Synthesis, structure, optical properties, and electronic structure of NaLiCdS₂

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Abstract

The new compound NaLiCdS₂ has been synthesized by the reaction of Cd and a Li₂S/S/Na₂S flux at 773 K. This compound, which has the Ce₂O₂S structure type, crystallizes with one formula unit in space group \( P\overline{3}m1 \) of the trigonal system in a cell at \( T = 153 \) K with \( a = 4.1320(3) \) Å and \( c = 6.8666(11) \) Å. The structure consists of two-dimensional \( \frac{1}{2}[\text{LiCdS}_2] \) layers stacked perpendicular to the [001] direction. The two-dimensional layers are formed by corner-sharing LiS₄ or CdS₄ tetrahedra. The Na atoms are between these layers. Li incorporation in the compound is confirmed by an SIMS chemical composition map and by ICP measurements. The Li and Cd atoms are disordered in the crystal structure. First-principles calculations show that the optical excitations arise primarily from S–Cd charge-transfer transitions at 1.0 eV (very weak) and 2.4 eV (strong). Calculations also indicate that Na contributions around the Fermi level are significant. Polarized single-crystal optical measurements indicate an indirect optical band gap of 2.37 eV for light perpendicular to the (001) crystal face, in good agreement with theory. The compound NaLiZnS₂ has also been synthesized and is found to be isostructural with NaLiCdS₂.

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1. Introduction

Many ternary and quaternary alkali-metal chalcogenides have been synthesized [1], mainly by the reactive flux method [2]. Most of these contain the heavier alkali metals Cs, Rb, or K. Although it is more difficult to obtain chalcogenides containing the lighter alkali metals Na or Li by this method some have been synthesized. Examples include LiAuS [3], Li₃AuS₂ [3], Li₄GeS₄ [4], Li₀.₅Pb₁.₇₅GeS₄ [5], LiEuPSe₄ [6], Li₂PbGeS₄ [7], Li₃EuGeS₄ [7], Na₉Pb₂Ge₃S₁₂ [8], Na₆Pb₃(PS₄)₄ [9], Na₁.₅Pb₁.₇₅GeS₄ [5], and Na₁.₅Pb₀.₇₅GeS₄ [5].

More recently, the reactive flux method was extended to the synthesis of mixed alkali-metal chalcogenides. Thus, the six new Li-containing compounds K₃LiVS₄, Rb₂LiVS₄, Cs₂LiVS₄, Rb₂LiNbS₄, Cs₂LiNbS₄, and Rb₂LiTaS₄ were synthesized in Li₁S/S/A₂S₃ (A = K, Rb, Cs) fluxes [10]. These Li₁S/A₂S₃ fluxes were observed to have even lower melting points than A₂S₃ fluxes and thus are suitable for the facile incorporation of the lighter alkali metals. Here, we show that Li₁S/S/Na₂S fluxes may also be used successfully. We report the synthesis of NaLiCdS₂, together with details on its crystal structure, optical properties, and electronic structure. The synthesis of the isostructural compound NaLiZnS₂ is also reported.

2. Experiment section

2.1. Syntheses of NaLiCdS₂ and NaLiZnS₂

The following reactants were used as obtained: Na₂S powder (Reacton, 99.9%), Li metal rods (Reacton, 99.9%), Cd powder (Aldrich, 99.9%), Zn powder (Strem, 99.9%), S
2.2. Analysis of NaLiCdS₂

The chemical composition map of NaLiCdS₂ was taken by SIMS (TRIFT III ToF-SIMS) with the use of 15 keV Ga ions as the primary ions. Positive Na, Li, Cd, and negative S secondary ions were used to form the images of a selected crystal. The images were taken with an area of 240 μm × 240 μm (Fig. 1). These maps confirm the presence of Li but do not quantify it. To determine the Cd:Li and Li:Na ratios, 3.2 mg of NaLiCdS₂ crystals were dissolved in 10 mL of a 3% acid solution of Omni Trace HNO₃ in ultra pure water. The solution was then further diluted to 1 mL in 10 and to 1 mL in 3 to bring the concentrations of Cd and Na, respectively, within the limits of a Varian VISTA-MPX ICP instrument. Four standards each for Li, Cd, and Na were used to calibrate the instrument. Found were Cd:Li = 1.06(1):1; Li:Na = 0.99(2):1.

2.3. Structure determinations

Single crystal X-ray diffraction data for NaLiCdS₂ and NaLiZnS₂ were collected with the use of graphite monochromatized MoKα radiation (λ = 0.71073 Å) at 153 K on a Bruker Smart-1000 CCD diffractometer [11]. The crystal-to-detector distance was 5,023 cm. Crystal decay was monitored by re-collecting 50 initial frames at the end of data collection. Data were collected by a scan of 0.3° in ω in groups of 606 frames for each of the φ settings 0°, 90°, 180°, and 270°. The collections of the intensity data were carried out with the program SMART [11]. The exposure time was 15 s/frame. Cell refinement and data reduction were carried out with the use of the program SAINT [11] and face-indexed absorption corrections were performed numerically with the use of the program XPREP [12]. Then the program SADABS [11] was employed to make incident beam and decay corrections.

The positions of the Na, Cd, and S atoms of NaLiCdS₂ in space group P̅3m1 were found with the use of the direct-methods program SHELXS [12]. There is one formula unit in the cell; the Na atom is at the 1a position (0,0,0), the S atoms are at 2d positions ±(1/3,2/3,z), and the Cd atoms are at 2d positions at half occupancy. With the use of the least-squares program SHELXL [12] this solution refined nicely. The ensuing difference electron density map was featureless. The structure comprises Na octahedrally coordinated by six S atoms and Cd tetrahedrally coordinated by four S atoms. In sulfides Li is often four-coordinated, for example in ALiS (A = Na, K) [13], KLiMS₂ (M = Mn, Zn) [14], and LiGaS₂ [15,16]. Because Cd:Li = 1.06(1):1 from the ICP results and because Cd²⁺ and Li¹⁺ have similar crystal radii [17] of 0.92 and 0.73 Å, respectively, it is reasonable to assume that the Cd and Li atoms share equally the same 2d positions. In this way charge balance is achieved with the formal oxidation states Na⁺ Li⁺ Cd²⁺ S²⁻. Given the small X-ray scattering power of Li compared to Cd, detection of the presumed Li position in the vicinity of the Cd position is not possible. Accordingly, the Li coordinates, displacement parameters, and occupancy were made equal to those of Cd. A refinement in which the (Cd/Li) occupancy was varied led to a value of 0.994, which was set equal to 1.00 in the final refinement. The program STRUCTURE TIDY [18] was then employed to standardize the atomic coordinates. The structure of NaLiZnS₂ was refined similarly. Additional experimental details are shown in Table 1 and in Supporting information. Selected metrical details are given in Table 2.

2.4. Single-crystal absorption measurement of NaLiCdS₂

A selected single crystal of NaLiCdS₂ was face-indexed, and its dimensions were measured by means of the video attachment of a Bruker Smart-1000 CCD diffractometer. Optical measurements were performed with the use of an Ocean Optics model S2000 spectrometer coupled fiber-
Table 1
Crystal data and structure refinements for NaLiMS$_2$ ($M = $ Cd, Zn)$^a$

<table>
<thead>
<tr>
<th></th>
<th>NaLiCdS$_2$</th>
<th>NaLiZnS$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>206.45</td>
<td>159.42</td>
</tr>
<tr>
<td>Space group</td>
<td>$P\bar{3}m$</td>
<td>$P\bar{3}m$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>4.1320(3)</td>
<td>3.9711(3)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>101.530(19)</td>
<td>91.755(19)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>6.8666(11)</td>
<td>6.7186(12)</td>
</tr>
<tr>
<td>$\mu$ (Å$^2$ cm$^{-1}$)</td>
<td>2.6051(7)</td>
<td>2.429(1)</td>
</tr>
<tr>
<td>$\mu$ (Å$^2$ cm$^{-1}$)</td>
<td>62.66</td>
<td>76.75</td>
</tr>
<tr>
<td>$R_1$</td>
<td>0.0139</td>
<td>0.0229</td>
</tr>
<tr>
<td>$R_w$</td>
<td>0.0329</td>
<td>0.0684</td>
</tr>
<tr>
<td>$S$–S distances for NaLiZnS$_2$ and NaLiCdS$_2$ of 2.9100(5) and 2.9590(3) Å, respectively.</td>
<td>2.9100(5)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$For both structures $T = 153(2)$ K and $\beta = 0.71073$ Å.

3. Results and discussion

3.1. Syntheses and structure

The compounds NaLiCdS$_2$ and NaLiZnS$_2$ have been synthesized in a mixed Na$_2$S/Li$_2$S flux at 773 K. The yields are about 80% for NaLiCdS$_2$ and 50% for NaLiZnS$_2$.

These two compounds are isostructural. The Li and ($M = $ Cd or Zn) atoms are disordered. The compounds possess the Ce$_2$O$_2$S structure type [25], with $M$/Li in the Ce positions, S in the O positions, and Na in the S position. The structure of NaLiMS$_2$ is shown in Fig. 2. It consists of two-dimensional $\overset{\perp}{c}$[Li/MS$_2$] layers stacked perpendicular to the [001] direction. The two-dimensional layers, which are ruffled, are formed by corner-sharing LiS$_4$ tetrahedra or MS$_4$ tetrahedra, as indicated in Fig. 3. The layers are separated by Na atoms (site symmetry $3m$) that are surrounded by six S atoms, three from each layer. The Li or $M$ atoms, which have site symmetry $3m$, are coordinated to one axial and three equatorial S atoms. The interatomic distances in these compounds are reasonable when compared to those in structures in which the given atoms have similar coordination geometries. For example, the Na–S distances for NaLiZnS$_2$ and NaLiCdS$_2$ of 2.9100(5) and 2.5939(2) Å, respectively, are close to the values of 2.9100(5) and 2.5939(2) Å, respectively, in NaLiCdS$_2$.
and 2.9590(3) Å, respectively, are comparable to those in Na₃TaS₄ (2.852(3) to 3.239(2) Å) [26]. The M–S distances of 2.3987(3) and 2.429(1) Å for NaLiZnS₂ and 2.5039(2) and 2.6051(7) Å for NaLiCdS₂ may be compared to those of 2.416(4) Å for Zn–S or Li–S in KLiZnS₂ [15], 2.473(2) to 2.671(3) Å for Cd–S in K₂Cd₁S₄ [27], and 2.52(2) to 2.53(1) Å for Li–S in LiAuS [3].

3.2. Absorbance spectrum

The absorbance spectrum obtained with polarized light perpendicular to the (0 0 1) crystal face of a single crystal of NaLiCdS₂ is shown in Fig. 4a. Electronic structure calculations indicate that NaLiCdS₂ is semiconducting (see below). In order to determine the nature of the transition at about 2.4 eV the scaled absorption value and the crystal thickness were used to calculate the absorption coefficient α [28]. Plots of (zhv)² vs. hv (Fig. 4b) and (zhv)¹/² vs. hv (Fig. 4c) show that the optical transition is indirect [29,30]. The optical transition was determined to be indirect because the fit in Fig. 4b is superior to that in Fig. 4c. The intersection of the least-squares lines of baseline and band edge [28] lead to an optical band gap of 2.37 eV. This value is consistent with the reddish-yellow color of the compound and agrees well with theory.

3.3. Electronic structure

The total and partial density of states (DOS) of NaLiCdS₂ are shown in Fig. 5. The Na, Li, Cd, and S orbitals are highly overlapped in the valence band and the conduction band, which can be seen from the overlap among them around the Fermi level. The heavier alkali metals (Cs, Rb, K) usually make no contributions around

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![Fig. 3. The structure of the two-dimensional $\frac{1}{2}[LiMS_2]$ layer.](image-url)

![Fig. 4. (a) Absorbance spectrum of NaLiCdS₂; (b) plot for an indirect transition; and (c) plot for a direct transition.](image-url)
the Fermi level and hence exert almost no effects on the electronic structures of comparable compounds, for example KSm₂CuS₄ [31], RbLnSe₂ [32], and CsLn₅MSe₃ (M = Zn, Cd, Mn) [28]. However, in NaLiCdS₂ the contributions of the Na 3s electrons around the Fermi level, and thus to the electronic structure, cannot be ignored. These contributions are about 30% of those of the Li 2s and Cd 5s electrons. The latter contributions are mainly in the conduction band. In the region from −5 eV to the Fermi level, the Li 2s and Cd 5s electrons also contribute. The Cd 4d orbitals are highly localized, as can be seen from the sharp peak near −8 eV. Because the Li and Cd atoms are disordered in the crystal structure, the electronic structure in the region from −5 eV to the Fermi level should be the average of the contributions of Li and Cd. The S 3s electrons are highly localized and exhibit a sharp peak near −13 eV. The S 3p orbitals lie mostly in the valence band, where Na–S, Li–S, and Cd–S interactions are formed.

The smallest direct transition between the valence band and the conduction band is only about 1.0 eV (Fig. 6), which is much smaller than the measured band gap of 2.37 eV. Although the theory employed underestimates band gaps, from our experience with other metal chalcogenide systems, for example KSm₂CuS₄ [31], K₂CuSbS₃ [33], and RbLnSe₂ [32], the underestimation should be less than 1.0 eV. Therefore, the band structure (Fig. 6) was calculated in order to obtain additional insight into the band gap. There is only one band in the region from +1.0 to 4.0 eV above the Fermi level. This region consists mainly of Cd 5s orbitals. The bands below the Fermi level are mainly composed of S 3p orbitals. The smallest direct transition, about 1.0 eV, is located at the G (0,0,0) point, as shown in Fig. 6. Note that the dispersion in the Cd 5s band is very large at the G (0,0,0) point. A large dispersion (steep bands with a large slope dE/dk in a band structure) corresponds to small density states, and small dispersion (flat bands with a small slope dE/dk in the band structure) corresponds to large density states [34], which can also be seen from the comparison of Figs. 5 and 6. Therefore, there only a few states at the G (0,0,0) point and the direct transition at this point is too weak to be measured. The strong optical transitions are due to flat bands from the valence band to the conduction band. A flat curve is found along the G point to the A point in the valence band as well as along the M point to the G point in the conduction band. The transition from G → A to M → G (dashed arrows in Fig. 6) exhibits a gap of about 2.4 eV, in agreement with the experimental value of 2.37 eV. More importantly, the transition is indirect as is also deduced from the absorption data.

The dielectric function was calculated to provide more information about the optical absorption. Fig. 7 shows the imaginary component of the dielectric tensor ε̅, which is directly proportional to the absorption properties of the (001) face. There is a weak optical absorption at about 1.0 eV and a strong absorption at about 2.4 eV; this confirms our assignment of the optical transition. On this basis, we conclude that the main band-gap excitations for NaLiCdS₂ arise primarily from S→Cd charge-transfer transitions at 1.0 eV (very weak) and 2.4 eV (strong); these result in the observed red–yellow color of the material.
4. Supporting information

The crystallographic files in cif format for NaLiCdS$_2$ and NaLiZnS$_2$ have been deposited with FIZ Karlsruhe as CSD Nos. 417089 and 417088, respectively. These data may be obtained free of charge by contacting FIZ Karlsruhe at +49 7247 808 666 (fax) or crysdata@fix-karlsruhe.de (e-mail).

Acknowledgments

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