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EXTENDED ABSTRACT BOOK

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Tuning the Electronic and Optical Properties of ZnO by Ag Doping: A DFT+*U* Investigation

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ABSTRACT

The structural, electronic and optical properties of Ag-doped ZnO were examined using first-principles calculations. The density functional theory plus Hubbard *U* correction (DFT+*U*) was incorporated to ensure an accurate analysis of the electronic structure. The inclusion of Ag dopants was found to introduce new impurity levels that significantly reduce the ZnO bandgap from 3.362 eV to 2.810 eV. Consequently, absorption in the visible light spectrum is greatly enhanced, providing valuable theoretical guidance for the development of Ag-doped ZnO for solar energy applications.

Keywords: DFT+*U*, Ag-doped ZnO, Structural Properties, Electronic Properties, Optical Properties.

1. INTRODUCTION

Zinc oxide (ZnO) is a versatile II-VI semiconductor with a wide, direct bandgap of 3.37 eV, making it suitable for many applications (Sharma et al., 2022). However, this wide bandgap is also its primary limitation for solar energy conversion, as it restricts optical absorption almost exclusively to the UV portion of the solar spectrum, which accounts for only 4% of available energy (López-López et al., 2022). To enhance its efficiency, the electronic and optical properties of ZnO must be modified to utilize the more abundant visible light spectrum.

Doping with transition metals is a proven strategy to modifying the structural, electronic and optical properties of ZnO (Gopalakrishnan & Ashokkumar, 2024). Silver (Ag) is considered a particularly promising dopant because of its ability to modify the electronic structure of zinc oxide and enhance its luminescence properties. Density functional theory (DFT) is a powerful tool for studying such systems. However, standard DFT methods often fail to accurately predict the electronic properties of strongly correlated materials like ZnO. This study addresses this

gap by employing the DFT+*U* method to conduct a rigorous first-principles investigation into the effects of varying Ag concentrations (x = 0.0625, 0.125 and 0.1875) on the structural, electronic and optical properties of ZnO, providing a more accurate theoretical foundation for its practical application.

2. COMPUTATIONAL METHOD

First-principles calculations were performed using the Cambridge Serial Total Energy Package (CASTEP) code. A 2×2×2 wurtzite ZnO supercell, containing 16 Zn and 16 O atoms, served as the basis for the models. Ag-doped systems ($Zn_{1-x}Ag_xO$) were created by substitutionally replacing one, two and three Zn atoms with Ag atoms to achieve concentrations of x = 0.0625, 0.125 and 0.1875, respectively.

Structural optimizations were performed using the generalized gradient approximation of Perdew-Burke-Ernzerhof for solids (GGA-PBEsol) to treat the exchange-correlation functional. To correct for the underestimation of the bandgap inherent in standard DFT, the electronic and optical properties were calculated using the GGA-PBEsol+*U* method. Based on previous studies, the Hubbard *U* parameters were applied to account for strong on-site Coulomb interactions, with values set to U_d = 5 eV for Zn-3*d* states, U_p = 9 eV for O-2*p* states and U_d = 6 eV for Ag-4*d* states (Hamzah et al., 2023; Wang et al., 2020). A plane-wave cut-off energy of 340 eV and a 4×4×1 Monkhorst-Pack *k*-point mesh were used for all calculations.

3. RESULTS AND DISCUSSION

3.1 Structural Properties

Structural optimization revealed that the lattice parameters (*a*, *b*, *c*) and unit cell volume increase systematically with higher Ag concentrations. This expansion is attributed to the larger ionic radius of the substituting Ag^+ ion (1.15 Å) compared to the host Zn^{2+} ion (0.74 Å), which is consistent with experimental observations.

3.2 Electronic Properties

The GGA-PBEsol+*U* method proved essential for accuracy. While standard GGA-PBEsol severely underestimated the bandgap of pure ZnO at 0.620 eV, the Hubbard *U* correction yielded a bandgap of 3.362 eV, in excellent agreement with the experimental value of 3.37 eV (Harun et al., 2017). Upon doping, the bandgap of ZnO was significantly reduced. The calculated bandgaps for Ag concentrations x =0.0625, 0.125 and 0.1875 were 3.120 eV, 2.970 eV and 2.810 eV, respectively. At the highest concentration, this represents a 16.4% reduction from the calculated pure ZnO value.

Analysis of the density of states (DOS) reveals the mechanism behind this bandgap narrowing. The hybridization of Ag-4*d* and O-2*p* orbitals introduces new, occupied impurity states at the top of the valence band. This effectively raises the valence band maximum, thereby reducing the energy required to excite an electron to the conduction band.

3.3 Optical Properties

The engineered reduction in the electronic bandgap has a direct and beneficial impact on the optical properties. The optical absorption edge of Ag-doped ZnO exhibits a significant redshift

(a shift to longer wavelengths) compared to pure ZnO. The redshift pushes the absorption threshold from the UV region into the visible light spectrum (380-780 nm), especially at higher Ag concentrations (x = 0.125 and 0.1875). This enhanced absorption of lower-energy photons means that a greater portion of the solar spectrum can be utilized by the material.

4. CONCLUSION

This study used DFT+U calculations to show that doping ZnO with Ag can effectively improve its properties for solar energy use. Ag doping expands the crystal structure and significantly reduces the bandgap by introducing Ag-4d states that mix with O-2p states. As a result, the material shows a redshift in light absorption, allowing better use of visible light. These findings suggest that Ag-doped ZnO is a strong candidate for photocatalytic and photovoltaic applications, providing useful guidance for future experiments.

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