First-principles calculation of $M_3Ta_6Si_4O_{26}$ ($M = Ba, Sr$) using Tran-Blaha exchange potential

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The first-principles energy band calculation for $M_3Ta_6Si_4O_{26}$ ($M = Ba, Sr$) with optimized structure is performed using the Tran-Blaha (TB) exchange potential combined with correlation potential from the local density approximation (LDA). The theoretical minimum band gaps of $Ba_3Ta_6Si_4O_{26}$ and $Sr_3Ta_6Si_4O_{26}$ are estimated to be 4.39 and 4.46 eV, respectively. These results are in large contrast to the underestimation based on the generalized gradient approximation calculation. The band gaps of $M_3Ta_6Si_4O_{26}$ ($M = Ba, Sr$) hardly changed with the spin-orbit interaction. The main conduction band can be divided into two energy regions near 7.6 eV due to the octahedral crystal-field splitting based on the interaction between Ta-d and O-p states. On the other hand, the main valence band in the energy range of -5.3 to 0 eV is constructed from O-p states, where the Ta-d states hybridize strongly with the O-p states. The optical properties of $M_3Ta_6Si_4O_{26}$ ($M = Ba, Sr$) are predicted from the complex dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. Polarized peaks in the z-direction appear at 5.5 and 6.4 eV for $Ba_3Ta_6Si_4O_{26}$, 5.6 and 6.6 eV for $Sr_3Ta_6Si_4O_{26}$ in the $\epsilon_2(\omega)$ function, respectively. The absorption coefficient estimated from the TB-LDA is very similar to the experimental result obtained in the literature.

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1. Introduction

Solid-state materials with a wide band gap such as $M_3Ta_6Si_4O_{26}$ ($M = Ba, Sr$) have been intensively investigated to obtain accurate insight for decomposition of water under UV light irradiation.^{1)–3)} This is because the energy positions of valence band maximum (VBM) and conduction band minimum (CBM) of wide-band-gap materials are far from the reduction potential for H_2O to H_2 and the oxidation potential for H_2O to O_2 , respectively.^{3)–6)} To understand the fundamental properties of the photocatalysts, it is indispensable to clarify the electronic structure of the solid-state material. However, there are no reports to date for the electronic structure of $M_3Ta_6Si_4O_{26}$ ($M = Ba, Sr$) as far as our knowledge.

In a first-principles energy band approach based on density functional theory, the generalized gradient approximation (GGA) and local density approximation (LDA) methods have been generally used to solve the Kohn-Sham equation.^{7)–9)} It is known that these approaches underestimate the energy gaps of semiconductor and insulator materials. Recently, Tran and Blaha (TB) improved the Becke-Johnson exchange potential and accurately showed the band gaps of various solid-state materials.^{10)–13)} Although the TB exchange potential has a high computational efficiency, its accuracy is almost equal to that of much more sophisticated method such as the GW calculation within the quasi-particle approach.^{14)–16)}

In the present study, we carried out a first-principles band calculation of $M_3Ta_6Si_4O_{26}$ ($M = Ba, Sr$) to determine the band-

gap energy, the characteristics of the valence and conduction bands, and the optical properties using the TB potential combined with the LDA correlation (TB-LDA). Furthermore, based on the TB-LDA band calculation, the results were compared with those of a GGA calculation using the Perdew-Burke-Ernzerhof (PBE) potential.

2. Methods and computational details

The crystal structure of $M_3Ta_6Si_4O_{26}$ ($M = Ba, Sr$) was optimized by relaxing all the lattice constants and atomic positions using the Quantum ESPRESSO code.¹⁷⁾ The exchange and correlation interaction was treated within the framework of the GGA scheme proposed by Perdew, Burke, and Ernzerhof (PBE-GGA).⁹⁾ The cutoff energy of plane-wave expansions was chosen 816 eV. Valence electrons were handled with Vanderbilt-type nonlocal ultra-soft pseudo-potentials, which describe effective potentials of ions and tightly bound core electrons.^{18),19)} The reciprocal-space integration was carried out using 12 irreducible k -points, which correspond to $4 \times 4 \times 4$ k -points grid.²⁰⁾ The electronic structure calculation of $M_3Ta_6Si_4O_{26}$ ($M = Ba, Sr$) was then performed by using the scalar-relativistic full potential linearized augmented plane wave plus local orbital (FLAPW+ lo) method based on the TB-LDA and the PBE-GGA methods.²¹⁾ For the valence states, relativistic effects were included in a scalar relativistic approximation and optionally spin-orbit interaction was treated with the second-variation method, while core states were fully treated relativistically. The wave functions were expanded by APW basis functions that are composed of plane waves in the interstitial region and linear combinations of radial functions multiplied by spherical harmonics inside the muffin-tin

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(MT) region. The MT spheres radii (R_{MT}) of the M (M = Ba, Sr), Ta, Si, and O atoms were chosen as respectively 2.50, 1.98, 1.50, and 1.45 a.u. The plane wave cutoff was $R_{MT} * K_{max} = 7.0$, which gave the 7603 plane waves for $Ba_3Ta_6Si_4O_{26}$ and 7357 plane waves for $Sr_3Ta_6Si_4O_{26}$. In the calculation for density of states (DOS), the Brillouin-zone integration was carried out with modified tetrahedron method on a special mesh of $8 \times 8 \times 8$ k -points grid. The optical properties of $M_3Ta_6Si_4O_{26}$ (M = Sr, Ba) were derived using the complex dielectric function, $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$.²²⁾ The imaginary part of the dielectric function, $\epsilon_2(\omega)$ was calculated numerically from the momentum matrix elements between the unoccupied and occupied electronic states and the real part $\epsilon_1(\omega)$ was converted from $\epsilon_2(\omega)$ using the Kramers-Kronig relation.

3. Results and discussion

$M_3Ta_6Si_4O_{26}$ (M = Ba, Sr) crystallizes into a hexagonal structure with space group $P6_2m$ and consists of one chemical formula of a total of 39 atoms (Fig. 1).¹⁾ This structure contains one independent M (Ba or Sr) atom (Wyckoff 3g), one independent Ta atom (Wyckoff 6i), one independent Si atom (Wyckoff 4h),

Fig. 1. Crystal structure of $M_3Ta_6Si_4O_{26}$ (M = Ba, Sr). M (Ba, Sr) atoms are green, TaO_6 octahedrons yellow ocher and SiO_4 tetrahedrons blue. This structure contains five independent O atoms (Wyckoff 2c, 3f, 6i, 12l, and 3g, O1 to O5).

and five independent O atoms (Wyckoff 2c, 3f, 6i, 12l, and 3g, O1 to O5). The calculated lattice constants of $Ba_3Ta_6Si_4O_{26}$ and $Sr_3Ta_6Si_4O_{26}$ agree well with the experimental values within 1.4% for the a axis and 1.1% for the c axis for $Ba_3Ta_6Si_4O_{26}$ and 1.3% for the a axis and 1.4% for the c axis for $Sr_3Ta_6Si_4O_{26}$. The atomic positions of these crystals were also in good agreement with the experimental positions, as summarized in Table 1.¹⁾ The difference in total energy was estimated to be 95.2 meV/atom for $Ba_3Ta_6Si_4O_{26}$ and 78.9 meV/atom for $Sr_3Ta_6Si_4O_{26}$, respectively, before and after the optimization. Thus, using these data of the lattice parameters and atomic positions, we calculated the electronic structure of $M_3Ta_6Si_4O_{26}$ (M = Ba, Sr).

Figures 2(a) and 2(b) show the self-consistent band structures of $Ba_3Ta_6Si_4O_{26}$ and $Sr_3Ta_6Si_4O_{26}$, respectively, along the symmetry lines of the Brillouin zone, obtained from the TB-LDA calculation. The energy is measured in electron volts (eV) and the origin of the energy is arbitrarily set at the valence band maximum. It is uncertain whether $Ba_3Ta_6Si_4O_{26}$ and $Sr_3Ta_6Si_4O_{26}$ are a direct-gap material or an indirect-gap material, since the energy difference between the direct and indirect transitions is very small. The minimum forbidden gaps of $Ba_3Ta_6Si_4O_{26}$ and $Sr_3Ta_6Si_4O_{26}$ are estimated to be 4.39 and 4.46 eV, respectively. The value of $Ba_3Ta_6Si_4O_{26}$ is close to the experimental optical band gap (4.3 eV),²⁾ while there is no report for $Sr_3Ta_6Si_4O_{26}$, to the best of our knowledge. On the other hand, in the PBE-GGA calculation, the band gaps of $Ba_3Ta_6Si_4O_{26}$ and $Sr_3Ta_6Si_4O_{26}$ are estimated to be 3.11 and 3.14 eV as shown in Figs. 2(c) and 2(d), respectively. The underestimation of energy gaps is due to a lack of consideration for the self-interaction correction as well as integer discontinuity in the exchange-correlation energy and the potential with changing the number of electrons.^{23),24)} The improved agreement between the calculated band gap by TB-LDA method and the experimental one makes it favorable to analyze the electronic structure of the system. In addition, spin-orbit coupling may have an influence on the band gaps of $Ba_3Ta_6Si_4O_{26}$ and $Sr_3Ta_6Si_4O_{26}$.²⁵⁾ However, the band gaps of $Ba_3Ta_6Si_4O_{26}$ and $Sr_3Ta_6Si_4O_{26}$ are calculated to be 4.30 and 4.37 eV, which hardly

Table 1. Structure-optimized lattice parameters and atomic positions of $M_3Ta_6Si_4O_{26}$ (M = Ba, Sr) by using Quantum ESPRESSO code

Chemical formula		Ba ₃ Ta ₆ Si ₄ O ₂₆			Sr ₃ Ta ₆ Si ₄ O ₂₆			
Lattice parameter (Å)		<i>a</i>	<i>b</i>	<i>c</i>		<i>a</i>	<i>b</i>	<i>c</i>
Experimental ^a		9.001	9.001	7.734		8.913	8.913	7.633
Calculated		9.125	9.125	7.821		9.027	9.027	7.742
Atomic position		<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Experimental ^a	Ba	0.595	0	1/2	Sr	0.589	0	1/2
	Ta	0.242	0	0.239	Ta	0.242	0	0.241
	Si	1/3	2/3	0.207	Si	1/3	2/3	0.209
	O1	1/3	2/3	0	O1	1/3	2/3	0
	O2	0.314	0	0	O2	0.307	0	0
	O3	0.809	0	0.242	O3	0.799	0	0.246
	O4	1/2	0.174	0.279	O4	0.498	0.169	0.278
	O5	0.208	0	1/2	O5	0.212	0	1/2
Calculated	Ba	0.602	0	1/2	Sr	0.596	0	1/2
	Ta	0.238	0	0.245	Ta	0.238	0	0.246
	Si	1/3	2/3	0.206	Si	1/3	2/3	0.209
	O1	1/3	2/3	0	O1	1/3	2/3	0
	O2	0.276	0	0	O2	0.278	0	0
	O3	0.823	0	0.236	O3	0.814	0	0.235
	O4	0.488	0.183	0.283	O4	0.491	0.177	0.291
	O5	0.230	0	1/2	O5	0.221	0	1/2

^a Ref. 1.

Fig. 2. Self-consistent band structures of (a) $Ba_3Ta_6Si_4O_{26}$ TB-LDA, (b) $Sr_3Ta_6Si_4O_{26}$ TB-LDA, (c) $Ba_3Ta_6Si_4O_{26}$ PBE-GGA, (d) $Sr_3Ta_6Si_4O_{26}$ PBE-GGA. Fermi energy is referenced to the valence band maximum.

changed with the spin-orbit interaction. Another feature in Fig. 2 is that the valence bands near VBM have a very weak dispersion, while the conduction bands near CBM show relatively wide dispersion in the Γ -A direction. The weak and wide band dispersions indicate a low mobility of photogenerated holes and a high mobility photogenerated electrons, respectively. In fact, the effective masses of the electrons and holes are respectively calculated to be $0.46m_0$ and $3.59m_0$ for $Ba_3Ta_6Si_4O_{26}$ and $0.44m_0$ and $4.79m_0$ for $Sr_3Ta_6Si_4O_{26}$ from parabolic fitting along Γ -A, where m_0 is the electron rest mass.

Figure 3(a) shows total densities of states (TDOS) and the partial densities of states (PDOS) for Ba, Ta, Si, and O1-O5 atoms obtained from TB-LDA calculation for the unit cell of $Ba_3Ta_6Si_4O_{26}$. For the sake of comparison, TDOS obtained by PBE-GGA calculation is also shown in Fig. 3. The CB can be divided into two energy regions near 7.6 eV due to the octahedral crystal-field splitting based on the interaction between Ta and O. The Ba-d states appear at energies above 7.7 eV. The main valence band in the energy range of -5.3 to 0 eV is constructed from O-p states, where the Ta-d states hybridize strongly with the O-p states. Atomic-like states below the main VB are ascribed to the interaction between Si-s states and O1/O4 -p states, where O1 and O4 atoms are the nearest neighbors of Si atom. A noticed feature in Fig. 3(a) is that a sharp peak of O-p states is seen near the VBM for O2, O3, O4, and O5 atoms, although there is no sharp peak in O1 atom, which is combined with only Si atom. O2, O3, O4, and O5 atoms are the nearest neighbors of Ta atom. O2, O3, and O5 atoms are combined with only Ta atom, while O4 atom is shared with Si and Ta atoms. Further, Ta-O3 and Ta-O4 bonds are placed in ab -plane of $Ba_3Ta_6Si_4O_{26}$, while Ta-O2 and Ta-O5 bonds are parallel to the c -axis. The difference in these coordination environment is reflected to the PDOS of $Ba_3Ta_6Si_4O_{26}$. Similar result is also obtained for $Sr_3Ta_6Si_4O_{26}$ as shown in Fig. 3(b). Moreover, from analysis of projected weights, we found that the bands near CBM, which show large dispersion along Γ -A, originate from Ta-dxz and dyz hybridized with O2-pz and O5-pz. Namely, one-dimensional network of -O2-Ta-O5-Ta- is responsible to these anisotropic bands.

Figure 4 shows the real and imaginary parts of the theoretical dielectric function, $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$, respectively, obtained from the TB-LDA approach. Due to the hexagonal structure of $M_3Ta_6Si_4O_{26}$ ($M = Ba, Sr$) crystal, $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ can be sepa-

rated into two diagonal components, xx and zz , whereas the off-diagonal components are zero. The black and red lines in Fig. 4 represent the dielectric functions along the x and z directions, respectively. The real part $\varepsilon_1(0)$ is equal to the square of the refractive index. As shown in Fig. 4(a), the refractive index of $Ba_3Ta_6Si_4O_{26}$ is calculated to be 1.89 for the GGA calculation and 1.58 for the TB-LDA calculation. Similar result is also obtained for $Sr_3Ta_6Si_4O_{26}$ as shown in Fig. 4(b). We note that the refractive index from the TB-LDA approach is smaller than that of the GGA approach. This result could be explained on the basis of the Penn model, where $\varepsilon(0)$ is inversely proportional with $E_g^{26,27}$. However, these estimated values have not been verified owing to its unknown experimental data. Also, the imaginary part $\varepsilon_2(\omega)$ is related to the absorption spectrum due to the electronic transitions from the VB to CB. Several peaks in $\varepsilon_2(\omega)$ are mainly ascribed to the transitions from the O-p VB to the Ta-d CB by comparison with their DOS characteristics. A distinctive feature in $\varepsilon_2(\omega)$ is a strong peak of the zz component at an energy below 6.0 eV, which is absent from the xx component. This difference may be attributed to the anisotropy of the momentum matrix elements between the VB and CB. Of course, note that a peak in $\varepsilon_2(\omega)$ does not correspond to a single interband transition because many direct and indirect transitions contribute to each peak.

Furthermore, the absorption coefficients $I(\omega)$ for $M_3Ta_6Si_4O_{26}$ ($M = Ba, Sr$) crystals were also estimated from the following equation;

$$I(\omega) = \left(\sqrt{2}\omega/c \right) \left[\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega) \right]^{1/2} \quad (1)$$

where c is the velocity of the light in vacuum. Since the coefficient was derived from the dielectric function, the two polarization components, $I(\omega)_{xx}$ and $I(\omega)_{zz}$, are similar to the corresponding two diagonal components of the dielectric function. There are some peaks below ca. 8 eV in **Fig. 5**. These may be mainly related to the interband transitions from the O-p VB to the Ta-d CB as expected from the DOS analysis. The $I(\omega)_{xx}$ and $I(\omega)_{zz}$ are distinguishable, which implies that $M_3Ta_6Si_4O_{26}$ ($M = Ba, Sr$) exhibits optical anisotropies. In particular, polarized peaks in the z -direction appear at 5.5 and 6.4 eV for $Ba_3Ta_6Si_4O_{26}$, 5.6 and 6.6 eV for $Sr_3Ta_6Si_4O_{26}$ in the $\varepsilon_2(\omega)$ function, respectively. The band gaps can be estimated from extrapolating the linear portion of calculated $I(\omega)$, i.e., from the values corresponding to $I = 0$.

Fig. 3. Density of states and projected density of states for (a) $\text{Ba}_3\text{Ta}_6\text{Si}_4\text{O}_{26}$ and (b) $\text{Sr}_3\text{Ta}_6\text{Si}_4\text{O}_{26}$ obtained from TB-LDA calculation. For the top graph (total DOS), the result of PBE-GGA calculation (dotted line) is also shown for comparison. Fermi energy is referenced to the valence band maximum.

Fig. 4. Real part $\varepsilon_1(\omega)$ and imaginary part $\varepsilon_2(\omega)$ of theoretical dielectric function for (a) $\text{Ba}_3\text{Ta}_6\text{Si}_4\text{O}_{26}$ and (b) $\text{Sr}_3\text{Ta}_6\text{Si}_4\text{O}_{26}$ obtained from TB-LDA calculation.

Fig. 5. Absorption coefficient $I(\omega)$ for (a) $Ba_3Ta_6Si_4O_{26}$ and (b) $Sr_3Ta_6Si_4O_{26}$ obtained from TB-LDA calculation.

As the results, the optical band gaps for $Ba_3Ta_6Si_4O_{26}$ and $Sr_3Ta_6Si_4O_{26}$ are 4.8 and 5.1 eV, respectively, which values are in good agreement with those in Fig. 2. The present theoretical study concerned optical properties might be helpful for the further experimental study of $M_3Ta_6Si_4O_{26}$ ($M = Ba, Sr$) to use as photocatalytic materials.

4. Conclusion

In this article, we have investigated the electronic structure of $M_3Ta_6Si_4O_{26}$ ($M = Ba, Sr$) with the TB-LDA energy band calculation. We have successfully predicted the accurate band gap, the detailed characteristics of the valence and conduction bands, the DOS, and the optical properties of $M_3Ta_6Si_4O_{26}$ ($M = Ba, Sr$). These results will improve the understanding of the photocatalytic properties of $M_3Ta_6Si_4O_{26}$ ($M = Ba, Sr$). We hope that the results presented in this research will also spur the fundamental understanding of other photocatalyst materials.

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