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The synthesis, single-crystal structure, optical absorption, and resistivity of Th_2GeSe_5

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ABSTRACT

The compound Th_2GeSe_5 has been synthesized by the reaction of the elements at 1273 K. From a single-crystal study Th_2GeSe_5 crystallizes in the Ba_5Si_3 structure type with four formula units in the space group $D^8_{4h}-P4/ncc$ of the tetragonal system in a cell with dimensions $a=7.4968(4)$ Å and $c=13.6302(9)$ Å at 100 (2) K. From optical absorption measurements Th_2GeSe_5 is found to have an optical band gap of 1.92 eV (indirect) or 1.98 eV (direct), consistent with its red color. Th_2GeSe_5 is a wide gap semiconductor, as indicated by its electrical resistivity at 298 K of $4.37(2)\times10^9$ Ω cm measured on a single crystal.

1. Introduction

The solid-state inorganic chemistry of ternary Th or U/group14/group16 compounds is largely unexplored. Six classes of compounds are known: (1) silicates and germanates, $AnZO_4$ (An=Th, U; Z=Si, Ge) [1–3]; (2) the carbonate UCO_5 [4]; (3) the uranates $PbUO_4$ [5], Pb_3UO_6 [6], and $Pb_3U_{11}O_{36}$ [7]; (4) the carbide U_2CS [8]; (5) the 1:1:1 compounds AnZQ (An=Th, U; Z=Si, Ge; Q=S, Se, Te) and USnTe [9,10]; and (6) the 2:1:5 compounds U_2PbQ_5 (Q=S, Se) [11]. Of these 23 known compounds, only eight contain Th. As part of an exploration of the Th/Ge/Q system we report here the synthesis, structure, optical absorption, and resistivity measurements of the new compound Th_2GeSe_5.

2. Experimental

2.1. Synthesis

Caution! ^{232}Th is an α-emitting radioisotope and as such is considered a health risk. Its use requires appropriate infrastructure and personnel trained in the handling of radioactive materials.

Th (MP Biomedicals, 99.1%), Ge (Aldrich, 99.99%), Se (Cerac, 99.999%), and Sb (Aldrich, 99.5%) were used as received. Sb_2Se_3 was prepared from the direct reaction of the elements in a sealed fused-silica tube at 1123 K.

A fused-silica tube was loaded with Th (30 mg, 0.129 mmol), Ge (9.4 mg, 0.129 mmol), and Se (10.2 mg, 0.129 mmol), evacuated to near 10^{-4} Torr, flame sealed, and placed in a computer-controlled furnace. It was heated to 1273 K in 24 h, kept at 1273 K for 99 h, cooled to 673 K in 198 h, and then rapidly cooled to 298 K in 4 h. The resulting brown powder (35 mg) was loaded with Sb_2Se_3 (70 mg, 0.146 mmol) in a fused-silica tube and heated as before. This tube contained brown powder and red-black rods. The elemental composition of these rods was determined to be Th/Ge/Se in an approximate ratio of 2:1:5, as measured on an EDX-equipped Hitachi S-3400 SEM.

2.2. Structure determination

X-ray diffraction data for a 0.042 mm × 0.106 mm × 0.116 mm crystal of Th_2GeSe_5 were collected with the use of graphite-monochromatized Mo$K\alpha$ radiation ($\lambda=0.71073$ Å) at 100 K on a Bruker APEX2 diffractometer [12]. The crystal-to-detector distance was 6 cm. The data collection strategy was optimized with the algorithm COSMO in the program APEX2 [12] as a series of 0.3° scans in ϕ and ω. The exposure time was 10 s/frame. The collection of intensity data as well as cell refinement and data reduction were carried out with the use of the program APEX2 [12]. Face-indexed absorption, incident beam, and decay corrections were performed with the use of the program SADABS [13]. The structure was solved with the direct-methods program SHELXS and refined

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Table 1
Crystal data and structure refinement for Th_2GeSe_5.

Space group	$D_{4h}^8 - P4/ncc$
Crystal system	Tetragonal
a (Å)	7.4968(4)
c (Å)	13.6302(9)
V (Å^3)	766.04(8)
Z	4
T (K)	100 (2)
Formula mass (g mol^{-1})	931.47
ρ (g cm^{-3})	8.077
μ (mm^{-1})	66.28
λ (Å)	0.71073
$R_1[F^2 > 2\sigma(F^2)]$[a]	0.0261
$R_w(F^2)$[b]	0.0648

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.
[b] $R_w(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4\}^{1/2}$ for all data. $w^{-1} = \sigma^2(F_o^2) + (0.0221F_o^2)^2$ for $F_o^2 \geq 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$.

Table 2
Selected interatomic distances (Å) and angles (deg) for Th_2GeSe_5.

	Distance or angle
Th1 – Se1	2.9586(6) × 2
Th1 – Se1	2.9975(7) × 2
Th1 – Se2	3.0100 (4) × 2
Th1 – Se1	3.0165 (6) × 2
Th2 – Se2	3.051(1)
Th2 – Se1	3.1113(5) × 4
Th2 – Se1	3.1122(5) × 4
Ge1 – Se1	2.520(1) × 2
Ge1 – Se2	2.7520(6) × 2
Se1 – Ge1 – Se1	105.57(8)
Se1 – Ge1 – Se2	78.86(4) × 2
Se1 – Ge1 – Se2	83.28(4) × 2
Se2 – Ge1 – Se2	150.28(9)

with the full-matrix least-squares program SHELXL [14]. The atomic positions were standardized with the program STRUCTURE TIDY [15]. Molecular graphics were generated with the program CrystalMaker [16]. Additional experimental details are given in Table 1 and in the Supporting material.

2.3. Resistivity

Resistivity data were collected at 298 K with the use of a Keithley 6517B electrometer. Electrical contacts were made with fast-drying silver paint (Ted Pella, Inc; Electrodag 1415 M) and copper wire of 0.025 mm thickness (Omega). A maximum bias of ± 10 V was applied on a single crystal of Th_2GeSe_5 0.13 mm long × 0.11 mm wide × 0.08 mm high. A two-probe geometry in a guarded home-made enclosure was used to collect current as a function of voltage.

2.4. Optical absorption

Optical absorption spectra were collected on a Hitachi U-6000 spectrophotometer at 298 K on thin fragments of the single crystal used for the resistivity measurement.

3. Results

3.1. Synthesis

The compound Th_2GeSe_5 was discovered while exploring the system Th/Ge/Se. The stoichiometric ratio of Th:Ge:Se during

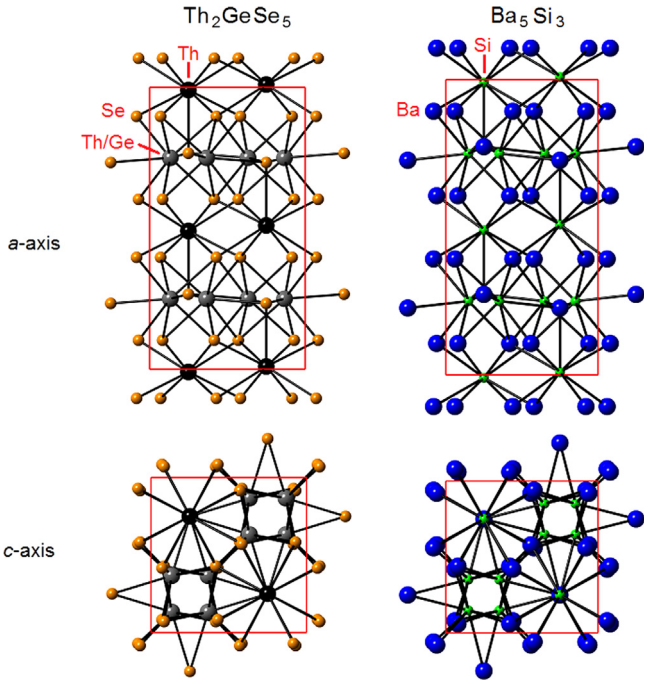

Fig. 1. Comparison of the structures of Th_2GeSe_5 and Ba_5Si_3, as viewed down the a- and c-axes. The unit cells are outlined.

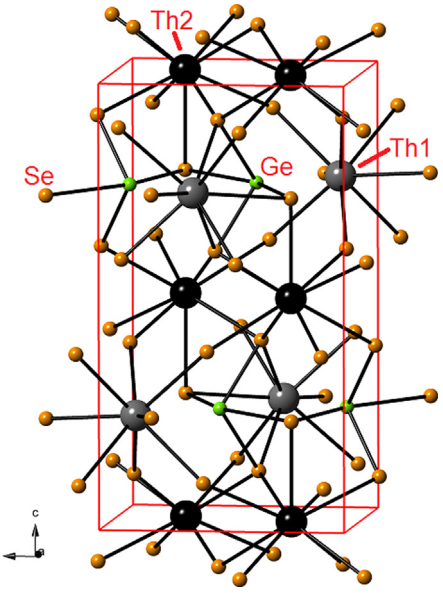

Fig. 2. View of Th_2GeSe_5. Th1 and Ge positions have been chosen to maximize Th1–Th1 and Ge–Ge distances. The unit cell is outlined.

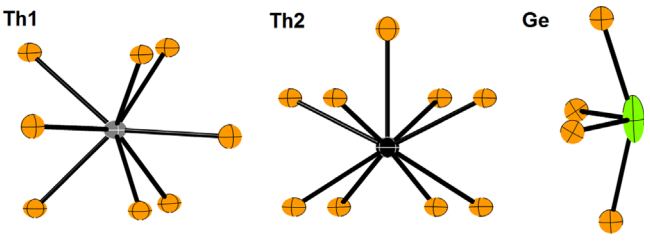

Fig. 3. The bonding environments around the Th1, Th2, and Ge positions. The 95% probability ellipsoids are shown.

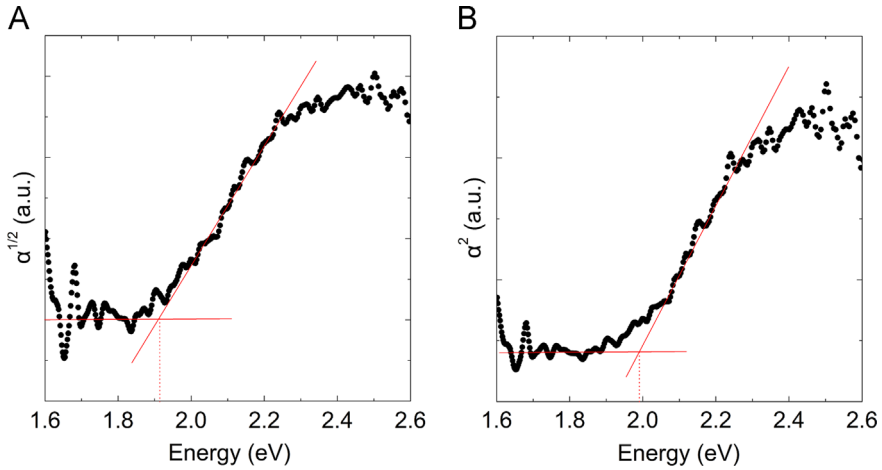

Fig. 4. Optical absorption spectrum of a fragment of a red Th_2GeSe_5 crystal plotted (a) for an indirect transition and (b) for a direct transition.

loading was 1:1:1. The reaction yielded crystals of Th_2GeSe_5 when powder from the initial reaction was reloaded with excess Sb_2Se_3. Because the yield of crystals of Th_2GeSe_5 was approximately 80% based on Se, no attempts at a reaction with a Th:Ge:Se ratio of 2:1:5 were made.

3.2. Structure

Dithorium(IV) germanium(II) pentaselenide, Th_2GeSe_5, crystallizes with four formula units in space group D_{4h}^8-P4/ncc of the tetragonal system. Additional metrical data and structure refinement details can be found in Tables 1 and 2 and Supporting material. The 2:1:5 compounds U_2PbQ_5 (Q=S, Se) [11] crystallize in the U_3S_5 structure type [17], but Th_2GeSe_5 is of the Ba_5Si_3 structure type [18], if one ignores the Th/Ge disorder. The substitution is as follows: Se2 for Ba1, Se1 for Ba2, Th2 for Si1, and Th1/Ge for Si2. A comparison of the structures of Th_2GeSe_5 and Ba_5Si_3 is shown in Fig. 1.

The site symmetries of the crystallographically independent atoms in Th_2GeSe_5 are: Th1,..2; Ge1,..2; Th2, 4..; Se1, 1; Se2, 4... The structure (Fig. 2) comprises two types of alternating layers. The first layer is composed of edge-sharing monocapped square-antiprismatic Th_2Se_5 polyhedra; the second contains Th1 and Ge disordered 1:1 in the cation site. Atom Th1 is coordinated by eight Se atoms in a bicapped trigonal-prismatic arrangement. Owing to its smaller size, the Ge atom lies 0.703 (2) Å away from the Th1 atom to be within bonding distance of four of the eight Se atoms in a saw-horse arrangement (Fig. 3). The Th1 and Ge positions are ordered in any given layer; otherwise Th1 sits too close to its symmetry-generated neighbor $(1/2-x, 3/2-y, z)$ at a distance of 2.483(1) Å. No evidence was found for a superstructure; thus, these layers are ordered throughout the crystal. The resultant structure shows one cation site split between the eight-coordinate Th1 atom and the four-coordinate Ge atom. Because there are no Se–Se bonds in the structure, oxidation states in Th_2GeSe_5 can be assigned to Th, Ge, and Se as +4, +2, and −2, respectively, with the occupancies of Th1 and Ge1 each fixed at 50%.

The interatomic distances in Th_2GeSe_5 (Table 2) are comparable to those in other chalcogenide compounds containing Th or Ge. The Th–Se interatomic distances in Th_2GeSe_5 vary between 2.9586(6) Å and 3.1122(5) Å with the square antiprismatic Se cap at a distance of 3.051(1) Å from Th2, whereas in ThGeSe they range from 2.995(1) Å to 3.163(1) Å [9]. The Ge–Se interatomic distances in Th_2GeSe_5 vary between 2.520(1) Å and 2.7520(6) Å, whereas in Fe_2GeSe_4 they vary between 2.496(8) Å and 2.730(6) Å [19].

3.3. Optical results

In Fig. 4 the optical data obtained from a single crystal are plotted both for an indirect and a direct transition. Band gaps of 1.92 eV and 1.98 eV, respectively, were calculated from these data, consistent with the dark red color of the crystals. Usually, a plot of the square root of absorption vs energy (Fig. 4a) deviates from linearity when the gap is indirect. Consequently, we favor the direct band gap (Fig. 4b).

3.4. Resistivity

A plot of current versus voltage of a single crystal of Th_2GeSe_5 measured at 298 K leads to a resistivity of $4.37(2)\times10^9\ \Omega$ cm. Thus, Th_2GeSe_5 is a wide gap semiconductor.

4. Conclusions

Th_2GeSe_5, the second compound in the system Th–Ge–Se, was prepared from the elements in an Sb_2Se_3 flux at 1123 K. The compound crystallizes in the space group D_{4h}^8–$P4/ncc$ of the tetragonal system. The structure comprises $ThSe_8$, $ThSe_9$, and $GeSe_4$ polyhedra and is unusual for its disorder between Th and Ge. The crystals appear red when thin and black when thick and the optical band gap is 1.92 eV (indirect) or 1.98 eV (direct), consistent with the red color. Electrical resistivity measured on a single crystal is $4.37(2)\times10^9\ \Omega$ cm confirming that Th_2GeSe_5 is a wide gap semiconductor.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jssc.2013.06.031. The crystallographic data in cif format for Th_2GeSe_5 have been deposited with FIZ Karlsruhe as CSD number 425988. These data may be obtained free of charge by contacting FIZ Karlsruhe at +497247808666 (fax) or crysdata@fiz-karlsruhe.de (email).

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