Calculation of the electronic structure of delafossite AgTaN₂ from first principles

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The electronic structure (band structure, DOS and COHP) of the delafossite nitride AgTaN₂ was investigated on the basis of density-functional theory using the generalized-gradient approximation (GGA). AgTaN₂ is predicted to be a semiconductor with an indirect band gap. The characters of the top of the valence band and the bottom of the conduction band are attributed to Ag–N antibonding and Ta–N antibonding interactions, respectively. These results were compared to the bonding situation in isostructural AgGaO₂. With increasing pressure, the electronic structure of AgTaN₂ changes. At a pressure of ca. 42 GPa, the indirect band gap should transform into a direct one, and at even higher pressures (above 65 GPa) AgTaN₂ should become metallic.

Key-words : Delafossite, Nitride, Density-functional theory, Chemical bonding, Band gap, High-pressure

1. Introduction

Cu- and Ag-delafossite oxides have been studied due to their potential for application as luminescence materials,¹ photo-catalysts²–⁶ and transparent conductors.⁷ Although a number of nitrides and oxynitrides, such as GaN⁸–¹² GaZnON⁹ and TaON⁹ have been used for the use as photonic and photo-electronic material, there is a quite limited number of publications on delafossite nitrides even in terms of synthesis and structural analysis. CuTaN₂ has been synthesized about two decades ago.¹⁰⁻¹² While AgTaN₂ has been found very recently,¹³ AgTaN₂ is a dark red powder which is, surprisingly enough, stable toward air and moisture at room temperature, and it is the first ternary nitride with a direct bonding interaction between Ag and N. This motivates us to examine its bonding features.

The electronic structures (band structures and density-of-states) of Cu- and Ag-delafossite oxides have been intensely investigated.¹⁴⁻¹⁷ These reports show that the oxides have an indirect band gap or exhibit metallic behavior. The electronic structures of delafossite nitrides, however, have not yet been calculated or analyzed. Within this report, the electronic structure and the structural properties of the delafossite nitride AgTaN₂ were investigated on the basis of density-functional theory using the generalized-gradient approximation (GGA). The bonding feature between Ag and N in AgTaN₂ was examined. In addition, the findings were compared to an isostructural oxide, α-AgGaO₂. The reasons for choosing AgGaO₂ are obvious: First, both oxide and nitride form linear X–Ag–X (X: N, O) bonding. Second, the ionic radii of Ga³⁺ (0.62 Å¹⁸) and Ta³⁺ (0.64 Å¹⁹) are similar. Third, both compounds exhibit optical absorbance for visible light, thus having potential applications for pigments or photocatalysts.

2. Theoretical method

The ab initio calculations were performed on the basis of the plane-wave pseudopotential strategy using the computer program VASP (Vienna Ab Initio Simulation Package).¹⁹ Here, the projector-augmented wave approach²⁰,²¹ and the generalized-gradient approximation of PBE-type were used.²² An energy cutoff of 400 eV was chosen, and the atomic positions were optimized until the residual force was less than 0.01 eV/Å. The lattice parameters were also allowed to relax. For the rhombohedral delafossite cells, a k-point grid of 13 × 13 × 13 was automatically generated according to the method by Monkhorst and Pack.²³ The Brillouin zone of the rhombohedral 3R delafossites follows the standard labeling such that the high symmetry points, in terms of the reciprocal basis, are Γ (0,0,0), Φ (1/2,1/2,0), L (0,1/2,0) and Z (1/2,1/2,1/2). The chemical bonding analyses were carried out by means of the crystal orbital Hamilton population (COHP) method²⁴ implemented in the all-electron scalar-relativistic TB-LMTO-ASA program package.²⁵ When comparing the electronic structures calculated by VASP and LMTO, we noted small differences going back to the differing basis sets but the general DOS shape was alike. For the pressure investigations, the lattice parameters and atomic positions were optimized under a fixed volume constraint. Afterwards, the band structures were calculated.

3. Results and discussion

Figure 1 shows the crystal structure of the delafossite compounds AgTaN₂ and AgGaO₂. Ag⁺ is occupying Wyckoff position 3a and can be found in a linear coordination by two X anions (either O²⁻ or N³⁻), whereas the Wyckoff position 3b is occupied by Ga³⁺ or Ta³⁺ located in the center of an X octahedron, either six O²⁻ or N³⁻. The structural parameters of AgGaO₂ and AgTaN₂ after relaxation are shown in Table 1. The larger lattice parameter of the nitride are primarily due to the larger N³⁻ anion than the O²⁻ anion.¹³ We find the calculated lattice parameters in good agreement (slight overestimate) to the experimental values,¹³,²⁶ and the agreement seems to be even better for the nitride case. There is less than 0.3% of difference.
from the previously reported lattice parameters,\textsuperscript{13} which is mostly due to different sets of k-points.

The band structures of AgGaO\(_2\) and AgTaN\(_2\) are shown in Fig. 2. An indirect band gap is detected for AgGaO\(_2\), as reported in a previous study.\textsuperscript{21} Although the energetic details of the band structure are slightly different, the overall similarity is clearly confirmed. We now turn to AgTaN\(_2\). The valence band maximum sits at \(Z\) (−0.54 eV) and the second highest point is located at \(L\) (−0.77 eV). The conduction band minimum is found at the \(L\) point (0.52 eV). Thus, AgTaN\(_2\) is a semiconductor with an indirect band gap of ca. 1 eV. Upon comparing the band structures, one observes that the dispersion of the conduction bands in AgGaO\(_2\) is slightly less pronounced than the one of AgGaO\(_2\). The indirect band gap of AgTaN\(_2\) is clearly larger, by 0.65 eV, than for AgGaO\(_2\). There is a significant discrepancy between the calculated values and experimental band gap estimated by optical absorbance of AgTaN\(_2\) (roughly 2.0 eV)\textsuperscript{13} and AgGaO\(_2\) (2.4 eV).\textsuperscript{22} This difference can be attributed to the typical band-gap underestimation by density-functional theory, the forbidden direct transition at the \(\Gamma\) point,\textsuperscript{16,17} and/or optical absorption related to impurities or defect levels in AgGaO\(_2\) and AgGaO\(_2\) powders.

Figure 3 shows the partial density-of-states (pDOS) of AgGaO\(_2\) and AgTaN\(_2\). In Figs. 3(a) and 3(c), the contribution from Ag and Ga/Ta orbitals can be found both in the valence and conduction bands, thereby indicating some covalent bonding features for Ag–O/N and also Ga–O/Ta–N. The N-2s and O-2s states are located around −14 and −18 eV, respectively, and they are not shown for reasons of conciseness.

The valence band of AgGaO\(_2\) between −8 and 0 eV mainly consists of Ag-4d and O-2p states in addition to occupied Ga-4s and Ga-4p orbitals, and the composition of the empty conduction band is similar to that [Fig. 3(a)]. Both valence and conduction bands have a mixed Ag-5s and -5p character, and the band edges exhibit more significant contribution from Ag-5s [Fig. 3(b)].

The features of the valence band of AgTaN\(_2\) in the same energy range are occupied Ag-4d, Ta-5d and N-2p states [Fig. 3(c)]. On the other hand, the conduction band of the nitride consists mainly of Ta-5d and N-2p states. Ag-5s and -5p contribute as minor components, and the contribution from Ag-5s is more significant at the band edges [Fig. 3(d)].

The bonding situation within AgGaO\(_2\) and AgTaN\(_2\) close to the band gap was examined in more detail by performing a COHP analysis, as shown in Fig. 4. For the case of AgGaO\(_2\) (left frame), we find that both interactions, Ag–O (solid line) and Ga–O (dashed line), are mostly bonding up to Fermi level, while the interactions above the Fermi level become antibonding. The bonding situation in AgTaN\(_2\) (right frame) differs from the oxide. While the Ta–N interaction (dashed line) is bonding up the Fermi level, the Ag–N interaction (solid line) is antibonding between −2.5 eV and the Fermi level, surprisingly enough. This indicates that the Ag–N bonding is more susceptible to oxidation (loss of electron density in the highest occupied bands) than the Ag–O bonding. Above the Fermi level, strongly antibonding Ta–N interaction is observed in AgTaN\(_2\), while only weakly antibonding Ag–N interaction is found.

In order to focus on the linear X–Ag–X (X: O/N) bonding along the \(z\) axis, we calculated the COHP of the Ag 4s/4d\({}^2\)-N/O combination around the band gap (Fig. 5). In the AgGaO\(_2\) case, below the Fermi level, Ag \(d_{\parallel}\)–O is antibonding while Ag s–O is bonding. Above the Fermi level, there are only antibonding behaviors. In the case of AgTaN\(_2\), a similar bonding situation can be found below the Fermi level, as antibonding Ag \(d_{\parallel}\)–N and bonding Ag s–N states can be found. Little contribution for the Ag s– and Ag \(d_{\parallel}\)–N are found above Fermi level. Below the Fermi level, however, the antibonding character of Ag \(d_{\parallel}\)–N is more significant when compared with the oxide case, a consequence of the larger overlap and higher covalency in the case of nitrogen.

In order to examine the effect of pressure on the delafossite nitride, the lattice parameters and the electronic structures of AgTaN\(_2\) were calculated at different volumes under the assumption that phase transition and decomposition do not occur. With increasing pressure, both \(a\)-axis and \(c\)-axis decrease (\(a = 2.954\) Å

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**Table 1. Theoretical lattice parameters and atomic positions of AgTaN\(_2\) and AgGaO\(_2\) in space group \(R\bar{3}m\). The experimental values\textsuperscript{13,20} are given in brackets.**

<table>
<thead>
<tr>
<th></th>
<th>(a) (Å)</th>
<th>(c) (Å)</th>
<th>N position (z)</th>
</tr>
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<tbody>
<tr>
<td>AgTaN(_2)</td>
<td>3.143 (3.141)</td>
<td>19.000 (18.810)</td>
<td>0.111</td>
</tr>
<tr>
<td>AgGaO(_2)</td>
<td>3.036 (2.989)</td>
<td>18.834 (18.534)</td>
<td>0.113</td>
</tr>
</tbody>
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**Fig. 1. Crystal structure of delafossite AgTaN\(_2\) or AgGaO\(_2\). Ag is described by large spheres linearly coordinated to anions (either N or O) shown as small spheres, and Ta/Ga are located in octahedra of the anions (either N or O). This scheme is drawn by VESTA.\textsuperscript{27}**

**Fig. 2. Band structures of AgGaO\(_2\) (left) and AgTaN\(_2\) (right) as calculated by density-functional theory.**
and $c = 18.294 \text{Å}$ at 41.6 GPa, $a = 2.888 \text{Å}$ and $c = 18.102 \text{Å}$ at 64.7 GPa). Figure 6 shows these band structures at different pressures. As mentioned above, an indirect band gap is found at ambient pressure (Fig. 2). When pressure is applied, the $c/a$ ratio changes in order to compensate the external force. This is also reflected in the electronic structure as a larger overlap results in more disperse bands. Thus, we find that the conduction band is declining and the valence band is rising. In addition, we find that the strength of the dispersion of the bands is dependent on the $k$-points as the variation in terms of energy is stronger at point $L$ compared with the variation at point $Z$. At a pressure of about 42 GPa (Fig. 6 left), the bands at the point $L$ have changed quite a lot and the valence-band maximum is shifted from the point $Z$ to the point $L$; as a consequence, the indirect band gap is converted into a direct band gap. A further increase of pressure (above 64.7 GPa) finally results in a metallization of AgTaN$_2$ (Fig. 6 right).

Fig. 3. Partial densities-of-states (pDOS) of AgGaO$_2$ (a–b) and AgTaN$_2$ (c–d). (a) contributions from Ag-$d$ (black solid line), Ga-$s$ + Ga-$p$ (black dotted line) and O-$p$ (grey solid line) are shown. (b) Ag-$d$ (black solid line), Ag-$p$ (black dotted line) and Ag-$s$ (grey solid line) are represented on an expanded scale of pDOS. (c) Ag-$d$ (black solid line), Ta-$d$ (black dotted line) and N-$p$ (grey solid line) are exhibited. (d) Ag-$d$ (black solid line), Ag-$p$ (black dotted line) and Ag-$s$ (grey solid line) are shown on an expanded scale of pDOS.

Fig. 4. Crystal Orbital Hamilton Population (COHP) analysis of Ag–O (solid line) and Ga–O (dashed line) bonding within AgGaO$_2$ (left) and Ag–N (solid line) and Ta–N (dashed line) bonding within AgTaO$_2$ (right).

Fig. 5. Crystal Orbital Hamilton Population (COHP) analysis of Ag–O (dashed line) and Ag $d_{z^2}$–O (solid line) bonding within AgGaO$_2$ (left) and Ag–N (dashed line) and Ag $d_{z^2}$–N (solid line) bonding within AgTaN$_2$ (right).

Fig. 6. Band structures of AgTaN$_2$ at (left) 41.6 GPa and (right) 64.7 GPa as calculated by density-functional theory.
The characteristic features of AgTaN\(_2\) are its antibonding Ag–N states just below the Fermi level and the Ta 5d contribution in the conduction band when compared with the isostructural AgGaO\(_2\). Above the Fermi level, the 5d contribution from Ta is significant. This Ta 5d contribution would make the less dispersed conduction band, which perhaps enables the transition of electronic structure under pressure.

4. Conclusion

The electronic structure and the bonding features of AgTaN\(_2\) have been calculated and compared to the isostructural oxide AgGaO\(_2\). Both nitride and oxide exhibit indirect band gaps, but the characteristics of the conduction bands are different between AgTaN\(_2\) and AgGaO\(_2\); the antibonding interaction between the Ta-5d and N-2p-states dominates the conduction band which is slightly less dispersed than in the case of the oxide. The electronic structure of the nitride is sensitive to pressure; it will change into a direct band gap at 42 GPa, while the band gap will disappear at 65 GPa. Further experimental and theoretical investigations on structurally related nitrides are currently in process.

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References