First principles study of electronic structure, chemical bonding and elastic properties of BiOCuS

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Abstract: The electronic structures, chemical bonding and elastic properties of the tetragonal phase BiOCuS were investigated by using density-functional theory (DFT) within generalized gradient approximation (GGA). The calculated energy band structures show that the tetragonal phase BiOCuS is an indirect semiconductor with the calculated band gap of about 0.503 eV. The density of states (DOS) and the partial density of states (PDOS) calculations show that the DOS near the Fermi level is mainly from the Cu-3d state. Population analysis suggests that the chemical bonding in BiOCuS has predominantly ionic character with mixed covalent–ionic character. Basic physical properties, such as lattice constant, bulk modulus, shear modulus, elastic constants, were calculated. The elastic modulus and Poisson ratio were also predicted. The results show that tetragonal phase BiOCuS is mechanically stable and behaves in a ductile manner.

Key words: BiOCuS; first principles; electronic structures; chemical bonding; elastic properties

1 Introduction

Since the discovery of superconductivity in LaOFeP, LaNiOP and LaFeAsO(F) [1–3], the quaternary oxypnictides and oxysulfides layered compounds with the ZrCuSiAs-type structure (space group P4/nnm, Z=2) have received considerable attention because of their interesting electrical, optical and magnetic properties [4–8].

BiCuOS, which is isostructural to the layered rare-earth oxysulfides LnCuOS (Ln=La–Eu), is an indirect gap semiconductor with band gap of about 1.1 eV in experimental investigation [7] or about 0.48 eV in theoretical calculation [9]. KUSAINOVA et al [10] synthesized BiOCuS by a high-temperature reaction in evacuated sealed quartz ampoules. SHEETS et al [8] synthesized BiOCuS by a single-step hydrothermal reaction at low temperature (250 °C) and pressure (<2×10⁶ Pa). They studied the optical properties of BiCuOS with diffuse reflectance. The absorption spectrum of BiCuOS is high across the entire visible region (2–3 eV), indicating that the optical band gap of BiCuOS is much smaller (<1.5 eV). HIRAMATSU et al [7] prepared BiOCuS samples by solid-state reaction method, and estimated the band gap of BiCuOS (about 1.1 eV) by diffuse reflectance spectra method. SHEIN et al [9] investigated the electronic band structure, density of states and inter-atomic bonding picture for BiOCuS. The results showed that the BiOCuS phase behaves as an ionic semiconductor with the calculated indirect band gap of about 0.48 eV. Very recently, superconductivity below Tc=5.8 K was reported for the tetragonal Cu-deficient BiOCu1−xS samples, which declared BiOCuS as a parent phase for novel layered superconductors [11–13].

To the best of our knowledge, there are no reports on the elastic properties of BiOCuS. However, it is important for fundamental physics and potential applications to study elastic properties of BiOCuS. Elastic properties provide information on interatomic potentials, interatomic bonding, equations of state, phonon spectra, specific heat capacity, thermal expansion, Debye temperature, etc [14]. In addition, elastic
properties are essential for many practical applications related to the mechanical properties of solid: load deflection, internal strain, thermoelastic stress, sound velocities and fracture toughness [14].

In this study, the electronic structures, chemical bonding and elastic properties of the tetragonal phase of BiOCuS were studied using first-principles calculations based on DFT.

2 Calculation details

The first principles calculations described here were based on DFT using a plan-wave expansion of the wave function [15,16]. The exchange correlation energy was calculated by the GGA with the Perdew-Burke-Ernzerhof (PBE) function [17]. The ionic cores were represented by ultra-soft pseudopotentials for Bi, O, Cu and S atoms. The Bi 6s26p3 electrons, O 2s22p4 electrons, Cu 3d104s1 electrons, and S 3s23p4 electrons were explicitly treated as valence electrons. The Monkhorst and Pack scheme of k-point sampling was used for integration over the first Brillouin zone [18]. The cutoff energy was chose to be 600 eV, and the Brillouin-zone sampling k-point set mesh parameters are 10×10×5. This set of parameters assured the total energy convergence of 5.0×10^{-6} eV/atom, the maximum force of 0.01 eV/Å, the maximum stress of 0.02 GPa and the maximum displacement of 5.0×10^{-4} Å.

3 Results and discussion

3.1 Geometry and structure properties

The crystal structure of the tetragonal phase of BiOCuS belongs to the space group P4/nmm, Z=2 (ZrCuSiAs type), where blocks [BiO] are sandwiched with [CuS] blocks as depicted in Fig. 1. There are four inequivalent atomic positions: Bi at 2c site (1/4, 1/4, z_{Bi}), O at 2a site (3/4, 1/4, 0), Cu at 2b site (3/4, 1/4, 1/2), and S at 2c site (1/4, 1/4, z_{S}) [7], where z_{Bi} and z_{S} are the internal coordinates of Bi and S, respectively. The experimental lattice parameters are a=b=3.8691 Å and c=8.5602 Å, and the internal coordinates of Bi and S, were reported as z_{Bi}=0.14829 and z_{S}=0.6710 [7], respectively.

At the first stage, the full structural optimization of this phase was performed both over the lattice parameters and the atomic positions including the internal coordinate z_{Bi} and z_{S}. The calculated optimization lattice parameters a, c, V and atomic coordinates compared with available experimental data [7] for BiOCuS are summarized in Table 1, which shows that the calculated values of GGA calculation are in agreement with the experimental results. The differences between our values and the experimental data may be due to the use of an approximate DFT. It is well known that the GGA leads to volume slightly overestimated in relation to the experimental value.

<table>
<thead>
<tr>
<th>Method</th>
<th>a/Å</th>
<th>c/Å</th>
<th>V/Å³</th>
<th>z_{Bi}</th>
<th>z_{S}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>3.8691</td>
<td>8.5602</td>
<td>0.1281456</td>
<td>0.1483</td>
<td>0.6710</td>
</tr>
<tr>
<td>GGA-USP</td>
<td>3.8680</td>
<td>8.5654</td>
<td>0.1281483</td>
<td>0.1491</td>
<td>0.6674</td>
</tr>
</tbody>
</table>

3.2 Electronic and chemical bonding

The calculated energy band structure of BiOCuS along with the high-symmetry points of the Brillouin zone by GGA is shown in Fig. 2. The top of the valence band is taken as the zero of energy. This compound is found to have indirect band gap. The valence band maximum (VBM) is at the Z point and the conduction band minimum (CBM) is on the M−Γ line.
calculated band gap value is 0.503 eV by GGA, which is smaller than the experimental value of 1.1 eV [7] due to the well-known underestimation of conduction band state energies in DFT calculations.

The total and partial densities of states (DOS) of BiOCuS calculated by GGA are shown in Fig. 3 and Fig. 4. It is found that the lower valence bands (between $-20.56$ and $-17.67$ eV) are essentially dominated by O-2s states and show hybridization with Bi-6s and Bi-6p states. The structure situated in the range from $-14.46$ to $-12.30$ eV originates predominantly from S-3s, and the one in the range from $-12.10$ to $-8.73$ eV originates predominantly from Bi-6s states. The upper valence bands are composed mainly of Cu-3d character and show hybridization with S-3p state. The conduction bands are dominated by Bi-6p state and hybridized Cu-4p and S-3p states. The calculated results are in agreement with the previous results [9].

The Mulliken bond population is useful for evaluating the bonding character in a material. A high value of the bond population indicates a covalent bond, and a low value indicates an ionic bond. Positive and negative values indicate bonding and anti-bonding states, respectively [19,20]. The Mulliken atomic population of BiOCuS reported in Table 2 shows a significant charge transfer from [BiO] block to [CuS] blocks, indicating that the internal of [BiO] block and the [CuS] block is ionic character. The bond population reported in Table 3 shows that the intra-block of Bi–O and Cu–S is covalent character. The chemical bonding in BiOCSu has predominantly ionic character with mixed covalent–ionic character, which is in agreement with the results of Ref. [12].

3.3 Elastic properties

Elastic properties are very important for materials because they provide information on the interatomic

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**Fig. 3** Total DOS of BiOCSu (the zero of energy is at the Fermi level)

**Fig. 4** PDOS of Bi (a), O (b), Cu (c) and S(d) of BiOCSu calculated by GGA
satisfy the Born’s stability criteria [23]:

For the tetragonal crystal, its mechanical stability is relatively soft material [23−25]. The single crystal bulk modulus

is about 85 GPa, which is smaller than that of the ZrCuSiAs-type Fe-based superconductor parent compound LaFeAsO (98 GPa) and is close to that of YZnAsO/LaZnAsO (78/87 GPa), meaning that BiOCuS is relatively soft material [23−25].

Table 2 Mulliken atomic population of BiOCuS

<table>
<thead>
<tr>
<th>Species</th>
<th>s</th>
<th>p</th>
<th>d</th>
<th>Total</th>
<th>Charge/e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>1.79</td>
<td>1.72</td>
<td>0.00</td>
<td>3.51</td>
<td>1.49</td>
</tr>
<tr>
<td>O</td>
<td>1.91</td>
<td>4.97</td>
<td>0.00</td>
<td>6.88</td>
<td>−0.88</td>
</tr>
<tr>
<td>Cu</td>
<td>0.58</td>
<td>0.80</td>
<td>9.79</td>
<td>11.17</td>
<td>−0.17</td>
</tr>
<tr>
<td>S</td>
<td>1.82</td>
<td>4.62</td>
<td>0.00</td>
<td>6.44</td>
<td>−0.44</td>
</tr>
</tbody>
</table>

Table 3 Mulliken bond population of BiOCuS

<table>
<thead>
<tr>
<th>Bond</th>
<th>Population</th>
<th>Length/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi−O</td>
<td>0.29</td>
<td>0.231760</td>
</tr>
<tr>
<td>Cu−S</td>
<td>0.54</td>
<td>0.240757</td>
</tr>
<tr>
<td>Cu−Cu</td>
<td>0.47</td>
<td>0.273507</td>
</tr>
<tr>
<td>O−O</td>
<td>−0.24</td>
<td>0.273507</td>
</tr>
</tbody>
</table>

Table 4 Calculated single crystal elastic constants \( C_{ij} \), bulk modulus and compressibility coefficient \( \beta \) of BiOCuS

<table>
<thead>
<tr>
<th>( C_{ij} )</th>
<th>( B )/GPa</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>152.99</td>
<td>118.90</td>
<td>34.68</td>
</tr>
<tr>
<td>50.19</td>
<td>63.86</td>
<td>57.08</td>
</tr>
<tr>
<td>75.98</td>
<td>85.13</td>
<td>0.01175</td>
</tr>
</tbody>
</table>

From Table 4, we can see that these criteria are all satisfied, which indicates that BiOCuS is mechanically stable. The single crystal bulk modulus \( B \) of BiOCuS is about 85 GPa, which is smaller than that of the ZrCuSiAs-type Fe-based superconductor parent compound LaFeAsO (98 GPa) and is close to that of YZnAsO/LaZnAsO (78/87 GPa), meaning that BiOCuS is relatively soft material [23−25].

Table 5 Calculated polycrystalline elastic constants, elastic modulus \( E \), Poisson ratio \( \nu \) and \( B/G \) of BiOCuS

<table>
<thead>
<tr>
<th>( B_y )</th>
<th>( B_g )</th>
<th>( G_y )</th>
<th>( G_g )</th>
<th>( B_y/G_y )</th>
<th>( E/GPa )</th>
<th>( \nu )</th>
</tr>
</thead>
<tbody>
<tr>
<td>86.77</td>
<td>85.13</td>
<td>85.95</td>
<td>40.37</td>
<td>39.35</td>
<td>39.86</td>
<td>2.16</td>
</tr>
<tr>
<td>103.57</td>
<td>0.2992</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is known that the values of the Poisson ratio \( \nu \) for BiOCuS are minimal for covalent materials \((\nu=0.1)\), and increase for ionic systems [29]. In our case, the calculated Poisson ratio is 0.2992, which means a sizable ionic contribution in intra-bonding.

3.4 Debye temperature

The Debye temperature \( (\Theta_D) \) is a fundamental parameter of a material, which is linked to many physical properties, such as specific heat capacity, elastic constants, and melting point. At low temperatures, the vibration excitations arise solely from acoustic vibrations. Hence, at low temperatures, the Debye temperature calculated from elastic constants is the same as that determined from specific heat capacity measurements. It can be obtained from the average wave velocity by the following equation [29]:

\[
\Theta_D = \frac{h}{k} \left[ \frac{3n}{4\pi} \left( \frac{N_A \rho}{M} \right)^{1/3} \right]^{1/3} \nu_m = \frac{h}{k} \left[ \frac{3n}{4\pi \nu_0} \right]^{1/3} \nu_m
\]
where $h$ is the Planck constant; $k$ the Boltzmann constant; $N_A$ the Avogadro number; $\rho$ the density; $n$ the number of atoms per formula unit; $M$ the relative molecular mass per formula unit; $V_0$ the volume of per formula unit; $v_0$ is the average wave velocity and is approximately estimated by

$$v_m = \left[ \frac{1}{3} \left( \frac{2}{v_T^2} + \frac{1}{v_L^2} \right) \right]^{1/3}$$

(13)

where $v_T$ and $v_L$ are transverse and longitudinal elastic wave velocities, respectively, which can be determined by the shear modulus $G$ and the bulk modulus $B$ from Navier’s equation:

$$v_s = \sqrt{\frac{G}{\rho}}, \quad v_L = \sqrt{\frac{B + 4G/3}{\rho}}$$

(14)

The calculated average, longitudinal and transverse elastic wave velocities and Debye temperature for BiOCuS are given in Table 6. However, no other theoretical or experimental data exist for comparison with the present values.

<table>
<thead>
<tr>
<th>$V/\text{nm}^3$</th>
<th>$\rho/(\text{g cm}^{-3})$</th>
<th>$v_s/(\text{m s}^{-1})$</th>
<th>$v_L/(\text{m s}^{-1})$</th>
<th>$v_T/(\text{m s}^{-1})$</th>
<th>$\Theta_D/\text{K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12815</td>
<td>8.31</td>
<td>2189.98</td>
<td>4091.00</td>
<td>2445.90</td>
<td>288.87</td>
</tr>
</tbody>
</table>

### 4 Conclusions

1) The GGA calculated structural parameters of the tetragonal phase BiOCuS are in agreement with the experimental data.

2) The electronic band structures present that BiOCuS has indirect band gap with 0.503 eV by GGA. The DOS and the PDOS calculations show that the DOS near the Fermi level is mainly from the Cu-3d state.

3) The chemical bonding was analyzed, which shows that BiOCuS has mainly ionic character with mixed covalent-ionic character.

4) The elastic constants were calculated and the bulks and shear modulus, elastic modulus, Poisson ratio were derived. All results show that BiOCuS is mechanically stable and behaves in a ductile manner.

### References


BiOCuS 电子结构、化学键和弹性性质的第一性原理研究

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摘要: 利用基于密度泛函理论 (DFT) 的广义梯度近似 (GGA) 研究四方相 BiOCuS 的电子结构、化学键和弹性性质。能带结构显示, BiOCuS 为间接带隙半导体, 带隙宽为 0.503 eV; 态密度和分态密度的结果表明, 费米能级附近的态密度主要来自 Cu-3d 态。布居分析表明, BiOCuS 中的化学键具有以离子性为主的混合离子−共价特征。计算得到四方相 BiOCuS 的晶格参数、体模量、剪切模量和单晶的弹性常数, 由此导出弹性模量和泊松比。结果表明, BiOCuS 是力学稳定的, 且具有一定的延展性。

关键词: BiOCuS; 第一性原理; 电子结构; 化学键; 弹性性质

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