Preparation, structures, and band gaps of RbInS₂ and RbInSe₂

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Abstract

The two compounds RbInS₂ and RbInSe₂ have been synthesized at 773K by means of the reactive flux method. These isostructural compounds crystallize in space group C\textsubscript{2}/c of the monoclinic system with 16 formula units in a cell at 153K of dimensions a = 11.0653(7) Å, b = 11.0643(7) Å, c = 15.5796(9) Å, and β = 100.244(1)° for RbInS₂, and a = 11.477(3) Å, b = 11.471(3) Å, c = 16.186(6) Å, and β = 100.16(2)° for RbInSe₂. The In atoms are four-coordinated. The structure consists of two-dimensional 2\textsubscript{1/2}In\textsubscript{Q} layers perpendicular to [001] separated from the Rb\textsuperscript{+} cations. Adamantane-like In\textsubscript{4}Q\textsubscript{10} units are connected by common corners to form the layers. Band structure calculations indicate that these compounds are direct band-gap semiconductors with the smallest band gap at the Γ point. The calculated band gaps are 2.8 eV for RbInS₂ and 2.0 eV for RbInSe₂, values that are consistent with the colors of the compounds.

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Keywords: Synthesis; Crystal structure; Band gaps; Chalcogenide; Indium

1. Introduction

The ternary chalcogenides A/\(\text{M}/Q\) (where \(A\) = alkali metal; \(M\) = p-block metal; \(Q\) = S, Se, Te) have attracted much interest owing to their rich structural chemistry. When \(M\) = In, the structures vary widely as a function of composition. For example, the structure of Rb₆In₂S₆ [1] contains isolated [In₂S₆]\textsuperscript{6⁻} anions but the structure of Rb₄In₂S₅ [1] contains connected [In₂S₆] units. The structure of Na₅InTe₂ [2] contains isolated [InTe₄] tetrahedra, whereas that of Na₃In₂Te₆ [2] contains one-dimensional \(\frac{1}{2}[\text{InTe}_2\text{Te}_5^{2–}]\) chains formed by corner-sharing [InTe₄] tetrahedra. The coordination number of the In center in chalcogenides also varies. It is often four (LiInTe₂ [3], NaInTe₂, KInTe₂ [4], and KInS₂, [5]), but six is also common (NaInS₂ and NaInSe₂ [6]). The composition and coordination versatility play important roles in the structural diversity of the A/In/Q family.

For the AIn\textsubscript{2}Q\textsubscript{2} family there exist three common structural types. NaInTe₂ is isostructural with TiSe, crystallizing in space group I\textsubscript{4}/mcm of the tetragonal system [4]. NaInS₂ exhibits the \(\alpha\)-NaFeO₂ structure (space group R\textsubscript{3}m of the trigonal system) [6], which is an ordered structure of a rock salt derivative. These two structural types are usually high-pressure forms in the AIn\textsubscript{2}Q\textsubscript{2} system. The ambient-pressure forms of KInS₂ [5] and KInSe₂ [7] crystallize in space group C\textsubscript{2}/c of the monoclinic system.

Here we provide details of the syntheses, structures, and electronic structures of RbInS₂ and RbInSe₂. Although the lattice constants for RhInS₂ have been determined in a powder X-ray diffraction study [8], insofar as we can determine full single-crystal structure determinations have not been reported for either of these compounds.
2. Experimental

2.1. Syntheses

The following reagents were used as obtained: Rb (Aldrich, 98+%), In (Strem, 99.5%), S (Alfa Aesar, 99.5%), and Se (Alfa Aesar, 99.5%). Rb$_2$S$_3$ and Rb$_2$Se$_3$, the reactive fluxes [9] employed in the syntheses, were prepared by the stoichiometric reactions of the elements in liquid NH$_3$. Each compound was synthesized by the reaction of 1.0 mmol of In, 2.0 mmol of Se, and 0.5 mmol of Rb$_2$Q$_3$ (Q = S or Se). A reaction mixture was loaded into a fused-silica tube under an Ar atmosphere in a glove box. The tube was sealed under a 10$^{-3}$ Torr atmosphere and then placed in a computer-controlled furnace. The sample was heated to 773 K in 10 h, kept at 773 K for 72 h, and then slowly cooled at 4 K/h to 293 K. The products were washed with deionized water and dried with methanol. Unoptimized yields of RbIn$_2$ crystals were about 30%, based on In. No attempt was made to optimize yields. Other products were binary chalcogenide powders. Selected crystals, which were easily separated from the side products, were examined with an EDX-equipped Hitachi S-3500 SEM. The results were consistent with the stated compositions. RbInS$_2$ is pale brown whereas RbInSe$_2$ is red-yellow in color.

2.2. Crystallography

Single-crystal X-ray diffraction data were obtained with the use of graphite-monochromatized MoK$\alpha$ radiation ($\lambda = 0.71073$ Å) at 153 K on a Bruker Smart-1000 CCD diffractometer [10]. The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by recollecting 50 initial frames at the end of data collection. Data were collected by a scan of 0.3° in $\omega$ in four groups of 606 frames at $\phi$ settings of 0°, 90°, 180°, and 270°. The exposure time was 15 s/frame. The collection of the intensity data was carried out with the program SMART [10]. Cell refinement and data reduction were carried out with the use of the program SAINT [10] and face-indexed absorption corrections were performed numerically with the use of the program XPREP [11]. Then the program SADABS [10] was employed to make incident beam and decay corrections.

The structures were solved with the direct methods program SHELXS and refined with the full-matrix least-squares program SHELXL of the SHELXTL suite of programs [11]. Each final refinement included anisotropic displacement parameters and a secondary extinction correction. The program STRUCTURE TIDY [12] was then employed to standardize the atomic coordinates. Additional crystallographic details are given in Table 1 and in Supplementary information. Table 2 presents selected metrical details.

### Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>RbInS$_2$</th>
<th>RbInSe$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>264.41</td>
<td>358.21</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
<td>C2/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>11.0653(7)</td>
<td>11.477(3)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>11.0643(7)</td>
<td>11.471(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>15.5796(9)</td>
<td>16.186(6)</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>100.244(1)</td>
<td>100.16(2)</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>1877.0(2)</td>
<td>2097.5(1)</td>
</tr>
<tr>
<td>Z</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>$\rho_i$ (g/cm$^3$)</td>
<td>3.743</td>
<td>4.537</td>
</tr>
<tr>
<td>$\mu$ (cm$^{-1}$)</td>
<td>160.2</td>
<td>274.2</td>
</tr>
<tr>
<td>$R(F)$</td>
<td>0.0252</td>
<td>0.0395</td>
</tr>
<tr>
<td>$R_w(F^2)$</td>
<td>0.0663</td>
<td>0.1143</td>
</tr>
</tbody>
</table>

*For both structures $T = 153$ K and $\lambda = 0.71073$ Å.

### Table 2

| Table 2 Crystal data* and structure refinements for RbInS$_2$ and RbInSe$_2$ |
|-----------------------------|-----------------------------|
| **Compound** | **RbInS$_2$** | **RbInSe$_2$** |
| **Formula weight** | 264.41 | 358.21 |
| **Space group** | C2/c | C2/c |
| **a (Å)** | 11.0653(7) | 11.477(3) |
| **b (Å)** | 11.0643(7) | 11.471(3) |
| **c (Å)** | 15.5796(9) | 16.186(6) |
| **$\beta$ (°)** | 100.244(1) | 100.16(2) |
| **V (Å$^3$)** | 1877.0(2) | 2097.5(1) |
| **Z** | 16 | 16 |
| **$\rho_i$ (g/cm$^3$)** | 3.743 | 4.537 |
| **$\mu$ (cm$^{-1}$)** | 160.2 | 274.2 |
| **$R(F)$** | 0.0252 | 0.0395 |
| **$R_w(F^2)$** | 0.0663 | 0.1143 |

### 2.3. Electronic structure calculation

Electronic structures were calculated by the TB-LMTO program, which is a self-consistent, scalar relativistic linearized muffin-tin orbital program by Andersen and co-workers within the atomic sphere approximation (ASA) [13-15]. This method splits the crystal space into overlapping atomic spheres (Wigner–Seitz spheres). To achieve space filling with the ASA, nine empty spheres and eight empty spheres were introduced for RbInS$_2$ and RbInSe$_2$, respectively. The positions and radii of the empty spheres were calculated automatically. The radii for the Rb, In, S, and Se atoms were also determined automatically to provide overlaps of more than 16% for any two atom-centered spheres. The calculated radii were 4.23, 2.79, and 2.59 a.u. for Rb, In, and S, and 2.39 a.u. for Se. The calculated radii were used within the local density approximation (LDA) [16]. All k-space integrations were performed with the tetrahedron method with the use of 242 k points [17,18]. The basis sets consisted of the valence 5s electrons for Rb; 5s and 5p electrons for In; 3s and 3p electrons for S; 4s and 4p electrons for Se; and 1s states for empty spheres. The 5p and 5d electrons for Rb, 4d electrons for In, 3d electrons for S, 4d electrons for Se, and p–d states for empty spheres were downfolded by means of the technique described by Löwdin [19].

### 3. Results and discussion

RbInS$_2$ and RbInSe$_2$ have been synthesized in about 30% yield by the reactions of the elements in Rb$_2$S$_3$ and
Rb$_2$Se$_3$ fluxes at 773 K. These compounds are stable in air for at least 1 week. After about 2 months crystals degrade into gray powders.

The isostructural compounds RbInS$_2$ and RbInSe$_2$ crystallize with 16 formulas in space group $C2/c$ of the monoclinic system, and are isostructural with their K analogues [5,7]. Fig. 1 shows a view of the crystal structure down the [100] direction. The structure consists of two-dimensional $\frac{3}{2}[\text{InQ}_2]$ layers separated by Rb$^+$ cations. The structure of the $\frac{3}{2}[\text{InQ}_2]$ layer is shown in Fig. 2. These layers stack perpendicular to the [001] direction. Each layer is related to the ones above and below it by a two-fold rotation. A given layer consists of corner-sharing adamantane-like [In$_4$Q$_{10}$] units comprising four corner-sharing [InQ$_4$] tetrahedra, as shown in Fig. 3 for $Q = S$. It was noted recently [16] that highly ordered crystals of RbInS$_2$ can be prepared easily. Consistent with this, the displacement ellipsoids shown in Fig. 3 provide no indication of disorder arising from stacking faults of the $\frac{3}{2}[\text{InQ}_2]$ layers.

In RbInS$_2$, each Rb$^+$ cation is surrounded by eight S atoms in an irregular polyhedron, with six shorter and

<table>
<thead>
<tr>
<th>Distance or angle</th>
<th>$Q = S$</th>
<th>$Q = \text{Se}$</th>
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<tbody>
<tr>
<td>In1–Q3</td>
<td>2.452(1)</td>
<td>2.567(1)</td>
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<tr>
<td>In1–Q1</td>
<td>2.456(1)</td>
<td>2.566(1)</td>
</tr>
<tr>
<td>In2–Q1</td>
<td>2.453(1)</td>
<td>2.565(1)</td>
</tr>
<tr>
<td>In2–Q5</td>
<td>2.456(1)</td>
<td>2.565(1)</td>
</tr>
<tr>
<td>Rb1–Q1</td>
<td>3.312(1)</td>
<td>3.447(2)</td>
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<td>Rb1–Q3</td>
<td>3.482(1)</td>
<td>3.598(2)</td>
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<tr>
<td>Rb1–Q5</td>
<td>3.483(1)</td>
<td>3.600(2)</td>
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<td>Rb2–Q5</td>
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<td>Q4–In1–Q2</td>
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<td>Q1–In2–Q3</td>
<td>111.77(4)</td>
<td>112.17(4)</td>
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<tr>
<td>Q3–In2–Q5</td>
<td>111.23(3)</td>
<td>112.29(3)</td>
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<tr>
<td>Q3–In2–Q2</td>
<td>108.08(4)</td>
<td>107.70(4)</td>
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</table>

![Fig. 1. Unit cell of RbInQ$_2$ ($Q = S$, Se) viewed down [100].](image1)

![Fig. 2. The two-dimensional $\frac{3}{2}[\text{InQ}_2]$ layer viewed down [001].](image2)
two longer Rb–S interactions. The shorter distances range from 3.312 (1) to 3.4828 (5) Å, comparable to those of 3.247 (2) to 3.7951(4) Å in RbNd₃CuS₄ [17].

The In–S distances range from 2.452 (1) to 2.458 (1) Å, which are also comparable to those of 2.421(3) to 2.482 (3) Å in KInS₂ [5]. The S–In–S bond angles in RbInS₂ range from 105.52(4)° to 111.81(3)°, close to those of 105.1(1)° to 113.3(1)° in KInS₂ [5].

In RbInSe₂, each Rb⁺ cation has six shorter and two longer Rb–Se interactions. The shorter Rb–Se distances range from 3.402(1) to 3.600(2) Å, which are consistent with those of 3.3814(9) to 3.4599(8) Å in RbLnSe₂ (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Ho, Er, Lu) [18].

The In–Se distances range from 2.563(1) to 2.573(1) Å, which are comparable to those of 2.537(2) to 2.856(2) Å in Pr₃InSe₆ [19]. The InSe₄ tetrahedra are somewhat more distorted than the InS₄ tetrahedra, with the Se–In–Se bond angles ranging from 104.15(4)° to 112.29(3)°.

Fig. 4 shows the total and partial densities of states (DOS) of RbInSe₂. The Rb electrons make almost no contribution around the Fermi level. Therefore, the electronic properties are mainly determined by the [InS₂] layers. As indicated in Fig. 4, most of contributions in the conduction band are from In (5s) and In (5p) electrons.

In the valence band, S (3p) electrons are hybridized with In (5s) and In (5p) electrons to form In–S bonds. The In (5s) electrons are mainly localized in the region from −5 to −4 eV, whereas the In (5p) electrons are mainly localized in the region from −2.5 eV to the Fermi level. The band structure of RbInSe₂ is shown in Fig. 5. The bands near the Fermi level are very flat with little dispersion, consistent with the localization of In (5s) and In (5p) electrons in the valence band. The valence band maximum and conduction band minimum are both located at the Γ point. Therefore, RbInSe₂ is a...
direct band-gap semiconductor. The DOS and band structure of RbInSe$_2$ (not shown) are similar to those of RbInS$_2$. However, the energy level of the S ($3p$) orbitals is lower than that of the Se ($4p$) orbitals; this leads to a higher energy level of Se for the valence band of RbInSe$_2$ and thus to a smaller band gap. From the band structures, the direct band gaps of RbInS$_2$ and RbInSe$_2$ are 2.8 and 2.0 eV, respectively, consistent with their respective colors of pale brown and red-yellow.

Supplementary information

The crystallographic files in cif format for RbInS$_2$ and RbInSe$_2$ have been deposited as CSD numbers 415086 and 415087, respectively. The data may be obtained free of charge by contacting FIZ Karlsruhe at +49 7247 808 666 (fax) or crysdata@fiz-karlsruhe.de (email)

Acknowledgments

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