Magnetic, Photoluminescent and Semiconductor Properties of a 4f-5d Bromide Compound

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Dedicated to Professor Jin-Shun Huang on the occasion of his 80th birthday.

Abstract
A novel 4f–5d material (HgDy₆Br₁₂)Hg₈Br₃₄ (1) is prepared by hydrothermal reactions and structurally characterized by single crystal X-ray diffraction. Compound 1 is characterized by a two-dimensional (2D) layered structure. A photoluminescence measurement with solid-state samples shows that this compound exhibits a strong emission in the blue region. A narrow optical band gap of 1.97 eV is revealed by a solid-state UV/Vis diffuse reflectance spectrum. The variable-temperature magnetic susceptibility obeys the Curie-Weiss law (χ_m = c/(T–θ)) with C = 0.78 K and a Weiss constant θ = –0.38 K as revealed by the magnetic measurements, suggesting the existence of an antiferromagnetic interaction.

Keywords: Lanthanide; mercury; magnetism; photoluminescence; semiconductor

1. Introduction
Lanthanide compounds have recently gained more and more attention because of their attractive photoluminescent, magnetic, catalytic and other performances.1–9 Nowadays, scientists from chemistry and material domains have completed a large number of explorations on different lanthanide compounds, in order to find out their application potentials in luminescent probes, light-emitting diodes (LEDs), electrochemical displays, and magnetic materials and so on.10–14 The attractive photoluminescent and magnetic performances of lanthanide compounds mainly come from the abundant 4f electrons of lanthanide (LN) ions. Generally speaking, lanthanide compounds may show strong photoluminescence only when the electronic transitions of the 4f electron of the lanthanide ion can efficiently happen. Moreover, a number of lanthanide compounds are interesting due to their fascinating magnetic and magneto-optical performances.15–20 As a result, a great number of researchers have devoted themselves into the exploration of design, preparation and characterization of new lanthanide-containing magnetic compounds. However, the semiconductor performances of lanthanide compounds are rarely explored yet in comparison with the studies on the photoluminescent and magnetic properties of the lanthanide materials.21

Group 12 (IIB) metals are zinc, cadmium and mercury and they have drawn much attention due to the following aspects: various coordination modes, photoluminescent and photoelectric properties, as well as the vital role played in the biosystem by zinc.22,23 The IIB metals are also very important components in semiconductor compounds and, up to date, many semiconductor compounds containing IIB metals have so far been reported.24–27 Since many years ago, photoluminescent, magnetic and semiconductor compounds have become one of research hotspots. The LN-IIB-VIIA (LN = lanthanide, VIIA = halogen) compounds have become one of research hotspots.
due to the attractive crystal structure, photoluminescence, magnetism and semiconductor performances. In this work, the synthesis, crystal structure, gas adsorption, magnetism, photoluminescence, and semiconductor performances of a 4f–5d material (HgDyBr$_{12}$)Hg$_8$Br$_{24}$ (1) with a 2-D layered structure are reported. It should be pointed out that some ternary LN–IIB–VIIA compounds have thus far been reported, but most of them are fluorides and an iodide with cadmium or zinc.

2. Experimental Section

2.1. Materials and Characterization

The chemicals were purchased via commercial sources and directly used. The photoluminescence experiments were carried out on a F97XP photoluminescent spectrometer. A solid-state UV/vis diffuse reflectance spectrum was measured at room temperature on a computer-controlled TU1901 UV/vis spectrometer equipped with an integrating sphere in the wavelength range of 190–900 nm. The barium sulfate powder was applied as a reference.

2.2. Synthesis of 1

A mixture of Dy(NO$_3$)$_3$·6H$_2$O (1 mmol, 458 mg), HgBr$_2$ (1 mmol, 360 mg) and distilled water (10 mL) was sealed into a 23 mL Teflon-lined stainless steel vessel. The vessel was heated to 473 K and kept there for one week under autogenous pressure. When the vessel was slowly cooled to room temperature, colorless block-like crystals were obtained. The yield was 21% based on HgBr$_2$.

2.3. Crystal Structure Determination and Refinement

A carefully selected single crystal (0.08 × 0.07 × 0.06 mm$^3$) was adhered onto the tip of a glass fiber and then mounted to a SuperNova CCD diffractometer. The X-ray source is graphite monochromated Mo-Kα radiation with the λ = 0.71073 Å. The intensity data were obtained at 293(2) K with the ω scan mode. For data reduction and empirical absorption correction, CrystalClear software was applied. The crystal structure of the title compound was solved by using the direct methods. The final structure was refined on $P^2_1$ by full-matrix least-squares using the Siemens SHELXTL™ V5 crystallographic software package. All of the atoms were generated on the difference Fourier maps and refined anisotropically. The high max./min. residual electron density is ghost peak around the heavy atom. The crystal data as well as the details of the data collection and refinement are given in Table 1, while the selected bond lengths and bond angles are listed in Table 2.

| Table 1. Crystal data and structure refinement details. |
| --- |
| Formula | Br$_{56}$Dy$_{6}$Hg$_8$ |
| Mr | 5656.7 |
| Crystal system | orthorhombic |
| Space group | Pbam |
| $a$ (Å) | 13.0997(11) |
| $b$ (Å) | 13.6459(13) |
| $c$ (Å) | 27.906(3) |
| $V$ (Å$^3$) | 4988.4(8) |
| $Z$ | 2 |
| $2\theta_{max}$ (º) | 50 |
| Reflections collected | 12182 |
| Independent, observed reflections ($R_{int}$) | 3855, 2167 (0.0437) |
| $d_{calc}$ (g/cm$^3$) | 3.741 |
| $\mu$ (mm$^{-1}$) | 31.850 |
| $F(000)$ | 4722 |
| $R_1$, w$R_2$ | 0.1122, 0.3031 |
| $S$ | 1.032 |
| $\Delta\rho$ (max, min) (e/Å$^3$) | 1.956, –2.820 |

| Table 2. Selected bond lengths (Å) and bond angles (º). |
| --- |
| Hg1-Br5 | 2.400(4) |
| Hg1-Br6 | 2.748(4) |
| Hg1-Br7 | 2.617(5) |
| Hg1-Br8 | 2.767(6) |
| Hg2-Dy#1 | 2.961(2) |
| Hg2-Dy2 | 2.961(2) |
| Hg2-Dy1#2 | 3.037(2) |
| Hg2-Dy1#3 | 3.037(2) |
| Hg2-Dy3 | 3.431(2) |
| Hg2-Dy3#1 | 3.431(2) |
| Hg3-Br10 | 2.370(4) |
| Hg3-Br11 | 2.397(4) |
| Dy1-Br1#4 | 2.390(3) |
| Dy1-Br1 | 2.390(3) |
| Dy1-Br2#5 | 3.425(6) |
| Dy1-Br3#6 | 3.310(6) |
| Dy2-Br2 | 2.420(5) |
| Dy2-Br3 | 2.390(5) |

Symmetry transformations used to generate equivalent atoms: #1 $-x + 3$, $-y - 2$, $-z - 1$; #2 $-x + 3/2$, $y + 1/2$, $z$; #3 $x - 1/2$, $-y - 5/2$, $-z - 1$; #4 $x$, $y$, $-z - 1$; #5 $x + 1/2$, $-y - 5/2$, $-z - 1$; #6 $-x + 3/2$, $y - 1/2$, $z$; #7 $-x + 3$, $-y - 2$, $-z - 1$.

3. Results and Discussion

As revealed by the single crystal X-ray diffraction, the title compound crystallizes in the space group Pbam of the orthorhombic system with two formula units in one cell. The asymmetric unit of compound 1 includes...
three mercury ions (Hg1 in full occupancy, Hg2 in 0.25 occupancies, Hg3 in full occupancy), three dysprosium ions (Dy1, Dy2, Dy3; all in 0.5 occupancies) and eleven bromine ions (from Br1 to Br11; Br2, Br3, Br6, Br9 in 0.5 occupancies, while others in full occupancy), as depicted in Fig. 1. Most of the crystallographically independent ions are located in the general positions, but all dysprosium ions as well as Hg2, Br2, Br3, Br6, and Br9 ions are resided at the special positions. Results of the bond valence calculations indicate that all dysprosium ions are in +3 oxidation state (Dy1: 3.395, Dy2: 3.246, Dy3: 3.231), while mercury ions Hg1 and Hg3 are in +2 oxidation state (Hg1: 2.318, Hg3: 2.093).33,34 The bond valence of Hg2 is not available because it contains only metal-metal bonds.

The Hg1 ion is coordinated by four bromine atoms and yields a slightly distorted HgBr4 tetrahedron with the bond angles of Br-Hg1-Br locating in the span of 93.27(16)° to 124.2(2)° and the bond lengths of Hg-Br locating in the range of 2.400(4) Å to 2.767(6) Å, which is comparable with those reported previously.35–37 Differently, the Hg2 ion is surrounded by six dysprosium ions and forms a HgDy6 octahedron. The distances of Hg-Dy are in the range of 2.961(2) Å to 3.431(2) Å. The Hg3 ion, however, is coordinated by two bromine ions to give an almost linear geometry of HgBr2 with the bond angle of Br10-Hg3-Br11 being of 174.89(19)° and the bond lengths of Hg-Br being of 2.370(4) Å and 2.397(4) Å. All dysprosium ions are surrounded by four bromine ions. The bond distance of Dy-Br is located in the range of 2.390(3) Å to 3.425(6) Å. The bond angle of Br-Dy-Br is in the span of 90.74(13)° to 173.99(19)°. Two HgBr4 tetrahedra connect together via a corner-sharing bromide ion to yield a dimer, as shown in Fig. 2a. The dimers then interconnect together via the bromide ions to form a one-dimensional (1-D) chain running along the a axis. The chains and HgBr2 moieties are in the same plane and form an Hg-Br layer (Fig. 2a and the purple layers in Fig. 3). The HgDy6 octahedra interconnect together via Dy-Dy interactions to yield a two-dimensional (2-D) Hg-Dy-Br layer extending parallel to the ab plane. The Dy-Dy distance is 3.468(3) Å, which is comparable with those reported in the literature.38,39 These Hg-Br layers and Hg-Dy-Br layers stack along the c axis in the number of 2-1-2 to yield a crystal packing structure of compound 1, as presented in Fig. 3.

Lanthanide materials can usually exhibit photoluminescence and, nowadays, a large number of lanthanide materials have been reported for the photoluminescent performance and for potential applications as photoluminescent emitting materials like electrochemical displays, LEDs, chemical sensors and so on.40–42 As a dysprosium-containing compound, the title compound is possible to display photoluminescence. The photoluminescence property of compound 1 was explored in the solid state at room temperature. The results of the photoluminescence experiments are given in Fig. 4. The photoluminescence spectrum of compound 1 obviously shows an effective energy absorption residing in the wavelength span of 400 to 430 nm. The photoluminescence excitation spectrum using the emission wavelength of 445 nm yields one sharp
excitation peak at 418 nm. The corresponding photoluminescence emission spectrum of compound 1 is also measured, with the irradiation wavelength at 418 nm. The photoluminescence emission spectrum is characteristic of one sharp peak residing at 445 nm of blue region. Therefore, the title compound can be a candidate for potential blue photoluminescence materials.

Mercury is well-known as an important component of semiconductor materials. The title compound contains mercury and it is supposed to display semiconductor property. So, the solid-state UV/Vis diffuse reflectance spectrum is explored with solid state samples at room temperature and the data of the diffuse reflectance spectrum were treated using the Kubelka-Munk function, namely, \( \alpha/S = (1-R)^2/2R \). In this function, \( \alpha \) means the absorption coefficient, \( S \) is the scattering coefficient that is practically wavelength independent when the particle size is larger than 5 \( \mu \)m, while \( R \) is the reflectance. The optical band gap value can be determined by extrapolating from the linear part of the absorption edges of the \( \alpha/S \) vs. energy diagram, as presented in Fig. 5. The solid-state diffuse reflectance spectrum shows that compound 1 has a narrow optical band gap of 1.97 eV and, therefore, compound 1 can be a candidate for narrow band gap semiconductor materials. The solid-state diffuse reflectance spectrum displays a slow slope of the optical absorption edge that indicates an indirect transition process. The optical band gap value of 1.97 eV of compound 1 is larger than that of CuInS\(_2\) (1.55 eV), CdTe (1.5 eV) and GaAs (1.4 eV) which are efficient photovoltaic materials.

Trivalent lanthanide ions-containing compounds can generally display magnetic performance. Therefore, the title compound is supposed to exhibit magnetic behaviors. The \( \chi_M \) vs. \( T \) and \( \mu_{\text{eff}} \) vs. \( T \) curves for the title compound are presented in Fig. 6. The \( \chi_M \) is the magnetic susceptibility per Dy-containing molecule. When the temperature is decreased, the \( \chi_M \) vs. \( T \) diagram continuously increases from 0.06 emu mol\(^{-1}\) at 300 K to 0.39 emu mol\(^{-1}\) at 2 K. Such a \( \chi_M \) vs. \( T \) diagram of compound 1 indicates an antiferromagnetic-like performance. The essence of this antiferromagnetic-like performance is not clear yet, but it
is supposed to be originated from the gradual thermal de-
population of the Stark components of the dysprosium ions. The magnetic susceptibility diagram agrees well with
the Curie-Weiss law, namely, $\chi_m = c/(T - \theta)$. The data
of the magnetic susceptibility is fitted from 300 K to 2 K
using this Curie-Weiss law and it results in the value of $C$
being 0.78 K and a Weiss constant $\theta$ being of $-0.38$ K,
as presented in Fig. 6. The negative Weiss constant con-
firms the presence of the antiferromagnetic-like perfor-
mance in compound 1. When the temperature was de-
creased, the $\mu_{\text{eff}}$ vs. $T$ diagram continuously decreases
from 11.89 $\mu_B$ at 300 K to 2.45 $\mu_B$ at 2 K, which also con-
firms the presence of the antiferromagnetic-like perfor-
mance in compound 1, as shown in Fig. 6. The field de-
pendence of the magnetization of compound 1 was car-
rried out at 2 K, as given in Fig. 7. This diagram shows a
very small coercive field of about 40 Oe and a remnant
magnetization of around 0.002 Nβ. The magnetization di-
gram increases fast with the increased field from $-80$
kOe to 80 kOe. A saturation value cannot be obtained
even at 80 kOe. The value is 0.49 Nβ at 80 kOe.

4. Conclusions

A novel 4f-5d bromide compound (HgDy$_6$Br$_{12}$)Hg-
$_8$Br$_{24}$ has been synthesized and structurally characterized
by single crystal X-ray diffraction. This compound is char-
acteristic of a 2-D layered structure. The solid-state photo-
luminescence measurement shows that it displays a strong
emission in the blue region. A solid-state UV/Vis diffuse
reflectance spectrum shows that this compound has a nar-
row optical band gap of 1.97 eV. This compound exhibits
an antiferromagnetic interaction with $C = 0.78$ K and a
Weiss constant $\theta = -0.38$ K. As a result, this compound
is probably a candidate of photoluminescence, semiconduc-
tive or magnetic materials.

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Supplementary Material

Crystallographic data in CIF format have been de-
posited with FIZ Karlsruhe with the following CSD num-
ers: 1947021. These data can be obtained from the
Fachinformationszentrum Karlsruhe, 76344 Eggen-
stein-Leopoldshafen, Germany, (fax: (49) 7247-808-666;
e-mail: crysdata@fiz.karlsruhe.de).

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**Povzetek**

S hidrotermalno sintezo smo pripravili 4f–5d material (HgDy$_3$Br$_7$)Hg$_8$Br$_{24}$ (1) in ga strukturno okarakterizirali z rentgensko monokristalno analizo. Spojine 1 ima dvodimenzionalno plastovito strukturo. Fotoluminiscenca v trdnem stanju kaže močno emisijo v modrem območju. Ozek optični pasovni razmak 1.97 eV je bil določen z UV/Vis difuzno refleksijo v trdnem. Magnetna susceptibilnost pri različnih temperaturah je v skladu z Curie-Weissovim zakonom ($c_{mw} = c/\left(T-\theta\right)$) z $C = 0.78 \, \text{K}$ in z Weissovo konstanto $\theta = -0.38 \, \text{K}$, kar kaže na obstoj antiferomagnetnih interakcij.