Jai Prakash, Adel Mesbah, Jessica Beard, Dario Rocca, Sébastien Lebègue,
Christos D. Malliakas and James A. Ibers*

Two new ternary chalcogenides Ba$_2$ZnQ$_3$ (Q = Se, Te) with chains of ZnQ$_4$ tetrahedra: syntheses, crystal structure, and optical and electronic properties

Abstract: Single crystals of Ba$_2$ZnQ$_3$ (Q = Se, Te) were obtained by solid-state reactions at 1173 K. These isostructural compounds crystallize in the K$_2$AgI$_3$ structure type. The Zn atoms in this structure are coordinated to four Q atoms (2 $Q1$, 1 $Q2$, 1 $Q3$) and these form a distorted tetrahedron around each Zn atom. Each ZnQ$_4$ tetrahedron shares two corners with neighboring ZnQ$_4$ tetrahedra resulting in the formation of infinite chains of [ZnQ$_4^{4-}$] units. The absorption spectrum of a single crystal of Ba$_2$ZnTe$_3$ shows an absorption edge at 2.10(2) eV, consistent with the dark-red color of the crystals. From DFT calculations Ba$_2$ZnSe$_3$ and Ba$_2$ZnTe$_3$ are found to be semiconductors with electronic band gaps of 2.6 and 1.9 eV, respectively.

Keywords: crystal structures; DFT calculations; optical band gap; syntheses.

*Corresponding author: James A. Ibers, Department of Chemistry, Northwestern University, Evanston, IL 60208-3113, USA, e-mail: ibers@northwestern.edu
Jai Prakash, Jessica Beard and Christos D. Malliakas: Department of Chemistry, Northwestern University, Evanston, IL 60208-3113, USA
Adel Mesbah: Department of Chemistry, Northwestern University, Evanston, IL 60208-3113, USA; and ICSM, UMR 5257 CEA/CNRS/ UM2/ENSCM, BP 17171, 30207 Bagnols-sur-Cèze cedex, France
Dario Rocca and Sébastien Lebègue: Laboratoire de Cristallographie, Résonance Magnétique et Modélisations (CRM2, UMR CNRS 7036), Institut Jean Barriol, Université de Lorraine, BP 239, Boulevard des Aiguillettes, 54506 Vandoeuvre-lès-Nancy, France

1 Introduction

The search for new solid-state metal chalcogenides is motivated by their diverse crystal chemistry and exciting physical properties, such as superconductivity [1–4], magnetism [5], charge and spin density waves [6], and optical [7, 8] and thermoelectric properties [9]. Examples of superconducting chalcogenides are Chevrel phases M_xMo$_6$Q$_8$ (M = metal, Q = chalcogen) [2–4] and Fe$_{1+x}$Q-based compounds [1] that exhibit magnetism and superconductivity which can be tuned by variation of the metal content and the type of Q atom. Metal chalcogenides, such as β-K$_2$Hg$_3$Ge$_2$S$_8$ [7], Na$_2$Ge$_2$Se$_5$ [8], Li$_2$CdGeS$_4$ [10], and Ba$_4$CuGa$_5$Q$_{12}$ (Q = S, Se) [11], have applications in nonlinear optical devices. These examples show that a variety of physical properties can be achieved by combination of suitable metal and chalcogen.

The alkaline-earth based compounds with the general formula Ak_2MQ_3 (Ak = Sr, Ba; M = 3d metal; Q = S, Se, Te) [12–15] are of interest because of their magnetic and fluorescent properties. The Mn-activated Ba$_2$ZnS$_3$ [15] and Eu(II)-activated Sr$_2$ZnS$_3$ compounds [12] are important fluorescent materials and have applications in lamps and in color displays [15]. The emission colors of these compounds can be tuned by substitution at the Zn site or at the Ak sites. In this report, we present the syntheses, structure, and optical and electronic band structures of the two new compounds, Ba$_2$ZnSe$_3$ and Ba$_2$ZnTe$_3$, of the Ak_2MQ_3 family.

2 Results and discussion

2.1 Syntheses

Initially, single crystals of Ba$_2$ZnSe$_3$ and Ba$_2$ZnTe$_3$ were obtained by solid-state reactions in an attempt to discover

new quaternary compounds in Ba–Th–Zn–Se and Ba–U–Zn–Te systems. Subsequently, Ba$_2$ZnSe$_3$ and Ba$_2$ZnTe$_3$ single crystals were produced in high yields at 1173 K from stoichiometric reactions of the elements.

2.2 Crystal structure

The isostructural compounds Ba$_2$ZnQ$_3$ (Q = Se, Te) crystallize in the K$_2$AgI$_3$ structure type [16] with four formula units in the space group D_{2h}^{16}-Pnma of the orthorhombic crystal system (Table 1). As expected, the unit cell constants for Ba$_2$ZnTe$_3$ are larger than those for Ba$_2$ZnSe$_3$. The crystal structure of these compounds is shown in Fig. 1. There are six atoms in the asymmetric unit of the structure all with site symmetry.*m*.: two Ba atoms, one Zn atom, and three Q atoms. The Zn atoms in this structure are coordinated to four Q atoms (2 Q1, 1 Q2, 1 Q3) and these form a distorted tetrahedron around each Zn atom. Each ZnQ$_4$ tetrahedron shares two corners (formed by Q1 atoms) with neighboring ZnQ$_4$ tetrahedra resulting in the formation of infinite chains of [ZnQ$_4^{4-}$] units along the *b* axis (Fig. 2). The Ba atoms in this structure act as space fillers and separate these [ZnQ$_4^{4-}$] chains. Both the Ba1 and Ba2 atoms are surrounded by seven Q atoms in a monocapped trigonal-prismatic geometry.

The ZnQ$_4$ tetrahedra in these structures are distorted with three different Zn−Q interatomic distances and four different Q−Zn−Q interatomic angles (Table 2). The ZnTe$_4$ tetrahedron in Ba$_2$ZnTe$_3$ is slightly less distorted than the ZnSe$_4$ tetrahedron in Ba$_2$ZnSe$_3$. The Zn−Se distances in Ba$_2$ZnSe$_3$ (2.4541 (6) to 2.5730 (5) Å) are in good agreement with the corresponding distances in ZnIn$_2$Se$_4$ (2.544(1) to 2.559(1) Å) [17], ZnGa$_2$Se$_4$ (2.438(1) Å)
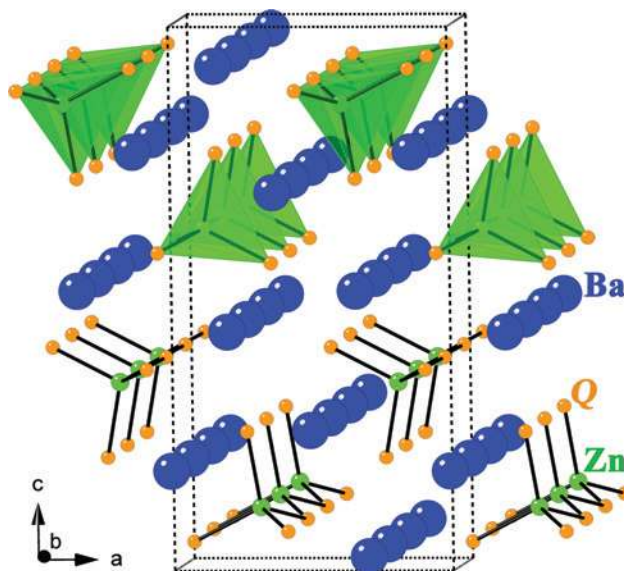

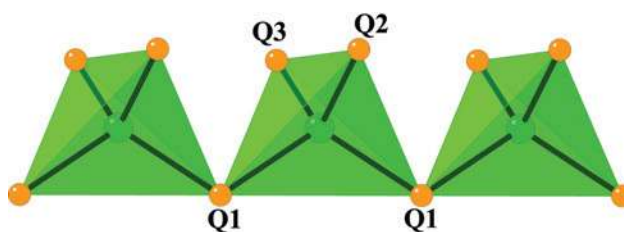**Fig. 1:** The Ba$_2$ZnQ$_3$ structure viewed along the *b* axis.

Fig. 2: Local coordination of the Zn atoms and connectivity of the ZnQ$_4$ tetrahedra.

Table 2: Interatomic distances (Å) and angles (deg) for Ba$_2$ZnSe$_3$ and Ba$_2$ZnTe$_3$.

Compound	Ba$_2$ZnSe$_3$	Ba$_2$ZnTe$_3$
Zn1−Q1	2.5730(5) × 2	2.7482(3) × 2
Zn1−Q2	2.4541(6)	2.6432(5)
Zn1−Q3	2.4739(6)	2.6568(5)
Q2−Zn1−Q3	107.29(2)	108.26(2)
Q2−Zn1−Q1	107.77(1) × 2	108.02(1) × 2
Q3−Zn1−Q1	108.03(1) × 2	108.37(1) × 2
Q1−Zn1−Q1	117.54(2)	115.59(2)
Ba1−Q	3.1966(5) to 3.4225(8)	3.4007(2) to 3.6408(3)
Ba2−Q	3.2534(5) to 3.3476(5)	3.4605(2) to 3.6054(3)

[18], Zn$_4$Ga$_{16}$Se$_3$ (2.375(1) to 2.445(1) Å) [19], CsHoZnSe$_3$ (2.435(1) to 2.552(1) Å) [20], and Cs$_2$ZnGe$_3$Se$_8$ (2.448(1) to 2.485(1) Å) [21]. The Zn−Te distances in Ba$_2$ZnTe$_3$ (2.6432(5) to 2.7482(3) Å) are also consistent with the Zn−Te distances in related compounds such as CsLaZnTe$_3$ (2.649(1) to 2.806(1) Å) [22], CsSmZnTe$_3$ (2.646(1) to 2.763(1) Å) [22], and KCuZnTe$_2$ (2.682(1) Å) [23]. The Ba−Se and Ba−Te distances

Table 1: Crystallographic data and structure refinement details.[a]

	Ba$_2$ZnSe$_3$	Ba$_2$ZnTe$_3$
Space group	D_{2h}^{16}-Pnma	D_{2h}^{16}-Pnma
a, Å	9.0757(19)	9.6695(3)
b, Å	4.4003(11)	4.6507(1)
c, Å	17.629(3)	18.7944(6)
V, Å^3	704.0(3)	845.18(4)
ρ, g cm^{-3}	5.433	5.681
μ, mm^{-1}	29.82	22.07
R(F)[b]	0.010	0.013
$R_w(F_o^2)$[c]	0.021	0.027

[a]λ = 0.71073 Å, *T* = 100(2) K, *Z* = 4; [b]$R(F) = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ for $F_o^2 > 2\,\sigma(F_o^2)$; [c]$R_w(F_o^2) = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma wF_o^4\}^{1/2}$; for $F_o^2 < 0$, $w^{-1} = \sigma^2(F_o^2)$, for $F_o^2 \geq 0$, $w^{-1} = \sigma^2(F_o^2) + (qF_o^2)^2$ where q = 0.0070 for Ba$_2$ZnSe$_3$ and 0.0027 for Ba$_2$ZnTe$_3$.

in Ba$_2$ZnQ$_3$ (*Q* = Se, Te) are also normal. These structures do not feature any short *Q*–*Q* interactions and hence their charge balance is Ba$_2^{2+}$Zn^{2+}(*Q*$^{2-}$)$_3$.

2.3 Optical band gap measurement

The absorption spectrum collected at 298 K on a single crystal of Ba$_2$ZnTe$_3$ shows an absorption edge at 2.10(2) eV. Analysis of the square and square root of absorbance data as a function of energy (Fig. 3) gives the same value for the direct and indirect band gap components suggesting that the band gap of Ba$_2$ZnTe$_3$ is direct at 2.10(2) eV. Furthermore, the edge of the absorption spectrum is consistent with the dark-red color of the crystals. Crystals of the Se analogue, Ba$_2$ZnSe$_3$, are pale yellow in color and their absorption falls outside the range of our spectrophotometer.

2.4 DFT calculations

Ba$_2$ZnSe$_3$ and Ba$_2$ZnTe$_3$ are found to be semiconductors with electronic band gaps of 2.6 and 1.9 eV, respectively, as seen on the computed total density of states (upper plots of Figs. 4 and 5). From the partial density of states (PDOS) plots (lower plots of Figs. 4 and 5), it is seen that the top of the valence states corresponds essentially to *p* states from the chalcogens (Se in Ba$_2$ZnSe$_3$ and Te in Ba$_2$ZnTe$_3$), while the bottom of the conduction states in both compounds comprise Ba-*d* states and Zn-*s* states. The electronic band gap of Ba$_2$ZnTe$_3$ of 1.9 eV is in very good agreement with the measured optical band gap of 2.1 eV.

3 Conclusions

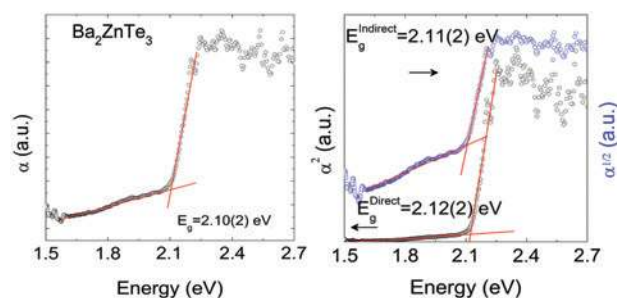Single crystals of Ba$_2$ZnQ$_3$ (*Q* = Se, Te) were obtained by solid-state reactions at 1173 K. These isostructural
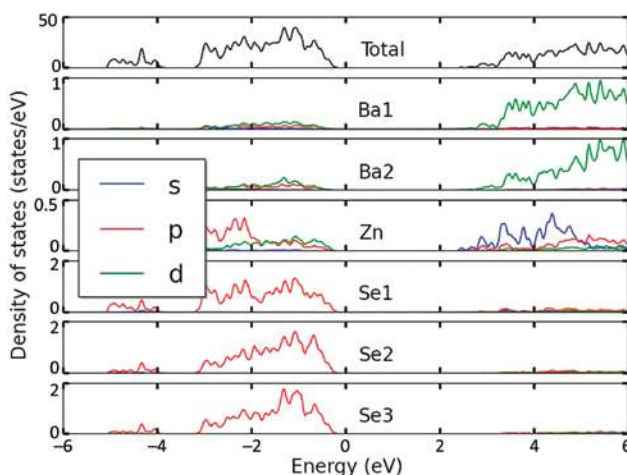

Fig. 4: Computed total density of states (upper plot) and partial density of states (lower plots) for Ba$_2$ZnSe$_3$.
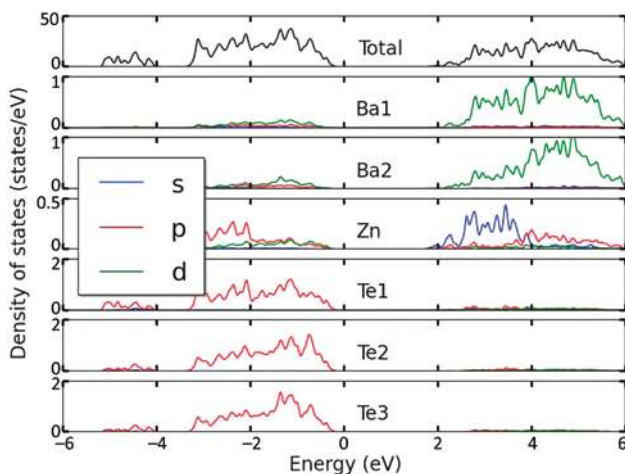

Fig. 5: Computed total density of states (upper plot) and partial density of states (lower plots) for Ba$_2$ZnTe$_3$.

compounds crystallize in the K$_2$AgI$_3$ structure type in the space group D_{2h}^{16}-*Pnma* of the orthorhombic crystal system with four formula units in the cell. The Zn atoms in this structure are coordinated to four *Q* atoms (2 *Q*1, 1 *Q*2, 1 *Q*3) and these form a distorted tetrahedron around each Zn atom. Each ZnQ$_4$ tetrahedron shares two corners (formed by *Q*1 atoms) with neighboring ZnQ$_4$ tetrahedra resulting in the formation of infinite one-dimensional chains of [ZnQ$_4^{4-}$] units. The Ba atoms in this structure act as space fillers and separate these [ZnQ$_4^{4-}$] chains. Both the Ba1 and Ba2 atoms are surrounded by seven *Q* atoms in a monocapped trigonal-prismatic geometry. The absorption spectrum collected at 293 K on a single crystal of Ba$_2$ZnTe$_3$ shows an absorption edge at 2.10(2)

Fig. 3: Optical absorption spectrum of a Ba$_2$ZnTe$_3$ single crystal (right) and plots of α^2 and $\alpha^{1/2}$ vs. energy (left).

eV. Analysis of the square and square root of absorbance data as a function of energy gives the same value for both direct and indirect band gap components suggesting that the band gap of Ba$_2$ZnTe$_3$ is direct. The edge of the absorption spectrum is consistent with the dark-red color of the crystals. From DFT calculations Ba$_2$ZnSe$_3$ and Ba$_2$ZnTe$_3$ are found to be semiconductors with electronic band gaps of 2.6 and 1.9 eV, respectively. The latter value is in very good agreement with the measured optical band gap.

4 Experimental section

4.1 Syntheses

The following reactants were used as obtained: Ba (Johnson Matthey, 99.5 %), Zn (Aldrich, 99.5 %), Se (Cerac, 99.999 %), Te (Aldrich, 99.8 %), and Th (MP Biomedicals, 99.1 %). U powder was obtained by hydridization and decomposition of depleted U turnings (IBI Labs) in a modification [24] of a literature method [25]. Reactions were performed in sealed 6 mm carbon-coated fused-silica tubes. Chemical manipulations were performed inside an Ar-filled dry box. The reactants were weighed and transferred into tubes that were then evacuated to 10^{-4} Torr, flame sealed, and placed in a computer-controlled furnace. Semi-quantitative EDX analyses of the products of the reactions were obtained with the use of a Hitachi S-3400 SEM microscope.

4.2 Synthesis of Ba$_2$ZnSe$_3$

Yellow single crystals of Ba$_2$ZnSe$_3$ were obtained in an attempt to synthesize the hypothetical quaternary compound Ba$_3$ZnThSe$_6$ of the 2H hexagonal perovskite family [26–28]. The reaction mixture comprised Ba (35 mg, 0.255 mmol), Th (19.7 mg, 0.085 mmol), Zn (5.56 mg, 0.085 mmol), and Se (40.13 mg, 0.508 mmol) in 100 mg of CsCl flux. The loaded tube was heated to 1173 K in 48 h, held there for 4 d, cooled to 673 K at 2.5 K h^{-1}. Then the furnace was turned off. The reaction produced rectangular-shaped yellow single crystals in an approximate yield of 20 wt%. For these crystals the EDX analysis gave Ba:Zn:Se ≈ 2:1:3. Byproducts included BaSe and ThOSe. Afterwards, a rational stoichiometric synthesis provided Ba$_2$ZnSe$_3$ in a yield of about 80 wt%. Crystals of BaSe and ZnSe were also detected.

4.3 Synthesis of Ba$_2$ZnTe$_3$

Red crystals of Ba$_2$ZnTe$_3$ were obtained by a reaction of Ba (35 mg, 0.599 mmol), U (10.1 mg, 0.042 mmol), Zn (5 mg, 0.076 mmol), and Te (86.8 mg, 0.680 mmol). The reaction mixture was heated to 1023 K in 24 h and held there for 10 h. The reaction mixture was then heated to 1173 K in 24 h followed by annealing there for 99 h. It was then cooled to 873 K in 99 h, and then finally to 373 K in 99 h. The reaction product contained red lath-shaped crystals of Ba$_2$ZnTe$_3$ (Ba:Zn:Te≈2:1:3), black plate-shaped crystals of UOTe (U:Te ≈1:1) [29], and crystals of BaTe (Ba:Te ≈1:1). A similar reaction with Th powder instead of U powder also produced Ba$_2$ZnTe$_3$ crystals in high yield. Ba$_2$ZnTe$_3$ can also be synthesized in the absence of U or Th.

4.4 Structure determinations

The crystal structures of both compounds were determined from single-crystal X-ray diffraction data collected with the use of graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at 100(2) K on a Bruker APEX2 diffractometer. The algorithm Cosmo implemented in the program Apex2 [30] was used to establish the data collection strategy with a series of 0.3° scans in ω and φ. The exposure time was 10 sec per frame and the crystal-to-detector distance was 60 mm. The collection of intensity data as well as cell refinement and data reduction were carried out with the use of the program Apex2 [30]. Face-indexed absorption, incident beam, and decay corrections were performed with the use of the program Sadabs [31]. Both crystal structures were solved and refined in a straightforward manner with the use of the Shelx-14 algorithms of the Shelxtl program package [32]. The program Structure tidy [33] in Platon [34] was used to standardize the atomic positions. Further details are given in Table 1.

Further details of the crystal structure investigations in cif format may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition numbers CSD-430578 (Ba$_2$ZnTe$_3$) and 430579 (Ba$_2$ZnSe$_3$).

4.5 Optical absorption measurement

A single-crystal absorption spectrum was obtained at 298 K on a Hitachi U-6000 Microscopic FT spectrophotometer mounted on an Olympus BH2-UMA microscope.

A crystal of Ba$_2$ZnTe$_3$ was placed on a glass slide and positioned over the light source where the transmitted light was recorded from above. The background signal of the glass slide was subtracted from the collected intensity.

4.6 DFT calculations

To conduct the calculations we have used density functional theory [35, 36] as implemented in the Vienna ab Initio Simulation Package (VASP) [37, 38] using projector augmented waves [39] as the basis set. We have used the HSE (Heyd-Scuseria-Ernzerhof) [40–42] functional for the exchange and correlation while the geometry (cells and atomic positions) were taken from the experiments. A 4×8×2 mesh was used to sample the Brillouin zone, and the default cutoff was used for the plane wave part of the wave function.

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