The effect of co-existing cations on optical conductivity and absorption in Hf$_{0.5}$Zr$_{0.5}$O$_2$ system: A first-principles study

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Abstract. We report the optical properties of monoclinic Hf$_x$Zr$_{0.5}$O$_2$ system calculated using the plane-wave method within the generalized gradient approximation. We also calculated the properties of monoclinic ZrO$_2$ and HfO$_2$ systems as the references. As a result, the systems show the significant optical dichroism between $xy$ plane and $z$-axis indicated by the significant differences between the real-part optical conductivities along both directions. Additionally, the increase of dielectric constant is proportional with the absorption edge decrease for each axis, which verifies the Penn model. This work shows that the doping treatment significantly tunes the optical properties of Hf$_{1-x}$Zr$_x$O$_2$ system. This report presents the essential properties for novel functional device applications.

1. Introduction
Hafnia (HfO$_2$) and zirconia (ZrO$_2$), which are stable in the monoclinic structure [1], have attracted many investigations because of their interesting physical phenomena. These systems show the large dielectric constants, the wide bandgaps ($E_0$), and the hysteresis of electrical polarization, leading to the ferroelectricity [2, 3]. The previous theoretical report showed the band structures of systems for different space groups by using many-body perturbation theory in $GW$ approximation. Both systems exhibit the similar quasiparticle band structures [4]. The systems show low compressibility for hard materials [5]. The electrical ferroelectricity of Hf$_{1-x}$Zr$_x$O$_2$ system has been investigated in several reports [6-11]. The ferroelectricity, described by the Gibbs/Helmholtz free energy model [12], opens a possible application in nonvolatile FRAM [11]. The experimental and theoretical approaches have been used to reveal the electronic structures of oxygen (O) vacancies [13-15]. Using the theoretical approach, the increase of Zr concentration induces the structural transition. The previous report has also shown that the conduction band (CB) edge can be tuned by changing $x$ [16]. However, there are limited reports of optical properties of the system, such as optical conductivity ($\sigma$).
In this work, we calculated electronic and optical properties of Hf$_{0.5}$Zr$_{0.5}$O$_2$ system. The plane-wave generalized gradient approximation method (GGA) was used [17]. We use ZrO$_2$ and HfO$_2$ systems as the references. We reveal any possible tuning of optical properties by doping treatment in Hf$_{1-x}$Zr$_x$O$_2$ system.
2. Numerical Method
The plane-wave density-functional method within the Quantum ESPRESSO code [18] was used to calculate ground-state electronic and optical properties of monoclinic systems of ZrO$_2$, HfO$_2$, and Hf$_{0.5}$Zr$_{0.5}$O$_2$ systems (space group: P2$_1$/c). Figure 1 presents the crystal structures of the systems. The GGA with the PBE-type exchange-correlation functional energy [17] is employed, which were used for various systems in our previous reports [19-21]. The Trouiller–Martins-approach-based norm-conserving pseudopotentials [22-24] were used as the approximations of sophisticated all-electron potentials. Threshold energy of ~0.014 eV, kinetic cutoff energy of ~1 keV, and a $\Gamma$-point-centered $k$-point mesh of 6 × 6 × 6 were employed. Threshold force of ~0.05 eV/Å was used in a ‘vc-relax’ calculation to optimize lattice constants, atomic positions, angles between $a$ and $c$ axes within the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [25-28]. The structural properties of HfO$_2$ and ZrO$_2$ systems from the previous report [29] are adopted as initial parameters of the calculation.

The optical properties calculation employs the Drude-Lorentz model [30], which covers the interband ($\varepsilon_{2r}(\omega)$) and intraband parts ($\varepsilon_{1f}^{'}(\omega)$) of dielectric functions [31]. The Kramers-Kronig relation [32, 33] connect both real and imaginary parts of dielectric functions ($\varepsilon_1$, $\varepsilon_2$) by

$$\varepsilon_1(\omega) = \frac{1}{\pi} \int_0^{\infty} \frac{\omega \varepsilon_2(\omega')}{\omega^2 - \omega'^2} d\omega',$$

and

$$\varepsilon_2(\omega) = -\frac{1}{\pi} \int_0^{\infty} \frac{\omega' \varepsilon_1(\omega')}{\omega^2 - \omega'^2} d\omega',$$

where

$$P\int_0^{\infty} d\omega'/(\omega'^2 - \omega^2) = 0.$$

We suggest that the plasmon frequency ($\omega_p$) lies at an energy where $\varepsilon_1 = 0$ and $d\varepsilon_1/d\omega > 0$ [34]. Loss function ($L$) spectrum calculated by $L = -\text{Im}(1/\varepsilon)$ would accurately show the peaks of plasmonic states. Additionally, $L$ spectrum will be reported elsewhere.

![Figure 1](image_url)

**Figure 1.** Crystal structure of ZrO$_2$ or HfO$_2$ systems illustrated using VESTA [35]: (a) Diagonal view showing polyhedral AO$_7$ sites and (b) view along $b$-axis showing the angle of $\beta$ between $a$ and $c$. 
3. Results and Discussions

Figure 2 presents real-part optical conductivity ($\sigma_1$) of the pure ZrO$_2$ and HfO$_2$, as well as Hf$_{0.5}$Zr$_{0.5}$O$_2$ systems, which are obtained from [33]

$$\sigma_1 = \frac{\omega \varepsilon_1}{4\pi}. \quad (4)$$

We find significant optical dichroism by the differences of $\sigma_1$ between $xy$ plane and $z$-axis. However, small differences of $\sigma_1$ between $x$ and $y$ axes are found, indicating weak optical dichroism between both axes. The significant optical dichroism between $xy$ plane and $z$-axis is similar with that of the tetragonal anatase TiO$_2$ [36]. Furthermore, we find an absorption edge ($E_a$) of 3.54 eV along $x$ axis and 3.96 eV along $z$ axis in ZrO$_2$ and HfO$_2$ systems, respectively. Note that $E_a$ corresponds to $E_g$. We find $E_a$ of 3.67 eV along $z$ axis in Hf$_{0.5}$Zr$_{0.5}$O$_2$ system. This value is between that of the other systems as well as the intensity peak of $\sigma_1$. However, Hf$_{0.5}$Zr$_{0.5}$O$_2$ system shows the lowest $\sigma_1$ width among the systems.

In Figure 3, the increase of $E_a$ decreases $\varepsilon_0$ for each axis, which will be reported elsewhere. This result verifies the Penn model for semiconductors formulated by [37, 38]

$$\varepsilon_0 = 1 + \left(\frac{\hbar \omega_p}{E_a}\right). \quad (5)$$

![Figure 2. Energy-dependences of real-part optical conductivities ($\sigma_1$) in (a) ZrO$_2$, (b) HfO$_2$, and (c) Hf$_{0.5}$Zr$_{0.5}$O$_2$ systems. The $\sigma_1$ width are presented.](image)

![Figure 3. Trend of dielectric constants and absorption edges of ZrO$_2$, HfO$_2$, and Hf$_{0.5}$Zr$_{0.5}$O$_2$ systems.](image)

All the systems show the highest $\varepsilon_0$ along $y$ axis. However, the highest $E_a$ values are found along $z$, $y$, and $x$ axes for ZrO$_2$ and HfO$_2$, and Hf$_{0.5}$Zr$_{0.5}$O$_2$ systems, respectively. By using the relation between the zero-energy refractive index ($n_0$) and $\varepsilon_0$ as
for semiconductor where the extinction coefficient ($k$) is zero, $n$ of HfO$_2$ and ZrO$_2$ systems are in a good agreement with that of the previously reported values [3]. Hf$_{0.5}$Zr$_{0.5}$O$_2$ system exhibits $n_0$ which is between that of the other systems. The details of $n$ and $k$ have previously reported [39]. Thus, the coexistence of both cations, i.e., Zr$^{4+}$ and Hf$^{4+}$ ions, significantly tunes the optical properties of either ZrO$_2$ and HfO$_2$ systems. The optical properties of Hf$_{0.5}$Zr$_{0.5}$O$_2$ system are essential to guide possible future experiments.

The results highlight the tune of optical properties by the doping treatment. The optical properties of Hf$_{1-x}$Zr$_x$O$_2$ system cannot be achieved in the pure HfO$_2$ or ZrO$_2$ systems. Notably, the use of $x$ other than 0.5 might promote a fine tuning of the optical properties. Hence, this study provides prospective potential technological uses in novel functional devices.

4. Conclusions

Using the GGA, we have studied the optical properties of the monoclinic ZrO$_2$, HfO$_2$, Hf$_{0.5}$Zr$_{0.5}$O$_2$ systems. $\sigma$ curves of the systems indicate the significant optical dichroism between xy plane and z-axis. Moreover, the increase of dielectric constant is proportional with the decrease of absorption edge for each axis. This result verifies the Penn model for semiconductors. Hence, this study shows that the doping treatment is essential to tune the optical properties of Hf$_{1-x}$Zr$_x$O$_2$ system. Overall, this study presents the essential optical properties for novel functional device applications.

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6. References

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