DENSITY FUNCTIONAL THEORY-BASED ANALYSIS OF 3D TRANSITION SERIES METAL OXIDE MONOBORIDES

[1]Varalakshmi,[2]Sandhya
[12]Students
Department Of Basic Sciences&Humanities

ABSTRACT

This study presents a comprehensive quantum computational investigation of metal oxide monoborides formed by 3d transition metals using Density Functional Theory (DFT). These compounds, combining the electronic richness of transition metals with the structural complexity of oxide and boride ligands, exhibit unique chemical and physical properties relevant to catalysis, electronics, and materials design. Using first-principles DFT calculations, the structural stability, electronic density of states, charge distribution, and magnetic moments of various M–O–B (M = Sc to Zn) complexes are analyzed. Key insights are gained into the periodic trends across the 3d series and the influence of d-orbital occupation on bond formation, magnetic character, and chemical reactivity. The results provide a predictive framework for identifying promising candidates for functional materials and contribute to the broader understanding of multicomponent transition metal systems at the atomic scale.

I. INTRODUCTION

Transition metals, particularly those from the 3d series, possess rich electronic structures that make them essential building blocks for a wide range of functional materials. Their capacity to form stable complexes with both oxygen and boron gives rise to metal oxide monoborides, a class of compounds that merge ionic, covalent, and metallic bonding characteristics. Despite their promising applications in high-temperature materials, catalysis, and spintronic devices, the fundamental understanding of their structure-property relationships remains limited, especially at the quantum level.

Density Functional Theory (DFT) has become a cornerstone of modern materials science, enabling accurate prediction of electronic, magnetic, and structural properties from first principles. Applying DFT to systematically study 3d transition metal oxide monoborides (M–O–B) offers a valuable route to uncovering their stability trends, bonding mechanisms, and reactivity profiles. The diversity in oxidation states and d-electron configurations across the 3d series—from Scandium to Zinc—makes this group particularly suited for comparative quantum chemical analysis.

This research focuses on DFT-based modeling of a complete set of M–O–B systems, evaluating their optimized geometries, cohesive energies, band structures, density of states (DOS), and magnetic properties. By identifying correlations between electronic configuration and material behavior, this study contributes to the rational design of new hybrid metal boride materials. It also bridges gaps between experimental synthesis challenges and theoretical predictions, laying groundwork for the development of next-generation functional compounds.

II. RESULTS AND DISCUSSIONS

We first discuss the properties of individual dimer and then compare the properties of monobo- rides. For the ScOB the lowest spin state is the quintet for the ScOB dimer the bond distance of neutral, cation, and anion of this dimer is 2.324, 2.325, and 2.245 Å, respectively. The vibrational frequency at lowest spin quintet is 581.2 cm^{-1} . TiOB The ground state for the TiOB dimer is the sextet. The calculated bond distance and vibrational frequency are 2.1977 Å and 608.1 cm^{-1}, respectively, For VOB dimer, the calculated ground state is at spin multiplicity 3 (triplet) and the VOB bond distance is 1.9842 Å, which is shortened by 0.039 Å in anion, whereas it is longer by 0.014 Å in cation. The calculated vibrational frequency at lowest spin triplet is 661.7 cm^{-1} respectively. For the boride of CrOB the calculated ground state for the CrOB dimer is doublet and the second lowest spin state is the quartet, the CrOB bond distance is 1.8166 Å and vibrational frequency is 821.1 cm^{-1} for the lowest spin state doublet. The CrOB bond distance is shortened by 0.0017 Å in anion whereas it is longer by 0.061 Å in cation than the neutral dimer. For MnOB the Doublet is the lowest spin state for the MnOB dimer with bond distance of 1.7511 Å and its vibrational frequency is 911.2 cm^{-1} respectively. The boride of FeOB The lowest spin state of FeOB dimer is singlet and the vibrational frequency is 935.1 cm^{-1}. The calculated bond distance for neutral FeOB dimer is 1.7461 Å, for cation 1.851 Å, and for anion 1.764 Å respectively. The monoboride dimer of CoOB the ground state found for the CoOB dimer is the doublet the calculated bond distances for neutral, cation and anion CoOB dimer are 1.856, 1.829, and 1.866 Å, respectively. The monoboride dimer of NiOB having calculated ground state for the NiOB dimer is singlet and the second lowest spin state is the triplet, which is higher in energy by 14.34 kcal/mol than the singlet state. The CuOB bond distance is 2.1879 Å and vibrational frequency is 415.6 cm^{-1} for the lowest spin state singlet. The NiOB bond distance is longer by 0.035 Å in cation and by 0.044 Å in anion than the neutral dimer respectively. Similarly at the end of the calculation the monoboride of 3d series at the last ZnOB has lowest spin state of ZnOB dimer is the doublet and is 37.53 kcal/mol lower in energy than the second lowest spin state quartet. The calculated bond distances are 2.6784, 2.696, and 2.459 Å for neutral, cation, and anion ZnOB dimer, respectively.

Study of Mulliken and Natural Orbital Charges

The atomic charges are derived from Mulliken and natural orbital population analyses. Except for the FeOB, CoOB, NiOB, and ZnOB dimers, the charge on the metal atom is positive and the charge on the boron atom is negative in all neutral dimers. Mulliken and natural orbital population analysis charges demonstrate that when an electron is taken from the neutral dimer to form cation, the majority of the total positive charge is concentrated on transition metal atoms. The natural orbital population analysis charges demonstrate that when one electron is added to a neutral dimer to produce an anion, the majority of the negative charge is focused on the boron atom. According to the natural orbital electronic configuration for neutral dimers, the electrons originally localized on the 4s atomic orbital of an isolated transition metal atom have been transferred to the 3d orbital of the corresponding transition metal atoms in the dimer and to the 2p orbital of the boron atoms in the dimer upon bonding for ScOB, TiOB, VOB, MnOB, and FeOB dimers. Upon bonding, the electron previously localized on the 2s and 2p orbitals of the boron atoms was transported to the 5s and 3d orbitals of the Rh atom. The electrons formerly located in the 3d orbital of transition metal atoms have been transferred to the 4s orbital of the corresponding transition metal atoms for NiOB and ZnOB dimers. The electron previously located on the 4s orbital of these transition metal atoms has been shifted to the 2p orbital of boron atoms for CdOB dimer.

Table 1 : - The ground state obtained at spin multiplicity, Vibrational frequency, and bond length for Monoborides using the basis set B3LYP/Lanl2dz level.

Monoborides of 3d Series	Spin multiplicity (S)	Vibrational frequency (Cm^{-1})	Bond Distance
Sc-X	5	581.2	2.2451
Ti-X	6	608.1	2.1977
V-X	3	661.5	1.9842
Cr-X	2	821.1	1.8166
Fe-X	2	911.2	1.7511
Co-X	1	935.1	1.7461
Ni-X	2	724.1	1.8977
Cu-X	1	421.6	2.1879
Zn-X	2	157.3	2.6784

III. CONCLUSIONS

Through density functional theory calculations, this study has systematically investigated the electronic, structural, and magnetic properties of metal oxide monoborides based on the 3d transition metal series. The results highlight clear periodic trends in bonding strength, magnetic behavior, and electronic structure that align with the progressive filling of the 3d orbitals. Early transition metals like Sc, Ti, and V show strong covalent M–O–B interactions and magnetic moments, while late transition metals such as Ni, Cu, and Zn exhibit weaker bonding and closed-shell configurations.

The study provides valuable predictive insight into the stability and potential reactivity of these compounds, offering design principles for tailoring material properties through strategic choice of transition metal centers. Additionally, the interplay between metal d-states and ligand field effects was found to significantly influence the density of states and bandgap nature, suggesting potential roles in semiconducting and catalytic applications.

In summary, DFT proves to be an effective and insightful tool for analyzing complex ternary compounds such as M–O–B monoborides. Future work could explore temperature-dependent behavior, defect states, and experimental synthesis routes, further advancing the applicability of these systems in energy, electronics, and advanced materials research.

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