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Synthesis, Crystal and Band Structures, and Optical Properties of a New Quaternary Metal Pnictidehalide: $(Hg_2Cd_2As_2Br)Br$

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A new quaternary cadmium and mercury pnictidehalide semiconductor $(Hg_2Cd_2As_2Br)Br$ (**1**) has been prepared by the solid-state reaction of $HgBr_2$ with elemental Cd and As at 420 °C. Compound **1** crystallizes in the space group *Pmma* of the orthorhombic system with two formula units in a cell: $a = 8.791(4)$ Å, $b = 4.701(2)$ Å, $c = 9.779(6)$ Å, $V = 404.2(3)$ Å^3. The structure of **1** is composed of parallel slabs bridged by linearly coordinated Hg atoms to form a 3D cationic network with the channels occupied by discrete Br anions, in which the layer consists of interlinks of linear $(HgAs_2Br_2)$ tetrahedral chains and $(CdAs_2Br)$ trigonal chains. The optical properties were investigated in terms of the diffuse reflectance and Fourier transform infrared spectra. The electronic band structure along with the density of states (DOS) calculated by the DFT method indicate that compound **1** is a semiconductor with an indirect band gap and that the optical absorption mainly originates from the charge transitions from the Br2-4p and As-4p to Cd-5s and Hg-6s states.

Introduction

Pnictides have been investigated extensively because of their structural diversity and physical properties since the beginning of the 1960s. For instance, pnictide semiconductors with the formula IIB−IV−V_2, such as $CdSiP_2$, $CdGeP_2$, and $CdSnP_2$, have been widely studied because of their possible technological applications as photovoltaic detectors, solar cells, light-emitting diodes, and nonlinear optics.[1] The semiconducting metal pnictides of IIB−V−VΠ type, which are also known as cadmium and mercury pnictidehalides, are attractive in advanced material research because of their abundant structural features and distinctive electronic properties.[2] Until now, a large number of ternary cadmium and mercury pnictidehalides $M_aZ_bX_c$ (M = Cd, Hg; Z = P, As, Sb; X = Cl, Br, I) have been discovered, which generally can be distinguished into five types on the basis of their crystal structures, containing (1) separate Z^{3-} anions, (2) binuclear Z_2^{4-} anions, (3) Z^{3-} and Z_2^{4-} bianions, (4) finite Z_3^{5-} anions, and (5) one-dimensional infinite $^{1}_{\infty}(Z^-)$ polyanions. Among them, the majority belong to the second, third, or fifth type, whereas only seven compounds with separate Z^{3-} anions, Cd_3PCl_3,[3a] Cd_3PI_3,[3a] Cd_3AsCl_3,[3b] Hg_3PCl_3,[3c] Cd_3AsI_3,[3d] $Cd_5P_2Br_4$,[3e] and $Hg_5P_2Br_4$,[3f] have been synthesized.

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(1) (a) Choi, I. H.; Yu, P. Y. *Phys. Rev. B* **1997**, *55*, 9642. (b) Yoodee, K.; Woolley, J. C.; Yakanit, V. S. *Phys. Rev. B* **1984**, *30*, 5904. (c) Shay, J. L.; Buehler, E.; Wernick, J. H. *Phys. Rev. B* **1970**, *2*, 4104. (d) Shay, J. L.; Buehler, E.; Wernick, J. H. *Phys. Rev. B* **1971**, *3*, 2004. (e) Shay, J. L.; Wernick, J. H. *Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties and Applications*; Pergamon Press: Oxford, 1974. (f) Webb, D. J.; Cohen, R.; Klavins, P.; Shelton, R. N.; Chan, J. Y.; Kauzlarich, S. M. *J. Appl. Phys.* **1998**, *8*, 7192. (g) Chiker, F.; Abbar, B.; Tadjer, A.; Bresson, S.; Khelifa, B.; Mathieu, C. *Physica B* **2004**, *349*, 181.

(2) (a) Olenev, A. V.; Baranov, A. I.; Oleneva, O. S.; Vorontsov, I. I.; Antipin, M. Y.; Shevelkov, A. V. *Eur. J. Inorg. Chem.* **2003**, 1053. (b) Olenev, A. V.; Oleneva, O. S.; Lindsjö, M.; Kloo, L. A.; Shevelkov, A. V. *Chem.—Eur. J.* **2003**, 3201. (c) Oleneva, O. S.; Olenev, A. V.; Dikarev, E. V.; Shevelkov, A. V. *Eur. J. Inorg. Chem.* **2004**, 4006. (d) Shevelkov, A. V.; Shatruk, M. M.; *Russ. Chem. Bull., Int. Ed.* **2001**, *50*, 337. (e) Rebbah, A.; Yazbeck, J.; Lande, R.; Deschanvres, A. *Mater. Res. Bull.* **1981**, *16*, 525. (f) Olenev, A. V.; Shevelkov, A. V. *Angew. Chem., Int. Ed.* **2001**, *40*, 2353.

(3) (a) Rebbah, A.; Yazbeck, J.; Deschanvres, A. *Rev. Chim. Miner.* **1981**, *19*, 43. (b) Donobue, P. C. *J. Solid State Chem.* **1972**, *5*, 71. (c) Lemoult, P. *C. R. Acad. Sci.* **1907**, *9*, 1175. (d) Rebbah, A.; Yazbeck, J.; Deschanvres, A. *Acta Crystallogr., Sect. B* **1980**, *36*, 1744. (e) Shatruk, M. M.; Reshetova, L. N.; Shevelkov, A. V.; Popvkin, B. A. *Russ. J. Inorg. Chem.* **2000**, *45*, 495. (f) Shevelkov, A. V.; Mustyakimov, M. Y.; Dikarev, E. V.; Popvkin, B. A. *J. Chem. Soc., Dalton Trans.* **1996**, *1*, 147.

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Table 1. Crystal Data and Structural Refinement for **1**

empirical formula	$Hg_2Cd_2As_2$Br2
fw	935.64
cryst size (mm^3)	0.05 × 0.05 × 0.04
cryst syst	orthorhombic
space group	*Pmma*
a (Å)	8.791(4)
b (Å)	4.701(2)
c (Å)	9.779(6)
V ($Å^3$)	404.2(3)
Z	2
D_{calcd} (g cm^{-3})	7.688
μ (mm^{-1})	60.966
F(000)	784
R_1,[a] wR_2[b] [$I > 2\sigma(I)$]	0.0633, 0.1262
R_1, wR_2 (all data)	0.1067, 0.1357
GOF on F^2	1.003
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e $Å^{-3}$)	2.411 and −2.521

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

In comparison with the large number of ternary cadmium and mercury pnictidehalides whose structures were well-characterized, little is known about quaternary phases that contain only group 12, 15, and 17 elements. To the best of our knowledge, only seven examples, including $(Hg_9As_4)(BiBr_6)_2$,[4a] $(Hg_6As_4)(BiCl_6)Cl$,[4b] $(Hg_6Sb_4)(BiBr_6)Br$,[4b] $(Hg_{13}As_8)(ZnCl_4)_4$,[4c] $(Hg_{23}As_{12})(ZnBr_4)_6$,[4c] $(Hg_2As)_2(ZnI_4)$,[4c] and $(Hg_2P)_2(ZnI_4)$,[4d] in which mercury pnictides construct 3D cationic frameworks while metal halides act as guest anions, have been reported in the literature. Prior to the present work, no compounds containing two kinds of group 12 metals coordinated by pnicogen and halogen atoms to construct the host frameworks had been characterized. In this paper, we report the synthesis, crystal and band structures, and optical properties of a new quaternary cadmium and mercury pnictidehalide, $(Hg_2Cd_2As_2Br)Br$ (**1**).

Experimental Section

Synthesis. Crystals of **1** were synthesized by the solid-state reaction of $HgBr_2$ (0.5 mmol, 180 mg), Cd (0.5 mmol, 56 mg), and As (0.5 mmol, 38 mg). The starting materials were ground into fine powders in an agate mortar and pressed into a pellet, followed by being loaded into a Pyrex tube, evacuated to 1×10^{-4} Torr, and flame-sealed. The tube was placed into a computer-controlled furnace, heated from room temperature to 300 °C at a rate of 50 °C/h and kept at 300 °C for 4 h. The tube was then heated to 420 °C at 20 °C/h, kept at 420 °C for 120 h, and then slowly cooled to 100 °C at a rate of 2.5 °C/h; it was finally cooled to room temperature in 5 h. A crop of dark red crystals of **1** was obtained. Semiquantitative microscope analysis using energy-dispersive X-ray spectroscopy (EDS) was performed on a JSM6700F scanning electron microscope (SEM) on a single crystal of **1**, which confirmed the presence of Hg, Cd, As, and Br in the approximate molar ratio 1.0: 0.6: 0.8: 1.1. No other elements were detected. The exact composition was established from the X-ray structure determination.

Single-Crystal Structure Determination. A dark red single crystal of **1** was mounted on a glass fiber for X-ray diffraction analysis. Data were collected on a Rigaku AFC7R diffractometer equipped with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. Intensities was corrected for LP factors and for empirical absorption using the ψ scan technique. The structure was solved by direct methods and refined by full-matrix least-squares techniques using the Siemens SHELXTL version 5 package of crystallographic software.[5] The final refinements included anisotropic displacement parameters for all atoms. Crystallographic data for **1** are listed in Table 1, and selected bond lengths and bond angles are given in Table 2.

Physical Measurements. The UV−vis spectrum was recorded at room temperature on a computer-controlled PE Lambda 900 UV−vis spectrometer equipped with an integrating sphere in the wavelength range 200−2000 nm. A $BaSO_4$ plate was used as a reference, on which the finely ground powder of the sample was coated. The absorption spectrum was calculated from reflection spectra by the Kubelka−Munk function:[6] $\alpha/S = (1 - R)^2/2R$, where α is the absorption coefficient, *S* is the scattering coefficient that is practically wavelength independent when the particle size is larger than 5 μm, and *R* is the reflectance. The energy gap was determined as the intersection point between the energy axis at the absorption offset and the line extrapolated from the linear portion of the absorption edge in the α/S versus *E* (eV) plot. The IR spectrum was recorded by using a Nicolet Magana 750 FT-IR spectrophotometer in the range of 4000−400 cm^{-1}. The powdery sample was pressed into pellets with KBr. The IR spectrum is given in Figure S1 of the Supporting Information.

Computational Descriptions. The crystallographic data of the present compound determined by X-ray were used to calculate the electronic band structure. Calculation of the electronic band structure along with density of states (DOS) was carried out with density functional theory (DFT) using one of the three nonlocal gradient-corrected exchange-correlation functionals (GGA-PBE) and performed with the CASTEP code,[7] which uses a plane wave basis set for the valence electrons and norm-conserving pseudopotential[8] for the core electrons. The number of plane waves included in the basis was determined by a cutoff energy E_c of 450 eV. Pseudoatomic calculations were performed for Br-$4s^24p$,^{5} As-$4s^24p^3$, Cd-$4d^{10}5s^2$, and Hg-$5d^{10}6s^2$. The parameters used in the calculations and convergence criteria were set by the default values of the CASTEP code.[7]

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1[a]

Hg(1)−As(1) × 2	2.530(4)	Cd(1)−As(1) × 2	2.363(1)
Hg(1)−Br(1) × 2	2.962(5)	Cd(1)−Br(1)	2.967(7)
Hg(2)−As(1) × 2	2.502(6)		
As(1)#1−Hg(1)−As(1)	160.8(3)	Hg(1)−Br(1)−Cd(1) × 4	119.19(7)
As(1)−Hg(1)−Br(1) × 4	95.82(9)	Cd(1)−As(1)−Hg(1) × 2	92.2(1)
Br(1)#2−Hg(1)−Br(1)#3	105.1(3)	Cd(1)−Br(1)−Cd(1)#6	73.4(2)
As(1)#4−Hg(2)−As(1)	180.0	Cd(1)−As(1)−Cd(1)#7	168.1(3)
As(1)−Cd(1)−As(1)#5	168.1(3)	Cd(1)−As(1)−Hg(2) × 2	95.4(2)
As(1)−Cd(1)−Br(1) × 2	95.9(2)	Hg(2)−As(1)−Hg(1)	92.8(2)
Hg(1)#2−Br(1)−Hg(1)#3	105.1(3)		

[a] Symmetry codes: #1 $-x + {}^1/_2, -y + 1, z$; #2 $-x, -y, -z + 1$; #3 $-x, -y + 1, -z + 1$; #4 $-x, -y + 1, -z + 2$; #5 $x, y - 1, z$; #6 $-x - {}^1/_2, -y, z$; #7 $x, y + 1, z$.

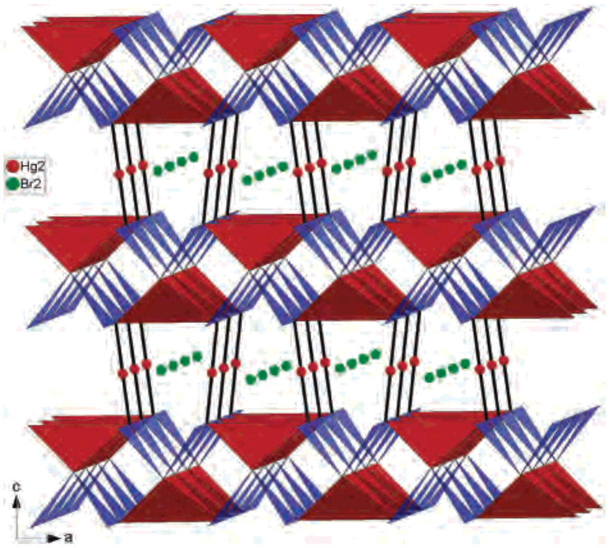

Figure 1. View of the 3D structure of **1** as a sequence of polyhedron (Hg1 tetrahedra and Cd1 trigons are drawn as red and blue colors, respectively).

Results and Discussion

The crystal structural novelty of **1** derives from the fact that its three-dimensional cationic network consists of parallel layers connected by linearly coordinated mercury atoms (Figure 1). The layer consists of interlinks of ($HgAs_2Br_2$) tetrahedral chains and ($CdAs_2Br$) trigonal chains, in which the Hg tetrahedra share corners with each other through the Br1 atoms to form a linear Hg tetrahedral chain extending along the *b* direction; the Cd trigons also share corners with each other through the As1 atoms to yield a linear Cd trigonal chain extending along the *b* direction (see Figure S2 of the Supporting Information). Two Cd trigonal chains share the Br1 atoms to form a V-shaped chain (see Figure S2 of the Supporting Information). The V-shape chains and the linear tetrahedral chains share the As1 and Br1 atoms along the *a* direction to form slabs, which are bridged by Hg2 atoms along the *c* direction to form a cationic network with channels along the *b* direction (Figure 1). The discrete Br2 anions are embedded in the channels with the shortest Br2−Hg distance being 3.228 Å. It is worthy to note that the V-shaped Cd chains and the linear Hg tetrahedral chains in the present compound are found for the first time in cadmium and mercury pnictidehalides.[2]

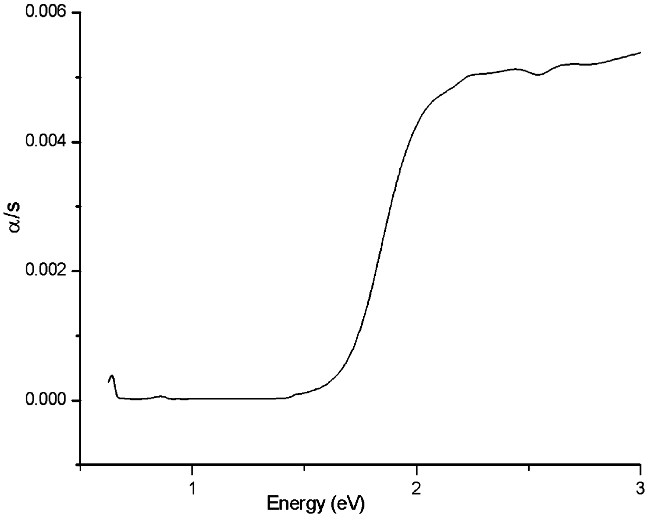

Figure 2. Diffuse reflectance spectrum of **1**.

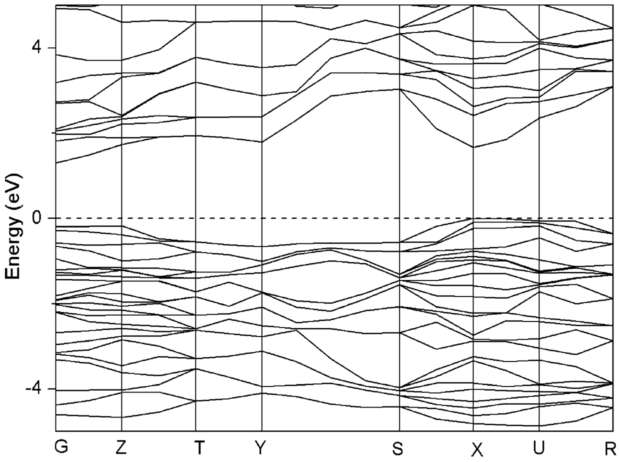

Figure 3. Band structure of **1** (bands are shown only between −5 and 5 eV for clarity, and the Fermi level is set at 0 eV).

Unlike most of cadmium and mercury pnictidehalides,[2b,2d] in which the pnicogen atoms often show an oxidation state of −2 and form P_2, As_2, or Sb_2 dumbbells, or show an oxidation state of −1 and form one-dimensional infinite $^{1}_{\infty}(Z^-)$ chains, the arsenic atom in the present compound shows an oxidation state of −3 and becomes a four-coordination anion. It is notable that the present compound exhibits a new structural type ($(M_2M'_2Z_2X)X$), different from the known cadmium and mercury pnictidehalides with separate Z^{-3} anions categorized into three types of M_3ZX_3, $M_5Z_2X_4$, and $(Hg_2Z)_2(ZnX_4)$.[3,4]

There are two crystallographic independent mercury atoms in the structure of **1**. Analogous to the cadmium and mercury pnictidehalides M_3ZX_3,[3b,3c] among which the metal atoms have linear and distorted tetrahedral coordination environments, the Hg1 atom is tetrahedrally surrounded by two arsenic atoms and two bromine atoms, whereas the Hg2 atom is linearly coordinated by two arsenic atoms in the present compound. The Hg1−As bond distance of 2.530(4) Å is a little longer than the Hg2−As bond distance of 2.502(6) Å;

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(4) (a) Puff, H.; Grönke, M.; Kilger, B.; Möltgen, P. *Z. Anorg. Allg. Chem.* **1984**, *518*, 120. (b) Beck, J.; Hedderich, S.; Neisel, U. *J. Solid State Chem.* **2000**, *154*, 350. (c) Olenev, A. V.; Shevelkov, A. V.; Popvokin, B. A. *Zh. Neorg. Khim.* **1999**, *44*, 1853. (d) Olenev, A. V.; Shevelkov, A. V.; Popovkin, B. A. *Zh. Neorg. Khim.* **1999**, *44*, 1814.

(5) *Siemens SHELXTL Version 5 Reference Manual*; Siemens Energy & Automation Inc.: Madison, WI, 1994.

(6) (a) Wendlandt, W. W.; Hecht, H. G. *Reflectance Spectroscopy*; Interscience Publishers: New York, 1966. (b) Kortüm, G. *Reflectance Spectroscopy*; Springer-Verlag: New York, 1969.

(7) (a) Segall, M.; Linda, P.; Probert, M.; Pickard, C.; Hasnip, P.; Clark, S.; Payne, M. *Materials Studio CASTEP*, version 2.2; Accelrys: San Diego, CA, 2002. (b) Segall, M.; Linda, P.; Probert, M.; Pickard, C.; Hasnip, P.; Clark, S.; Payne, M. *J. Phys.: Condens. Matter* **2002**, *14*, 2717.

(8) Hamann, D. R.; Schluter, M.; Chiang, C. *Phys. Rev. Lett.* **1979**, *43*, 1494.

(9) (a) Shevelkov, A. V.; Dikarev, E. V.; Popvkin, B. A. *J. Solid State Chem.* **1996**, *126*, 324. (b) Shevelkov, A. V.; Dikarev, E. V.; Popvkin, B. A. *Zh. Neorg. Khim.* **1995**, *40*, 1496.

(10) (a) Shevelkov, A. V.; Dikarev, E. V.; Popvkin, B. A. *J. Solid State Chem.* **1991**, *93*, 331. (b) Shevelkov, A. V.; Dikarev, E. V.; Popvkin, B. A. *J. Solid State Chem.* **1993**, *104*, 177.

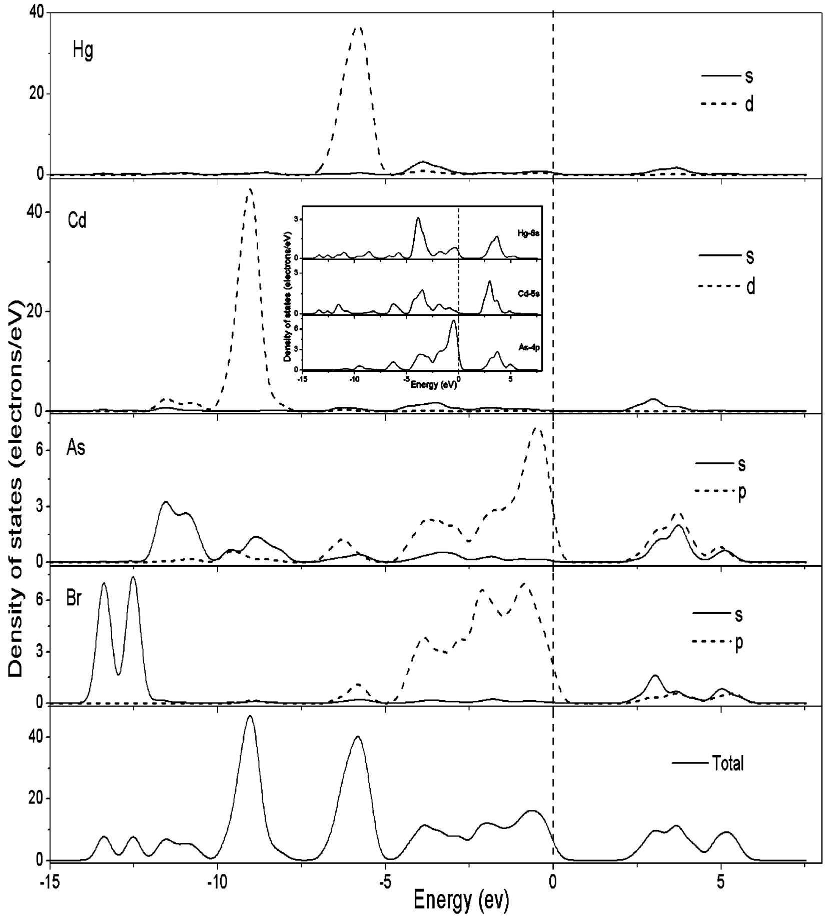

Figure 4. Total and partial DOS of **1** (the Fermi level is set at 0 eV). The Hg-6s, Cd-5s, and As-4p states are drawn in the inset for clarity.

they both lie in the normal range of the Hg−As separations in cadmium and mercury arsenidehalides.[2d,9] The Hg−Br bond distance of 2.962(5) Å also lies in the normal range of Hg−Br separations in cadmium and mercury pnictidehalides.[10] Unlike most cadmium and mercury pnictidehalides,[2d] in which the cadmium atoms often adopt linear, tetrahedral, or octahedral coordination environments, the cadmium atom in the present compound is coordinated by two arsenic atoms and one bromine atom to form a triangular plane. The Cd−As bond distance of 2.363(1) Å is much shorter than those found in cadmium arsenides, whereas the Cd−Br bond distance of 2.967(7) Å is close to those observed in cadmium pnictidehalides.[11]

The diffuse reflectance spectrum of **1** reveals the presence of an optical gap of 1.67 eV (Figure 2), which suggests that compound **1** is a semiconductor and consistent with its color. The IR spectrum of **1** shows no obvious absorption in the range of 4000−400 cm^{-1}, indicating the absence of direct As−As bonds, consistent with its single-crystal structure. The absence of IR absorption supports the idea that the compound may be potentially used as window material for laser delivery media and infrared transmitting for optical fiber applications in telecommunication.[12]

The calculated band structure of **1** along high symmetry points of the first Brillouin zone is plotted in Figure 3, where the labeled *k*-points are present as G (0.0, 0.0, 0.0), Z (0.0, 0.0, 0.5), T (−0.5, 0.0, 0.5), Y (−0.5, 0.0, 0.0), S (−0.5, 0.5, 0.0), X (0.0, 0.5, 0.0), U (0.0, 0.5, 0.5), and R (−0.5, 0.5, 0.5). It is found that valence bands (VBs) and conduction bands (CBs) are both disperse, which indicates the differing nature of the bonds between Br, As and Cd, Hg. The lowest energy (1.30 eV) of CBs is localized at the G point, and the highest energy (0.00 eV) of VBs is localized at the X point. So, compound **1** shows a semiconductor character with an indirect band gap of 1.30 eV, which is comparable with the experimental value (1.67 eV). The bands can be assigned according to total and partial densities of states (DOS), as plotted in Figure 4. The Hg-5d and Cd-4d states, mixing with small Br-4s and As-4s states, create the VBs localized at about −15.0 and −5.0 eV. The VBs between energy −5.0 eV and the Fermi level (0.0 eV) are mostly formed by Br-4p and As-4p states mixing with a small amount of the s

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[11] (a) Shevelkov, A. V.; Dikarev, E. V.; Popvkin, B. A. *J. Solid State Chem.* **1994**, *113*, 116. (b) Pietraszko, A.; Lukaszewicz, K. *Acta Crystallogr., Sect. B* **1969**, *25*, 988. (c) Cervinka, L.; Hruby, A. *Acta Crystallogr., Sect. B* **1970**, *26*, 457. (d) Eisenmann, B.; Klein, J.; Somer, M. *Z. Kristallogr.* **1991**, *197*, 271. (e) Marsh, R. E.; Herbstein, F. H. *Acta Crystallogr., Sect. B* **1979**, *35*, 2197. (f) Shevelkov, A. V.; Reshetova, L. N.; Popovkin, B. A. *J. Solid State Chem.* **1997**, *134*, 282.

[12] (a) Harrington, J. A. *Infrared Fibers and Their Applications;* SPIE Press: Bellingham, WA, 2004; p 83. (b) Marchese, D.; De Sario, M.; Jha, A.; Kar, A. K.; Smith, E. C. *J. Opt. Soc. Am. B* **1998**, *15*, 2361.

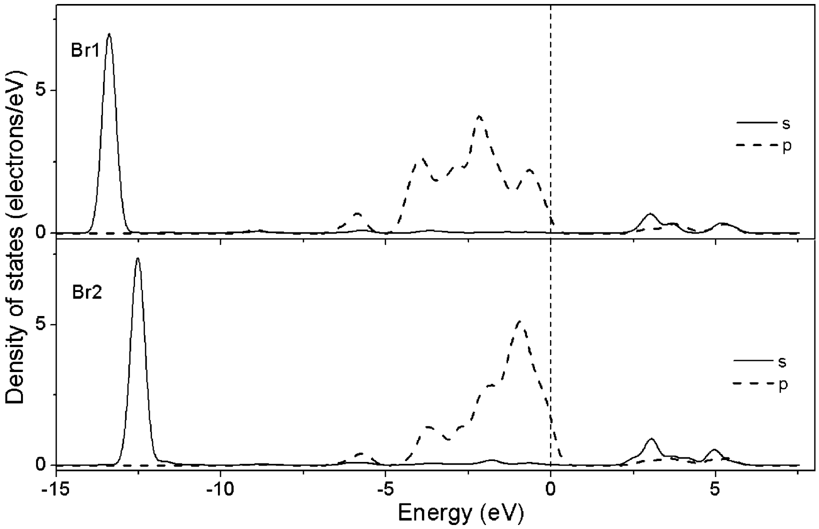

Figure 5. Partial DOS of Br1 and Br2 (the Fermi level is set at 0 eV).

orbital of the transition metals, whereas the CBs between 1.3 and 8.0 eV are mostly a contribution from Cd-5s, Hg-6s, Br-4s, As-4s, and As-4p states hybridized with a small amount of the Br-4p state.

In addition, if the partial DOS of the two different bromine atoms are compared (Figure 5), the DOS of the Br2−4p state is much higher than that of the Br1−4p state at the top of the VBs. This shows the charge transitions mostly come from Br2-4p rather than Br1-4p to Cd-5s and Hg-6s states. Therefore, the optical absorption of **1** is mainly ascribed to the charge transitions from the Br2-4p and As-4p to Cd-5s and Hg-6s states.

In addition, we calculated the atomic site and angular momentum projected DOS of **1** to elucidate the nature of the electronic band structure and chemical bonds. As shown in Figure 4, we observed that the density and shape of As-4p are similar to those of the Cd-5s and Hg-6s states between −5.0 and −2.5 eV, which shows that there are strong covalent interactions between As and the metal atoms Hg and Cd. As for the bromine atoms, it can be found that the density and shape of Br-4p are much different from those of the Cd-5s and Hg-6s states between −5.0 eV and the Fermi level, which shows that there are only weak contributions to the covalence bond, implying that the Hg−Br and Cd−Br bonds are both ionic in character.

Semiempirical population analysis allows for a more quantitative bond analysis. The calculated bond orders of the Cd−Br1, Cd−Br2, Hg−Br1, Hg−Br2, Cd−As, and Hg−As bonds are 0.18, 0.08, 0.36, 0.29, 1.49, and 0.64 to 0.86 e in a unit cell of **1** (covalent single-bond order is generally 1.0 e), respectively. Accordingly, it indicates that the covalent interactions of the Cd−As bond are larger than those of the Hg−As bond, but the ionic character of the Cd−Br bond is larger than that of Hg−Br in the present compound. As for the two different bromine atoms, the covalent character of the M−Br1 (M = Hg, Cd) bonds is larger than that of the M−Br2 bonds.

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Supporting Information Available: IR spectrum, molecular structure figures, and X-ray crystallographic file (CIF format) for the structure determination of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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