Inorganic Chemistry

Communication

pubs.acs.org/IC

Quaternary Tellurides with Different Valent Ge Centers: $Cs_2Ge_3M_6Te_{14}$ (M = Ga, In)

Cheng-Yi Zhang,[†,‡] Liu-Jiang Zhou,[†,‡] and Ling Chen*,[†]

[†]Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

[‡]Graduate University of Chinese Academy of Sciences, Beijing 100039, People's Republic of China

Supporting Information

ABSTRACT: New quaternary tellurides, $Cs_2Ge_3M_6Te_{14}$ (M = Ga, In), were discovered by solid-state reactions. These compounds crystallize in space group $P3\bar{m}1$ (No. 164), with $a = b = 8.2475(2)$ Å, $c = 14.2734(8)$ Å, and $V = 840.82(6)$ Å^3 ($Z = 1$) for $Cs_2Ge_3Ga_6Te_{14}$ (**1**) and $a = b = 8.5404(2)$ Å, $c = 14.6766(8)$ Å, and $V = 927.07(6)$ Å^3 ($Z = 1$) for $Cs_2Ge_3In_6Te_{14}$ (**2**). The remarkable structural feature is the novel three-dimensional $[Ge_3M_6Te_{14}]^{2-}$ anionic framework made by condensed In_6Te_{14} (or Ga_6Te_{14}) layers that are connected alternately by dimeric $Ge^{3+}{}_2Te_6$ units and $Ge^{2+}Te_6$ octahedra along the c direction. The presence of Ge centers with different oxidation states is also supported by the results of the electron localization function calculation and X-ray photoelectron spectroscopy measurement.

Ternary or quaternary germanium tellurides are interesting because of not only their diverse structural chemistry but also their desired physical properties, which show wide potential applications. For example, $Ba_4Ag_{3.95}Ge_2Te_9$[1] and Tl_2MGeTe_4 (M = Cd, Hg)[2] exhibit thermoelectric properties, and M_3GeTe_2 (M = Fe, Ni)[3] show magnetic properties. In general, Ge can adopt three different oxidation states in chalcogenides, i.e., Ge^{2+}, Ge^{3+}, or Ge^{4+}. Interestingly, each oxidation state has been found in its own distinct local coordination geometry, such as a $Ge^{4+}Q_4$ tetrahedron in Li_2CdGeS_4,[4] $K_4Cu_8Ge_3S_{12}$,[5] and $Rb_3(AlS_2)_3(GeS_2)_7$,[6] a dimeric $Ge^{3+}{}_2Q_6$ unit with a covalent Ge−Ge bond in $Na_8Sn(Ge_2S_6)_2$,[7] $Sr_2Ge_2Se_5$,[8] and $Ba_4Ag_{3.95}Ge_2Te_9$,[1] and octahedral $Ge^{2+}Q_6$ in $Ge_3Sb_2Te_6$[9] and As_4GeTe_7.[10] More interestingly, a few compounds illustrate that Ge atoms with mixed oxidation states can occur in a single compound, such as $Tl_2Ge^{2+}Ge^{4+}S_4$[11] and $Ba_2Ge^{2+}Ge^{4+}Se_5$.[8] Moreover, a unique compound, $\{[Mn(en)_3]_2(Ge_5Te_{10})\}_n$, contains multivalent Ge sites, e.g., Ge^{2+}, Ge^{3+}, and Ge^{4+}, simultanously.[12] Besides chalcogenides, the interesting Ge−Ge bonding can also be found in phosphides or halides, such as $NaGe_3P_3$[13] and Ge_6Cl_6.[14]

To date, quaternary A/Ge/M/Te telluride (A = alkali metals; M = transition metals or main-group metals) remains less explored. Ternary A/Ge/Te tellurides, i.e., $K_6Ge_2Te_6$,[15] K_2GeTe_4,[16] and Cs_4GeTe_6,[17] are reported. Herein, we report the first quaternary $Cs_2Ge_3M_6Te_{14}$ [M = Ga (**1**), In (**2**)], which contain both Ge^{2+} and Ge^{3+} centers. These compounds were synthesized from a mixture of 0.6 mmol of M, 0.3 mmol of Ge, and 1.4 mmol of Te, together with 1.2 mmol of flux CsCl at 820 °C by solid-state reactions. It turned out that CsCl worked as both a flux and a cesium source in these reactions (experimental details are listed in the Supporting Information, SI). X-ray diffraction (XRD) analyses indicated that the yields of the target products (after washing by distilled water) were about 90%, and the minor second phase was Ga_2Te_3 or In_2Te_3. Pure-phased products can be obtained by manually picking crystals (black block crystals; Figure S1 in the SI), and the corresponding XRD patterns are shown in Figures S2 and S3 in the SI. The energy-dispersive X-ray analyses gave stoichiometries of $Cs_{1.7(4)}Ge_3Ga_{5.9(4)}Te_{14.2(5)}$ for **1** and $Cs_{1.6(6)}Ge_3In_{6.8(8)}Te_{14.6(7)}$ for **2**, which are in good agreement with the refined compositions obtained from single-crystal diffraction data (Figures S4 and S5 in the SI).

$Cs_2Ge_3M_6Te_{14}$ (M = Ga, In) crystallizes in the $P3\bar{m}1$ space group, with $a = b = 8.2475(2)$ Å, $c = 14.2734(8)$ Å, and $V = 840.82(6)$ Å^3 for **1** and $a = b = 8.5404(2)$ Å, $c = 14.6766(8)$ Å, and $V = 927.07(6)$ Å^3 for **2**. The remarkable structural feature of these compounds is the novel $[Ge_3M_6Te_{14}]^{2-}$ anionic three-dimensional framework made by layers of condensed $InTe_4$ (or $GaTe_4$) tetrahedra, which are connected alternately by dimeric $(Ge1)^{3+}{}_2Te_6$ units and $(Ge2)^{2+}Te_6$ octahedra along the c direction (Figure 1).

Each In or Ga atom is coordinated by one Te1, one Te2, and two Te3 atoms in a distorted tetrahedral geometry, as shown in Figure 1, with the M−Te distance varying from 2.6004(9) to 2.6637(7) Å in **1** and from 2.7606(7) to 2.7951(6) Å in **2**, which are comparable with 2.64 Å in Ga_2Te_5[18] and 2.77 Å in $AgIn_5Te_8$[19] (Table S3 in the SI). Each M_6Te_{14} layer is constructed of condensed MTe_4 tetrahedra via sharing of 3-fold μ_3-Te2 bridging atoms (shared by three coplanar tetrahedra) and 2-fold μ_2-Te2 bridging atoms (shared by two coplanar tetrahedra); see Figure S6 in the SI. Neighboring M_6Te_{14} layers are operated to each other by the 3-fold inversion axis located at (0, 0, z).

There are two crystallographically independent Ge sites: Ge1 (Wyckoff 2c site) and Ge2 (Wyckoff 1b site). Ge1 atoms lying at (0, 0, z) are dimerized by a covalent Ge1−Ge1 bond (Figure 1, blue bonds), which connect two neighboring M_6Te_{14} layers via six Ge1−Te1 bonds. The Ge1−Ge1 bond lengths 2.438(2) Å in **1** or 2.432(2) Å in **2** are comparable with 2.45 Å in $Tl_6Ge_2Te_6$,[20] 2.49 Å in $K_6Ge_2Te_6$,[15] and 2.43 Å in

Received: March 22, 2012
Published: June 15, 2012

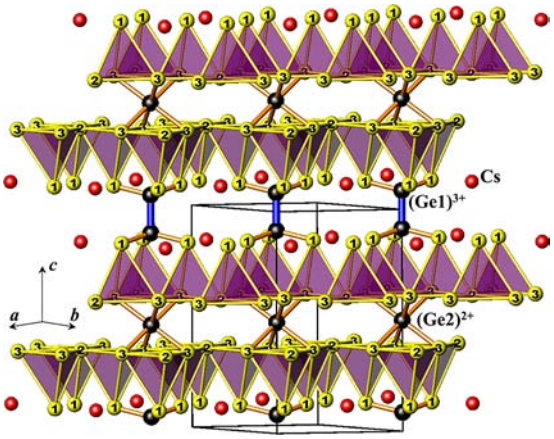

Figure 1. Structure of $Cs_2Ge_3M_6Te_{14}$ with the Ge1−Ge1 (blue line) and Ge−Te (orange line) bonds outlined. Color code: red, Cs; black, Ge; yellow, Te; purple tetrahedra, MTe_4 (M = Ga, In), in which the centering M atoms and M−Te bonds are omitted for clarity.

$Ba_4Ag_{3.95}Ge_2Te_9$.[1] The Ge1−Te1 bond distances are 2.5671(5) Å in **1** and 2.5842(6) Å in **2**, which are comparable with 2.58 Å in $Tl_6Ge_2Te_6$.[20] Differently, Ge2 centers a $Ge2Te_6$ octahedron that is constructed of six Te3 atoms, of which three come from the upper layer and three come from the lower one so as to interlink the neighboring M_6Te_{14} layers (Figure 1). The Ge2−Te bond distances 3.0880(5) Å in **1** and 3.0208(5) Å in **2** are comparable with 2.916 Å in As_4GeTe_7[10] and 2.993 Å in GeTe.[21]

The Cs^+ cation centers a $CsTe_{12}$ anticubooctahedron constructed of nine Te1 and three Te3 atoms, as shown in Figure S7 in the SI, with Cs−Te distances ranging from 4.1272(2) to 4.4369(2) Å (Table S3 in the SI). These values are comparable to those found in $CsTaTe_3$ (3.99−4.01 Å),[22] CsAuTe (4.02−4.09 Å),[23] and $Cs_2Mo_2O_{14}P_2Te$ (4.25−4.44 Å).[24]

The shortest Te−Te interactions in **1** and **2** are 3.907 and 4.037 Å, which are much longer than the sum of the covalent radius 2.7 Å and are comparable with the sum of the van der Waals radius 4.1 Å; thus, all Te atoms are viewed as Te^{2-}. The $(Ge1)_2Te_6$ unit contains a Ge−Ge covalent bond in a typical geometry that is characteristic of the trivalent Ge^{3+}, as reported in $Na_8Sn(Ge_2S_6)_2$,[7] $Sr_2Ge_2Se_5$,[8] and $Tl_6Ge_2Te_6$.[20] The formal oxidation state of Ge2 can be assigned as Ge^{2+} according to its octahedral coordination environment, which is the common geometry for the bivalent Ge^{2+}, as found in $Ge_3Sb_2Te_6$[9] and As_4GeTe_7.[10] Therefore, the charge-balanced formula of **1** and **2** can be described as $Cs_2Ge_3M_6Te_{14} \equiv (Cs^+)_2(Ge1^{3+})_2(Ge2)^{2+}(M^{3+})_6(Te^{2-})_{14}$.

The presence of two different oxidation states of Ge (namely, Ge^{2+} and Ge^{3+}) in **1** or **2** can be proven by both the electron localization function (ELF; Figure S8 in the SI) and X-ray photoelectron spectroscopy (XPS) results (Figure 2). Figure S8 in the SI shows the ELF contours of a plane within the $[Ge_3Ga_6Te_{14}]^{2-}$ anion in **1**. The covalent Ge−Ge bond can be clearly seen as the black pane indicated. XPS results of compound **1** indicated the presence of two different binding energies (31.6 and 32.5 eV), which correspond to those of Ge^{2+} and Ge^{3+}, respectively. Furthermore, the Ge^{2+}:Ge^{3+} atomic ratio calculated from the area of the XPS peaks is 0.49:1, which agrees well with the 0.5:1 obtained from the single-crystal data refinement.

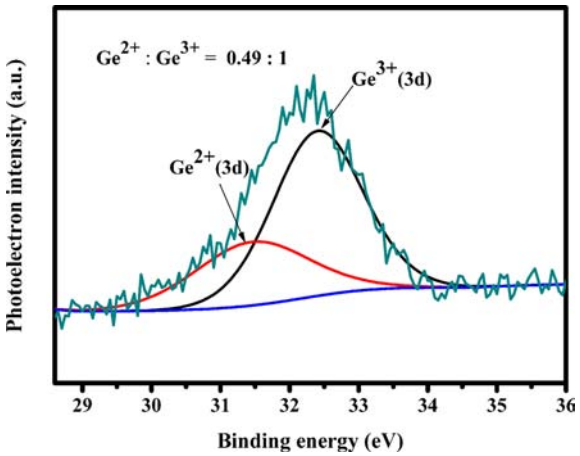

Figure 2. XPS of compound **1**.

To understand the distribution of the states near the Fermi level, the densities of states (DOS) of **1** and **2** were calculated (Figures 3a and S9 in the SI). The valence band (VB) near the Fermi level is dominated by the Ga 4p, Ge 4p, and Te 5p states, whereas the conduction band (CB) has most of its contributions coming from Te 5p, Ge 4s, Ga 4s, Ge 4p, and Ga 4p with minor Cs 6s and Cs 5p contributions. In the band structure of **1**, the VB maximum and CB minimum locate at

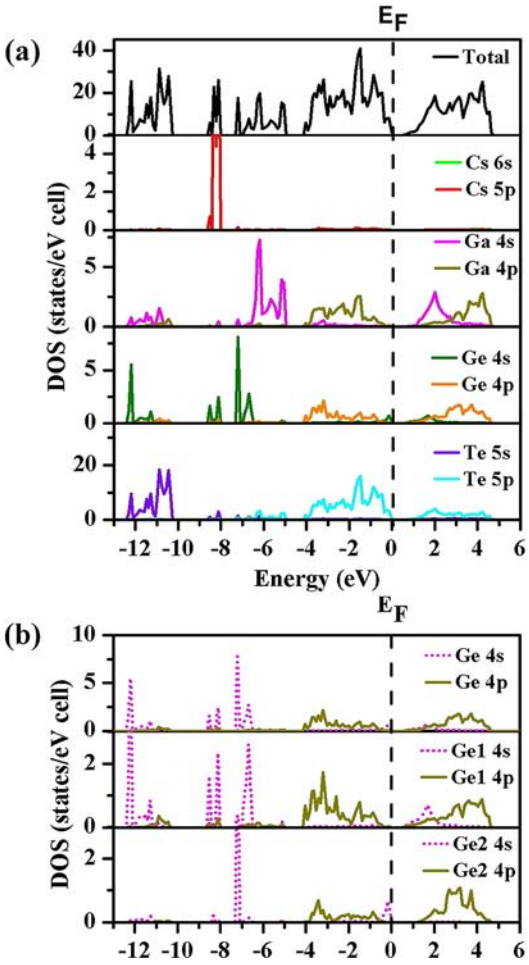

Figure 3. (a) Total and partial DOSs of **1**. (b) Enlarged DOSs of Ge1 and Ge2.

different k points, indicating a computational indirect narrow band of about 0.53 eV (Figure S10 in the SI). Compound **2** has a similar band structure but a slightly larger computational band gap of about 0.63 eV (Figure S11 in the SI). According to the DOSs, $(Ge1)^{3+}$ has less 4s states below E_F than $(Ge2)^{2+}$ does because some $(Ge1)^{3+}$ 4s states distribute above E_F, whereas $(Ge2)^{2+}$ 4s states almost distribute below E_F (Figure 3b).

In conclusion, the first two quaternary three-dimensional telluride frameworks, $Cs_2Ge_3M_6Te_{14}$ (M = Ga, In), with Ge in different oxidation states in the A/Ge/M/Te system (A = alkali metals; M = transition metals or main-group metals), have been discovered. The presence of Ge^{3+} and Ge^{2+} is revealed by characteristic coordination geometries around Ge centers according to the single-crystal diffraction data, as well as the results of the ELF calculation and XPS measurement. The primary electron structure analyses indicate small-band-gap semiconducting nature of these compounds, and further investment on their physical properties is worth trying.

■ ASSOCIATED CONTENT

Supporting Information

CIF data, experimental and theoretical methods, and additional tables and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: chenl@fjirsm.ac.cn. Tel: (011)86-591-83704947.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the National Natural Science Foundation of China under Projects 90922021, 20973175, and 21171168 and the "Knowledge Innovation Program of the Chinese Academy of Sciences" (Grant KJCX2-YW-H20).

■ REFERENCES

(1) Cui, Y. J.; Assoud, A.; Kleinke, H. *Inorg. Chem.* **2009**, *48*, 5313.
(2) McGuire, M. A.; Scheidemantel, T. J.; Badding, J. V.; DiSalvo, F. J. *Chem. Mater.* **2005**, *17*, 6186.
(3) Deiseroth, H. J.; Aleksandrov, K.; Reiner, C.; Kienle, L.; Kremer, R. K. *Eur. J. Inorg. Chem.* **2006**, 1561.
(4) Lekse, J. W.; Moreau, M. A.; McNerny, K. L.; Yeon, J.; Halasyamani, P. S.; Aitken, J. A. *Inorg. Chem.* **2009**, *48*, 7516.
(5) Zhang, R. C.; Yao, H. G.; Ji, S. H.; Liu, M. C.; Ji, M.; An, Y. L. *Inorg. Chem.* **2010**, *49*, 6372.
(6) Rothenberger, A.; Shafaei-Fallah, M.; Kanatzidis, M. G. *Inorg. Chem.* **2010**, *49*, 9749.
(7) Marking, G. A.; Kanatzidis, M. G. *J. Alloys Compd.* **1997**, *259*, 122.
(8) Johrendt, D.; Tampier, M. *Chem.—Eur. J.* **2000**, *6*, 994.
(9) Matsunaga, T.; Kojima, R.; Yamada, N.; Kifune, K.; Kubota, Y.; Takata, M. *Appl. Phys. Lett.* **2007**, *90*, 161919.
(10) Shu, H. W.; Jaulmes, S.; Flahaut, J. *J. Solid State Chem.* **1988**, *74*, 277.
(11) Eulenberger, G. *J. Less-Common Met.* **1985**, *108*, 65.
(12) Zhang, Q. C.; Armatas, G.; Kanatzidis, M. G. *Inorg. Chem.* **2009**, *48*, 8665.
(13) Feng, K.; Yin, W. L.; He, R.; Lin, Z. S.; Jin, S. F.; Yao, J. Y.; Fu, P. Z.; Wu, Y. C. *Dalton Trans.* **2011**, *41*, 484.
(14) Beattie, I. R.; Jones, P. J.; Reid, G.; Webster, M. *Inorg. Chem.* **1998**, *37*, 6032.
(15) Dittmar, G. *Z. Anorg. Allg. Chem.* **1979**, *453*, 68.
(16) Eisenmann, B.; Schrod, H.; Schäfer, H. *Mater. Res. Bull.* **1984**, *19*, 293.
(17) Brinkmann, C.; Eisenmann, B.; Schäfer, H. *Mater. Res. Bull.* **1985**, *20*, 1207.
(18) Julien-Pouzol, M.; Jaulmes, S.; Alapini, F. *Acta Crystallogr., Sect. B* **1977**, *33*, 2270.
(19) Mora, A. J.; Delgado, G. E.; Pineda, C.; Tinoco, T. *Phys. Status Solidi A* **2004**, *201*, 1477.
(20) Eulenberger, G. *J. Solid State Chem.* **1984**, *55*, 306.
(21) Parker, S. G.; Pinnell, J. E.; Swink, L. N. *J. Mater. Sci.* **1974**, *9*, 1829.
(22) Pell, M. A.; Vajenine, G. V. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 5186.
(23) Bronger, W.; Kathage, H. U. *J. Alloys Compd.* **1992**, *184*, 87.
(24) Guesdon, A.; Raveau, B. *Chem. Mater.* **2000**, *12*, 2239.