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Article

Electronic Structure and Magnetic Properties of 4d and 5d Transition Metal Halide Lead-Free Perovskites for Possible Spintronic Applications

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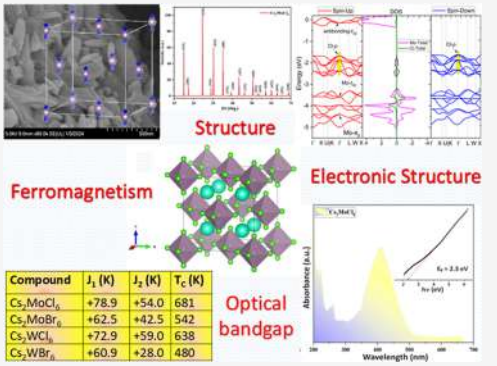
ABSTRACT: The present report aims at the detailed investigation of structural dynamics, ferromagnetism, and band profiles of cesium−molybdenum (Cs_2MoX_6) and cesium−tungsten (Cs_2WX_6)-based halide perovskites, where X = Cl and Br. A ferromagnetic ground state originates from the only 4d-states of Molybdenum and 5d-states of tungsten in both the cases, respectively. The relaxed lattice systems provide the precise atomic arrangements in agreement with the previous experimental data. Experimentally, Cs_2MoCl_6 and Cs_2WCl_6 exhibit cubic structures with semiconducting properties, while Cs_2MoBr_6 and Cs_2WBr_6 are assumed for comparison only. Present calculations of elastic constants predict these systems as stable, and positive phonon modes ensure the dynamic stability as well, where all the optical modes are similar to a considerable difference in low phonon manifolds having mixed optical and acoustic characteristics. Contrary to the previous theoretical studies on Cs_2MoCl_6, the spin-polarized HSE06 calculations decide the spin-up semiconducting nature of all these isostructural systems with a maximum gap in (Mo/W)Br compared to their Cl counterparts. Ferromagnetic exchange interactions between magnetic atoms via nonmagnetic halogen atoms constitute a total spin magnetic moment $\mu \sim 2.0\ \mu B$ for each material, where a transition metal atom only contributes the magnetic moment to the whole unit cell. The magnetic moment is primarily contributed by the transition metal atoms, and the compounds display high Curie temperatures (T_C) ranging from 480 to 681 K. The magnetic properties confirm a second-order phase transition, with the derivative of magnetization (dM/dT) revealing sharp variations at T_C. Magnetocaloric properties show a linear dependence of magnetic entropy change and relative cooling power on external magnetic fields. These findings highlight the potential of Cs_2Mo/WX_6 compounds for spintronic, optoelectronic, and energy-efficient magnetic refrigeration applications.



INTRODUCTION

Electronic structure and magnetism of transition metal systems are generally described by the spin-degree of freedom, where the d-orbital angular momentum is quenched by the crystal field splitting, and such spin-only predictions are rationally accurate for 3d-species only.[1−3] Spin, charge, and orbit couplings or both fall within the quantum domain of effects hence shape the striking electronic and magnetic situations/states in the 3d/4d/5d transition metal compounds.[4−6] Probing synthesis-related issues, chemical or strain tuning, and structure-dependent property characterization of these compounds is inevitable and increasingly a thrust area in view of both fundamental research and application-related outlooks. Nevertheless, these phenomenal states are extremely sensitive to the structural orientations and bonding strengths of the host materials.[7] For example, the orbital effects in 4d and 5d species are even more substantial as the crystal field splitting Δ_0 is enhanced significantly; therefore, the valence electrons in 3d/5d systems entirely adopt a low-spin configuration. Consequently, additional factors including octahedral distortion-induced splitting of the t_{2g} states and spin−orbit coupling play a fundamental role in determining the electronic ground state.[7,8] Hence, a thorough study on the mixing of t_{2g} and e_g d-orbital states induced by the interaction or coupling of spin−orbit in a cubic environment, mostly common in transition metal oxides, needs to be undertaken carefully.

Lead-free perovskite halides are key materials for optoelectronic, bioimagining, sensors, and long-wave communication applications due to their adjustable band gaps, near-infrared (NIR) region emission, and maximum forbearance of defects, as well as atomic configuration-dependent transport behavior.[9,10] Being luminescent, these perovskite materials exhibit

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