Electronic structure of photoresponsive $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$)

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The electronic structures of $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$) are investigated by the scalar-relativistic full potential linearized augmented plane wave plus local orbital (FLAPW+lo) method using the modified Becke-Johnson (MBJ) potential combined with the local density approximation (LDA) correlation. For $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$), the valence band maximums (VBM) are approximately located at the X (Si) or A (Ge) and the conduction band minimums (CBM) at the Γ both, indicating that $\text{Ag}_6\text{M}_2\text{O}_7$ are an indirect energy gap material. The fundamental band gaps of $\text{Ag}_6\text{Si}_2\text{O}_7$ and $\text{Ag}_6\text{Ge}_2\text{O}_7$ are calculated to be 1.69 and 1.42 eV, respectively, in the MBJ-LDA calculation. The results are a remarkably contrast to the underestimation based on the generalized gradient approximation (GGA) calculation. On the other hand, there is no distinct difference in the effective masses of photogenerated holes and electrons near the VBM and CBM between MBJ-LDA and GGA approaches. The optical properties of $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$) are contemplated from spectral dependence of the complex dielectric function, $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$.

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1. Introduction

Since the finding of Fujishima-Honda effect for a TiO_2 photochemical electrode, photocatalysis of TiO_2 has been widely studied from the viewpoint of the utilization of solar energy for several decades.¹⁾ TiO_2 shows some of advantages such as stability, low cost, and nontoxic. However, it is well known that TiO_2 shows no photocatalytic activity under visible light irradiation because of its relative large band gap. Thus, a visible light responsible photocatalyst has been the focus of intense research interest. In the latest research, photoresponsive silicate is attracted considerable attention due to its low cost and abundant resource.^{2),3)} Lou and co-workers reported that $\text{Ag}_6\text{Si}_2\text{O}_7$ is a photoactive material in the visible light region ($\lambda < 740 \text{ nm}$) and has higher photocatalytic activity for the degradation of methylene blue (MB) than those of Ag_2O , Ag_3PO_4 , and N-doped TiO_2 (P25). In our opinion, similar photoresponsive properties are expected for the isostructural material such as $\text{Ag}_6\text{Ge}_2\text{O}_7$, because the photoresponsive properties of $\text{Ag}_6\text{Si}_2\text{O}_7$ might related with its structural characteristics, although photocatalytic activity of $\text{Ag}_6\text{Ge}_2\text{O}_7$ should be examined experimentally. However, there is no report on $\text{Ag}_6\text{Ge}_2\text{O}_7$ material as a photocatalyst. Moreover, the electronic structure of photoresponsive silicate and isostructural

germanate has not been elucidated sufficiently due to their complex structure.

In the present study, the first-principles energy band calculation of $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$) has conducted to determine the accurate band-gap energy, the type of optical transition, the characteristics of band structure, and optical properties by using the MBJ potential combined with the LDA correlation (MBJ-LDA) method. The results of our band calculations were compared with those from standard GGA calculation using a PBE function.

2. Calculation method

The lattice constants and atomic positions of $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$) were taken from the reported values.⁴⁾ The electronic structure calculation of the crystals was performed with the scalar-relativistic full potential linearized augmented plane wave plus local orbital (FLAPW+lo) method based on a semilocal exchange–correlation potential improved by Tran and Blaha (referred to as MBJ-LDA) and as well as on the standard GGA of Perdew, Burke, and Ernzerhof (abbreviate as PBE-GGA) using the WIEN2k code.^{5)–9)} The FLAPW method is the most accurate of all energy band calculation methods, because the shape approximation of potential is not adopted. The wave functions were expanded by APW basis functions which are composed of plane waves in the interstitial region and linear combinations of radial functions multiplied by spherical harmonics inside the muffin-tin (MT) region. The MT spheres radii (R_{MT}) of the Ag, Si, and O atoms for $\text{Ag}_6\text{Si}_2\text{O}_7$ were respectively 2.11, 1.51, and

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1.51 a.u. and Ag, Ge, and O atoms for $\text{Ag}_6\text{Ge}_2\text{O}_7$ were 2.12, 1.62, and 1.62 a.u. All the calculations were carried out fixing the product of $R_{\text{MT}} \times K_{\text{max}} = 6.0$, which gave the 6397 and 5601 plane waves respectively for $\text{Ag}_6\text{Si}_2\text{O}_7$ and $\text{Ag}_6\text{Ge}_2\text{O}_7$, where R_{MT} denotes the smallest MT radius and K_{max} is the largest wavenumber of the basis set. In the calculation for density of states (DOS), the Brillouin-zone (BZ) integration was carried out with modified tetrahedron method on a special mesh ($10 \times 5 \times 3$) of 45 k points in the first BZ. The spin-orbit coupling effect was taken into consideration through the second variational method because of the relativistic effect in Ag and Ge atoms. The optical properties of $\text{Ag}_6\text{Si}_2\text{O}_7$ and $\text{Ag}_6\text{Ge}_2\text{O}_7$ 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 calculated numerically from the momentum matrix elements between the unoccupied and occupied electronic states using selection rules. These properties were broadened by Lorentzian functions with $\gamma = 0.10$ eV. The real part $\varepsilon_1(\omega)$ was converted from $\varepsilon_2(\omega)$ using the Kramers-Kronig relation.

3. Results and discussion

Figure 1 shows the crystal structure of $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$). Linke and co-workers reported that $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$) crystals have a space group $P2_1$ and unit-cell parameters: $a = 0.53043(5)$ nm, $b = 0.97533(7)$ nm, $c = 1.59283(13)$ nm, and $\beta = 91.165(8)^\circ$ for $\text{Ag}_6\text{Si}_2\text{O}_7$ and $a = 0.53713(4)$ nm, $b = 0.99835(8)$ nm, $c = 1.62249(14)$ nm, and $\beta = 90.904(8)^\circ$ for $\text{Ag}_6\text{Ge}_2\text{O}_7$.⁴⁾ All constituent atoms occupy Wyckoff positions 2a sites in both oxides. These crystals contain two independent $\text{M}_2\text{O}_7^{6-}$ ($\text{M} = \text{Si}, \text{Ge}$) anions, where one is a staggered conformation and the other is an eclipsed conformation, and the MO_4 tetrahedral are corner-shared to form M_2O_7 units.^{2),4)} There are symmetrically twelve independent Ag atoms (from Ag1 to Ag12), four independent M (Si or Ge) atoms (from M1 to M4), and fourteen independent O atoms (from O1 to O14). **Table 1** lists bond lengths of Ag–O, Si–O, and Ge–O, respectively. In $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$) crystals, there are three kinds of AgO_n units ($n = 2, 3, 4$), that is, AgO_2 (Ag9 and Ag12), AgO_3 (Ag1, Ag2, Ag3, Ag5, Ag6, Ag10, and Ag11), and AgO_4 (Ag4, Ag7, and Ag8) and Ag–O bond lengths distribute widely from 2.1164 to 2.5965 Å for $\text{Ag}_6\text{Si}_2\text{O}_7$ and from 2.1268 to 2.5947 Å for $\text{Ag}_6\text{Ge}_2\text{O}_7$. Ge–O bond is approximately 7% larger than Si–O bond because of larger ionic radius of Ge^{4+} than Si^{4+} .

Fig. 1. Crystal structure of $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$).

Figures 2(a) and **2(b)** present the calculated self-consistent energy band structure of $\text{Ag}_6\text{Si}_2\text{O}_7$ and $\text{Ag}_6\text{Ge}_2\text{O}_7$, respectively, along the symmetry direction of the first BZ obtained by the MBJ-LDA method. Γ , X, A, Y, and Z are symmetry points for the BZ of $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$) crystal and the coordinate are respectively (0, 0, 0), (0.5, 0, 0), (0.5, 0.5, 0), (0, 0.5, 0), and (0, 0, 0.5) in units of g_1^* , g_2^* and g_3^* , where g_1^* , g_2^* and g_3^* are the relevant reciprocal-space vectors. The origin of energy was taken at the valence band maximum (VBM). As shown in Fig. 2(a), the VBM is ranging from the X to the A, while the conduction band minimum (CBM) locates at the Γ . This means that $\text{Ag}_6\text{Si}_2\text{O}_7$ is an indirect energy gap material. As shown in Fig. 2(b), similar result is also obtained for $\text{Ag}_6\text{Ge}_2\text{O}_7$. The energy gaps of $\text{Ag}_6\text{Si}_2\text{O}_7$ and $\text{Ag}_6\text{Ge}_2\text{O}_7$ are respectively calculated to be 1.69 and 1.42 eV when the MBJ potential was used. The value of $\text{Ag}_6\text{Si}_2\text{O}_7$ is close to the experimental optical band gap (1.58 eV) and theoretical band gap (1.5 eV) using Heyd-Scuseria-Ernzerhof (HSE06) hybrid-functional,^{3),10),11)} while there is no report for $\text{Ag}_6\text{Ge}_2\text{O}_7$, to the best of our knowledge. For $\text{Ag}_6\text{Si}_2\text{O}_7$, the band gap estimated from the PBE-GGA calculation was 0.40 eV, almost 75% smaller than experiment (**Fig. 3**). The energy gap of $\text{Ag}_6\text{Ge}_2\text{O}_7$ was calculated to be only 0.10 eV from the PBE-GGA method. It is well known that the GGA and local density approximation (LDA) methods underestimate the energy gaps of semiconductors and insulators, known as band gap problem.¹²⁾ This result is because the self-interaction correction and the integer discontinuity in the exchange–correlation energy and potential upon changing the number of electrons are not taken into account, as already reported.^{13),14)} The large discrepancy from experimental value makes the precise analysis of the electronic structure of solid-state materials to be difficult. Furthermore, the calculated band gaps may change by the inclusion of spin-orbit interaction. However, it was found that the band gap of $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$) obtained with the MBJ-LDA slightly changes below 0.1 eV with the spin-orbit interaction as a perturbation of the scalar-relativistic result. Thus, the spin-orbit effect is not considered in the following calculations for $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$). The energy bands near the CBM and VBM have a relative wide dispersion in the Γ -Y and A-Y directions. In the MBJ-LDA calculation, the effective masses of the electrons and holes are respectively calculated to be $0.53m_0$ and $2.38m_0$ for $\text{Ag}_6\text{Si}_2\text{O}_7$ and $0.43m_0$ and $2.86m_0$ for $\text{Ag}_6\text{Ge}_2\text{O}_7$ from parabolic fitting, where m_0 is the electron rest mass. In the

Table 1. Bond distances of Ag–O, Si–O, and Ge–O

$\text{Ag}_6\text{Si}_2\text{O}_7$		$\text{Ag}_6\text{Ge}_2\text{O}_7$	
Average bond length/Å		Average bond length/Å	
Ag1–O	2.2684	Ag1–O	2.2739
Ag2–O	2.2355	Ag2–O	2.2439
Ag3–O	2.5548	Ag3–O	2.5397
Ag4–O	2.3754	Ag4–O	2.5305
Ag5–O	2.4314	Ag5–O	2.4314
Ag6–O	2.5111	Ag6–O	2.5109
Ag7–O	2.4180	Ag7–O	2.3904
Ag8–O	2.4028	Ag8–O	2.3955
Ag9–O	2.4286	Ag9–O	2.4268
Ag10–O	2.3144	Ag10–O	2.3191
Ag11–O	2.2990	Ag11–O	2.3030
Ag12–O	2.5286	Ag12–O	2.3030
Si1–O	1.6308	Ge1–O	1.7544
Si2–O	1.6359	Ge2–O	1.7641
Si3–O	1.6318	Ge3–O	1.7515
Si4–O	1.6308	Ge4–O	1.7543

Fig. 2. Calculated self-consistent energy band structure of $\text{Ag}_6\text{Si}_2\text{O}_7$ (a) and $\text{Ag}_6\text{Ge}_2\text{O}_7$ (b) obtained from MBJ-LDA approach.

Fig. 3. Calculated self-consistent energy band structure of $\text{Ag}_6\text{Si}_2\text{O}_7$ (a) and $\text{Ag}_6\text{Ge}_2\text{O}_7$ (b) obtained from PBE-GGA approach.

Fig. 4. Total density of states calculated from MBJ-LDA and PBE-GGA methods for $\text{Ag}_6\text{Si}_2\text{O}_7$ (a) and $\text{Ag}_6\text{Ge}_2\text{O}_7$ (b).

GGA calculation, the effective masses of the electrons and holes are respectively calculated to be $0.45m_0$ and $2.37m_0$ for $\text{Ag}_6\text{Si}_2\text{O}_7$ and $0.35m_0$ and $2.97m_0$ for $\text{Ag}_6\text{Ge}_2\text{O}_7$. The effective masses of the electrons and holes for $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$) have not been estimated experimentally, i.e., the obtained value of this study may contribute to the further investigation of $\text{Ag}_6\text{M}_2\text{O}_7$ materials. In addition, the semiconducting properties such as the fact of an indirect energy gap material as well as these structurally derived values such as effective masses are to be base for the further discussion of optical/electrical properties, though the correlation between the narrow band gap energy and visible light responsibility was confirmed in the present state.

Figures 4(a) and 4(b) compare the total density of states (TDOS) obtained from the PBE-GGA and MBJ-LDA calculations for $\text{Ag}_6\text{Si}_2\text{O}_7$ and for $\text{Ag}_6\text{Ge}_2\text{O}_7$, respectively. The origin of the energy in Fig. 4 was set to accord with that in Figs. 2 and 3. For $\text{Ag}_6\text{Si}_2\text{O}_7$, there is no distinct difference in the shapes of the VBs between both calculations, although the VB calculated from the MBJ potential are slightly narrower than that calculated from the GGA potential. As described above, the CB given by the MBJ potential is 1.29 eV higher than that given by the GGA potential, resulting in a close band gap to that measured by optical measurement. Similar result is also obtained for $\text{Ag}_6\text{Ge}_2\text{O}_7$ as shown in Fig. 4(b).

Figure 5 compares the DOS for Ag, Si, and O atoms in $\text{Ag}_6\text{Si}_2\text{O}_7$ crystal obtained from the GGA and MBJ-LDA methods, respectively. Ag 5p and Si 3d states were excluded from the present analysis since they hardly contribute to the occupied electron states between -10 to 0 eV and have no significant roles in chemical bond. In the MBJ-LDA calculation, the VB lies mainly in the range from -7.19 to 0 eV, although a tiny internal band gap around -6.65 eV is recognized. The VB above -6.45 eV is mainly constructed from Ag 4d and O 2p and these states strongly hybridize each other. The small DOS in the range of -7.27 to -6.80 has Si 3s, 3p, and O 2p characters. In addition, highly localized states from -8.74 to -8.52 eV are ascribed to Si 3s and 3p, interacting with O 2s and 2p states. The CB mainly consists of the interaction between Ag 4d/5s and O 2p states. These assignments are almost identical to those for the GGA

calculation and the literature.³⁾ **Figure 6** shows the DOS for Ag, Ge, and O atoms in $\text{Ag}_6\text{Ge}_2\text{O}_7$ crystal calculated from the GGA and MBJ-LDA approaches. It is also clear that the interactions between Ag 4d and O 2p states as well as Ag 4d/5s and O 2p states play a dominant role in the VB and CB of $\text{Ag}_6\text{Ge}_2\text{O}_7$ crystal, respectively.

As mentioned above, the calculated CB of $\text{Ag}_6\text{Si}_2\text{O}_7$ has to be rigidly shifted upward by 1.29 eV and using a scissor operator to reproduce the optical band gap owing to its underestimation in the GGA calculation.³⁾ However, the shift using a scissor operator does not remove the essential errors of the LDA and GGA methods. On the other hand, there is no need for a scissor operator in the present calculation since the MBJ-LDA calculation gives a reasonable band gap.

Figures 7(a) and 7(b) show the real and imaginary parts of the theoretical dielectric function, which describes the response of the crystal to an electromagnetic field (E), obtained from the MBJ-LDA and GGA (without the scissor operator) approaches for $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$). In the present analysis, the dielectric function was resolved into two components $\varepsilon_{\parallel}$ ($E \parallel c$) and $\varepsilon_{\perp}$ ($E \perp c$) owing to the monoclinic structure of $\text{Ag}_6\text{M}_2\text{O}_7$ (biaxial crystal). For the monoclinic crystals, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are defined as $\varepsilon_{\parallel} = \varepsilon_x + \varepsilon_z - \varepsilon_y$ and $\varepsilon_{\perp} = \varepsilon_y$.¹⁵⁾ The real part $\varepsilon_1(0)$ is equal to the square of the refractive index. For $\text{Ag}_6\text{Si}_2\text{O}_7$, the resulting refractive indices, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, are respectively calculated to be 2.24 and 2.19 for the GGA and 1.62 both for the MBJ-LDA calculation. On the other hand, the refractive indices of $\text{Ag}_6\text{Ge}_2\text{O}_7$, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, were respectively estimated to be 2.57 and 2.52 for the GGA and 1.71 and 1.70 for the MBJ-LDA calculation. We note that the refractive index from the MBJ-LDA scheme is smaller than that of the GGA calculation. Also, the refractive index of $\text{Ag}_6\text{Si}_2\text{O}_7$ is smaller than that of $\text{Ag}_6\text{Ge}_2\text{O}_7$. These results could be explained on the basis of the Penn model, as reported by Reshak.¹⁶⁾ Penn described the relationship between $\varepsilon(0)$ and E_g as follows:^{17),18)}

$$\varepsilon(0) \approx 1 + \left(\frac{\hbar\omega_p}{E_g} \right)^2 \quad (1)$$

where E_g is some kind of averaged energy gap which could be related to the real energy gap,¹⁸⁾ ω_p is the classical plasma

Fig. 5. Partial density of states calculated from PBE-GGA (a) and MBJ-LDA (b) methods for $\text{Ag}_6\text{Si}_2\text{O}_7$.

Fig. 6. Partial density of states calculated from PBE-GGA (a) and MBJ-LDA methods for $\text{Ag}_6\text{Ge}_2\text{O}_7$.

frequency, and $\hbar$ is the Dirac constant. It is clear from the Eq. (1) that $\varepsilon(0)$ is inversely proportional with E_g . The imaginary part $\varepsilon_2(\omega)$ of the dielectric function is related to the absorption spectrum due to the electronic transitions from the VB to CB. For $\text{Ag}_6\text{M}_2\text{O}_7$ (M = Si, Ge), the several peaks in $\varepsilon_2(\omega)$ are mainly ascribed to the transitions from the Ag 4d VB or the O 2p VB to the Ag 4d/5s CB or the O 2p CB by comparison with their DOS characteristics. However, note that a peak in $\varepsilon_2(\omega)$ does not correspond to a single interband transition since many direct and

indirect transitions contribute to each peak. In the MBJ-LDA calculation, a distinctive feature in $\varepsilon_2(\omega)$ is that the $\varepsilon_{\parallel}$ component is stronger at an energy below 4.6–4.7 eV than the $\varepsilon_{\perp}$ component for $\text{Ag}_6\text{M}_2\text{O}_7$ (M = Si, Ge). This difference is attributed to the anisotropy of the momentum matrix elements between the VB and CB.

Furthermore, the absorption coefficient $\alpha(\omega)$ of $\text{Ag}_6\text{M}_2\text{O}_7$ (M = Si, Ge) were calculated by using MBJ-LDA scheme over the energy range of 0 to 10.0 eV. **Figure 8** shows three com-

Fig. 7. Dielectric function calculated from PBE-GGA and MBJ-LDA methods for $\text{Ag}_6\text{Si}_2\text{O}_7$ (a) and $\text{Ag}_6\text{Ge}_2\text{O}_7$ (b).

ponents α_{xx} , α_{yy} , and α_{zz} for $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$). The α_{xx} and α_{yy} (or α_{zz}) are distinguishable, which implies that $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$) exhibits optical anisotropies. The band gaps can be estimated from extrapolating the linear portion of calculated $\alpha(\omega)$, i.e., from the values corresponding to $\alpha = 0$. As the results, the optical band gaps for $\text{Ag}_6\text{Si}_2\text{O}_7$ and $\text{Ag}_6\text{Ge}_2\text{O}_7$ are 1.7 and 1.4 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 $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$) to use as photocatalytic materials widely.

4. Conclusion

$\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$) were found to be indirect-band-gap oxides and calculated band gaps were 1.69 eV for $\text{Ag}_6\text{Si}_2\text{O}_7$ and 1.42 eV for $\text{Ag}_6\text{Ge}_2\text{O}_7$, respectively, from the MBJ-LDA calculation. This value is consistent with the experimental optical band gap and the result hardly changes with the spin-orbit interaction. There is no distinct difference in the effective masses of holes and electrons near the VBM and CBM for the MBJ-LDA and GGA schemes. The VB is mainly constructed from Ag 4d and O 2p and these states strongly hybridize each other, whereas the CB mainly consists of the interaction between Ag 4d/5s and O 2p states. These assignments in the MBJ-LDA calculation are almost identical to those for the GGA calculation. These features of the DOS are well reflected by the optical transition between

Fig. 8. Calculated absorption coefficients $\alpha(\omega)$ of $\text{Ag}_6\text{M}_2\text{O}_7$ ($\text{M} = \text{Si}, \text{Ge}$) by MBJ-LDA scheme.

the upper VB and lower CB, as seen in the energy dependence of the dielectric function.

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