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Title of the Ph.D. Thesis: Study of perovskites and their derivatives for spintronics, optoelectronic and thermoelectric device applications.

Findings

This research work establishes a predictive framework for designing lead-free multifunctional materials that integrate spintronic stability, thermoelectric efficiency, and optoelectronic response within a single crystal platform. It demonstrates that halide double perovskites, vacancy-ordered derivatives, and transition-metal antiperovskites form a tunable materials class where exchange interactions, orbital hybridization, and lattice anharmonicity are co-engineered to couple electronic and thermal functionalities. All systems are studied using first-principles density functional theory within the full-potential linearized augmented plane wave method, employing GGA for structural optimization and HSE06/mBJ for electronic refinement. Thermoelectric transport is evaluated *via* Boltzmann theory, lattice dynamics through density functional perturbation theory, and thermodynamic properties within the quasi-harmonic Debye model. Negative formation enthalpies, low convex-hull energies, mechanically stable elastic tensors, and phonon spectra without imaginary modes confirm overall thermodynamic, mechanical, and dynamical stability.

In A_2CuMCl_6 , structural and thermodynamic stability is attained through negative decomposition enthalpies and low convex-hull energies, supported by mechanically stable elastic constants satisfying cubic Born criteria. Electronic structure via HSE06 calculations reveal indirect band gaps of 1.24 eV ($K_2CuSbCl_6$), 1.22 eV ($Rb_2CuSbCl_6$), 1.53 eV ($K_2CuBiCl_6$), and 1.50 eV ($Rb_2CuBiCl_6$). Electron effective masses range from 0.16 to 0.22 m_0 and hole masses from 0.25 to 0.29 m_0 . Longitudinal optical phonon frequencies are 157.86, 145.13, 165.23, and 154.32 cm^{-1} , with static dielectric constants between 3.64 and 4.71 and electron–phonon coupling constants α_e between 3.71 and 4.02, indicating intermediate Fröhlich coupling and large-polaron transport. At 300 K, Seebeck coefficients reach 2100, 2000, 2900, and 2600 $\mu V K^{-1}$, while lattice thermal conductivity remains low at 0.21–0.25 $W m^{-1} K^{-1}$. The

thermoelectric figure of merit attains 1.05 in $\text{K}_2\text{CuBiCl}_6$. Optical absorption coefficients are of the order of 10^4 cm^{-1} in the visible region.

The halide double perovskites $\text{Cs}_2\text{AgMBr}_6$ and $\text{Rb}_2\text{GeMBr}_6$ ($\text{M} = \text{V}, \text{Mn}, \text{Ni}$) exhibit robust magnetic ordering in the cubic $\text{Fm}\bar{3}\text{m}$ phase, with formation enthalpies of -1.22 to -1.58 eV and convex-hull energies as low as 0.0005 eV per atom. Young's moduli range from 21.05 to 35.41 GPa , while Debye temperatures of 273 – 285 K and Grüneisen parameters up to 2.49 indicate moderate lattice anharmonicity. GGA+mBJ calculations reveal ferromagnetic semiconducting behavior in $\text{Rb}_2\text{GeMBr}_6$ with spin-resolved gaps of $2.20/3.30 \text{ eV}$ (GeV), $1.92/2.95 \text{ eV}$ (GeMn), and $1.85/1.54 \text{ eV}$ (GeNi), alongside pronounced exchange splitting. In contrast, $\text{Cs}_2\text{AgMBr}_6$ compounds are intrinsically half-metallic with half-metallic gaps of 2.13 eV (AgV), 2.85 eV (AgMn), and 1.92 eV (AgNi), supported by strong crystal-field splitting and exchange interactions ($N_0\alpha$ down to -0.80 eV). Spin-up electron effective masses lie between 0.28 – $0.69 m_0$, while hole masses reach up to $1.95 m_0$, generating favorable carrier asymmetry. Integer magnetic moments of 2.00 – $4.00 \mu_B$ (Cs -series) and 3.00 – $5.00 \mu_B$ (Rb -series) are obtained. Mean-field Curie temperatures reach 658.44 K in $\text{Cs}_2\text{AgMnBr}_6$ and 680.23 K in $\text{Rb}_2\text{GeMnBr}_6$, confirming stable high-temperature ferromagnetism combined with half-metallic or spin-resolved semiconducting electronic structures.

Transition-metal antiperovskites A_3XN (Co_3CuN , Co_3ZnN , Fe_3CuN) crystallize in the cubic $\text{Pm}\bar{3}\text{m}$ structure and exhibit bulk moduli up to 205.76 GPa and Debye temperatures up to 935 K . Magnetic moments are $4.37 \mu_B$, $3.70 \mu_B$, and $7.61 \mu_B$, with Curie temperatures of 942.48 K , 692.7 K , and 1400.41 K . Spin polarization at the Fermi level reaches -20% in Fe_3CuN . At 300 K , Seebeck coefficients range from 15 to $25 \mu\text{V K}^{-1}$, electrical conductivity per relaxation time approaches $7.55 \times 10^{20} \Omega^{-1}\text{m}^{-1} \text{ s}^{-1}$, and zT reaches 0.041 in Co_3ZnN . Optical spectra display Drude-type metallic response. Vacancy-ordered perovskites Rb_2VCl_6 and K_2PtBr_6 show formation energies of -1.86 and -1.63 eV per atom and convex-hull energies of 0.0001 and 0.002 eV . Rb_2VCl_6 is a half-metallic ferromagnet with a spin-down gap of 2.59 eV and magnetic moment of $1.00 \mu_B$, while K_2PtBr_6 is a direct-gap semiconductor with $E_g = 1.29 \text{ eV}$. At 300 K , Seebeck coefficients reach 2200 and $2100 \mu\text{V K}^{-1}$, lattice thermal conductivity is 0.22 and $0.34 \text{ W m}^{-1} \text{ K}^{-1}$, and zT approaches unity. Optical absorption coefficients remain of the order of 10^4 cm^{-1} in the visible range. Overall, the results reveal that exchange splitting stabilizes magnetism, orbital hybridization controls electronic behavior, and lattice anharmonicity suppresses heat transport, enabling the design of sustainable materials that combine high-temperature ferromagnetism, strong spin polarization, and efficient thermoelectric and optoelectronic performance within a single platform.