Electronic structures and optical properties of CuMgVO$_4$ and AgMgVO$_4$: a first-principles study

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Electronic structures and optical properties of CuMgVO$_4$ and AgMgVO$_4$ with optimized structures were investigated using the generalized gradient approximation proposed by Perdew-Burke-Ernzerhof and the Heyd-Scuseria-Ernzerhof hybrid functional. From the energy band calculation, we found that CuMgVO$_4$ and AgMgVO$_4$ have indirect band gaps. The upper valence band is mainly composed of fully occupied Cu 3d (Ag 4d) states, and the lower is mainly comprises O 2p states. The conduction band can be divided into two regions because of the crystal-field splitting by the interaction between the V 3d and the O 2p states. The optical properties of CuMgVO$_4$ and AgMgVO$_4$ were predicted from the complex dielectric function, $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The static dielectric constants were estimated from the real part of the dielectric functions, $\varepsilon_1(\omega)$. The imaginary part of the dielectric functions, $\varepsilon_2(\omega)$, demonstrated optical anisotropy, with the component along the z (y) direction being larger than the others for CuMgVO$_4$ (AgMgVO$_4$) in the wavelength range of visible light. The absorption coefficient $I(\omega)$ was also calculated from the dielectric function.

Key-words : Oxide, Ab initio calculation, Electronic structure, Optical properties

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Recently, new vanadate single crystals CuMgVO$_4$ and AgMgVO$_4$ were synthesized by Yahia and co-workers.$^1$ They found that CuMgVO$_4$ and AgMgVO$_4$ crystallize with the Na$_2$CrO$_4$-type and maricite-type structures, respectively. However, no physical and chemical properties of CuMgVO$_4$ and AgMgVO$_4$, except for crystallographic data, have thus far been reported. Detailed information about the electronic structures of CuMgVO$_4$ and AgMgVO$_4$ are critical to understand their physical and chemical properties. In general, the local-density approximation and the generalized gradient approximation (GGA) have been adopted as an exchange-correlation functional to solve the Kohn-Sham equation in the density functional theory framework.$^{2,4}$ Although these approaches reproduce the structural properties of solid-state materials with high accuracy, they are known to underestimate the band gaps of semiconductors and insulators because the self-interaction correction and integer discontinuity are not described.$^{3,6}$ The large discrepancy between the experimental and theoretical band gaps makes difficult to analyze the electronic structure of solid-state materials correctly. To remedy the band-gap problem, the hybrid Hartree-Fock (HF) density functional$^7$ such as the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional$^8$ is widely used. The HSE06 functional is proper to predict band gaps of solid-state materials.$^9,10$

In this study, we carried out first-principles band calculations for CuMgVO$_4$ and AgMgVO$_4$ to reveal the band-gap energies, optical transition types, characteristics of their valence band (VB) and conduction band (CB), and their optical properties using the Perdew-Burke-Ernzerhof (PBE) GGA functional (PBE-GGA) and the HSE06 functional.

All first-principles calculations were performed within the projector augmented-wave method$^{11,12}$ as implemented in the Vienna Ab initio Simulation Package code$^{13,14}$ First, the structural parameters of CuMgVO$_4$ and AgMgVO$_4$ were optimized by relaxing all lattice constants and atomic positions under the constraints of space group $Pnma$ for AgMgVO$_4$ and $Cmcm$ for CuMgVO$_4$. In the structure optimization, the exchange-correlation interaction was treated within the framework of the PBE-GGA functional. The electronic structure calculations for CuMgVO$_4$ and AgMgVO$_4$ were then carried out using the PBE-GGA and the HSE06 approaches. We employed
a cutoff energy of 500 eV for both CuMgVO₄ and AgMgVO₄. The Cu 3d, 4s, Ag 4d, 5s, Mg 3s, 3p, V 3s, 3p, 3d 4s, and O 2s, 2p states were treated as valence electrons. The integration of Brillouin zone was performed using 8 × 8 × 6 k-points mesh (84 irreducible k-points) for CuMgVO₄, and 4 × 6 × 8 k-points mesh (60 irreducible k-points) for AgMgVO₄. After the ground-state electron densities were determined, the optical properties of CuMgVO₄ and AgMgVO₄ were estimated from the frequency-dependent dielectric matrices. The optical properties were derived using the complex dielectric function, \( \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \). The imaginary part of the dielectric function, \( \varepsilon_2(\omega) \), was numerically calculated from the momentum matrix elements between the unoccupied and occupied electronic states; the real part, \( \varepsilon_1(\omega) \), was converted from \( \varepsilon_2(\omega) \) using the Kramers-Kronig relation. In addition, we estimated the absorption coefficients \( I(\omega) \) from the complex dielectric function \( \varepsilon(\omega) \).

As depicted in Figs. 1(a) and 1(b), CuMgVO₄ and AgMgVO₄ have orthorhombic structures with space groups \( \text{Cmcm} \) (S.G. 63) and \( \text{Pnma} \) (S.G. 62), respectively. CuMgVO₄ has edge-sharing MgO₆ octahedra innumerably connected with each other in the c-axis direction, whereas AgMgVO₄ has the octahedra in the b-axis direction. As summarized in Table 1, the calculated lattice constants and atomic positions of CuMgVO₄ and AgMgVO₄ agree well with the previously reported experimental values. We then investigated the stability of CuMgVO₄ and AgMgVO₄ with respect to the binary oxides; Cu₂O, Ag₂O, MgO and V₂O₅, on the PBE-GGA level. It is found that CuMgVO₄ and AgMgVO₄ are more energetically favorable by 0.59 and 0.53 eV/formula unit than these binary oxides, respectively. Thus, we performed the electronic structure calculations of CuMgVO₄ and AgMgVO₄ using these relaxed structural parameters.

Figure 2 depicts the energy band structures of

Table 1. Experimental and calculated lattice constants and atomic positions for CuMgVO₄ and AgMgVO₄. Exchange-correlation interaction was treated within the framework of the PBE-GGA functional in the structure optimization.

| Chemical formula | CuMgVO₄ | AgMgVO₄ |
|------------------|---------|---------|
| Lattice parameter |         |         |
| Experimental     |         |         |
| \( a \)          | 5.6932  | 9.4286  |
| \( b \)          | 8.7055  | 6.7465  |
| \( c \)          | 6.2789  | 5.3360  |
| Error (%)        | 1.38    | 0.10    |
| Atomic position  |         |         |
| Experimental     |         |         |
| Cu               | 0       | 0.14979 |
| Mg               | 0       | 1/2     |
| V                | 0.7460  | 0.3663  |
| O₁               | 0.7610  | 0.1165  |
| O₂               | 0.3367  | 0.1158  |
| O₃               | 0.5256  | 0.4468  |
| Calculated       |         |         |
| Cu               | 0       | 0.1519  |
| Mg               | 0       | 1/2     |
| V                | 0.6430  | 0.1784  |
| O₁               | 0.7470  | 0.3653  |
| O₂               | 0.3384  | 0.4487  |

Fig. 1. Schematic illustration of the crystal structures of (a) CuMgVO₄ and (b) AgMgVO₄ obtained by the structure optimizations.
CuMgVO₄ and AgMgVO₄ along the symmetry lines of the first Brillouin zone, as obtained from the PBE-GGA and the HSE06 calculations. The origin of energy, so-called Fermi level, was taken at the valence-band maximum (VBM). Regarding CuMgVO₄ [Fig. 2(a)], the VBM and the conduction-band minimum (CBM) are respectively located near the T and the \( \nu \) points, indicating that CuMgVO₄ has an indirect gap. The minimum band gap of CuMgVO₄ was estimated to be 1.24 (PBE-GGA) and 2.60 eV (HSE06). The HSE06 functional leads to the larger gap than that obtained by the PBE-GGA because of the HF term in the hybrid functional. As shown in Fig. 2(b), AgMgVO₄ has also an indirect-type band gap because the VBM and the CBM are located near the T and the \( \Gamma \) points, respectively. The minimum bandgap of AgMgVO₄ was estimated to be 2.18 (PBE-GGA) and 3.74 eV (HSE06).

Figure 3 presents the total density of states (TDOS) and the projected density of states (PDOS) for each constituent atom of CuMgVO₄ and AgMgVO₄ crystals. The PBE-GGA calculation revealed that the VB of CuMgVO₄ lies in the range from \(-6.5\) to \(-2.3\) eV (lower VB) and from \(-1.3\) to 0 eV (upper VB) [Fig. 3(a)]. The upper VB is mainly composed of fully occupied Cu 3d states, and the lower VB mainly comprises O 2p states. The CB can be divided into two regions—from 1.3 to 1.9 eV (lower CB) and from 2.5 to 3.4 eV (upper CB)—because of the crystal-field splitting by the interaction between the V 3d and the O 2p states. The lower and upper CB regions both primarily originate in V 3d states, where O 2p states hybridize slightly with them. It is notable that the VB near the Fermi level is constructed not from O 2p states but from Cu 3d states, because in the case of typical metal-oxide semiconductors and insulators, VBM are derived from O 2p states with the strongly localized band. For AgMgVO₄, the PBE-GGA calculation leads to the VB from \(-5.2\) to 0 eV, as depicted in Fig. 3(b). In the range from approximately \(-1.5\) to 0 eV, the energy states are anchored by Ag 4d states. O 2p states are predominant below \(-1.5\) eV, where they hybridize with Ag 4d and V 3d states. The CB can
also be divided into two regions from 2.2 to 2.8 eV (lower CB) and from 3.0 to 5.7 eV (upper CB). Both CBs mainly arise from V 3d states as in the case of CuMgVO₄. In addition, the Mg atoms are irrelevant to the principal of the VB and CB in both CuMgVO₄ and AgMgVO₄. As previously mentioned, the HSE06 method increases the band gap compared with the PBE-GGA method; however, the shapes of the TDOS and PDOS are similar to those of the PBE-GGA calculation.

**Figure 4** depicts the real $\varepsilon_1(\omega)$ and the imaginary part $\varepsilon_2(\omega)$ of the dielectric function for CuMgVO₄ and AgMgVO₄, as calculated using the PBE-GGA and the HSE06 approaches. The dielectric tensor has three independent diagonal components—$\varepsilon_{xx}$, $\varepsilon_{yy}$, and $\varepsilon_{zz}$—and the off-diagonal components are zero because both CuMgVO₄ and AgMgVO₄ have orthorhombic crystal systems. For CuMgVO₄, the real part $\varepsilon_1(0)$, which corresponds to the static dielectric constant, was estimated to be 6.72 (PBE-GGA) and 3.48 (HSE06) from the average of three components, as depicted in Fig. 4(a). The $\varepsilon_2(\omega)$ of CuMgVO₄ is relevant to the absorption spectrum stemming from electronic transitions from the VB and CB. In the wavelength range of visible light, a large anisotropy is observed in the dielectric function: the component $\varepsilon_{zz}$ is larger than the components corresponding to the other two directions, whereas hardly any difference is observed between $\varepsilon_{xx}$ and $\varepsilon_{yy}$ [Fig. 4(b)]. The first and second strong peaks of component $\varepsilon_{zz}$ in $\varepsilon_2(\omega)$ are due to the transition from the Cu 3d state to the V 3d state, which is well illustrated through comparing the PDOS. In the case of AgMgVO₄, Fig. 4(c) shows that the static dielectric constant was estimated to be 5.31 (PBE-GGA) and 3.10 (HSE06). From the imaginary part of the dielectric function $\varepsilon_2(\omega)$ given in Fig. 4(d), optical anisotropy was also observed in the dielectric tensor with component $\varepsilon_{yy}$. The two distinctive strong peaks of components $\varepsilon_{yy}$ in $\varepsilon_2(\omega)$ originate from the transition from the Ag 4d state to the V 3d state. In addition, HSE06 predicts smaller corresponding peaks for both CuMgVO₄ and AgMgVO₄.

Finally, we estimated the absorption coefficient $I(\omega)$ from the dielectric function (Fig. 5). The absorption coefficient is given by
\[I(\omega) = \left( \frac{\sqrt{2} \omega}{c} \right)^2 \left[ \sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega) \right]^{1/2}\]

where \(c\) is the velocity of light in vacuum. Because the absorption coefficient is derived from the dielectric function, three components \(\varepsilon_{xx}\), \(\varepsilon_{yy}\), and \(\varepsilon_{zz}\) in \(I(\omega)\) are compatible with the diagonal components of the dielectric tensor. In Fig. 5(a), the component \(\varepsilon_{zz}\) in \(I(\omega)\) has two peaks resulting from the Cu 3\textit{d} \rightarrow V 3\textit{d} transition and anisotropy between \(z\) and the other directions occurs, similar to the imaginary part of the dielectric function. The optical band gap can be estimated by extrapolating the linear portion of the calculated \(I(\omega)\) or, equivalently, using the values corresponding to \(I = 0\). As a result, the optical bandgap was estimated to be 1.3 (PBE-GGA) and 2.6 eV (HSE06) from the average of the three components, which is exactly consistent with the values calculated in the energy band diagram. In regard to AgMgVO\(_4\), the two peaks of component \(\varepsilon_{yy}\) in \(I(\omega)\) because of the Ag 4\textit{d} \rightarrow V 3\textit{d} transition and the anisotropy between \(y\) and other directions are observed [Fig. 5(b)]. At the same time, the optical bandgap was estimated to be 2.3 (PBE-GGA) and 3.8 eV.
In this study, we investigated the electronic structures and optical properties of CuMgVO$_4$ and AgMgVO$_4$ on the basis of the PBE-GGA and the HSE06 approaches. We successfully predicted the band-gap energy, the type of optical transition, the characteristics of the VB and the CB, and the optical properties of CuMgVO$_4$ and AgMgVO$_4$. To further verify the results, experimental characterizations of CuMgVO$_4$ and AgMgVO$_4$ should be carried out in future work. We hope that the results presented in this research will promote a better understanding of the physical and chemical properties of CuMgVO$_4$ and AgMgVO$_4$.

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