First-principles study of electronic structure of Er-doped monoclinic ZrO₂

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The electronic structure of Er-doped monoclinic ZrO₂ was investigated by the generalized gradient approximation (GGA), GGA plus on-site Coulomb interaction (GGA + U) calculation, and modified Becke-Johnson (MBJ) exchange potential calculation. In the GGA calculation, the minimum bandgap energy of ZrO₂ was estimated to be 3.74 eV. The valence band was mainly composed of O 2p states, which strongly hybridized with the Zr 4d states. The conduction band was composed of Zr 4d and O 2p states. When an Er atom replaced one of the Zr atoms, seven-fold Er 4f states appeared in the forbidden gap of ZrO₂. Considering the spin–orbit coupling, the energy positions of the seven-fold Er 4f states in the forbidden gap hardly changed. Based on the GGA + U calculation, the Er 4f states shifted to the lower energy direction and entered into the valence band of ZrO₂ with an increase in the U parameter. In addition, the MBJ calculation gave similar results using a small U parameter in the valence band energy region, while the conduction band region is similar to the GGA + U calculation result with a large U parameter. Based on these results, we concluded that the GGA calculation is the most appropriate to describe the position of Er 4f states in the bandgap of Er-doped ZrO₂ phosphors among the three kinds of calculation methods examined in the present study.

Key-words : Oxides, Ab initio calculation, Supercell, Electronic structure

ZrO₂ is an ideal host material for producing phosphors doped with trivalent lanthanide (Ln) elements because it has thermal and chemical stabilities. Many researchers have prepared the Ln³⁺-doped ZrO₂ and investigated its photoluminescence properties; for example, Ce³⁺ doped by Zhu et al.,¹ Sm³⁺ doped by Nayak et al.,² Yb³⁺ doped by Rosa et al.³ and Er³⁺, Yb³⁺ co-doped by Singh et al.⁴,⁵ To understand the luminescence behavior, it is essential to understand the electronic structure of the solid, especially the energy level of the Ln 4f states. Dorenbos systematically researched the 4f energy levels of the Ln³⁺/Ln²⁺ doped into ZrO₂ and clarified that the Ln²⁺/Ln³⁺ 4f levels locate in the bandgap of ZrO₂.⁶ However, there are only a few theoretical reports about the electronic structure of the Ln³⁺-doped ZrO₂ due to the difficulty of strongly localized 4f electrons.⁷

For the density functional theory (DFT), local spin density approximation and generalized gradient approximation (GGA) methods have been generally applied as the exchange–correlation functional to solve the Kohn–Sham equation.⁸–¹⁰ It is well known that these approaches underestimate the bandgaps of semiconductors and insulators,¹¹,¹² although these approaches provide the structural properties of solid-state materials with a high accuracy. In order to improve the bandgap problem, the GGA plus on-site Coulomb interaction (GGA + U) proposed by Anisimov et al.¹³ and modified Becke-Johnson (MBJ) exchange potential proposed by Tran and Blaha¹⁴ are used. Moreover, the hybrid Hartree-Fock density functional method and the GW approximation based on the quasi-particle approach have been developed to reproduce the accurate electronic structure of solid-state materials.¹⁵,¹⁶ However, these sophisticated methods are still expensive for the large-scale system that the application of the supercell method is indispensable. In contrast, the GGA, GGA + U, and MBJ methods are reasonable for interpreting the experimental data of various practical materials with complex structures including many atoms, in view of the computational time and cost.

In this study, we performed a first-principles band calculation for the Er³⁺-doped ZrO₂ with a monoclinic structure to investigate the bandgap energy, valence and conduction band characteristics, and position of the Er 4f states in the bandgap in the framework of the GGA calculation. We also compared the calculation results obtained by the
GGA + $U$ and the MBJ methods with those of the GGA calculation.

Monoclinic ZrO$_2$ was classified into space group $P2_1/c$ and contained four formula units for a total of 12 atoms.\textsuperscript{17} All of the constituent atoms occupy the Wyckoff 4e sites. An Er-doped ZrO$_2$ supercell was constructed by substituting an Er atom for a Zr atom in the $2 \times 2 \times 2$ expanded cell (Fig. 1). In this supercell, there were 31 Zr atoms, 64 O atoms, and one Er atom. The supercell has the nominal composition of $\text{Er}_0.03\text{Zr}_{1.97}\text{O}_2$ and the space group $P1$. The electronic structure was calculated in two steps. First, the structure optimization calculation was performed in the framework of the GGA method using the CASTEP code.\textsuperscript{18} The structural parameters of the ZrO$_2$ unit cell ($P2_1/c$) were optimized by relaxing all lattice constants and atomic positions. For the Er-doped ZrO$_2$ supercell, the lattice constants were assumed to have the same values as those in the expanded cell and only the atomic positions were optimized. The pseudopotentials were constructed using the on-the-fly pseudopotential generator.\textsuperscript{19} The cutoff energy was set to 630 eV guaranteeing the convergence of the total energies less than 5.0 $\times$ 10$^{-8}$ eV/atom. The reciprocal space integration over the irreducible Brillouin zone (BZ) was approximated at two irreducible $k$-points using the 2 expanded tetrahedron method.\textsuperscript{20}

Secondly, the all-electron band calculations were performed with the full-potential linearized augmented plane wave and local orbital (FLAPW + lo) method based on the GGA approach.\textsuperscript{21} For the GGA + $U$ calculation, strong correlations among the $f$ electrons were considered through the effective screened interaction among electrons, $U_{\text{eff}} = U - J$, with Coulomb ($U$) and exchange ($J$) parameters, which are mean values for the Coulomb and exchange interactions in a considered shell.\textsuperscript{22} For the MBJ calculation, the parameter $c$ was self-consistently determined and $\alpha = -0.012$ and $\beta = 1.023$ bohr$^{1/2}$ were used.\textsuperscript{14} The muffin-tin radii ($R_{\text{MT}}$) values of the Er, Zr and O atoms for the Er$^{3+}$-doped ZrO$_2$ supercell were 2.21, 2.00 and 1.81 a.u. (atomic units), respectively. The plane wave cutoff was $R_{\text{MT}} \times K_{\text{max}} = 6.0$ (5.521 plane waves) for the Er$^{3+}$-doped ZrO$_2$ supercell. The electroneutral condition in the Er$^{3+}$-doped supercell was maintained by placing a background charge such as a jellium model. The BZ integration was performed by the modified tetrahedron method within the irreducible wedge. For the valence states, relativistic effects were included in either a scalar relativistic approximation or a spin–orbit coupling (SOC) that was considered by the second-variation method, while the core states were treated fully relativistically. In the density of states (DOS) calculation, the BZ integration was performed using the modified tetrahedron method on a special mesh of 32 $k$ points and 64 $k$ points without and with SOC, respectively.

Table 1 lists the optimized lattice constants of the ZrO$_2$ unit cell and the Er-doped ZrO$_2$ supercell. The calculated lattice constants of ZrO$_2$ agreed with the experimental values within 0.24% for the $a$-axis, 1.16% for the $b$-axis, 0.50% for the $c$-axis, and 0.13% for $\beta$. Table 2 shows the bond lengths of Zr–O in the unit cell and the bond lengths of Er–O in the supercell. In the monoclinic ZrO$_2$ structure, seven O atoms are coordinated around a cation. The coordination number did not change, the bond distance with oxygen increased when the Zr-site was replaced by an Er atom. The average bond length of Er–O is 0.2173 nm. Although the coordination number did not change, the bond distance with oxygen increased when the Zr-site was replaced by an Er atom. The average bond length of Er–O is 0.2173 nm. This is due to the difference in the ionic radius between Er$^{3+}$ (94.5 pm) and Zr$^{4+}$ (78 pm).

![Fig. 1](https://example.com/image.png)

**Fig. 1.** Schematic drawing of the monoclinic ZrO$_2$ unit cell as well as its extended supercell structure. Zr (gray), O1 (pale yellow), O2 (white), Er (green).

| Table 1. Calculated lattice constants obtained for ZrO$_2$ unit cell and Er-doped supercell. The supercell was obtained by expanding the ZrO$_2$ structure twice each in the directions of the $a$-, $b$-, and $c$-axes |
|---|---|---|---|---|
| Lattice constant/\(\text{nm}\) | ZrO$_2$ unit cell | Experimental$^{17}$ | Calculated |
| $a$ | 0.51849 | 0.51974 | 0.52980 |
| $b$ | 0.52367 | 0.53498 | 0.53767 |
| $c$ | 0.57689 | 0.5173 | 0.5966 |

| Table 2. Calculated bond lengths of Zr–O in ZrO$_2$ unit cell and Er–O in Er-doped supercell. Seven O atoms are coordinated around a cation |
|---|---|---|
| Bond length/\(\text{nm}\) | Zr–O | Er–O |
| Zr–O1 | 0.2055 | Er–O35 |
| Zr–O2 | 0.2164 | Er–O31 |
| Zr–O3 | 0.2166 | Er–O42 |
| Zr–O4 | 0.2172 | Er–O16 |
| Zr–O5 | 0.2271 | Er–O60 |
| Zr–O6 | 0.2299 | Er–O62 |

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is arbitrarily set as the valence band maximum (VBM). As shown in Fig. 2(a), the VBM and conduction band minimum (CBM) are located at $\Gamma$ and $Y_2$, respectively, indicating that the monoclinic ZrO$_2$ is an indirect-band transition. However, the energy difference between the direct and indirect transitions is very small. The forbidden gap between the VBM and the CBM was 3.74 eV, which is smaller than the experimental optical bandgap (5.5 eV). This value is due to a lack of consideration for the self-interaction correction and integer discontinuity in the exchange–correlation energy and potential with a changing number of electrons.

Figure 2(b) shows the total DOS and the partial DOS for the Zr and O atoms. The VB below $-15$ eV is constructed from O 2s and Zr 4p states. The VB in the energy range of $-4.29$ to 0 eV is mainly constructed from the O 2p states, which hybridized strongly with Zr 4d states, indicating stronger covalent bonding. On the other hand, the CB is mainly composed of Zr 4d states with a small O 2p contribution.

Figure 3 depicts the total DOS of the Er-doped ZrO$_2$ supercell from the GGA calculation. The forbidden gap of the host ZrO$_2$ was calculated to be 3.51 eV. Seven-fold Er 4f minority-spin states appear in the bandgap of ZrO$_2$ ($-0.27, -0.12, -0.02, 0.00, 1.15, 1.23$ and $1.34$ eV). This is because there are seven kinds of bond lengths between the Er and O atoms as listed in Table 2. These Er 4f minority-spin states are atomic-like peaks and strongly localized in the gap. In contrast, for the Er 4f majority-spin state, there are no energy states in the bandgap, and the Er 4f majority-spin states overlap with the O 2p states in the VB region. The Er 5d majority-spin and minority-spin states are widely spread in the CB. When the SOC is considered, the Er 4f majority-spin states also appear in the

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**Fig. 2.** Calculated band structure (a) and DOS (b) of monoclinic ZrO$_2$ using the GGA method. The highest occupied energy level with electrons was 0 eV. The band path is taken from Ref. 23.

**Fig. 3.** Density of states of Er-doped ZrO$_2$ supercell calculated from GGA without and with SOC. Sevenfold Er 4f states near 0 eV are inserted.
forbidden gap because the majority-spin and minority-spin states mix with the spin–orbit interaction. However, the energy positions of the seven-fold Er 4f states in the bandgap of ZrO$_2$ hardly changed (see the inserted figure, at $-0.40$, $-0.34$, $-0.04$, $0.00$, $1.00$, $1.09$ and $1.20$ eV).

We then performed the GGA + $U$ calculation using the $U$ parameter for the Er-doped supercell. The $U$ parameter can be generally prepared by fitting to the experimental results.\cite{25,29} However, it is difficult to choose the appropriate screening $U$ parameter, which often changes the obtained results. This means that the position of the Er 4f states in the bandgap depends on the strength of the Coulomb repulsion. We explored the behavior of the system for the $U$ values varying from $1.36$ eV ($0.1$ Ry) to $5.44$ eV ($0.4$ Ry).\cite{30} Figure 4 shows the Er-related DOS calculated from the GGA + $U$ without the SOC. The Er 4f majority-spin and minority-spin states shifted in the higher energy direction or lower energy direction by considering the $U$ parameter. As the $U$ parameter increases, the Er 4f minority-spin states strongly shift and enter into the VB and CB of ZrO$_2$. The Er 4f minority-spin states also gave a poor dispersibility by adding the $U$ correction in comparison the GGA method. In addition, we noted that the bandgap underestimation for ZrO$_2$ was hardly improved by adding the $U$ parameter ($E_g = 3.54$ eV @ $U = 5.44$ eV).

According to Dorenbos,\cite{30} the Er$^{3+}$ 4f levels locate in the bandgap of the host ZrO$_2$. Although it is a rough interpretation, our result obtained from the GGA calculation showed the tendency suggested by Dorenbos. Similar results are also obtained for ZrO$_2$: Yb$^{3+}$, Er$^{3+}$ by Pihlgren et al.\cite{31} and for Er$^{3+}$-doped Y$_2$O$_2$:S by Pokhrel et al.\cite{32} In addition, Pihlgren et al. pointed out that the Er$^{3+}$ 4f ground level ($^{4}I_{15/2}$) in ZrO$_2$ locates above the top of the VB at ca. $5000$ cm$^{-1}$ (0.62 eV).\cite{31} According to the information provided by these reports, the above results given by the GGA + $U$ calculation is not suitable to explain the 4f states of the Er-doped ZrO$_2$ phosphors. Thus, we examined the MBJ exchange potential method. However, as shown in Fig. 4, the MBJ calculation gave similar results using a small $U$ parameter in the VB energy region, while the CB region is similar to the GGA + $U$ calculation result with a large $U$ parameter. The MBJ calculation was also performed for the Er-doped ZnO, as reported by Alkahtani et al.\cite{33} However, the Er$^{3+}$ 4f energy states lie near the bottom of the CB of ZnO. This result differs from the prediction by Dorenbos,\cite{6} Pihlgren et al.,\cite{31} and Pokhrel et al.\cite{32} as already discussed.

Accordingly, we concluded that the GGA calculation is the most appropriate to describe the behavior of the Er$^{3+}$-doped ZrO$_2$ phosphors among the three kinds of calculation methods examined at the present time. Needless to say, it should be examined to give a proper treatment to the multiplet effects in the Er 4f energy states unfilled by electrons because the present calculations are essentially based on the one-electron equation in the DFT framework.\cite{32} We hope that the present study concerning electronic structures may be helpful for further experimental study of the Er$^{3+}$-doped ZrO$_2$ phosphors as a preliminary approach.

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