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Cryst. Growth Des., Just Accepted Manuscript • DOI: 10.1021/acs.cgd.6b01118 • Publication Date (Web): 28 Sep 2016

Downloaded from http://pubs.acs.org on October 4, 2016

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1418x759mm (55 x 55 DPI)

Mercury Chalcohalide Semiconductor Hg₃Se₂Br₂ for Hard Radiation Detection

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Abstract

Hg₃Se₂Br₂ is a wide band gap semiconductor (2.22 eV) with high density (7.598 g/cm³), and crystallizes in the monoclinic space group *C*2/*m* with cell parameters of *a* = 17.496 (4) Å, *b* = 9.3991 (19) Å, *c* = 9.776(2) Å, β = 90.46(3)°, *V* = 1607.6(6) Å³. It melts congruently at a low temperature, 566 °C, which allows for an easy single crystal growth directly from the stoichiometric melt. Single crystals of Hg₃Se₂Br₂ up to 1 cm long have been grown using the Bridgman method. Hg₃Se₂Br₂ single crystals exhibit strong photocurrent response when exposed to Ag X-ray and blue diode laser. The resistivity of Hg₃Se₂Br₂ measured by the two probe method is in the order of 10¹¹ Ω·cm and the mobility-lifetime product ($\mu\tau$) of the electron and hole carriers estimated from the energy spectroscopy under Ag X-ray radiation are ($\mu\tau$)_e ~ 1.4 ×10⁻⁴ cm²/V and ($\mu\tau$)_h ~ 9.2×10⁻⁵ cm²/V. Electronic structure calculations at the Density Functional Theory level indicate a direct band gap and a relatively small effective mass for carriers. Based on the photoconductivity and hard X-ray spectrum, Hg₃Se₂Br₂ is a promising candidate for X-ray and into detection at room temperature.

Keywords: chalcohalide, crystal growth, photoconductivity, mobility-lifetime product, X-ray detector, γ -ray detector.

Introduction

Solid state semiconductors for hard radiation detection at room temperature are needed in a number of applications such as medical imaging, cosmic ray astronomy, national security, and for several scientific research,¹ they generally provide better energy resolution than scintillator detectors.² The semiconductor CdZnTe (CZT) is the current benchmark material for room temperature X-ray and γ -ray detection.^{1a,3} However, due to some of its intrinsic physical properties, such as high Cd vapor pressure, high solubility of Te in CdTe at the crystal growth temperature, etc, CZT is prone to form macroscopic defects such as grains, cracks, twins and tellurium precipitates, which lead to low yield and high cost of the detector-grade single crystals.^{1a,4} Therefore, there is a great demand for superior and low cost semiconductor materials for radiation detection to meet the technological requirements.

Generally, among the required properties of a good semiconducting material for hard radiation detection at room temperature are: 1) band gap (E_g) in the range of 1.5 eV < Eg < 2.5 eV, which is large enough for high resistivity and small enough for small electron-hole ionization energy; 2) high average atomic number (Z) for high stopping power to ensure high absorption; 3) high mobility-lifetime products ($\mu\tau$) for rapid signal readout; and 4) cost effective and efficient growth of high quality single crystals. In the search of new detector materials, a variety of heavy metal chalcogenides (GaTe,⁵ Cs₂Hg₆S₇,⁶ TlGaSe₂⁷ etc.) and halides (PbI₂,^{2c,8} HgI₂,⁹ Hg₂Br₂,¹⁰ BiI₃,^{2b,11} TlBr,¹² CsPbBr₃¹³ etc.) have been investigated. Generally most binary heavy metal chalcogenides, such as HgQ (Q = Se and Te) possess high density, high average Z, and high carrier mobility but have very low or zero energy gap. On the other hand, heavy metal halides such as HgX_2 (X = Br, I) and TlBr have a suitable band gap for detector applications but they suffer from mechanical softness, polarization effects, and low carrier mobility to be good detector materials. One approach to obtain favorable properties in candidate materials is to combine attributes from both metal chalcogenides and halides by applying a lattice hybridization approach.¹⁴ This approach is based on the fact that heavy metal chalcogenides generally have band gaps that are too low for room temperature detection (giving high dark currents) while heavy metal halides tend to have band gaps that are too high (giving low carrier mobilities). On the basis of this concept, we have explored several chalcohalides (SbSeI, β -Hg₃S₂Cl₂, Hg₃Q₂Bi₂Cl₈(Q = S, Se, Te), TlHg₆Q₄Br₅ (Q

= S, Se) $)^{14c,15}$ and identified the thallium chalcohalides Tl₆SeI₄ and Tl₆SI₄, to be promising materials for hard radiation detection^{14a,16}

In this work, we extend the lattice hybridization concept to the mercury chalcohalide. Mercury is a heavy element that is chemically stable. High purity elemental mercury can be easily obtained and starting materials of mercury compounds such as mercury metal and mercury halides are also relatively inexpensive. Therefore, mercury chalcohalides could be low cost materials for Xray and γ -ray radiation detectors. Hg₃Se₂Br₂ was reported more than 50 years ago,^{4g,17} but single crystals of Hg₃Se₂Br₂ have not been grown and consequently the physical properties are unknown. Here, we report the synthesis, purification, and physical characterizations of large Hg₃Se₂Br₂ single crystals grown for the first time, which proposed as a very promising wide band gap semiconductor for hard radiation detection.

Experimental Section

Syntheses and Crystal Growth. The following reagents were used: (i) Mercury metal, 99.999%, Alfa Aesar, Ward Hill, MA; (ii) Selenium shot, 99.999+%, Alfa Aesar, Ward Hill, MA; (iii) Mercury Bromide, 99.99%, Alfa Aesar, Ward Hill, MA. HgSe was prepared as a stoichiometric mixture of mercury metal and selenium shot. Liquid mercury was added by pipetting into a ϕ 13mm and ~30 cm long fused silica tube and then selenium was loaded. The tube was flame sealed under ~ 10⁻⁴ mbar (the bottom part of the tube was cooled in liquid N₂ to prevent evaporation of Hg metal). One end of the reaction tube was extended to the outside of the tube furnace which was then set to 500 °C and stayed for three days. HgSe formed and condensed at the cool end of the tube. The "as synthesized" HgSe was transferred to a vial and stored in glove box for further use. The commercially purchased HgBr₂ was purified twice using vapor transport method. HgBr₂ was loaded into a long quartz tube and sealed under vacuum. The tube was placed in a box furnace vertically, with one end extended to the outside of the furnace, and the temperature was set at 300 °C. HgBr₂ was transported and condensed at the top part of the tube, while black non-volatile impurities were left at the bottom of the tube.

HgSe and HgBr₂ in the molar ratio of 2:1.05 were weighed and sealed in an evacuated thick wall quartz tube (O.D. 13mm x I.D. 7 mm) where the material mixture was loaded up to 80% of the inner volume. The crystal growth was processed without a seed crystal. Over a period of 12 h,

the tube was heated to 650 °C and then kept there for 24 h to ensure a homogeneous melt. The tube was then cooled to room temperature over 8 h. Then the tube was transferred to a three zone Bridgman furnace. Three zones in the furnace were set at 650 °C - 650 °C - 200 °C from the top. The temperature gradient in the growth zone was about 38° C/cm, as shown in Figure 1(a). The growth speed was 1 cm to 2.4 cm per day. The as grown Hg₃Se₂Br₂ ingots and crystals are shown in Figure 1(b).

Semi-quantitative elemental analysis by Energy Dispersive Spectroscopy (EDS) on several $Hg_3Se_2Br_2$ crystals cleaved from the ingot was performed using Hitachi S-3400 scanning electron microscope (SEM) equipped with a PGT energy dispersive X-ray analyzer with an accelerating voltage of 25 kV and a 60 s accumulation time for data acquisition.

Thermal Analysis. In order to investigate thermal behavior of Hg₃Se₂Br₂, Differential Thermal Analysis (DTA) was performed using a Shimadzu DTA-50 Differential Thermal analyzer. Crystalline materials (~36 mg) were flame sealed in a silica ampoule evacuated at 10^{-4} Torr. A similarly sealed ampoule of Al₂O₃ was used as a reference. Samples were heated to 650 °C at a rate of 5 °C/min and then cooled at 5 °C/min to 50 °C. This thermal cycle was repeated at the same condition to verify the thermal behavior. The residue was then examined by X-ray powder diffraction and compared to the diffraction patterns taken before DTA to verify that Hg₃Se₂Br₂ is congruently melting. Melting and crystallization points were measured at a minimum endothermic peak and a maximum exothermic peak.

X-ray Diffraction. Powder X-ray diffraction (XRD) for the samples randomly collected from the grown crystals to examine the phase purity was performed using a PanAlytical X'Pert Pro powder diffractometer (Cu K α radiation, $\lambda = 1.5418$ Å) over the 2 θ range of 10 - 70° with a step size of 0.017°. The diffractometer was operated at 45 kV/40 mA.

Single crystal X-ray Diffraction data were collected at 293K on a STOE 2T image plate diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å). Data reduction and numerical absorption corrections were done on the structures using STOE X-Area software package.¹⁸ The crystal structure was solved by direct methods and refined by full-matrix least square on F^2 (all data) using the SHELXTL software suite.¹⁹ Thermal displacement parameters were refined anisotropically for all atomic positions. The parameters for data collection and the details of the

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structure refinement are given in Table 1. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 2.

Optical Spectroscopy. The band gap energy of $Hg_3Se_2Br_2$ was determined using optical diffuse reflectance spectroscopy. The measurement was performed at room temperature using a Shimadzu Model UV-3101PC double-beam, double-monochromator spectrophotometer. BaSO₄ was used as a 100% reflectance standard. The absorption data were calculated based on the obtained reflectance spectra data using the Kubelka-Munk equation.²⁰

Electronic Band Structure Calculations. The electronic band structure of Hg₃Se₂Br₂ was investigated by first-principles electronic structure calculations within the Density Functional Theory (DFT) framework. We employed the plane-wave basis set and pseudo-potential scheme using the projector augmented wave method implemented in the Vienna Atomic Simulation Package (VASP) code. The cut-off energy for the plane-wave basis was set to 450 eV and a 3x7x7 k-point mesh was used for Brillouin zone sampling. For exchange-correlation functional, generalized gradient approximation (GGA) method is used with Perdew-Burke-Ernzerhof formalism.

Electrical Resistivity and Photoconductivity. Single crystals of $Hg_3Se_2Br_2$ were selected for the DC resistivity measurements by a two probe method using a Keithley 617 electrometer. Ti (5nm) and Pt (20nm) were evaporated on the front and back surfaces of the samples. The resistance measurement was conducted perpendicular to the (001) plane of the plate crystal. The electrical current from the two electrodes on the crystal sample was measured while voltage was applied from -300 V to 300 V.

Photoconductivity measurement was carried out using a home-built setup on two single crystal plates of Hg₃Se₂Br₂ with similar dimensions ($3.0 \times 2.1 \times 0.5 \text{ mm}^3$ and $3.9 \times 2.5 \times 0.6 \text{ mm}^3$) using the Amptek Mini-X Ag X-ray (50 kV, 40 µA) white radiation. The crystal was irradiated perpendicular to the (001) plane by the X-ray beam. The bias voltage was maintained constant at each value while the shutter on the X-ray source was switched ON and OFF manually. The resulting current was recorded as a function of time using a Keithley 6517B Electrometer. The X-ray induced photocurrent under different bias voltage was calculated by subtracting the X-ray OFF current from the X-ray ON current. The carrier mobility-lifetime ($\mu\tau$) products for electrons

and holes were obtained by fitting the photocurrent curves versus bias voltage using the Hecht equation:^{4f,21}

$$I(V) = \frac{I_0 \mu \tau V}{L^2} \left(1 - e^{\frac{-L^2}{\mu t V}} \right)$$
(1)

where I_0 is saturation current, L is the sample thickness, and V is the applied voltage. A qualitative measurement of laser response was conducted. A blue diode laser (473 nm, 50 mW) was focus on the crystal sample and turned ON and OFF every 20 seconds. The bias voltage was set constant at 100V. The resulting current was recorded as a function time.

X-ray spectroscopy measurement was performed by the same X-ray source (50 kV, 40 uA). $Hg_3Se_2Br_2$ single crystal was used to measure the X-ray radiation spectrum. One $Hg_3Se_2Br_2$ plate single crystal (3.9 × 2.5 × 0.6 mm³) was cleaved from the as grown ingot. The sample with large cleaved surfaces was not polished or etched. Ti and Pt metal contact were evaporated onto the two sides of the crystal. The single crystal was placed in an eV-480 test fixture attached to an eV-550 preamplifier box (eV Products Inc.). An ORTEC 572A amplifier (Ametek Inc.) with a gain of 1000 and 10 µs shaping time was used to amplify the signal before it is evaluated by a dual 16 K input multichannel analyzer (Model ASPEC-927), the spectrum data was recorded using MAESTRO-32 software.^{13,22}

Results and discussion

Synthesis and crystal growth. We synthesized $Hg_3Se_2Br_2$ directly using a stoichiometric combination of HgSe and HgBr₂.^{17,23} The thermal behavior of the product obtained from the synthesis was examined by DTA. In the DTA curves (Figure 2(a)), one endothermic peak at 566 °C on heating and one exothermic peak at 543 °C during cooling process and no change in a repeated cycle were observed. The sample after the DTA measurement was examined by PXRD to confirm that the sample remains as a single phase with no phase transitions or decomposition after two cycles of heating and cooling. The experimental X-ray diffraction pattern of the sample matches well with the calculated pattern from the crystal structure, Figure 3(a). This result suggests that single crystals of $Hg_3Se_2Br_2$ can be grown directly from stoichiometric melt by the Bridgman method. When the synthesis was scaled up to ~10 g, however, the binary phase HgSe

as an impurity was observed in PXRD of the final product. The presence of HgSe is caused by partial dissociation of Hg₃Se₂Br₂ due to high vapor pressure of HgBr₂, which was not noticed in a small scale synthesis. Accordingly, 5 mol% excess of HgBr₂ was added in the reaction mixture to compensate for the evaporation of HgBr₂ during synthesis and also the starting polycrystalline mixture of HgSe and HgBr₂ was filled up to > 80 % of total volume in the quartz tube to suppress evaporation of HgBr₂. A thick wall quartz tube (3 mm thick wall) was used to avoid explosion by excessive pressure of HgBr₂ vapor. After the crystal growth process by the Bridgman method, some white and light yellow polycrystalline coating (Figure S1) was observed on the surface of the Hg₃Se₂Br₂ ingots, which was identified as excess HgBr₂ by PXRD.

The obtained Hg₃Se₂Br₂ ingots are red in color and transparent to light as shown in Figure 1(b). Because of the layered structure, the ingots are apt to cleave along the (001) plane, which was determined from XRD as shown in Figure 3(b). The color of the Hg₃Se₂Br₂ crystals ranges from yellow (thin crystals ~ 0.3 mm) to red (thick crystals >1 mm) (Figure 1(b)). The crystal shows no noticeable change in ambient atmosphere for several weeks. EDS/SEM analysis on the crystals shows an average composition of Hg₃Se_{2.3}Br_{2.0} and no HgBr₂ inclusions were found in the SEM micrograph, although an excess of HgBr₂ was added in synthesis and crystal growth.

Crystal Structure The cell parameters of Hg₃Se₂Br₂ were previously determined by powder Xray diffraction as a = 9.42 Å, b = 9.74 Å, c = 8.78 Å.^{4g} Later, Yu. V. Minets et al. investigated the structure by single crystal X-ray diffraction and found Hg₃Se₂Br₂ crystallizes in the monoclinic space group C2/m with the cell parameters a = 17.529(6) Å, b = 9.408(4) Å, c =9.775(4) Å, and $\beta = 89.51(3)^{\circ}$.¹⁷ However the single crystal X-ray diffraction data had only 684 reflections, which is not sufficient to obtain an accurate structure for monoclinic space group. From our structural solution, the cell parameters a = 17.496(4) Å, b = 9.3991(19) Å, c = 9.776(2)Å, and $\beta = 90.46(3)^{\circ}$ were refined based on 7859 reflections (2294 independent reflections) collected. The data refinement resulted in very accurate atomic positions and consequently significantly more precise atom distances and angles, Table 2 and 3.

As shown in Figure 4, the structure of $Hg_3Se_2Br_2$ is built of $[Hg_3Se_2]$ layers spreading along the *ab* plane, which are separated by Br atoms. There are also Br atoms embedded in the grooves of the $[Hg_3Se_2]$ layers. The $[Hg_3Se_2]$ layers are formed by $[Hg_2Se_2]$ zig zag chains (Figure 5(a)) connected by Hg Se bonds between them (Figure 5(b)). The $[Hg_2Se_2]$ chains run parallel to the

crystallographic a axis. This chain is composed of Hg atoms linearly coordinated with two Se atoms. The asymmetric unit of Hg₃Se₂Br₂ contains five Hg atoms, four Br atoms, and two Se atoms. Selected distances and angles for Hg₃Se₂Br₂ are summarized in Table 3. The Hg-Se distances (2.490(1) Å to 2.524(1) Å) and Hg-Br (2.843(1) Å to 3.124(1) Å) are normal in the range found in Hg/Se and Hg/Br compounds^{4e,24}. The Hg-Se bond distances within the [Hg₃Se₂] layer are in good agreement with the sum of the Hg and Se covalent radii and the relatively long Hg-Br distances indicate weak metal-halogen interactions between the layers. This explains why the as grown crystals cleave easily along the (001) plane. The asymmetric unit of Hg₃Se₂Br₂ contains five Hg atoms, four Br atoms, and two Se atoms. Selected atom distances and angles for Hg₃Se₂Br₂ are summarized in Table 3. As shown in Figure 4, Hg₃Se₂Br₂ is built of infinite [Hg₃Se₂] layers along the *ab* plane loosely bound by the interlayer Br atoms along the c-axis. The [Hg₃Se₂] layers are formed by [Hg₂Se₂] zig-zag chains (Figure 5(a)) running parallel to the crystallographic *a*-axis. The linear Hg-Se bond distances in $[Hg_2Se_2]$ (Figure 5(b)) are ~2.5 Å which is in a good agreement with those reported in literatures.(ref. 4e, find one more from online) The structure of Hg₃Se₂Br₂ involves long interactions between Br and Hg atoms beyond the normal Hg-Br covalent distance which is in the range of 2.4 - 2.7 Å.²⁴ Br(1) and Br(4) enclosed inside the [Hg₃Se₂] layers are weakly bonded by Hg(2) and Hg(3) in a square planar geometry at the distance of 3.1448(14) - 3.3006(12) Å. Br(2) and Br(3) are bridging the [Hg₃Se₂] layers by long interactions with Hg(1), Hg (4), and Hg(5) at the distance of 2.8438(13) -3.1789(21) Å. The Hg-Br distances in these two circumstances are significantly longer than the sum (2.5 Å) of covalent radii of Hg and Br, implying that Hg₃Se₂Br₂ has a significant ionic character in the structure. All Hg atoms are surrounded by Br and Se atoms in distorted octahedral environments at the distance ranging from 2.844(1) to 3.741(1) Å and their detailed local geometries are shown in Figure S2. The structure of ternary Hg₃Se₂Br₂ retains motifs of linear Se-Hg-Se and octahedral HgBr₆ units observed in the parent binary compounds, HgSe²⁵ and HgBr2²⁶, respectively. The weak Br-Hg interactions between and inside the [Hg3Se2] layers accounts for easy cleavage of the Hg₃Se₂Br₂ crystals along the (001) plane as well as the partial decomposition into two binary HgBr₂ and HgSe during the Bridgman crystal growth process at 650 °C that we observed.

Band Gap Energy. The UV/Vis/NIR absorption spectrum of Hg₃Se₂Br₂ measured using ground crystalline powder is shown in Figure 2(b). From the well-defined absorption edges, the optical

band gap of $Hg_3Se_2Br_2$ is estimated as 2.22 eV, which is in the range of 1.5 to 2.5 eV suitable for hard radiation detectors at room temperature. The band gap of $Hg_3Se_2Br_2$ is between those of its parent binary compounds $HgSe (0.061 \text{ eV} at 300 \text{ K})^{27}$ and $HgBr_2 (3.65 \text{ eV})$,²⁸ which directly supports the feasibility of our chalcogenide-halide hybridization approach for band gap engineering.

Band Structure Calculations. To investigate the electronic properties related to the γ -ray detection mechanisms of Hg₃Se₂Br₂, first-principles calculations were performed. The calculations were carried with the lattice constants obtained by our single crystal analysis. The electronic band structure of Hg₃Se₂Br₂ is shown in Figure 6(a). The band gap is direct in nature and appears at the Γ point. The gap energy 1.25 eV is underestimated from the optical band gap 2.22 eV measured as it is typical for this kind of calculations.²⁹ The conduction bands of Hg₃Se₂Br₂ as depicted in Figure 6(a) are quite dispersive along Γ - X, Γ - Y and B - D directions, indicating small effective masses for electron carriers. The valence bands, on the other hand, are relatively flat, especially along the S – Y direction. As seen in the Projected-Density-of-States plot in Figure 6(b), the conduction bands are mainly composed of Hg *s*- and Se *p*-states and the valence bands are mixture of Br *p*-, Se *p*-, and Hg *s*-states.

Resistivity and Photoconductivity. The resistivity of a Hg₃Se₂Br₂ crystal was measured using a two probe method at room temperature. The voltage-current characteristics of the single crystal sample are shown in Figure 7(a). The I-V curve deviates from linearity at positive bias, which is a normal behavior for Schottky contact barriers and has often been observed in commercial CZT crystals.³⁰ The resistivity calculated from the slope of the I-V curve (-300 – 300 V) based on the dimensions of the crystal was 5.19 x $10^{11} \Omega$ ·cm and is sufficiently high to suppress dark current at room temperature, and also allowing for higher bias voltage be applied to increase detection resolution.

Hg₃Se₂Br₂ single crystals exhibit strong photoconductivity response when exposed to low flux Ag X-rays. Figure 8 shows the current as a function of time while the X-ray beam was turned ON-OFF. The X-ray induced current is ~3 times higher than dark current under 100 V bias. The photoconductivity response curve as a function of positive and negative bias voltage is shown in Figure 9, and the mobility-lifetime ($\mu\tau$) products for electrons and holes were fitted as described in the Experimental Section. The mobility-lifetime products of Hg₃Se₂Br₂ are ($\mu\tau$)_e = 1.13 × 10⁻⁴

cm²/V for electrons and ($\mu\tau$)_h = 1.26 × 10⁻⁵ cm²/V for holes. These values are promising for a relatively unexplored compound, grown here for the first time, and are comparable to ($\mu\tau$)_e = 8 × 10⁻⁴ cm²/V and ($\mu\tau$)_h = 3 × 10⁻⁵ cm²/V³¹ of α-HgI₂ a widely studied semiconductor for detector applications.^{1e,9a,17,32} Furthermore, the $\mu\tau$ of Hg₃Se₂Br₂ samples is higher than other layered materials studied for X-ray and γ-ray detectors, such as PbI₂ (($\mu\tau$)_e = 8 × 10⁻⁶ cm²/V, ($\mu\tau$)_h = 9 × 10⁻⁷ cm²/V),^{1e} CsHgInS₃ (($\mu\tau$)_e = 3.6 × 10⁻⁵ cm²/V, ($\mu\tau$)_h = 2.9 × 10⁻⁵ cm²/V),³³ CsCdInSe₃(($\mu\tau$)_e = 1.18 × 10⁻⁵ cm²/V, ($\mu\tau$)_h = 2.74 × 10⁻⁶ cm²/V),³⁴ TlGaSe₂ (($\mu\tau$)_e = 6 × 10⁻⁵ cm²/V, ($\mu\tau$)_h = 9.2 × 10⁻⁶ cm²/V),⁷ and GaSe (($\mu\tau$)_e = 6.8 × 10⁻⁶ cm²/V, ($\mu\tau$)_h = 5.8 × 10⁻⁷ cm²/V).³⁵ The $\mu\tau$ products of Hg₃Se₂Br₂ are lower than the leading room temperature detector material, CZT (($\mu\tau$)_e = 4.5 × 10⁻² cm²/V, ($\mu\tau$)_h = 1.0 × 10⁻⁴ cm²/V)³¹. Further purification of starting materials, reduction of trap defects in Hg₃Se₂Br₂ crystals, and wafer production with suitable chemical surface treatment are expected to produce the material with lower trap densities and higher $\mu\tau$ products.

 $Hg_3Se_2Br_2$ single crystal has also shown strong photocurrent response when illuminated by a blue diode laser (473 nm). The dark current and laser induced photocurrent under 100 V bias voltage was recorded when the laser was turned ON-OFF (Figure \$2\$3). The dark current under 100 V bias was ~ 0.09 nA. Upon laser illumination of 50 mW, the photocurrent increased to a peak value of ~7000 nA, indicating the photocurrent is >77,000 times larger than the dark current. The laser photocurrent was much higher than the Ag X-ray induced because the photon flux of the laser is thousands of times higher than that of the latter source.

Detector Property Hg₃Se₂Br₂ is composed of elements with high atomic numbers (Z_{Hg} =80, Z_{Se} =34 and Z_{Br} =35) and has a high density of 7.598 g/cm³, giving the material a high stopping power for X-ray and γ -ray radiation. The attenuation length of the material for hard radiation as a function of photon energy was calculated using the atomic attenuation coefficient tabulated by NIST³⁶ as shown in Figure 7(b). The compound Hg₃Se₂Br₂ has a much higher stopping power than CZT, especially at high photon energy range of 0.1 to 10 MeV. For example, at the energy of ¹³⁷Cs (i.e., 662 keV), the attenuation length of CZT is 2.28 cm, while Hg₃Se₂Br₂ is 1.39 cm, confirming the much higher absorption coefficient compared to CZT at this energy. Therefore, thinner crystals of the Hg₃Se₂Br₂ can be used to absorb the hard radiation. This property helps to relax some of the requirements for the high carrier mobility-lifetime products.

To assess the detection performance of the $Hg_3Se_2Br_2$ crystals for X-ray radiation, we performed Ag X-ray irradiation experiments at room temperature. The pulse height spectra obtained from the Hg₃Se₂Br₂ crystal are shown in Figure 10 (a) and Figure 11 (a) for electron and hole carriers, respectively. The sample was 0.6 mm thick, the bias voltage was set in the range of 30/40 – 800/900 V, and the counting time was 200 seconds. The recorded spectra clearly show responses over X-ray irradiation compared to the dark conditions (without X-ray) for both electron and hole carriers. The electron response exhibits well resolved two peaks, while the hole response shows a broad unresolved peak. The peak position shifts to the high channel numbers as the voltage increases, and then nearly becomes constant above 200 V. To get the mobility-lifetime $(\mu\tau)$ products, the average peak positions are plotted as a function of voltage applied for electron and hole responses in Figure 10 (b) and Figure 11 (b), respectively. The $\mu\tau$ values for both carriers were estimated using the maximal charge collection efficiency (CCE) under each bias voltage applied to the sample. The details of this method were presented in our previous report.³⁷ The estimated mobility-lifetime ($\mu\tau$) products of Hg₃Se₂Br₂ from these X-ray energy spectra are $(\mu\tau)_{\rm e} = 1.4 \times 10^{-4} \text{ cm}^2/\text{V}$ for electrons and $(\mu\tau)_{\rm h} = 9.2 \times 10^{-5} \text{ cm}^2/\text{V}$ for holes, which are in the same order of magnitudes as the vales obtained from photocurrent measurements.

The X-ray energy spectrum for electron response of a Hg₃Se₂Br₂ single crystal is shown in Figure 12(a) comparing with that of a commercial CZT crystal measured under 200 V bias voltage. The counting times for CZT and Hg₃Se₂Br₂ are set as the same of 200 seconds. Similar to the CZT, the characteristic lines of Ag K_a 22.2 keV and K_β 24.9 keV are well resolved in the spectrum detected by Hg₃Se₂Br₂ crystal. The count of K_a line from the Hg₃Se₂Br₂ crystal is comparable to that of CZT, while the signal for K_β is weaker. CZT has a low $\mu\tau$ for hole carriers and thus as expected did not show a hole response on X-ray irradiation at the same measurement condition. Furthermore, Hg₃Se₂Br₂ crystal has also exhibited counter response under Co⁵⁷ γ-ray irradiation. The pulse height energy spectra in Figure 12(b) shows obvious counting comparing to the dark condition under positive bias 500 V, 600 V and 700 V, respectively. This result from the Hg₃Se₂Br₂ crystal suggests comparable γ -ray spectroscopy capabilities found in Bi doped CZT.³⁸ Such results are encouraging considering the Hg₃Se₂Br₂ crystal is still at the early stage of development. There should be some impurities and defects in our crystal samples which act as traps for photo induced electrons and holes, better spectroscopy performance from Hg₃Se₂Br₂ can be achieved using improved crystal with better quality synthesized in the future.

Compared to other mercury chalcohalides β -Hg₃S₂Cl₂ in the same chemical series which we reported earlier,^{15a} Hg₃Se₂Br₂ crystal exhibit much stronger photo-induced response. The $\mu\tau$ product for electron carriers obtained under X-ray is 1.4×10^{-4} cm²/V for Hg₃Se₂Br₂ crystal which is ~ 4 times higher than 3.2×10^{-5} cm²/V of β -Hg₃S₂Cl₂. This high $\mu\tau$ of Hg₃Se₂Br₂ is confirmed by the pulse height spectra of Ag X-ray detected using Hg₃Se₂Br₂ crystal, while there was no Ag X-ray spectra reported using β -Hg₃S₂Cl₂ crystal. One of the main reasons could be the high quality with lower defect concentration in Hg₃Se₂Br₂ crystals that can be grown directly from stoichiometric melt, while β Hg₃S₂Cl₂ crystal is formed by decomposition process^{15a}-of quaternary Hg₃Bi₂S₂Cl₈-melt involving other phases in the product. One of the main reasons could be the high quality with lower defect concentration in Hg₃Se₂Br₂ crystals that were grown directly from stoichiometric melt, while β -Hg₃S₂Cl₂ crystal is formed by decomposition process^{15a}-of quaternary Hg₃Bi₂S₂Cl₈-melt involving other phases in the product. One of the main reasons could be the high quality with lower defect concentration in Hg₃Se₂Br₂ crystals that were grown directly from stoichiometric melt, while β -Hg₃S₂Cl₂ crystals were formed by decomposition process of quaternary Hg₃Bi₂S₂Cl₈ in which other phases may present in the product.

Conclusion

The mercury chalcohalide, Hg₃Se₂Br₂, is a promising candidate material for X-ray and possibly γ -ray radiation detection. It has a very high stopping power, suitable optical band gap and high resistivity for the detector applications. Large single crystals of Hg₃Se₂Br₂ up to 1 cm in length were grown by Bridgman method for the first time. Hg₃Se₂Br₂ crystallizes in a layered structure with 2-D layers weakly bonded by Br atoms. The single crystal exhibits strong photocurrent response to both Ag X-ray and blue laser radiation. Pulse height spectra of Ag Xray were obtained from Hg₃Se₂Br₂ crystal, where two peaks corresponding to the characteristic lines of Ag K_{α} 22.2 and K_{β} 24.9 keV were well resolved. The $\mu\tau$ products of HgSe₂Br₂ Hg₃Se₂Br₂ are comparable or superior to other layered materials such as PbI₂, CsHgInS₃, CsCdInSe₃, etc. Hg₃Se₂Br₂ is a low cost and promising material for X-ray and γ -ray detection, suggesting that further investigation and development to improve the quality of single crystals are warranted.

Acknowledgment

This work was supported by the Office of Nonproliferation and Verification Research and Development under National Nuclear Security Administration of the U.S. Department of Energy

under contract No. DE-AC02-06CH11357. Use of the Center for Nanoscale Materials, an Office of Science user facility, was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval

to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Supporting Information. The Supporting Information includes the following information: Figure S1, The HgBr₂ coating formed on the surface of as grown Hg₃Se₂Br₂ ingot. Figure S2, the coordination environment of Br and Hg atoms. Figure S2S3, Photocurrent response of Hg₃Se₂Br₂ single crystal to the blue laser radiation. Also, the crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Table 1. Crystal data and structure refinement for $Hg_3Se_2Br_2$ at 293(2) K.

Empirical formula	$Hg_3Se_2Br_2$
Formula weight	919.51
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/m
Unit cell dimensions	a = 17.496(4) Å, α = 90.00° b = 9.3991(19) Å, β = 90.46(3)° c = 9.776(2) Å, γ = 90.00°
Volume	1607.6(6) Å ³
Z	8
Density (calculated)	7.598 g/cm^3
Absorption coefficient	76.049 mm^{-1}
F(000)	3024
Crystal size	$0.1 \ge 0.09 \ge 0.02 \text{ mm}^3$
θ range for data collection	4.11 to 29.21°
Index ranges	-23<=h<=23, -12<=k<=12, - 13<=l<=13
Reflections collected	7859
Independent reflections	2294 [$R_{int} = 0.0729$]
Completeness to $\theta = 29.21^{\circ}$	99.2%
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2294 / 0 / 76
Goodness-of-fit	0.989
Final R indices $[>2\sigma(I)]$	$R_{obs} = 0.0339, wR_{obs} = 0.0563$
R indices [all data]	$R_{all} = 0.0613, wR_{all} = 0.0597$
Extinction coefficient	0.000052(9)
Largest diff. peak and hole	3.700 and -2.080 $e \cdot Å^{-3}$
$R = \Sigma F_o - F_c / \Sigma F_o , wR = \{\Sigma [w(F_o)] E_o \}$	$ _{o} ^{2} - F_{c} ^{2} ^{2}] / \Sigma[w(F_{o} ^{4})] \}^{1/2}$ and calc
$w=1/[\sigma^2(Fo^2)+(0.0109P)^2]$ where P=	$(Fo^2 + 2Fc^2)/3$

Label	Х	Y	Z	Occupancy	${\rm U_{eq}}^{*}$
Hg(1)	0.1239(1)	0.2245(1)	0.2017(1)	1	40(1)
Hg(2)	1/4	1/4	1/2	1	41(1)
Hg(3)	0	0.7641(1)	1/2	1	40(1)
Hg(4)	0.2722(1)	1/2	0.2154(1)	1	40(1)
Hg(5)	-0.0249(1)	1/2	0.2297(1)	1	43(1)
Br(1)	0.1236(1)	1/2	0.4779(2)	1	30(1)
Br(2)	0.1184(1)	0	0.0069(2)	1	32(1)
Br(3)	0.1249(1)	1/2	0.0229(2)	1	35(1)
Br(4)	0.1267(1)	0	0.4770(2)	1	32(1)
Se(1)	0.2657(1)	0.2363(2)	0.2459(2)	1	28(1)
Se(2)	-0.0179(1)	0.2359(2)	0.2464(2)	1	27(1)

Table 2. Atomic coordinates $(x10^4)$ and equivalent isotropic displacement parameters $(\text{\AA}^2 x10^3)$ for Hg₃Se₂Br₂ at 293(2) K with estimated standard deviations in parentheses.

 $^{*}U_{eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond lengths atom distances [Å] and Angles angles [deg] for Hg ₃ Se ₂ Br ₂ at 293(2) K with estimated standard deviations in parentheses. Hg(1)- Se(1)	2.5177(11)	Hg(4)-Br(2)	2.9070(19)
Hg(1)-Se(2)	2.5247(12)	Hg(4)- $Br(3)$	3.1789(21)
Hg(2)-Se(1) × 2	2.5045(12)	Hg(4)- $Br(4)$	3.4765(22)
Hg(3)-Se(2) × 2	2.4971(12)	Hg(5)-Br(1)	3.5410(21)
Hg(4)-Se(1) × 2	2.4994(13)	Hg(5)-Br(1)	3.3517(21)
Hg(5)-Se(2) × 2	2.4903(13)	Hg(5)-Br(3)	3.0152(21)
Hg(1)-Br(2)	2.8438(13)		
Hg(1)-Br(3)	3.1243(13)	Se(1)-Hg(1)-Se(2)	159.55(4)
Hg(1)-Br(4)	3.4195(16)	Se(1)-Hg(2)-Se(1)	180.0
Hg(2)-Br(1)	3.2326(11)	Se(2)-Hg(3)-Se(2)	179.99(7)
Hg(2)-Br(4)	3.1965(12)	Se(1)-Hg(4)-Se(1)	165.28(6)
Hg(3)-Br(1)	3.3006(12)	Se(2)-Hg(5)-Se(2)	170.68(6)
Hg(3)-Br(4)	3.1448(14)	Br(2)-Hg(1)-Br(3)	103.92(4)
Hg(1)-Se(1)	2.5177(11)	Hg(4)-Br(2)	2.9070(19)
Hg(1)-Se(2)	2.5247(12)	Hg(5)-Br(3)	3.015(2)
$Hg(2)$ Se(1) $\times 2$	2.5045(12)	Se(1) Hg(1) Se(2)	159.55(4)
$Hg(3)$ Se(2) $\times 2$	2.4971(12)	Se(1) Hg(2) Se(1)	180.0
$Hg(4)$ Se(1) $\times 2$	2.4994(13)	Se(2) Hg(3) Se(2)	179.99(7)
$Hg(5)$ Se(2) $\times 2$	2.4903(13)	Se(1) Hg(4) Se(1)	165.28(6)
$\frac{1}{Hg(1)-Br(2)}$	2.8438(13)	$\frac{Se(2)}{Hg(5)} \frac{Se(2)}{Se(2)}$	170.68(6)

Hg(1) Br(3)	3.1243(13)	Br(2)-Hg(1)-Br(3)	103.92(4)	



Figure 1. (a) Temperature profile of the Bridgman furnace, (b) As grown $Hg_3Se_2Br_2$ ingot and single crystals, the crystal cleaves along (001) plane.



Figure 2. (a) DTA curves of crystalline $Hg_3Se_2Br_2$, showing melting at 566 °C and crystallization at 541543 °C. The heating rate is 5 °C/min; (b) Optical absorption spectrum of $Hg_3Se_2Br_2$ ground powder showing a band gap of 2.22 eV.



Figure 3. (a) Powder X-ray diffraction patterns of ground $Hg_3Se_2Br_2$ crystals and the residue sample of the DTA experiments comparing to the simulated pattern; (b) X-ray diffraction pattern of a $Hg_3Se_2Br_2$ single crystal.



Figure 4. The structure of $Hg_3Se_2Br_2$ view down the *b*-axis.



Figure 5. (a) Infinite one dimensional $[Hg_2Se_2]$ zigzag chain as viewed down *b*-axis; (b) $[Hg_3Se_2]$ layer formed by $[Hg_2Se_2]$ chains connected by Hg-Se bonds.



Figure 6. (a) Calculated electronic band structure for $Hg_3Se_2Br_2$; (b) Element orbital contributions to the electronic density of states (per eV unit cell), as a function of the energy relative to the Fermi level at 0 eV.



Figure 7. (a) DC voltage-current curve from a $Hg_3Se_2Br_2$ single crystal; (b) Comparison of the attenuation length between $Hg_3Se_2Br_2$ and CZT.



Figure 8. Photocurrent response of on a Hg₃Se₂Br₂ plate crystal ($3.0 \times 2.1 \times 0.5 \text{ mm}^3$) along *c*-axis, (a) under positive bias and (b) under negative bias.



Figure 9. Ag X-ray induced photocurrent as a function of the bias voltage applied for electron and hole carriers measured on a Hg₃Se₂Br₂ plate crystal ($3.0 \times 2.1 \times 0.5 \text{ mm}^3$) along *c*-axis. Mobility-lifetime ($\mu\tau$) products for electron and hole carriers are $1.13 \times 10^{-4} \text{ cm}^2/\text{V}$ and $1.26 \times 10^{-5} \text{ cm}^2/\text{V}$, respectively.



Figure 10. (a) The pulse height energy spectra of unfiltered Ag X-ray for electron response from $Hg_3Se_2Br_2$ crystal (3.9 × 2.5 × 0.6 mm³) under bias voltage from 30 V to 800 V, (b) The average peak positions obtained as a function of bias voltage. The ($\mu\tau$)_e value was estimated from the fitted data.



Figure 11. (a) The pulse height energy spectra for hole response from Hg₃Se₂Br₂ crystal (3.9 × $2.5 \times 0.6 \text{ mm}^3$) under bias voltage from 40 V to 900 V, (b) The average peak positions obtained as a function of bias voltage. The ($\mu\tau$)_h value was estimated from the fitted data.



Figure 12. (a) The pulse height energy spectra of unfiltered Ag X-ray from Hg₃Se₂Br₂ crystal under 200 V applied. A spectrum obtained from a commercial CZT (black line, dimensions $5 \times 5 \times 5 \text{ mm}^3$) is shown for comparison. The counting time for both measurements was 200 seconds; (b) The pulse height energy spectra of Hg₃Se₂Br₂ crystal under Co⁵⁷ γ -ray irradiation under 200 V to 700 V applied for electron response.