Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting information

Spin exchange, electronic correlation, and thermoelectric transport in Rb_2GeMBr_6 (M = V, Mn, Ni) halide double perovskites from first principles calculations

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I. Phase stability diagrams

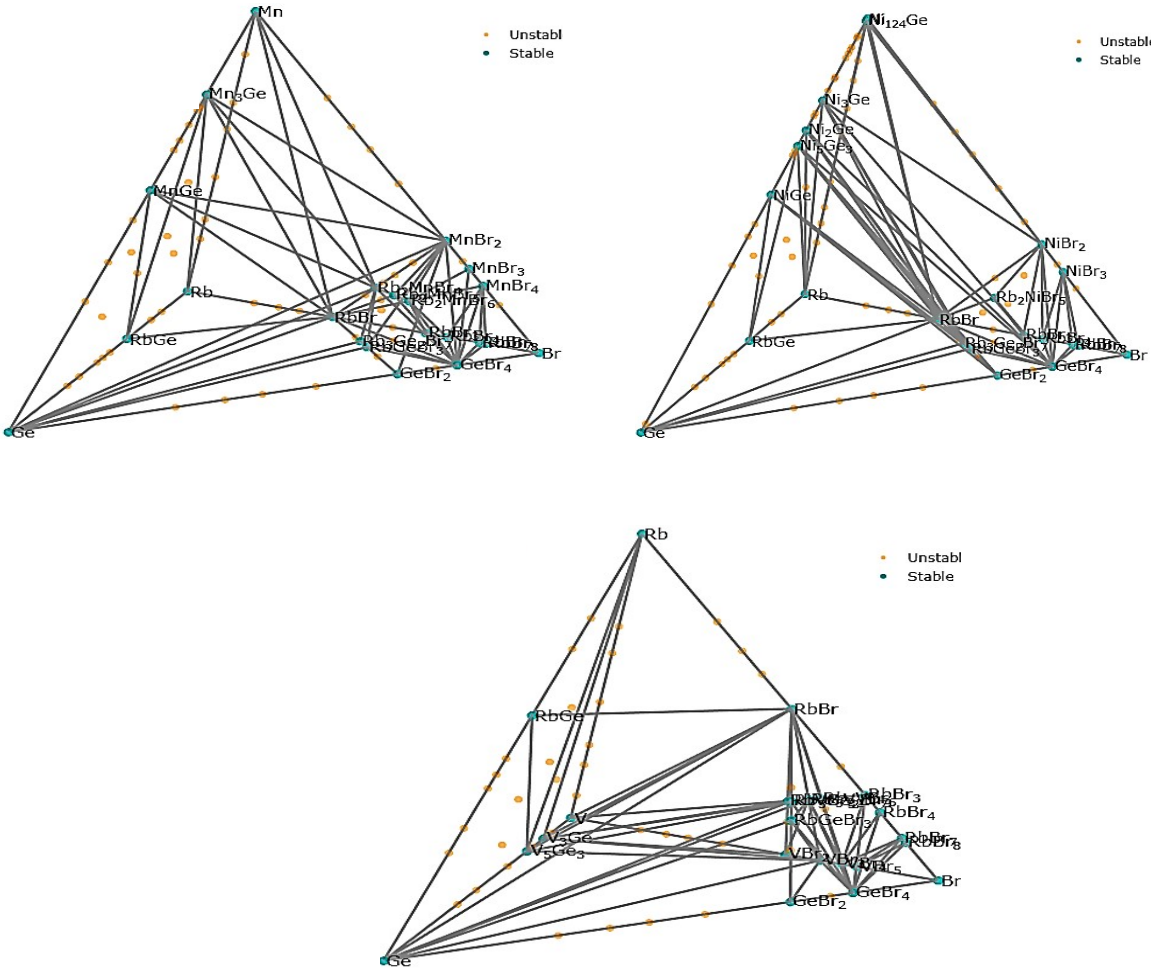

Figure S1. Phase stability diagrams of Rb_2GeMBr_6 (M = V, Mn, Ni) halide double perovskites, illustrating the thermodynamic equilibrium regions of stable compounds in the Rb-Ge-M-Br quaternary system.

The phase stability diagrams presented in **Figure S1** provide a detailed thermodynamic map of the compositional conditions necessary for the stable formation of Rb_2GeMBr_6 (M = V, Mn, Ni) halide double perovskites. Constructed using calculated chemical potentials and Gibbs free energy minimization, these triangular compositional diagrams delineate the equilibrium regions where each compound can coexist with its elemental and binary phases, offering a precise understanding of their thermodynamic stability. For Rb_2GeVBr_6, the stability region is defined by a clear phase boundary, surrounded by competing phases such as VBr_2, $GeBr_4$, and RbBr. This well-defined domain indicates the optimal chemical potential range for vanadium, ensuring the selective formation of the desired Rb_2GeVBr_6 phase while minimizing the risk of impurity phases. The robustness of this stability window is crucial for controlled synthesis, where slight deviations in chemical potential could result in the formation of undesirable byproducts. In the case of $Rb_2GeMnBr_6$, the phase stability diagram reveals a more complex landscape. The coexistence with $MnBr_2$ and other germanium halide species highlights the sensitivity of Mn-based perovskite stability to variations in chemical potential. The sharp phase boundaries reflect the delicate balance required to maintain the pure $Rb_2GeMnBr_6$ phase, where slight fluctuations in Mn or Br content can destabilize the desired structure. This sensitivity underscores the importance of precise compositional control during synthesis. The phase stability of $Rb_2GeNiBr_6$ is characterized by a relatively narrow stability region, tightly constrained by phase coexistence with $NiBr_2$, $GeBr_4$, and RbBr. This limited stability window emphasizes the need for precise chemical potential control to synthesize the pure Ni-based perovskite phase without contamination. The narrow region also suggests that $Rb_2GeNiBr_6$ is more susceptible to phase competition, requiring careful adjustment of reaction conditions for successful synthesis. Collectively, these phase stability diagrams are invaluable for guiding experimental synthesis of Rb_2GeMBr_6 perovskites. They provide a clear understanding of the chemical environments favorable for the formation of the target phases while avoiding the emergence of competing impurities.

II. Elastic properties

Table S1. Mechanical properties of Rb_2GeMBr_6 (M = V, Mn, Ni) double perovskites determined using Voigt, Reuss, and Hill averaging schemes.

Compound	Averaging	Bulk modulus (K) (GPa)	Young's modulus (E) (GPa)	Shear modulus (G) (GPa)	Poisson's ratio (v)
Rb_2GeVBr_6	Voigt	24.573	38.790	15.680	0.23691
	Reuss	24.573	36.356	14.503	0.25342
	Hill	24.573	37.581	15.091	0.24511
$Rb_2GeMnBr_6$	Voigt	24.050	37.292	15.018	0.24157
	Reuss	24.050	36.565	14.666	0.24661
	Hill	24.050	36.929	14.842	0.24408
$Rb_2GeNiBr_6$	Voigt	25.050	39.161	15.798	0.23944
	Reuss	25.050	38.812	15.628	0.24177
	Hill	25.050	38.987	15.713	0.24061

Table S1 summarizes the calculated elastic constants of Rb_2GeMBr_6 (M = V, Mn, Ni) double perovskites obtained using Voigt, Reuss, and Hill averaging schemes. All compounds exhibit comparable bulk moduli (≈ 24–25 GPa), moderate Young's moduli (≈ 36–39 GPa), and shear moduli (≈ 14–16 GPa), indicating their mechanically soft yet stable nature. The Poisson's ratios *(v* ≈ 0.24–0.25) suggest predominant central interatomic forces and ductile mechanical behavior. Overall, the consistency between Voigt and Reuss bounds confirms the mechanical stability and elastic isotropy of these compounds.