FIRST-PRINCIPLES INVESTIGATION OF 7% CU-DOPED SRTIO₃ USING MATERIAL STUDIO: STRUCTURAL, ELECTRONIC, AND OPTICAL PROPERTIES

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Abstract. *Perovskite strontium titanate, $SrTiO_3$, attracts particular attention due to its wide bandgap, excellent dielectric properties, and great thermal stability, promising excellent application prospects in photocatalysis, optoelectronics, and solar energy conversion devices. However, the intrinsic $SrTiO_3$ presents limited absorption of visible light as a result of the large band gap (~3.2 eV), restricting its realization in solar-driven applications [1], [2]. The transition metal doping is one of the active ways to enhance the optical absorption and tune electronic structure. Below, we report a detailed first-principles investigation of the structural, electronic, and optical properties for Cu-doped $SrTiO_3$ with 7 mol% copper substitution, using material models created and analyzed in BIOVIA Materials Studio. Finally, the doped system was modeled by replacing the sites of titanium (Ti) with the atoms of copper (Cu) within a $2 \times 2 \times 2$ supercell of $SrTiO_3$ to obtain approximately 7 mol% doping. The geometry optimization and calculations of the electronic structure were done within the GGA of the PBE functional, with the addition of Hubbard U corrections (GGA + U) toward the proper description of the strongly correlated Cu 3d states [3], [4]. The obtained values for the structural parameter were compared with experimental lattice constants for undoped $SrTiO_3$, which resulted in good agreement, thus allowing us to validate the computational setup [5].The crystal structure showed that Cu doping leads to small lattice distortion due to the difference between the ionic radii of Cu^{2+} (0.73 Å) and Ti^{4+} (0.605 Å), because of which the doped lattice got expanded with an enlarged lattice constant and modified bond lengths for both Sr–O and Ti–O. In fact, the optimized lattice parameters showed increased cell volume relative to pristine $SrTiO_3$, consistent with earlier theoretical and experimental reports on transition metal dopants [6]. Importantly, the Cu dopant location and its local coordination environment influenced the symmetry of the perovskite lattice, leading to subtle octahedral tilting and a reduction in space group symmetry compared to the ideal cubic structure.*

Keywords— *$SrTiO_3$, Cu doping, density functional theory (DFT), electronic structure, optical properties, Materials Studio.*

Calculations of electronic band structure and DOS revealed dramatic changes upon incorporation of Cu. A direct bandgap at the Γ point of about 3.2 eV, in good agreement with the values in literature [1], was obtained for pristine $SrTiO_3$. However, this bandgap

narrowed upon doping of Cu so that mid-gap states composed mainly of Cu 3d and O 2p hybridized orbitals appeared in the bandgap. The effective bandgap thereby decreased to about 1.8–2.1 eV with the resultant impurity states, which made possible absorption in the visible-light range. Partial DOS analysis showed that the VBM consisted mainly of O 2p states while the CBM has strong Ti 3d character. Cu 3d states within the gap furnish ideal intermediate levels that allow electron transition upon lower energy photons. Bandgap tuning through Cu doping presents a feasible means to enhance the visible light activity in $SrTiO_3$-based photocatalysts and photovoltaic materials.The frequency-dependent complex dielectric function $\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)$ was computed from the calculated electronic transitions, and then important optical constants, such as absorption coefficient, refractive index, and reflectivity spectra, were derived. It was noticed that the absorption edge for Cu-doped $SrTiO_3$ showed a huge redshift compared to the undoped one, confirming the results obtained for the electronic structure. Furthermore, enhanced optical absorption in the visible region (400–700 nm) has been observed, and thus, 7 mol% Cu-doped $SrTiO_3$ may be promising for better solar energy conversion. Moreover, the refractive index spectra show increased values at lower photon energies, which indicates modified light-matter interaction due to dopant states. In addition, reflectivity profiles are also modified upon doping in the low energy region indicating altered dielectric screening effects.Charge density difference plots and Bader charge analysis were employed to probe the charge redistribution upon doping. Results showed that a large portion of the charge is localized around the Cu dopant and the immediately surrounding oxygen atoms, indicating an enhanced degree of covalent bonding and henceforth defect state formation. Indeed, the enhanced charge density around Cu sites is in good agreement with the mid-gap states appearing in the DOS, further confirming the strong influence of Cu on the electronic structure. In addition, cohesive energies for the doped structures were computed to understand the thermodynamic stability of this particular configuration. From the calculated formation energies, this work confirmed that Cu substitution at the host Ti site is energetically viable under typical synthesis conditions. The structural, electronic, and optical analysis combined affirms the effectiveness of Cu doping in modifying the intrinsic properties of $SrTiO_3$. It is indicated that narrowing in the bandgap, enhanced visible region absorption, and modulation of optical constants could be potentially useful for photocatalytic water splitting, CO_2 reduction, and photoelectrochemical cells. Among the doped $SrTiO_3$ systems considered so far, the Cu doping exhibits competitive bandgap narrowing with moderate lattice distortion, where the functional enhancement is balanced with the structural integrity [7], [8]. First-principles calculations using material models in Materials Studio reveal that 7 mol% Cu-doped $SrTiO_3$ exhibits tailored structural parameters, reduced bandgap, and superior optical absorption characteristics suitable for visible-light-driven applications. Theoretical insights herein provide the basis for future experimental synthesis and optimization of Cu-doped $SrTiO_3$-based functional materials. Future studies incorporating temperature

effects and defect concentration variance may be used to further develop understanding of dopant behavior under realistic operating conditions.

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