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First-Principles Investigation of the Electronic Structure and Optical Properties of $NbCuO_3$ and Ag-Substituted $Nb_{13}AgO_{33}$ for Optoelectronic Applications

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Abstract

The search for advanced semiconductor materials with improved electronic and optical properties is crucial for the development of modern optoelectronic and photocatalytic devices. In this study, density functional theory (DFT) calculations were carried out using the CASTEP code within the GGA-PBE framework to investigate the structural, electronic, and optical properties of pristine $NbCuO_3$ and Ag-substituted $Nb_{13}AgO_{33}$. A plane-wave cutoff energy of 450 eV and a 4×4×4 Monkhorst–Pack k-point mesh were employed throughout the calculations. Structural optimization confirms that both compounds crystallize in the triclinic P1 crystal system. The electronic band structure reveals that Ag substitution reduces the band gap from 1.08 eV to 0.83 eV, indicating enhanced electronic conductivity and easier charge-carrier excitation. TDOS and PDOS analyses show significant hybridization between Nb-d, Cu-d, Ag-d, and O-p orbitals, with Ag introducing additional electronic states near the Fermi level. Optical calculations reveal enhanced absorption, dielectric response, optical conductivity, refractive index, and reflectivity upon the incorporation of Ag. These enhancements suggest stronger interaction with visible light and improved optoelectronic performance. Overall, the results indicate that Ag substitution effectively tailors the properties of $NbCuO_3$, making $Nb_{13}AgO_{33}$ a promising material for photovoltaic, photocatalytic, and other optoelectronic applications.

Keywords: Density Functional Theory (DFT); CASTEP; $NbCuO_3$; Ag substitution; Electronic Structure; Density of States; Optical Properties; Band Gap Engineering; Optoelectronic Materials.

Introduction

Transition-metal oxides (TMOs) have emerged as one of the most extensively studied classes of functional materials due to their exceptional structural stability, tunable electronic Properties, and remarkable optical properties[1, 2]. These materials exhibit a wide range of physical characteristics, including semiconducting, dielectric, catalytic, and magnetic behavior, making them attractive candidates for applications in photocatalysis, solar-energy conversion, optoelectronic devices, sensors, and energy-storage systems. The versatility of transition-metal oxides arises from the strong interaction between transition-metal d orbitals and oxygen p orbitals, which governs their electronic and optical characteristics [3, 4]. Among transition-metal oxides, niobium-based compounds have attracted increasing attention owing to their excellent chemical stability, relatively narrow band gap, high dielectric constant, and efficient charge-transport properties [5, 6]. These characteristics make niobium-containing materials

suitable for various technological applications, including photovoltaic devices, photodetectors, photocatalysts, and transparent electronic components [7, 8]. However, the performance of pristine niobium oxides is often limited by their intrinsic electronic structure and optical absorption, which restrict their efficiency in visible-light-driven applications [9, 10]. Consequently, tailoring their electronic properties through elemental substitution has become an effective strategy for improving their overall performance [11, 12]. Elemental substitution is one of the most effective approaches for engineering the structural and electronic properties of semiconductor materials [13, 14]. Introducing suitable dopant atoms into the crystal lattice can modify the atomic bonding environment, alter orbital hybridization, and generate additional electronic states near the Fermi level. These changes often result in band-gap narrowing, enhanced carrier mobility, improved electrical conductivity, and stronger optical absorption [15, 16]. Silver (Ag) is considered an attractive substitutional element because of its unique electronic configuration and its ability to modify the electronic distribution within oxide materials without significantly disturbing the crystal framework. Ag incorporation has been reported to improve charge separation, increase visible-light absorption, and enhance the optoelectronic performance of several oxide semiconductors. Density Functional Theory (DFT) has become one of the most reliable computational techniques for investigating the structural, electronic, and optical properties of crystalline materials before experimental synthesis. DFT enables accurate prediction of band structures, density of states, charge distribution, and optical spectra, providing valuable insight into the relationship between atomic structure and material performance. Such theoretical investigations significantly reduce the time and cost associated with experimental material development while providing a deeper understanding of the fundamental mechanisms governing electronic and optical behavior. In the present study, first-principles DFT calculations were performed using the CASTEP code within the framework of the Generalized Gradient Approximation (GGA) employing the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional to investigate pristine $NbCuO_3$ and Ag-substituted $Nb_{13}AgO_{33}$. The structural, electronic, and optical properties of both compounds were systematically examined. Particular emphasis was placed on the optimized crystal structure, electronic band structure, total density of states (TDOS), partial density of states (PDOS), dielectric function, absorption coefficient, optical conductivity, refractive index, reflectivity, and energy-loss function. The calculated results reveal that Ag substitution effectively modifies the electronic structure by reducing the band gap from approximately 1.08 eV to 0.83 eV, while simultaneously enhancing the optical response over a broad photon-energy range. These improvements indicate that Ag-substituted $Nb_{13}AgO_{33}$ possesses significant potential for future optoelectronic, photovoltaic, and photocatalytic applications.

Structural Properties

Results and Discussion

The calculated electronic band structures indicate that both $NbCuO_3$ and $Nb_{13}AgO_{33}$ exhibit semiconducting behavior. The pristine $NbCuO_3$ possesses a band gap of approximately 1.08 eV, whereas Ag substitution reduces the band gap to approximately 0.83 eV. This reduction suggests that Ag incorporation facilitates electronic excitation by lowering the energy required for electron transitions from the valence band to the conduction band. The narrowing of the band gap is attributed to the interaction between Ag electronic states and the host lattice, which modifies the electronic potential and introduces additional states close to the Fermi level [17, 18]. Consequently, $Nb_{13}AgO_{33}$ is expected to exhibit enhanced electrical conductivity and superior visible-light absorption compared with pristine $NbCuO_3$, indicating improved suitability for optoelectronic and photocatalytic applications. The optimized crystal structures of pristine $NbCuO_3$ and Ag-substituted $Nb_{13}AgO_{33}$ belong to the triclinic crystal system with the P1 space group. The calculated lattice parameters for $NbCuO_3$ are a = 9.6235 Å, b = 8.5923 Å, c = 6.7541 Å, with lattice angles of $\alpha = 90.00°$, $\beta = 91.05°$, and $\gamma = 90.00°$. After Ag substitution, the optimized $Nb_{13}AgO_{33}$ structure exhibits lattice constants of a = 22.6696 Å, b

= 3.8475 Å, and c = 15.6071 Å, while the lattice angles become α = 90.00°, β = 91.91°, and γ = 90.00°.

The incorporation of Ag atoms significantly modifies the lattice dimensions compared with pristine $NbCuO_3$, indicating structural rearrangement and lattice distortion caused by substitution. The slight deviation of the β angle from 90° confirms the low-symmetry triclinic nature of both structures [19]. Such structural modifications can alter the overlap between atomic orbitals, leading to changes in the electronic band structure, density of states, and optical response[20, 21]. Consequently, the structural distortion introduced by Ag substitution is expected to contribute to the observed reduction in the band gap and the enhancement of the optical properties, making $Nb_{13}AgO_{33}$ a promising material for optoelectronic and photocatalytic applications.

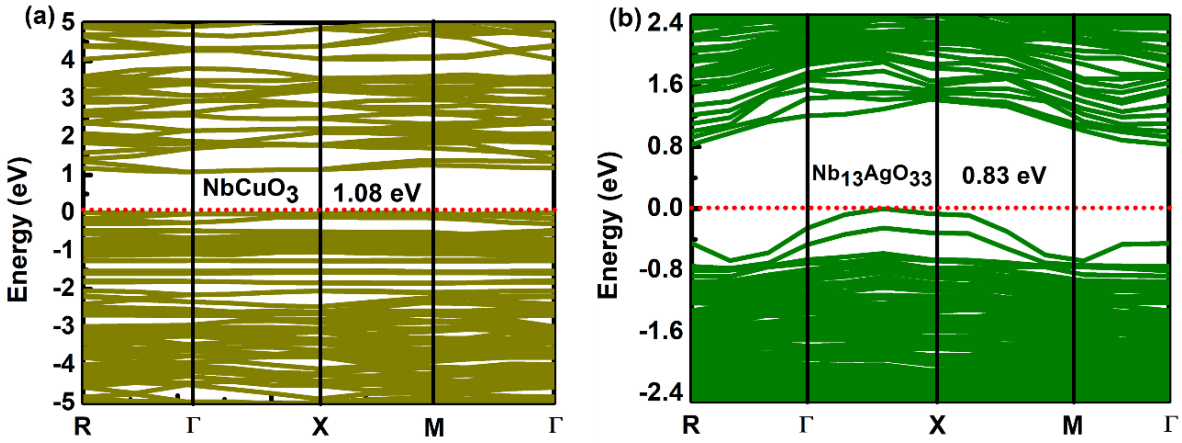

Fig 1: Band structure of (a) $NbCuO_3$ (b) $Nb_{13}AgO_{33}$

Total Density of States (TDOS)

The TDOS analysis provides valuable information regarding the electronic-state distribution around the Fermi level. For $NbCuO_3$, the valence band is mainly occupied below the Fermi level, while the conduction band begins above the band gap, confirming its semiconducting nature. After Ag substitution, the total density of states near the Fermi level increases noticeably. The emergence of additional electronic states decreases the band gap and enhances charge-carrier availability. This increased electronic-state density is expected to improve electrical conductivity and facilitate optical transitions, which is consistent with the observed band-gap reduction.

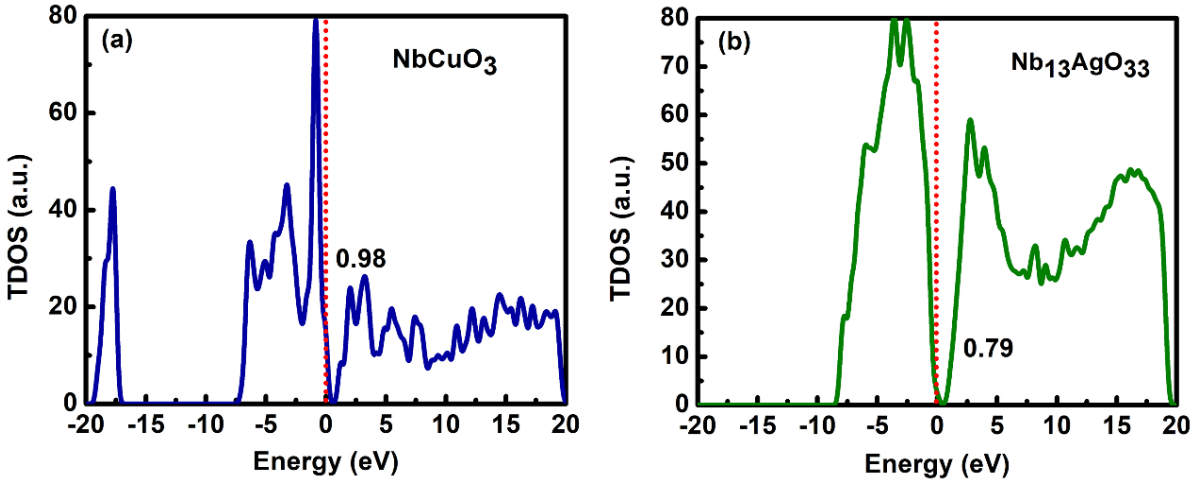

Fig 2: TDOS Lead Free double perovskites compound properties, (a) $NbCuO_3$, (b) $Nb_{13}AgO_{33}$
Partial Density of States (PDOS)

The PDOS analysis reveals the orbital contributions responsible for the electronic structure. The upper valence band is primarily formed by strong hybridization between O-2p orbitals and transition-metal d orbitals. The conduction band is dominated by Nb-4d states, while Cu-d states also contribute to the electronic structure. In $Nb_{13}AgO_{33}$, Ag-derived orbitals introduce additional electronic states near the Fermi level and strengthen hybridization with neighboring atoms. These modifications promote electronic transitions and explain the enhanced optical response observed in the substituted material.

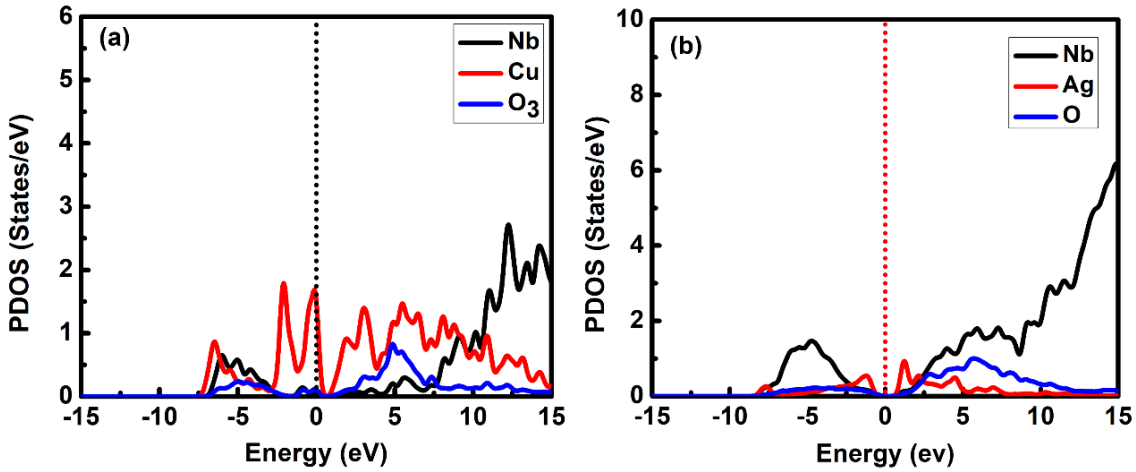

Fig 3: PDOS (a) $NbCuO_3$ (b) $Nb_{13}AgO_{33}$

Elastic Constants

Table: 1

Elastic Properties	$NbCuO_3$	$Nb_{13}AgO_{33}$
C_{11}	10.88	34.38
C_{12}	5.01	3.43
C_{44}	5.54	11.16
Bulk modulus B	6.96	13.74
Shear modulus G	4.28	12.72
Young's modulus E	11.10	29.45
Poisson's ratio ν	0.14	0.23
Pugh's ratio B/G	1.08	1.62
Elastic anisotropy	2.2	0.7

Optical Properties

The optical calculations demonstrate that both compounds possess significant optical activity over a broad photon-energy range. Compared with $NbCuO_3$, $Nb_{13}AgO_{33}$ exhibits stronger optical absorption, particularly in the visible region, owing to its reduced band gap. The dielectric function indicates enhanced polarization after Ag incorporation, reflecting stronger interaction between electromagnetic radiation and the material. Similarly, the optical conductivity increases because of the higher density of available electronic states participating in inter-band transitions. The refractive-index spectra suggest efficient light propagation within the material, while the reflectivity remains moderate, indicating that a substantial portion of incident light can penetrate the crystal. The energy-loss function exhibits characteristic plasmon peaks corresponding to collective oscillations of conduction electrons. Overall, the optical analysis confirms that Ag substitution significantly improves the light-harvesting capability and optoelectronic performance of $NbCuO_3$.

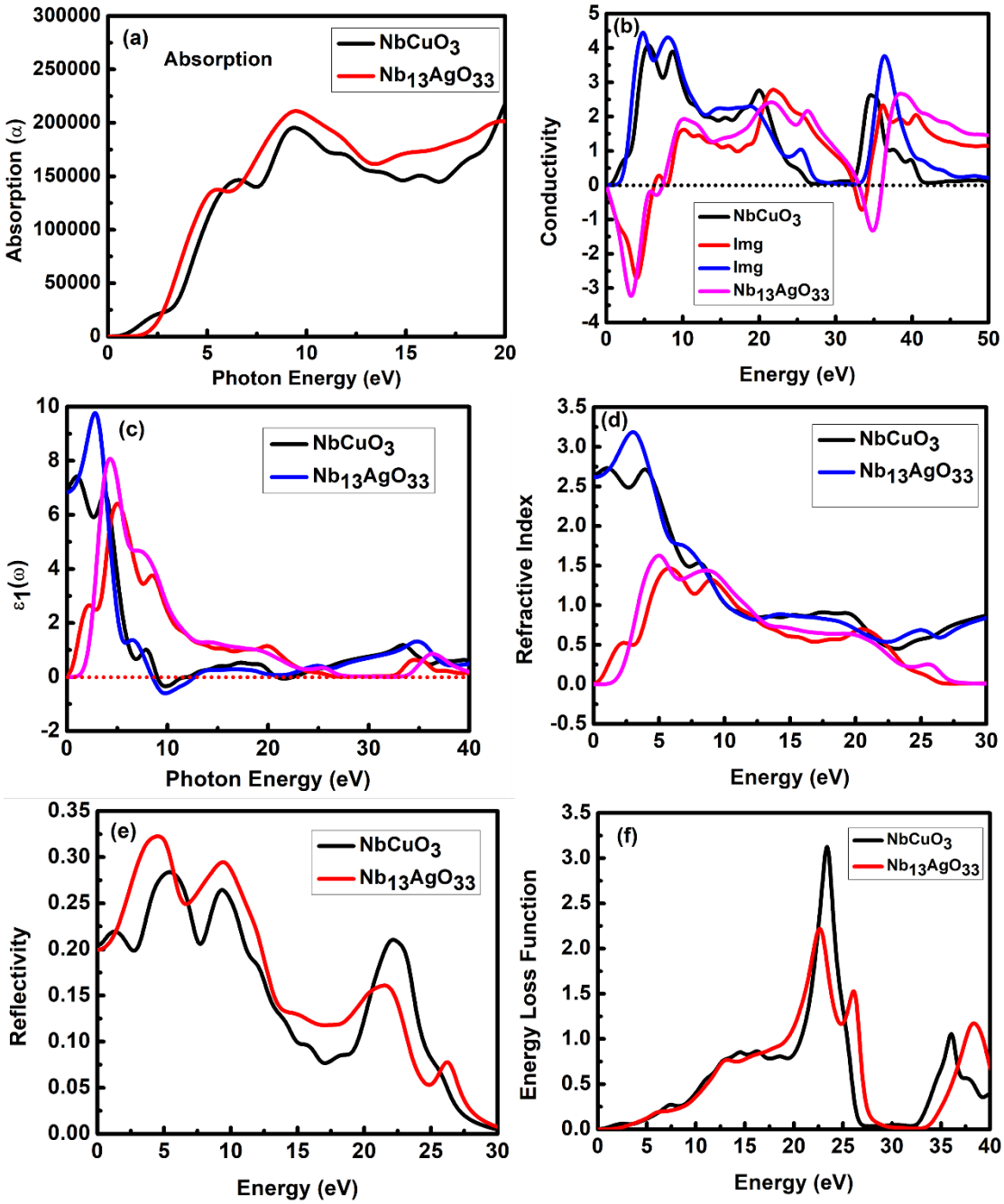

Fig 4. Optical aspects (a) Absorption (b) Optical conductivity (c) Dielectric Function (d) Refractive (e) Reflectivity (f) Loss of $NbCuO_3$ (b) $Nb_{13}AgO_{33}$

Conclusion

A comparative first-principles study of $NbCuO_3$ and Ag-substituted $Nb_{13}AgO_{33}$ demonstrates that Ag incorporation substantially modifies the electronic and optical properties of the host material. The calculated band gap decreases from approximately 1.08 eV for $NbCuO_3$ to approximately 0.83 eV for $Nb_{13}AgO_{33}$, enhancing electronic conductivity and visible-light absorption. The TDOS and PDOS analyses reveal increased electronic-state density and stronger orbital hybridization after Ag substitution. Furthermore, the optical calculations show improved absorption, dielectric response, optical conductivity, and refractive index, highlighting the beneficial effect of Ag on the material's optoelectronic behavior. These results suggest that $Nb_{13}AgO_{33}$ is a promising candidate for applications in photocatalysis, solar-energy conversion, photodetectors, and other optoelectronic devices.

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