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Synthesis, crystal structure, and electronic structure of Ba$_2$GeTe$_3$(Te$_2$)

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Keywords: Barium germanium telluride, solid-state synthesis; crystal structure, Te–Te single bond, electronic structure

Abstract

Black crystals of Ba$_2$GeTe$_3$(Te$_2$) were obtained by the “U-assisted” reaction of U, Ba, Ge, and Te at 1173 K using the sealed-tube method. The crystal structure of Ba$_2$GeTe$_3$(Te$_2$) was determined by a single crystal X-ray study at 100(2) K. It crystallizes in space group *Pnma* of the orthorhombic crystal system with four formula units in a cell with constants $a = 6.7900(14)$ Å, $b = 23.720(5)$ Å, and $c = 6.9300(14)$ Å. The crystal structure of Ba$_2$GeTe$_3$(Te$_2$) can be described as pseudo one-dimensional with zig-zag chains $1_∞[\text{GeTe}_3^{2-}]$ where each Ge atom is bonded to four Te atoms in a distorted tetrahedron. These chains are separated by the Ba$^{2+}$ cations and homoatomic dimers of Te$_2^{2-}$. Around each Ba atom there are nine Te atoms in a distorted tricapped trigonal prism. Charge balance in Ba$_2$GeTe$_3$(Te$_2$) is achieved with $2 \times$ Ba$^{2+}$, $1 \times$ Ge$^{4+}$, $3 \times$ Te$^{2-}$, and $1 \times$ Te$_2^{2-}$. Density functional theory (DFT) calculations suggest Ba$_2$GeTe$_3$(Te$_2$) is a metal with Ge- and Te-derived states contributing the most around the Fermi level.

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1. Introduction

The compounds A/Q/T and Ak/Q/T, where A = alkali metal = Li-Cs; Ak = alkaline-earth metal = Mg, Ca, Sr, Ba; Q = chalcogen = S, Se, and Te; and T = Si, Ge, and Sn, have been extensively studied because of their rich structural chemistry. These compounds show diverse physical properties, such as semiconducting, nonlinear optics (NLO) materials, thermoelectric properties, solar energy converters, and detector materials [1-4]. For example, Li₂Ga₂GeS₆ shows a strong second harmonic generation (SHG) effect [5] and the Li₂In₂TQ₆ (T = Si, Ge; Q = S, Se) compounds are the few examples of IR NLO materials [6].

The structures of most of these compounds contain tetrahedral TQ₄ units. The condensation of TQ₄ units results in the formation of infinite chains, layers, and networks of [TₓQₓ₋₄] units. Compounds such as Mg₂SnS₄ [2] and Ba₃GeS₅ [7] contain discrete units of [TQ₄₋₄] and are classified as zero-dimensional. Other examples of [TₓQₓ₋₄] units include the [Ge₄S₁₀₋₄] clusters in Ba₂Ge₄S₁₀ [8], the infinite chains of [GeS₃₋₂] in Ba₂Ge₂S₆ [1], and the [SnS₅₋₀] units in the BaSn₂S₅ structure [9]. Apart from TQ₄ units, a few compounds also contain ethane-like [T₂Q₆₋₄] units with homonuclear T–T bonds, an example being K₆Ge₂S₆ [10].

The current ICSD database [11] shows very few compounds in the ternary Ak/Ge/Q system: Ba₂Ge₄S₁₀ [8], Ba₂Ge₂S₆ [1], Ba₃GeS₅ [12], Ak₂GeQ₄ (Ak = Mg, Ca, Sr, and Ba; Q = S and Se) [1,2,12], Sr₂Ge₂Se₅ [13], Ba₂Ge₂Se₅ [13], and only one telluride Ba₂Ge₂Te₅ [14]. Most of these compounds contain Ge⁴⁺. However, there are few compounds with Ge³⁺ or mixed Ge²⁺/⁴⁺. For example, Sr₂Ge₂Se₅ [13] and Ba₂Ge₂Te₅ [14] contain exclusively Ge³⁺ whereas Ge²⁺ and Ge⁴⁺ coexist in a mixed-valence compound Ba₂Ge₂Se₅ [13]. Surprisingly, there appear to be no known Ak/Ge/Q compounds with structures that have any homoatomic Q–Q bonds. Here we present the first such example: the synthesis, crystal structure, and electronic structure of the new ternary polytelluride Ba₂GeTe₃(Te₂).
2. Experimental

2.1. Synthesis

**Caution!** Depleted uranium is an α-emitting radioisotope and its manipulation is considered a health risk. Its use requires appropriate infrastructure and personnel trained in the handling of radioactive materials.

The following reactants were used as received: Ba (Alfa 99.5%), Ge (Aesar 99.99%), and Te (Aldrich 99.8%). U powder was obtained through the hydridization of depleted-U turnings (Mfg Sci. Corp.) followed by decomposition of the hydride under vacuum [15].

*Synthesis of single crystals of Ba2GeTe3(Te2).* Black crystals of Ba2GeTe3(Te2) were serendipitously obtained by combining the elements Ba, Ge, U, and Te. The aim of the reaction was to synthesize a new quaternary compound of Ba, Ge, U, and Te. The reactants were loaded into carbon-coated fused-silica tubes in an Ar-filled glove box, evacuated to 10⁻⁴ Torr, and flame sealed. The reaction contained 0.0346 g (0.252 mmol) Ba, 0.01g (0.042 mmol) U, 0.0061g (0.084 mmol) Ge, and 0.0965g (0.756 mmol) Te. The sealed tube containing the reaction mixture was heated from 298 K to 1053 K in 36 h, held there for 15 h, further heated to 1173 K in 24 h, and held there for 192 h. The tube was then cooled to 993 K over 99 h and finally to 298 K in a further 122 h. Semi-quantitative elemental analysis of the products was carried out with the use of a Hitachi S-3400 SEM equipped for EDX analysis. The black irregular shaped crystals showed Ba:Ge:Te ≈ 2:1:5. The sizes of these crystals were in the range of ~ 30 μm to 150 μm. The reaction product also contained crystals of UOTe and BaTe. The crystals of Ba2GeTe3(Te2) were stable in air for at least one week as judged from unit-cell determinations.

2.2. Structure Determination

Single-crystal X-ray diffraction data were collected at 100(2) K on an APEX2 X-ray diffractometer equipped with graphite-monochromatized MoKα radiation [16]. The crystal-to-detector distance was 60 mm; the exposure time was 15 sec/frame. Collection of
intensity data, cell refinement, and data reduction were performed using APEX2 as a series of 0.3° scans in \( \phi \) and \( \omega \) [16]. Face-indexed absorption, incident beam, and decay corrections were performed by the program SADABS [17]. The crystal structure was solved using the SHELX14 suite of programs [18]. Atom positions were standardized using the program STRUCTURE TIDY [19]. Structure drawings were made using the program CRYSTALMAKER [20]. Further details are given in Tables 1 and 2, and in the Supporting Information.

2.3. Electronic structure calculation

To conduct our calculations we have used the VASP (Vienna ab Initio Simulation Package) [21] code which implements density functional theory [22,23] using the projector augmented wave basis set [24]. For the exchange-correlation functional, we have chosen the one of Heyd, Scuseria, and Ernzerhof [25-27]. The crystal structure was kept identical to the experimental one, while to ensure proper convergence of our calculations, a 12 \( \times \) 4 \( \times \) 12 mesh was used to integrate over the Brillouin zone. The default cut-off was used for the plane wave part of the wave functions.
3. Results and discussion

3.1. Synthesis and Structure

Black single crystals of Ba$_2$GeTe$_3$(Te$_2$) were first obtained using the sealed tube method by heating the elements Ba, Ge, U, and Te at 1173 K. A yield of Ba$_2$GeTe$_3$(Te$_2$) crystals was about 25% (based on Ge). The reaction of stoichiometric amount of Ba, Ge, and Te did not yield the target Ba$_2$GeTe$_3$(Te$_2$) phase, but instead a mixture of the phases BaTe, GeTe, Ba$_2$Ge$_2$Te$_5$, and unreacted Te powder was obtained. The reaction of Ba, Ge, and Te in the same ratio as loaded in the initial reaction that involved uranium also tried using the same heating profile. However, the reaction product showed the presence of Ba$_2$Ge$_2$Te$_5$ as a major phase. Our further attempts to synthesize this compound by varying the heating conditions failed. It appears that this compound cannot be synthesized without the participation of U in the reaction. There are other known examples of compounds such as CsTi$_5$Te$_8$ [28] that can only be synthesized by U-assisted reactions.

The single-crystal X-ray diffraction study of Ba$_2$GeTe$_3$(Te$_2$) shows that it crystallizes with four formula units in the space group $Pnma$ of the orthorhombic system in a cell of dimensions $a = 6.790(1)$, $b = 23.720(5)$, and $c = 6.930(1)$ Å. The site symmetries of the atoms in the asymmetric unit are: Ba1 (1), Ge1 (.m.), Te1 (1), Te2 (1), and Te3 (.m.). The crystal structure of Ba$_2$GeTe$_3$(Te$_2$) is one-dimensional (Fig. 1).
Fig. 1: The unit cell view of Ba$_2$GeTe$_3$(Te$_2$) structure along (a) [100] and (b) [001] directions. The Ba, Ge, and Te atoms are shown in blue, green, and orange, respectively.

It consists of the zigzag chains that are made up of Ge1, Te1, and Te3 atoms. Each Ge atom is bonded to two Te1 and two Te3 atoms in a distorted tetrahedral fashion. Each GeTe$_4$ tetrahedron shares its two corners with the two neighboring GeTe$_4$ tetrahedra forming the infinite zigzag chain of $1_x[\text{GeTe}_3^{2-}]$ composition (Fig. 2). The Ge1–Te distances are in the range of 2.571(1)–2.683(1) Å. These distances are in good agreement with the corresponding distances in some known related compounds (Table 3).

Fig. 2: A view of infinite zig-zag chain of $[\text{GeTe}_3^{2-}]$ in Ba$_2$GeTe$_3$(Te$_2$) structure.

The Ba atoms in Ba$_2$GeTe$_3$(Te$_2$) structure are surrounded by nine Te atoms (4 × Te1, 4 ×
Te2, and 1 × Te3) in a distorted tricapped trigonal prism geometry (Fig. 3).

**Fig. 3:** Local coordination environment of Ba atoms in Ba2GeTe3(Te2) structure. The Ba–Te interactions are shown as black lines and Te–Te bond is shown as a red solid line.

The Ba–Te distances range between 3.5323(5) to 3.7110(7) Å. Compare these distances with BaSbTe3, (3.406(1)–3.888(1) Å) [29], Ba2SnTe5 (3.583(1)–3.662(1) Å) [9], and BaBiTe3 (3.404(2)–3.887(2) Å) [30] where the local coordination environments of Ba atoms are similar. This structure also features homoatomic Te–Te bonding between two Te2 atoms forming a Te2dimer with a distance of 2.7924(5) Å. This distance is comparable to the single bond Te–Te distances found in Cs4GeTe6 (2.735(1) and 2.746(1) Å) [31], Cs2GeTe4 (2.780(1) Å) [32], Tl2GeTe5 (2.905(1) Å) [33], K2GeTe4 (2.736(1) Å) [34], α-ThTe3 (2.7631(8) Å) [35], and BaThTe4 (2.766(1) Å) [36].

The charge balance in this ternary Ba2GeTe3(Te2) compound can be achieved with 2 × Ba2+, 1 × Ge4+, 3 × Te2−, and 1 × Te22−. Hence, the chemical formula of this closed shell Zintl compound is best described as Ba2GeTe3(Te2).

### 3.2. Electronic structure

In Fig. 4 we present our computed total (upper plot) and partial (lower plots) density of states (DOS) for Ba2GeTe3(Te2), as obtained with the HSE functional. Although relatively small, the total density has a finite value at the Fermi level; thus Ba2GeTe5 is a metal.
Fig. 4: Density of states (DOS) for Ba$_2$GeTe$_3$(Te$_2$).

From our partial density of states, it can be seen that Ge- and Te-derived states contribute the most around the Fermi level, while the contribution from Ba is almost negligible.

4. Conclusions

Crystals of the new ternary polytelluride, Ba$_2$GeTe$_3$(Te$_2$), have been obtained by the solid-state “U-assisted” reaction of U, Ba, Ge, and Te at 1173 K. The single crystal X-ray study at 100(2) K indicates that Ba$_2$GeTe$_3$(Te$_2$) crystallizes in space group $Pnma$ of the orthorhombic crystal system with four units in a cell with constants of $a = 6.7900(14)$ Å, $b = 23.720(5)$ Å, and $c = 6.9300(14)$ Å. Charge balance in Ba$_2$GeTe$_3$(Te$_2$) is achieved with $2 \times$ Ba$^{2+}$, $1 \times$ Ge$^{4+}$, $3 \times$ Te$^{2-}$, and $1 \times$ Te$_2^{2-}$: (Te$-$Te $= 2.7924(5)$ Å). The crystal structure of Ba$_2$GeTe$_3$(Te$_2$) can be described as pseudo one-dimensional with zig-zag chains of $1_\infty[GeTe_3^{2-}]$, where each Ge atom, which has $m$ symmetry, is coordinated to four Te atoms that form a distorted tetrahedron. Each Ba atom is surrounded by nine Te atoms in a distorted tricapped trigonal prism. The Te$_2^{2-}$ units and Ba$^{2+}$ cations separate the $1_\infty[GeTe_3^{2-}]$ chains. Ba$_2$GeTe$_3$(Te$_2$) is predicted to be a metal from the DFT calculations with Ge and Te-derived states contributing the most around the Fermi level.

5. Supporting information

The crystallographic CIF file for Ba$_2$GeTe$_3$(Te$_2$) [i.e., Ba$_2$GeTe$_5$] has been deposited as entry CCDC-1935898 (https://www.ccdc.cam.ac.uk).

Acknowledgments
Use was made of the IMSERC X-ray Facility at Northwestern University, supported by the International Institute of Nanotechnology (IIN).
References


[17] G.M. Sheldrick, SADABS, 2008. Department of Structural Chemistry, University of
Göttingen, Göttingen, Germany.


Table 1. Crystallographic Data and Structure Refinement Details for Ba$_2$GeTe$_3$(Te$_2$) structure$^a$.

<table>
<thead>
<tr>
<th></th>
<th>Ba$_2$GeTe$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>Pnma</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>6.7900(14)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>23.720(5)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>6.9300(14)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>1116.1(4)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
<td>$\rho$ (g cm$^{-3}$)</td>
<td>5.863</td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>22.39</td>
</tr>
<tr>
<td>$R(F)^b$</td>
<td>0.016</td>
</tr>
<tr>
<td>$R_w(F_o^2)^c$</td>
<td>0.027</td>
</tr>
</tbody>
</table>

$^a$λ = 0.71073 Å, $T = 100(2)$ K.

$^bR(F) = \Sigma ||F_o|| - ||F_c|| / \Sigma |F_o| \text{ for } F_o^2 > 2\sigma(F_o^2)$.

$^cR_w(F_o^2) = \{ \Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4 \}^{1/2}$. For $F_o^2 < 0$, $w^{-1} = \sigma^2(F_o^2)$; for $F_o^2 \geq 0$, $w^{-1} = \sigma^2(F_o^2) + 0.0074 F_o^2$. 
Table 2: Selected Metrical Data for $\text{Ba}_2\text{GeTe}_3(\text{Te}_2)$.$^a$

<table>
<thead>
<tr>
<th>Atom pair</th>
<th>Distances (Å)</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge1–Te1</td>
<td>2.5713(5) × 2</td>
<td>Te1–Ge1–Te1 130.05(2)</td>
</tr>
<tr>
<td>Ge1–Te3</td>
<td>2.6316(7)</td>
<td>Te1–Ge1–Te3 102.44(1) × 2</td>
</tr>
<tr>
<td></td>
<td>2.6827(7)</td>
<td>Te1–Ge1–Te3 103.85(1) × 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Te3–Ge1–Te3 114.78(2)</td>
</tr>
<tr>
<td>Te2–Te2</td>
<td>2.7924(5)</td>
<td></td>
</tr>
<tr>
<td>Ba1–Te1</td>
<td>3.6048(7)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.6202(7)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.6332(7)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.7110(7)</td>
<td></td>
</tr>
<tr>
<td>Ba1–Te2</td>
<td>3.5323(5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.5381(5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.5678(5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.5859(5)</td>
<td></td>
</tr>
<tr>
<td>Ba1–Te3</td>
<td>3.5514(7)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Some entries have been rounded to three significant figures to facilitate comparisons.
Table 3: Ge!Te Distances in Some Related Compounds with 4-Coordinated Ge atoms$^a$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Ge!Te (Å)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$_2$GeTe$_5$</td>
<td>one-dimensional</td>
<td>2.571(1)−2.683(1)</td>
<td>this work</td>
</tr>
<tr>
<td>Cs$_4$GeTe$_6$</td>
<td>zero-dimensional</td>
<td>2.537(3)−2.623(2)</td>
<td>[31]</td>
</tr>
<tr>
<td>Cs$_2$GeTe$_4$</td>
<td>one-dimensional</td>
<td>2.549(1)−2.650(3)</td>
<td>[32]</td>
</tr>
<tr>
<td>Tl$_2$GeTe$_3$</td>
<td>zero-dimensional</td>
<td>2.580(3)−2.643(3)</td>
<td>[37]</td>
</tr>
<tr>
<td>α-Tl$_2$GeTe$_5$</td>
<td>zero-dimensional</td>
<td>2.604(1)−2.664(5)</td>
<td>[33]</td>
</tr>
<tr>
<td>β-Tl$_2$GeTe$_5$</td>
<td>zero-dimensional</td>
<td>2.616(1)−2.639(1)</td>
<td>[38]</td>
</tr>
<tr>
<td>K$_2$GeTe$_4$</td>
<td>one-dimensional</td>
<td>2.508(2)−2.640(2)</td>
<td>[34]</td>
</tr>
</tbody>
</table>

$^a$Some distances have been rounded for comparison. All the compounds contain germanium in +4 oxidation state.