NOTE

First-principles study of electronic structure of Er-doped monoclinic ZrO_2

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The electronic structure of Er-doped monoclinic ZrO_2 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 ZrO_2 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 ZrO_2 . 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 ZrO_2 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 ZrO_2 phosphors among the three kinds of calculation methods examined in the present study.

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ZrO_2 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 Ln^{3+} -doped ZrO_2 and investigated its photoluminescence properties; for example, Ce^{3+} doped by Zhu et al.,¹⁾ Sm^{3+} doped by Nayak et al.,²⁾ Yb^{3+} doped by Rosa et al.,³⁾ and Er^{3+} , Yb^{3+} 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 $\text{Ln}^{2+}/\text{Ln}^{3+}$ doped into ZrO_2 and clarified that the $\text{Ln}^{2+}/\text{Ln}^{3+}$ 4f levels locate in the bandgap of ZrO_2 .⁶⁾ However, there are only a few theoretical reports about the electronic structure of the Ln^{3+} -doped ZrO_2 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 Er^{3+} -doped ZrO_2 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

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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).

GGA + U and the MBJ methods with those of the GGA calculation.

Monoclinic ZrO_2 was classified into space group $\text{P}2_1/\text{c}$ and contained four formula units for a total of 12 atoms.¹⁷⁾ All of the constituent atoms occupy the Wyckoff 4c 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.¹⁸⁾ The structural parameters of the ZrO_2 unit cell ($\text{P}2_1/\text{c}$) 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.¹⁹⁾ The cutoff energy was set to 630 eV guaranteeing the convergence of the total energies less than 5.0×10^{-6} eV/atom. The reciprocal space integration over the irreducible Brillouin zone (BZ) was approximated at two irreducible k -points using the $2 \times 2 \times 2$ Monkhorst-Pack k -point grid.²⁰⁾

Secondly, the all-electron energy band calculations were performed with the full-potential linearized augmented plane wave and local orbital (FLAPW + l_o) method based on the GGA approach.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.²²⁾ For the MBJ calculation, the parameter c was self-consistently determined and $\alpha = -0.012$ and $\beta = 1.023 \text{ bohr}^{1/2}$ were used.¹⁴⁾ The muffin-tin radii (R_{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 planewave 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, rela-

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

		a/nm	b/nm	c/nm	$\beta/^\circ$
ZrO_2 unit cell	Experimental ¹⁷⁾	0.51974	0.52980	0.53498	99.53
	Calculated	0.51849	0.52367	0.53767	99.66
Er-doped supercell	Calculated	1.03698	1.04735	1.07534	99.66

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/nm		Bond length/nm	
Zr–O1	0.2055	Er–O35	0.2142
Zr–O1	0.2081	Er–O57	0.2189
Zr–O2	0.2164	Er–O31	0.2215
Zr–O1	0.2166	Er–O42	0.2250
Zr–O2	0.2172	Er–O16	0.2289
Zr–O2	0.2271	Er–O60	0.2299
Zr–O2	0.2299	Er–O62	0.2438

tivistic 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 β . **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 Zr atom, and the average bond length of Zr–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 0.2260 nm. This is due to the difference in the ionic radius between Er^{3+} (94.5 pm) and Zr^{4+} (78 pm).

Figure 2 shows the calculated band structure and the DOS for the monoclinic ZrO_2 . The origin of the energy

Fig. 2. Calculated band structure (a) and DOS (b) of monoclinic ZrO₂ using the GGA method. The highest occupied energy level with electrons was 0 eV. The band path is taken from Ref. 23.

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 Γ and Y_2 , respectively, indicating that the monoclinic ZrO₂ 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).²⁴ 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.^{11),12)} 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 ZrO₂ supercell from the GGA calculation. The forbidden gap of the host ZrO₂ was calculated to be 3.51 eV. Seven-fold Er 4f minority-spin states appear in the bandgap of ZrO₂ (-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

Fig. 3. Density of states of Er-doped ZrO₂ supercell calculated from GGA without and with SOC. Sevenfold Er 4f states near 0 eV are inserted.

Fig. 4. Density of states of Er-doped ZrO_2 calculated from the GGA + U using different U and MBJ methods. The shaded regions illustrate the Er majority-spin character. The red solid lines are the Er minority-spin character.

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.^{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).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,⁶⁾ 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 $\text{ZrO}_2\text{:Yb}^{3+}$, Er^{3+} by Pihlgren et al.³¹⁾ and for Er^{3+} -doped Y_2O_3 by Pokhrel et al.³²⁾ In addition, Pihlgren et al. pointed out that the Er^{3+} 4f ground level ($^4I_{15/2}$) in ZrO_2 locates above the top of the VB at ca. 5000 cm^{-1} (0.62 eV).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.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,⁶⁾ Pihlgren et al.,³¹⁾ and Pokhrel et al.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.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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