Solid-state Synthesis, Crystal and Band Structures, and Optical Properties of a Novel Ternary Sulfide Eu2Ga2S5 (Postprint)

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Abstract

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Full Text

Solid-state Synthesis, Crystal and Band Structures, and Optical Properties of a Novel Ternary Sulfide Eu Ga S

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ABSTRACT
One new ternary europium gallium sulfide, Eu Ga S , has been synthesized by a facile solid-state route with boron as the reducing reagent. It crystallizes in the orthorhombic space group Pbca, with a = 11.976(1), b = 11.074(1), c = 17.446(1) Å, V = 1650.6(3) Å³, and Z = 8. Its 3-D structure is built by the connection between EuS monocapped trigonal prisms and GaS tetrahedra, and the latter connect with each other to form layer-like slabs. Its optical energy gap is determined to be 2.17 eV, which is also verified by the electronic band structure calculation.

Keywords: rare-earth sulfide; solid-state reaction; crystal structure; band gap
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1 INTRODUCTION

Rare-earth chalcogenides have received increasing attention in recent years due to their rich crystal structures and diverse physical properties [1, 2]. To date, many rare-earth chalcogenides have been investigated as second-order nonlinear optical [3–5], photocatalytic [6], voltage-dependent [7], and magnetic materials [8, 9]. Encouraged by these applications, the exploration of novel rare-earth chalcogenides remains meaningful.

Among rare-earth metals, divalent Eu and Yb ions have similar ionic radii and coordination geometries to alkali-earth metal ions, which distinguish them from other trivalent rare-earth metal ions [10]. Recently, many alkali-earth metal chalcogenides have been studied extensively, particularly Ba- and Sr-based compounds such as BaGa S [11], BaGa SnSe [12], Ba Ga MS (M = Si, Ge) [13], and BaCdSnS [14]. Most of these compounds have been investigated as second-order nonlinear optical materials in the middle and far-infrared region. It would be interesting if Eu² ions could substitute the II² (II = Mg, Ca, Sr, Ba) ions in the structures of alkali-earth metal chalcogenides. These Eu-based chalcogenides could be expected to possess not only similar physical properties to alkali-earth metal chalcogenides, but also magnetic and photoluminescent properties due to the presence of f-electrons. In fact, many such compounds have already been reported, such as EuZrS [15] and EuGa S [16].

When examining the ICSD and Pearson' s Handbook, a large number of compounds with the formulae II III Q (III = B, Al, Ga, In; Q = S, Se) have been reported [17–21]. It might be possible to obtain Eu III Q compounds based on the above considerations. In our ongoing exploration of this hypothesis, one Eu III Q compound, Eu Ga S , was successfully obtained. Herein, we present its synthesis, crystal structure, band structure, and optical properties.

2 EXPERIMENTAL

2.1 Synthesis and Analyses

All starting materials were used as received without further purification. Single crystals of the title compound were obtained by solid-state reaction using KI as flux [22–26]. The starting materials were Eu O (99.9%), Ga O (99.9%), S (99.999%), and additional boron powder (99%). The sample had a total mass of 500 mg with an additional 400 mg of KI (99%), and the molar ratio of Eu:Ga:S:B was 2:2:5:4. The mixture of starting materials was ground into fine powder in an agate mortar and pressed into a pellet, then loaded into a quartz tube. The tube was evacuated to 1 × 10 torr and flame-sealed. The sample was placed in a muffle furnace, heated from room temperature to 573 K over 5 h, held at 573 K for 10 h, then heated to 923 K over 5 h, held at 923 K for 10 h, then

heated to 1223 K over 5 h, held at 1223 K for 7 days, and finally cooled to 573 K over 5 days before the furnace was powered off. Block-shaped brown crystals of Eu Ga S , stable in air and water, were obtained.

Semiquantitative microscopic elemental analyses on several single crystals were performed using a field-emission scanning electron microscope (FESEM, Hitachi S-4800II) equipped with an energy dispersive X-ray spectrometer (EDS, Bruker Quantax), which confirmed the presence of Eu, Ga, and S with an approximate molar ratio of 1.95:2.03:5.10 (Fig. 1 [Figure 1: see original paper]), and no other elements were detected. The exact composition was established from X-ray structure determination.

2.2 Structure Determination

Intensity data sets were collected on a Bruker D8 QUEST diffractometer with graphite-monochromated Mo-K radiation (= 0.71073 Å). The structure of Eu Ga S was solved by direct methods and refined by full-matrix least-squares techniques on F^2 with anisotropic thermal parameters for all atoms. All calculations were performed using Shelxtl-2014 [27] through the Olex2 [28] interface. The final refinements included anisotropic displacement parameters for all atoms and a secondary extinction correction.

Eu Ga S crystallizes in the orthorhombic space group Pbca with Z = 8, a = 11.976(1), b = 11.074(1), c = 17.446(1) Å, and V = 1650.6(3) $Å^3$. The final R and wR values for all data are 0.0307 and 0.0425, respectively. The bond lengths are listed in Table 1 .

2.3 Optical Properties

The infrared (IR) spectrum was recorded using a TENSOR27 FT-IR spectrophotometer in the range of 400–4000 cm^{-1}. Powdered sample was pressed into a pellet with KBr. The diffuse reflectance spectrum was recorded at room temperature on a computer-controlled Varian Cary 5000 UV-Vis-NIR spectrometer equipped with an integrating sphere. The measurement wavelength was set in the range of 300–1700 nm. A BaSO plate was used as a reference, on which the finely ground powdered sample was coated. The absorption spectrum was calculated from the reflection spectrum using the Kubelka-Munk function.

2.4 Theoretical Calculations

The calculation model was built directly from the single-crystal structure data of Eu Ga S . Its electronic band structure based on density functional theory (DFT) was performed using the Material Studio software [29]. The generalized gradient approximation (GGA) was chosen as the exchange-correlation functional, and a plane-wave basis with projector-augmented wave (PAW) potentials was used. A plane-wave cutoff energy of 480 eV and a threshold of 10 eV were set for the self-consistent-field convergence of the total electronic energy. The electronic configurations for Eu, Ga, and S were 5d and 4f, 4s and 4p, and 3s

and 3p, respectively. Numerical integration of the Brillouin zone was performed using 4 × 4 × 4 Monkhorst-Pack k-point meshes, and the Fermi level (E_f = 0 eV) was selected as the reference.

3 RESULTS AND DISCUSSION

Eu Ga S crystallizes in the orthorhombic space group Pbca (No. 61), belonging to the Mg Al Se structure type. There are two Eu (Eu(1) and Eu(2)), two Ga (Ga(1) and Ga(2)), and five S atoms in the crystallographically independent unit. Its structure is composed of two structural units, namely, EuS monocapped trigonal prisms (mtp) and GaS tetrahedra (Fig. 2 [Figure 2: see original paper]), in which all the Eu, Ga, and S atoms occupy the 8c sites.

The 3-D structure of Eu Ga S is constructed by the connection between EuS mtps and GaS tetrahedra (Fig. 3 [Figure 3: see original paper]). In fact, Ga(1)S and Ga(2)S tetrahedra connect with each other to form layer-like slabs parallel to the ac plane (Fig. 4 [Figure 4: see original paper]), and Eu(1) and Eu(2) atoms occupy the interlayer monocapped trigonal prismatic cavities. The 2-D slab features a cluster built by four Ga(1)S and four Ga(2)S tetrahedra as circled in Fig. 4. This polyanionic cluster can be formulated as [Ga S]^{1} , as only one S atom (S(5) for Ga(1)S tetrahedron and S(3) for Ga(2)S tetrahedron) in each GaS tetrahedron has no connection with the others, while each of the other three S atoms is shared by two neighboring GaS tetrahedra. It can be observed that Ga(1)S and Ga(2)S tetrahedra are connected alternately via sharing S corners. Each such cluster has four neighboring [Ga S]^{1} clusters.

The Eu–S bond distances in Eu Ga S are in the range of 2.927(2)–3.227(2) Å, which are in good agreement with those of corresponding compounds in the literature [15, 16]. The Ga–S bond lengths in the range of 2.221(2)–2.334(2) Å are consistent with those found in (K I)[SmB (GaS)] [5], EuGa S [16], and BaGa S [18].

The II III Q (II = Mg, Ca, Sr, Ba; III = B, Al, Ga, In; Q = S, Se) family compounds have been extensively investigated for a long time [17–21]. Known members include Mg Al Se , Sr Ga S , Ba Ga S , and Ba In Q (Q = S, Se). Most previous reports only studied their crystal structures, and only S. L. Pan has recently reported the electronic structures and optical properties of Ba In Q [21]. It is surprising that there has been no investigation of Eu III Q compounds until now. Since one Eu^{2} ion contains seven f-electrons, largely different from the II^{2} ions, it is more attractive to investigate the versatile physical properties of Eu-based chalcogenides.

In addition to II III Q compounds, some oxide variants have also been reported. Numerous II III O compounds, including Mg B O , Ca B O , Mg Al O , Ca Al O , Ba In O , and Sr Ga O , have been studied [30–33]. Moreover, the two III atoms in II III Q can be substituted by one divalent and one tetravalent atom, respectively, such as in Ba GeS . If a transition metal atom is introduced to replace one of the two II atoms in II III Q , several quaternary variants can

be obtained, with known examples including BaLn MS (Ln = rare-earth metal; M = Mn, Fe, Co, Zn) and BaLa Co(S Se) [34-37].

The IR and diffuse reflectance spectra of Eu Ga S are shown in Figs. 5 and 6. The measurement results show that Eu Ga S is transparent in the IR range of 400-4000 cm ^{1} (2.5-25 m), and exhibits an optical band gap of 2.17 eV, which is consistent with its brown color.

To investigate the electronic structures of Eu Ga S , its band structure computation based on DFT theory was performed using the CASTEP module in Material Studio software [29]. The calculated band structure along high-symmetry points of the first Brillouin zone is shown in Fig. 7 [Figure 7: see original paper], from which it can be seen that the band gap of Eu Ga S is calculated to be 2.21 eV, which is reasonable considering the calculation precision. Both the lowest conduction band (CB) and the highest valence band (VB) of Eu Ga S are located at the G point, indicating that it has a direct band gap.

In conclusion, a new ternary Eu-based sulfide Eu Ga S was obtained using high-temperature solid-state reaction. Its optical properties indicate that it may be used as IR window materials, and also has potential applications in the field of photoelectric materials in view of its direct band gap. It is expected that more Eu^{2} ion-substituted II III Q (II = Mg, Ca, Sr, Ba; III = B, Al, Ga, In; Q = S, Se) compounds can be discovered.

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Table 1. Bond Lengths for Eu Ga S

Dist.	Dist.
Eu(1)-S(1)#7 2.945(2)	Eu(2)-S(4)#5 3.162(2)
Eu(1)-S(1)#6 3.178(2)	Eu(2)-S(5)#5 3.113(2)

Dist.	Dist.
Eu(1)-S(2)#4 3.227(2)	Eu(2)-S(5)#9 3.157(2)
Eu(1)-S(3) 3.146(2)	Ga(1)-S(1)#2 2.334(2)
Eu(1)-S(3)#6 3.039(2)	Ga(1)-S(2) 2.277(2)
Eu(1)-S(5) 2.927(2)	Ga(1)-S(4) 2.290(2)
Eu(1)-S(5)#5 2.930(2)	Ga(1)-S(5) 2.245(2)
Eu(2)-S(1)#8 3.132(2)	Ga(2)-S(1) 2.330(2)
Eu(2)-S(2)#7 3.054(2)	Ga(2)-S(2) 2.290(2)
Eu(2)-S(3) 2.954(2)	Ga(2)-S(3) 2.221(2)
Eu(2)-S(3)#9 3.052(2)	Ga(2)-S(4)#4 2.296(2)

Symmetry transformations used to generate equivalent atoms: #1 1-x, -1/2+y, 1/2-z; #2 3/2-x, -1/2+y, z; #3 x, 3/2-y, 1/2+z; #4 1-x, 1-y, 1-z; #5 1-x, 1/2+y, 1/2-z; #6 -1/2+x, y, 1/2-z; #7 3/2-x, 1-y, -1/2+z; #8 x, 3/2-y, -1/2+z; #9 3/2-x, 1/2+y, z; #10 1/2+x, y, 1/2-z; #11 3/2-x, 1-y, 1/2+z

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Fig. 1. EDS analysis of Eu Ga S [Figure 1: see original paper]

Fig. 2. Coordination geometry of Eu Ga S [Figure 2: see original paper]

Fig. 3. 3-D crystal structure of Eu Ga S constructed by the connection between GaS tetrahedra (blue) viewed along the a direction, where the Eu-S bonds are omitted for clarity [Figure 3: see original paper]

Fig. 4. Connection between GaS tetrahedra in the crystal structure of Eu Ga S viewed parallel to the ab plane [Figure 4: see original paper]

Fig. 5. IR spectrum of Eu Ga S [Figure 5: see original paper]

Fig. 6. Diffuse reflection spectrum of Eu Ga S [Figure 6: see original paper]

Fig. 7. Calculated band structure of Eu Ga S . The Fermi level is chosen as the energy reference at 0 eV and the band gap is calculated to be 2.21 eV [Figure 7: see original paper]

Note: Figure translations are in progress. See original paper for figures.