



# Solid-state syntheses, crystal structures and properties of two novel metal sulfur chlorides— $\text{Zn}_6\text{S}_5\text{Cl}_2$ and $\text{Hg}_3\text{ZnS}_2\text{Cl}_4$

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## ABSTRACT

Two novel metal sulfur chlorides –  $\text{Zn}_6\text{S}_5\text{Cl}_2$  (**1**) and  $\text{Hg}_3\text{ZnS}_2\text{Cl}_4$  (**2**) – were obtained by solid-state reactions and structurally characterized by single-crystal X-ray diffraction. Compound **1** is characteristic of a 1-D tunnel-like structure, which connects to each other to construct a 3-D framework with the chlorine atoms locating at the voids. Compound **2** crystallizes in the acentric space group  $P6_3mc$  of the hexagonal system. Compound **2** features a 2-D layered motif, which is composed by the interconnected 12-membered  $\text{Hg}_6\text{S}_3\text{Cl}_3$  rings with chair-like conformation. There are  $\text{ZnSCl}_3$  tetrahedra located between the layers, yielding a sandwich-like structure. TG-DTA measurement shows that compound **1** is thermally stable up to 220 °C. Optical absorption spectra reveal the presence of sharp optical gap of 2.71 and 2.65 eV for **1** and **2**, respectively.

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## 1. Introduction

The transition metal and main group metal chalcogenides show rich structural chemistry and useful physical and chemical properties for potential applications in nonlinear optics [1–4], optical storage [5–9], solar energy conversion [10,11], thermal electrics [12–16], ion-exchange [17,18], second harmonic generation [19], chemical absorption [20–23], ferroelectrics [24] and so forth. Nowadays, many metal chalcogenides have been synthesized and some of them have been widely used in military and civil areas, famous examples including  $\text{CuInSe}_2$  and  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ , whose primary applications are found in photovoltaic devices for solar energy conversion and infrared detection [10,11,25]. However, among the known metal chalcogenides, many are  $A-M-Q$  ( $A$ =alkali metal or alkaline-earth metal;  $M$ =p-block metal;  $Q$ =S, Se, Te) systems, while group IIB- $Q-X$  ( $\text{IIB}=\text{Zn, Cd, Hg}$ ;  $X=\text{F, Cl, Br, I}$ ) systems are relatively rare. To obtain new materials which may possess the excellent photovoltaic and optical properties, our recent efforts in synthesizing novel IIB-based compounds have focused mainly on the systems containing both chalcogenide and halide anions. Herein, we describe the syntheses and characterizations of two novel metal sulfur chlorides:  $\text{Zn}_6\text{S}_5\text{Cl}_2$  (**1**) and  $\text{Hg}_3\text{ZnS}_2\text{Cl}_4$  (**2**). It should be pointed out that compound **1** is the first example of ternary zinc- $Q-X$  chalcogenides and compound **2** is the first example of quaternary IIB- $Q-X$  metal chalcogenides.

## 2. Experimental work

All reactants of analytical reagent grade were obtained commercially and used without further purification. The UV–vis spectra were recorded at room temperature on a computer-controlled PE Lambda 900 UV–vis spectrometer equipped with an integrating sphere in the wavelength range 190–2500 nm.  $\text{BaSO}_4$  plate was used as a reference (100% reflectance), on which the finely ground powder of the samples were coated. The absorption spectra were calculated from reflection spectra, using the Kubelka–Munk function [26,27]:  $\alpha/S=(1-R)^2/2R$ ,  $\alpha$  is the absorption coefficient,  $S$  is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5  $\mu\text{m}$ , and  $R$  is the reflectance. Semiquantitative microscope analysis was performed on a field emission scanning electron microscope JSM-35CF equipped with an energy dispersive X-ray spectroscope (EDS). Thermogravimetry-differential thermal analysis (TG-DTA) was performed under  $\text{N}_2$  atmosphere on a NETZSCH STA 449C analyzer.

**Synthesis of  $\text{Zn}_6\text{S}_5\text{Cl}_2$  (1):** it was prepared from the reaction of  $\text{ZnCl}_2$  (1 mmol, 136 mg), Zn (5 mmol, 325 mg) and S (5 mmol, 160 mg). The starting materials were ground into fine powders in an agate mortar before they were pressed into a pellet of 1 cm in diameter. Then the pellet was loaded into a glass tube, which was flame-sealed under a  $10^{-3}$  Torr atmosphere and subsequently placed into a furnace. The tube was heated to 500 °C in 12 h from room temperature and kept for 10 days, followed by cooling to 100 °C at a rate of 6 °C/h to promote crystal growth, then power off. The yield of **1** is 52% based on zinc. We have tried to synthesize compound **1** at 300 and 400 °C, but failed. Analyses of

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the products with SEM/EDS showed only the presence of Zn, S and Cl in a ratio of 6.2:4.9:2.1, which is close to the chemical formula of  $\text{Zn}_6\text{S}_5\text{Cl}_2$  established by the X-ray diffraction analysis. The products are very stable in air and water.

**Synthesis of  $\text{Hg}_3\text{ZnS}_2\text{Cl}_4$  (2):** this compound was prepared from the reaction of  $\text{HgCl}_2$  (2 mmol, 543.2 mg),  $\text{ZnS}$  (1 mmol, 97.4 mg) and  $\text{HgS}$  (1 mmol, 232.6 mg). The starting materials were loaded into a silica tube, which was flame-sealed under a  $10^{-3}$  Torr atmosphere and subsequently placed into a furnace. The tube was heated to 200 °C in 6 h from room temperature and kept for 24 h, then heated to 450 °C in 6 h and kept for 15 days, followed by cooling to 100 °C at a rate of 5 °C/h to promote crystal growth, then cooled to 35 °C in 5 h and power off. The yield of **2** is 45% based on mercury.

**X-Ray Data Collection, Reduction and Structure Solution:** the intensity data sets were collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda=0.71073$  Å) by using a  $\omega$  scan technique. CrystalClear software was used for data reduction and empirical absorption corrections

**Table 1**  
Summary of crystallographic data and structure analyses.

Compound	1	2
Formula	$\text{Zn}_6\text{S}_5\text{Cl}_2$	$\text{Hg}_3\text{ZnS}_2\text{Cl}_4$
Fw	623.42	873.06
Color	Light yellow	Yellow
Crystal size/mm <sup>3</sup>	0.46 0.10 0.07	0.05 0.03 0.03
Crystal system	Orthorhombic	Hexagonal
Space group	<i>Cmcm</i>	<i>P6<sub>3</sub>mc</i>
<i>a</i> (Å)	18.291(1)	7.257(4)
<i>b</i> (Å)	9.187(4)	7.257(4)
<i>c</i> (Å)	9.272(7)	10.848(8)
<i>V</i> (Å <sup>3</sup> )	1558(1)	494.7(5)
<i>Z</i>	4	2
$2\theta_{\text{max}}$ (°)	50	49.8
Reflections collected	4847	3057
Independent, observed reflections ( $R_{\text{int}}$ )	750, 353 (0.1407)	366, 203 (0.0670)
$d_{\text{calcd}}$ (g/cm <sup>3</sup> )	2.657	5.861
$\mu$ (mm <sup>-1</sup> )	10.057	50.224
<i>T</i> (K)	293(2)	293(2)
<i>F</i> (0 0 0)	1176	740
$R_1, wR_2$	0.0693, 0.1294	0.0540, 0.1170
<i>S</i>	0.875	0.993
Largest and mean $\Delta/\sigma$	0, 0	0, 0
$\Delta\rho$ (max/min) (e/Å <sup>3</sup> )	1.369, -1.467	2.083/-1.593

**Table 2**  
Selected bond lengths (Å) and bond angles (°).

$\text{Zn}_6\text{S}_5\text{Cl}_2$			
Zn(1)–S(1)	2.375(5)	S(1)–Zn(1)–S(1)#1	161.9(2)
Zn(1)–S(3)	2.839(3)	S(1)–Zn(1)–S(3)	98.8(1)
Zn(2)–S(1)	2.380(5)	S(1)–Zn(2)–S(1)#2	173.8(2)
Zn(3)–S(1)	2.430(5)	S(1)–Zn(3)–S(1)#3	165.5(2)
S(1)–S(2)	2.303(5)	S(1)–S(2)–S(1) #4	168.0(6)
$\text{Hg}_3\text{ZnS}_2\text{Cl}_4$			
Hg1–Cl1	2.295(3)	Cl2#1–Zn1–Cl2	115.22(9)
Hg1–S1	2.398(3)	Cl2#1–Zn1–Cl2#2	115.22(9)
Zn1–Cl2#1	2.244(3)	Cl2–Zn1–Cl2#2	115.22(9)
Zn1–Cl2	2.244(3)	Cl2#1–Zn1–S2	102.8(1)
Zn1–Cl2#2	2.244(3)	Cl2–Zn1–S2	102.8(1)
Zn1–S2	2.359(9)	Cl2#2–Zn1–S2	102.8(1)
Cl1–Hg1–S1	178.8(2)	Br4–Cd1–Br3	110.60(3)

Symmetry transformations used to generate equivalent atoms: #1 *x, y, -z+3/2*; #2  $-x+1, y, z$ ; #3 *x, -y+1, -z+1*; #4 *x, y, -z+1/2*.

Symmetry codes: #1  $-x+y, -x, z$ ; #2  $-y, x-y, z$ .

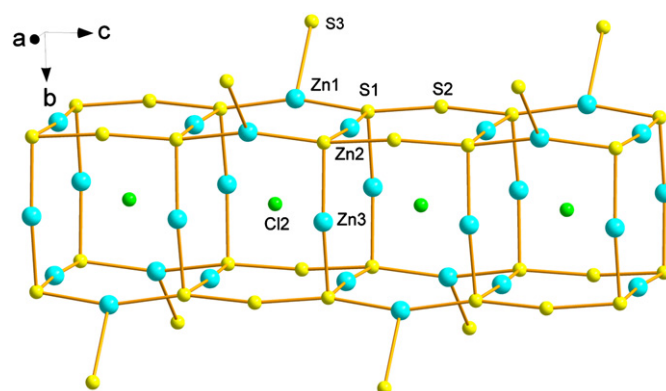
[28]. The structures were solved by the direct methods, using the Siemens SHELXTL™ Version 5 package of crystallographic software [29]. The difference Fourier maps based on these atomic positions yield all the atoms. The assignments of S and Cl positions are mainly based on the charge balance of the two compounds. The structures were refined using a full-matrix least-squares refinement on  $F^2$ . All atoms were refined anisotropically. A summary of crystallographic data and structure analyses is listed in Table 1, and selected bond distances and bond angles are given in Table 2.

Crystallographic data in CIF format have been deposited with FIZ Karlsruhe with the following CSD numbers: 419561, 420783 for **1** and **2**, respectively. These data can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: 49 7247 808 666; e-mail: crysdata@fiz.karlsruhe.de).

### 3. Results and discussion

Single-crystal X-ray diffraction analysis reveals that compound **1** features a 1-D tunnel-like structure. The three crystallographically different zinc atoms are on special positions and have different coordination geometries. The Zn1 atom has an approximately trigonal geometry, if we arbitrarily choose a cutoff of 2.88 Å for the Zn–S distances [30], coordinating with three sulfur atoms with the bond lengths of Zn1–S1, Zn1–S1(#1) and Zn1–S3 of 2.375(5), 2.375(5) and 2.839(3) Å, respectively, and the bond angles of S1–Zn1–S1(#1), S1–Zn1–S3 and S1(#1)–Zn1–S3 being 161.9(2), 98.77(13) and 98.77(13)°, respectively. The bond lengths of Zn–S are in the normal range. Differently, the Zn2 and Zn3 atoms have a twofold coordination geometry, coordinating with two sulfur atoms with the bond lengths of Zn2–S1 and Zn3–S1 being 2.380(5) and 2.430(5) Å, respectively, and the bond angles of S1–Zn2–S1(#2) and S1–Zn3–S1(#3) being 173.8(2) and 165.5(2)°, respectively. In **1**, ten zinc atoms and ten sulfur atoms interconnect to each other to form a cubane-like structure. Neighboring to this cubane are two upside-down cubanes compared to the former one. The cubanes and the upside-down cubanes face-share together alternatively to yield a 1-D tunnel running along the *c* direction, in which the isolated Cl2 atoms locate, as shown in Fig. 1. The tunnels link through weak S, ..., S interactions [S2, ..., S3(*x, -y, 0.5+z*)=2.788 (1) Å] to form a 2-D layer parallel to the *bc* plane and the isolated Cl1 atoms locate in the voids between two tunnels (Fig. 2). The 2-D layers are further connected by weak Zn, ..., S interactions [Zn3, ..., S3(0.5–*x, 0.5–y, 1–z*)=2.977 (2) Å, Zn3, ..., S3(0.5–*x, 0.5+y, 1.5–z*)=2.977 (2) Å] to construct a 3-D framework (Fig. 3).

Compound **2** is characterized by a 2-D layered structure, which contains interconnected 12-membered  $\text{Hg}_6\text{S}_3\text{Cl}_3$  rings with chair-like



**Fig. 1.** A 1-D tunnel of **1** running along the *c* direction.

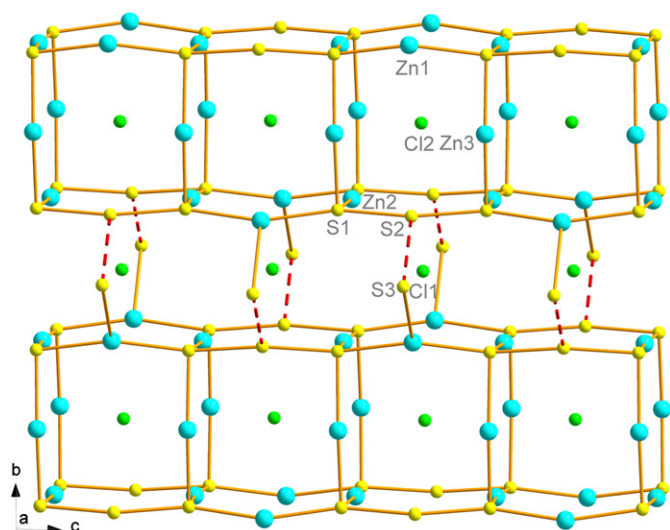


Fig. 2. A view of a 2-D layer formed by two tunnels through weak S, ..., S interactions (dashed lines), showing the locations of two different chlorine atoms.

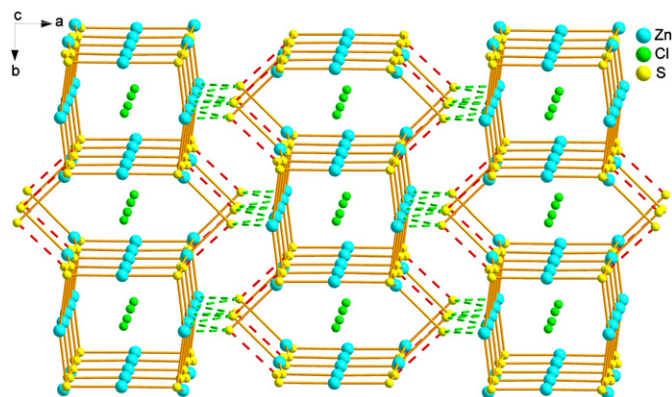


Fig. 3. A packing diagram of **1** with the red and green dashed lines representing weak S, ..., S and Zn, ..., S interactions, respectively.

conformation, and the layers sandwich the  $\text{ZnSCl}_3$  tetrahedra (Fig. 4). The Hg1 atom is coordinated by one chlorine atom and one sulfur atom with the bond lengths of Hg1–Cl1 and Hg1–S1 being of 2.295(3) and 2.398(3) Å, respectively, and the bond angle of Cl1–Hg1–S1 being of 178.8(2)°. The Zn1 atom has a tetrahedral geometry, coordinating with one sulfur atom and three chlorine atoms with the bond lengths of Zn1–S2, Zn1–Cl2, Zn1–Cl2(#1) and Zn1–Cl2(#2) of 2.359(9), 2.244(3), 2.244(3) and 2.244(3) Å, respectively, and the bond angles of Cl2–Zn1–S2 and Cl2–Zn1–Cl2(#2) being of 102.8(1) and 115.22(9)°, respectively. Six mercury atoms, three sulfur atoms and three chlorine atoms interconnect together to form a 12-membered  $\text{Hg}_6\text{S}_3\text{Cl}_3$  rings with chair-like conformation. Every such ring edge-shares to six neighboring rings to construct a layered structure (Fig. 5). The  $\text{ZnSCl}_3$  tetrahedra locate between the layers, yielding a sandwich-like structure (Figs. 6 and 7). To our knowledge, compound **2** is the first example of quaternary IIB–Q–X metal chalcogenides.

The shortest Hg, ..., Hg distance is of 3.568(3) Å, which is in the range of the sum of the van der Waals radii (3.4–4.0 Å) [31] and comparable with those of other mercury compounds [32–35], indicating the existence of the weak Hg, ..., Hg interaction. The weak Hg, ..., Hg interactions may solidify the structure of compound **2**.

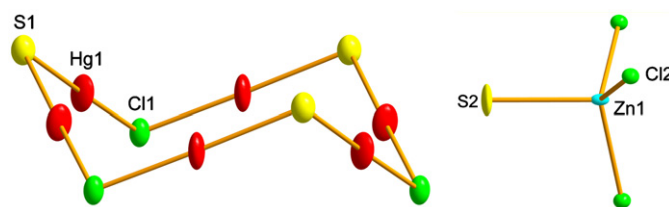


Fig. 4. An ORTEP drawing of **2** with 30% thermal ellipsoids, showing the coordination environments of the metal atoms. Left: the chair-like conformation of the  $\text{Hg}_6\text{S}_3\text{Cl}_3$  ring; Right: the tetrahedral configuration of  $\text{ZnSCl}_3$ .

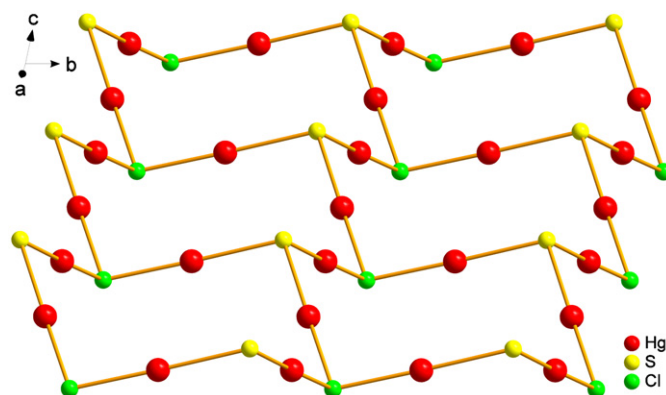


Fig. 5. A 2-D layer of **2** displays the interconnection of the 12-membered rings with chair-like conformation.

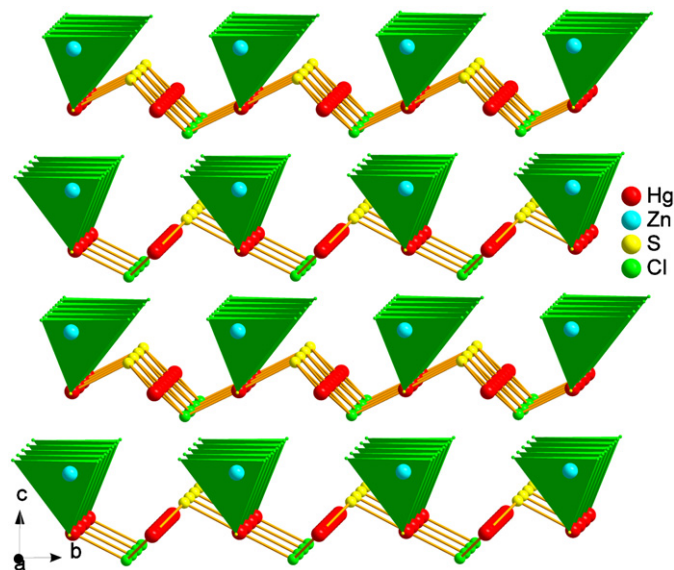


Fig. 6. A polyhedral perspective of **2** viewed along the *a*-axis.

A Flack *x* parameter of 0.0(4) for the structure of **2** was calculated, indicating a correct absolute structure [36]. Results of the bond valence calculations indicate that the mercury and zinc atoms are in +2 oxidation state (Hg1: 1.7, Zn1: 2.1) [37,38].

TG-DTA shows that the compound **1** is thermally stable up to 220 °C and underwent a three-step decomposition process (Fig. 8). The TG-DTA displays an initial mass loss of 16.56% with a beginning temperature of about 220 °C, corresponding to the losses of two chlorine atoms and one sulfur atom (calcd. 16.52%). A second weight loss of 40.91% is found in the range 220–316 °C,

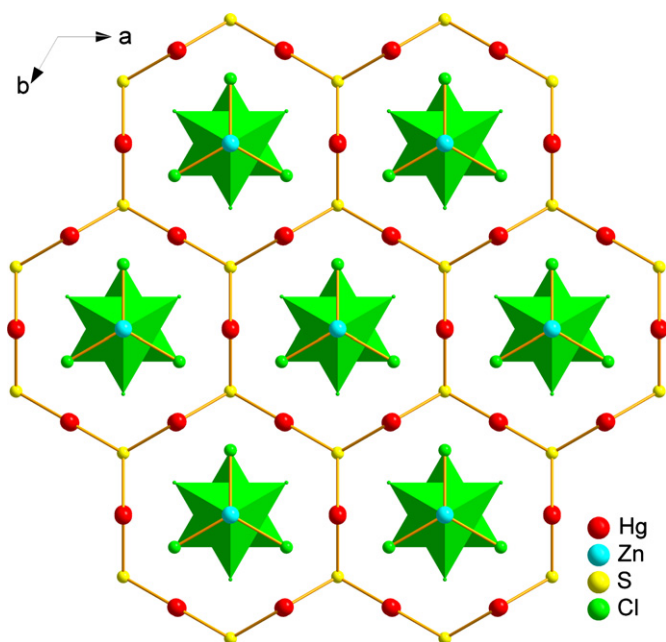


Fig. 7. A polyhedral representation of **2** viewed along the *c*-axis.

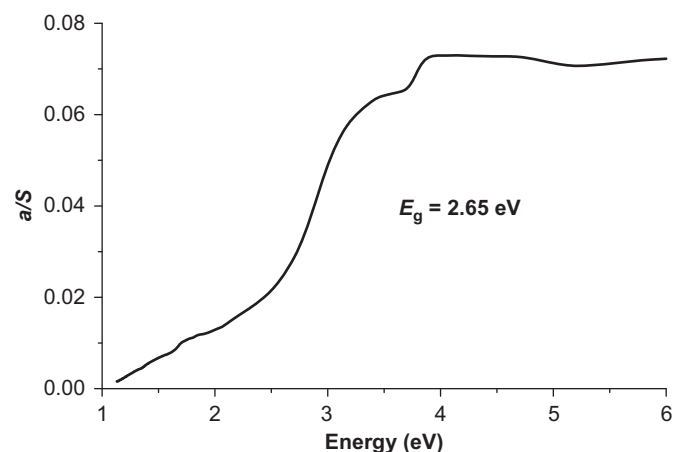


Fig. 10. The solid-state diffuse reflectance spectra of **2**.

suggesting the losses of the other sulfur atoms and two zinc atoms (calcd. 41.51%). The third weight loss of 42.59% has occurred in the range 316–820 °C, which is in accordance with the losses of the other zinc atoms (calcd. 41.97%). These results are well consistent with the X-ray crystal structure.

Optical absorption spectra of **1** and **2** reveal the presence of optical band-gaps of 2.71 and 2.65 eV (Figs. 9 and 10), which suggest that this material may be a potential semiconductor. The steep slope of the optical absorption edge of **1** is indicative of the existence of a direct transition, while the slow slope of the optical absorption edge of **2** is indicative of the existence of an indirect transition [39]. The band-gaps of **1** and **2** are larger than those of CdTe (1.5 eV), GaAs (1.4 eV), CuInS<sub>2</sub> (1.55 eV), CdSe (1.75 eV) and CdS (2.42 eV), all of which are highly efficient photovoltaic materials, but smaller than the band gap of LiNbO<sub>3</sub> (3.5 eV) [40–43].

#### 4. Conclusions

Two novel metal sulfur chlorides Zn<sub>6</sub>S<sub>5</sub>Cl<sub>2</sub> (**1**) and Hg<sub>3</sub>ZnS<sub>2</sub>Cl<sub>4</sub> (**2**) have been synthesized via solid-state reactions. The crystal structure of **1** is characterized by a 1-D tunnel-like structure, while that of **2** features a 2-D layered motif. Compound **1** is the first example of ternary zinc-Q-X chalcogenides and compound **2** is the first example of quaternary IIB-Q-X metal chalcogenides. Optical absorption spectra show that the title compounds may be the candidates for potential photovoltaic materials.

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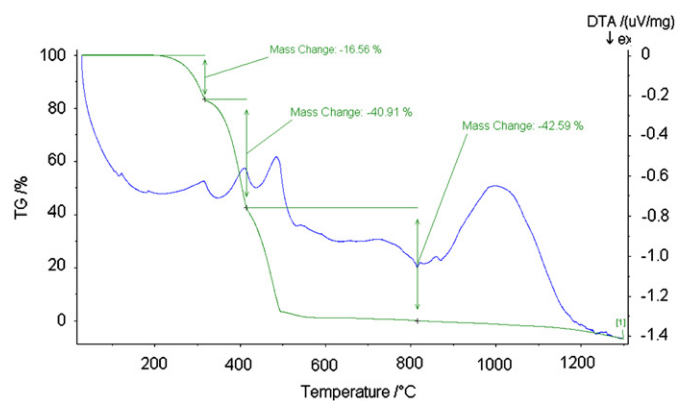


Fig. 8. A TG-DTA diagram showing the weight losses of **1**.

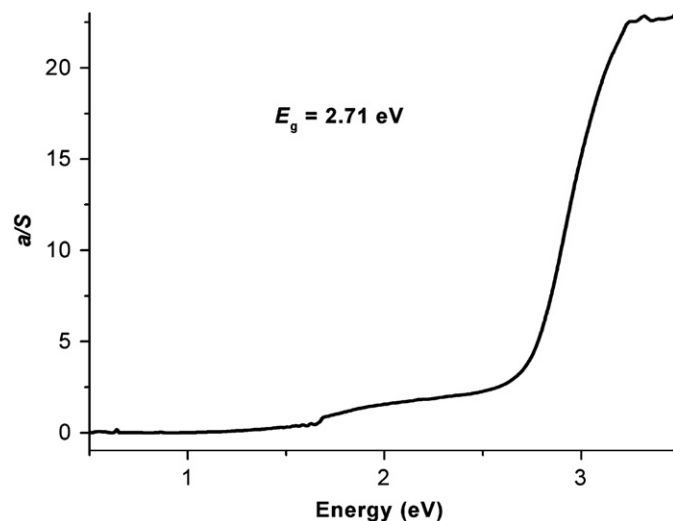


Fig. 9. The solid-state diffuse reflectance spectra for **1**.

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