.

range of 2.8–4.1 Å (Figure 3, top). The atomic displacement parameter (ADP) for the guest tellurium atom is almost twice as large as for other atoms, which is typical for clathrate structures.[4] The [$5^{12}6^2$] polyhedra, bonded through the alternation of regular and distorted hexagons, are packed into infinite columns (Figure 2 top), which, in turn, are bridged by sulfur atoms. It should be noted that one of the framework 18*h* positions is significantly disordered. Atoms of three types (Ge4, Ge5, P2) are located near this 18*h* position. Each of these atoms has characteristic distances to the adjacent framework atoms (see the Supporting Information).

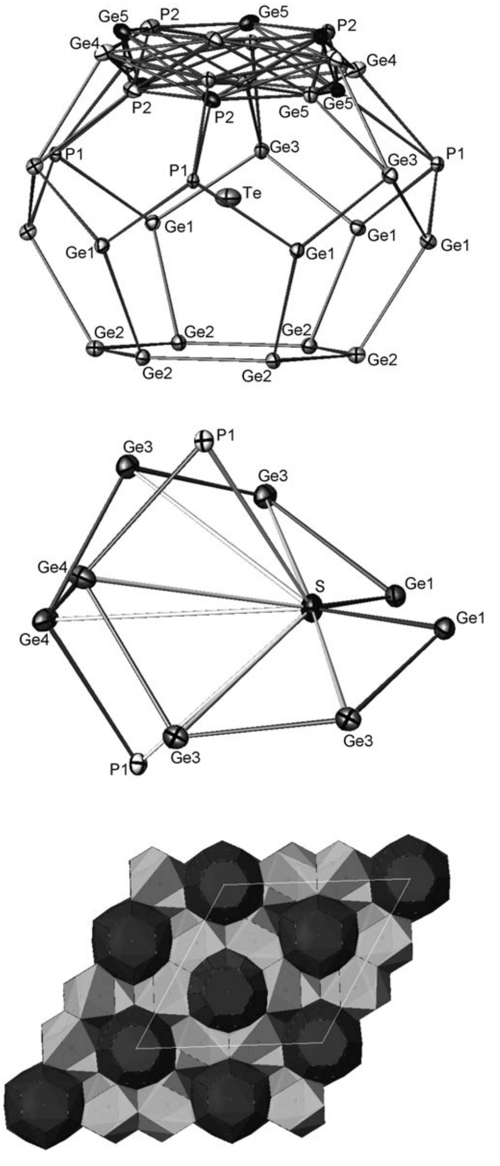

Figure 3. View of the distorted [$5^{12}6^2$] polyhedron (top), the environment of the S atoms (middle), and the complete polyhedral presentation of $Ge_{79}P_{29}S_{18}Te_6$ viewed along the *c* axis (bottom). [$5^{12}6^2$] polyhedra around Te are shown in dark gray; irregular 10-vertex polyhedra around S are drawn in light gray. The unit cell is outlined.

There are three groups of separations: 2.40–2.48 Å, 2.35–2.38 Å, and 2.20–2.33 Å, corresponding to the Ge–Ge, Ge–P, and P–P bonds, respectively. This finding explicitly indicates the presence of different chemical species at this position and explains the origin of the disordered structure: There are several kinds of regular and disordered polyhedra that randomly alternate along the *c* axis of the unit cell.

An analogy can be drawn between the crystal structure of the new clathrate and that of clathrate IX. In the latter structure, the polyhedra [5^{12}] are joined together into helical chains, which similarly do not fully occupy the space. Two other types of guest atoms are placed between these chains.[12] Their coordination is strongly distorted and cannot be simply described within a polyhedral model. Similarly, in the crystal structure of $Ge_{79}P_{29}S_{18}Te_6$ the sulfur atoms could be considered as the guest atoms in the unusual configuration, which can be described as a (2 + 8) environment (Figure 3, middle). The sulfur atom has two covalent bonds to Ge1 atoms, d(S–Ge1) = 2.25 Å, and eight noticeably longer bonds to other framework atoms. Therefore, in $Ge_{79}P_{29}S_{18}Te_6$ the sulfur atoms take part in the framework bridging and are at the same time guest atoms in the irregular environment (Figure 3); the same feature is sometimes observed in clathrate-related ice structures.[13]

$Ge_{79}P_{29}S_{18}Te_6$ behaves as a Zintl phase with reversed polarity.[14] The application of the Zintl electron-counting scheme gives a discrepancy from electroneutrality of less than one electron per formula of 132 atoms; this result is within the estimated standard deviation of the calculations, which stems from the accuracy of the determination of the atomic occupancy. Indeed, the magnetization and electrical resistivity measurements (not shown) confirm that the title compound is a diamagnetic semiconductor, which is typical for Zintl phases, with a rather high room-temperature resistivity of about 450 Ω m. No sign of superconductivity was observed down to 1.4 K.

In conclusion, $Ge_{79}P_{29}S_{18}Te_6$ represents the first example of a new clathrate structure type. According to the classification by Jeffrey,[1] the label type X can be assigned to this new clathrate crystal structure.

Experimental Section

Ge powder (99.999 %), Te pieces (99.99 %), S powder (99 %) and P powder (97 %) were used as starting materials. The two latter elements were purified according to standard methods. A mixture of the elements corresponding to the stoichiometry of the product was sealed in a silica tube under vacuum, heated at 600 °C for 24 h, annealed at 550 °C for five days, and then cooled with the furnace, providing a single-phase sample of $Ge_{79}P_{29}S_{18}Te_6$. Single crystals suitable for structure determination were prepared by heating the sample at 600 °C for four days with subsequent slow cooling to 200 °C over two days.

X-ray powder diffraction measurements were performed with a Stoe STADI-P diffractometer (Cu-$K_{\alpha 1}$ radiation). The single-crystal X-ray diffraction experiment was carried out with a CAD-4 (Nonius) diffractometer. The data were processed using the SHELX-97 package[15] $Ge_{79.28(17)}P_{29.12(7)}S_{18}Te_6$, $M_r = 6477.20\ \mathrm{g\,mol^{-1}}$, crystal size $0.05 \times 0.1 \times 0.2$ mm, trigonal, $R\bar{3}m$, $a = 17.120(2)$, $c = 10.609(2)$ Å, $V = 2692.9(8)$ Å^3, $Z = 1$, $\rho_{calc} = 3.994\ \mathrm{g\,cm^{-3}}$, $\mu = 21.129\ \mathrm{mm^{-1}}$, Mo-$K_\alpha$ radiation, $\lambda = 0.71073$ Å, $T = 293$ K, $2\theta_{max} = 29.97°$, reflections collected/unique = 5388/957, $R_{int} = 0.0872$, $R = 0.0297$, $wR = 0.0658$ ($I > 2\sigma(I)$); largest diff. peak and hole 1.008 and $-1.509\ \mathrm{e\,Å^{-3}}$. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. Complete X-ray crystallography data can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Fax: (+49) 7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de) on quoting the number CSD-422364.

SAED and CBED patterns were obtained with a Philips CM20 electron microscope operated at 200 kV. The sample was prepared by crushing the powder under ethanol and depositing drops of suspension onto holey carbon grid.

EDX analysis was carried out for a single crystal by means of a JEOL JSM-6490LV scanning electron microscope operating at 30 kV and equipped with an Oxford Instruments detector system. The data were collected for six points and then averaged. The resulting gross formula, normalized to six Te atoms, is $Ge_{72.56(16)}P_{30.73(18)}S_{17.9(5)}Te_6$.

DCS measurements were performed with a DSC 204 F1 Phoenix device in an argon atmosphere. Two sets of consecutive heating and cooling experiments were performed with the ramp rate of 10 K min^{-1}.

Magnetization measurements were performed with the Cryogenics S700 SQUID magnetometer in applied fields of 1.0 and 0.1 T. For electrical resistivity measurements, the sample was cold-pressed into a rectangular bar (8 × 2 × 2 mm) and transferred to the precalibrated original four-probe setup described in detail elsewhere.[16]

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