Supplementary Information

Scrutinizing the Stability and Exploring the Dependence of Thermoelectric Properties on Band Structure of *3d* Metal-Based Double Perovskites: An *ab-initio* Analysis

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Methods

The linearized augmented plane-wave basis set with $l_{max} = 10$ and $R_{MT}K_{max} = 7$ (here R_{MT} is the radius of the smallest sphere and K_{max} represent maximum *k*-value) has been used. The integrals over the Brillouin zone (BZ) are evaluated by dividing BZ into a dense *k*-mesh of 1000 integration points crucial for the convergence of the results. The iterations for solving the K-S are allowed till the charge for successive cycles converges up to 0.0001e order and energy up to 0.0001Ry, respectively.

The onsite Coulomb repulsion in transition metal-based materials is strong enough to localize the electrons. However, GGA parameterization does not precisely define the exchange potential and therefore does not predict the required splitting of d-states for such alloys. The GGA needs to be supported to explain the electronic structure and magnetic properties more sophisticatedly. There are several alternatives like the inclusion of Hubbard (U_{eff} = U-J) or mBJ potentials to GGA or even hybrid functions can be used as a replacement to GGA. Here, we have used the used GGA+mBJ scheme to define electronic properties more efficiently. The choice of choosing mBJ over other alternatives is that it is a facile and purely *ab-initio* technique working very well for systems with d-electrons. The unit cell volume is shared among muffin tin spheres surrounding the motif (with radii R_{MT}) and interstitial space. The Seebeck (S), electrical conductivity (σ) and electronic thermal conductivity (κ_e) coefficients can be evaluated by using relation relations;

$$S = \frac{ek_B}{\sigma}\int\left(-\frac{\partial f_0}{\partial \varepsilon}\right)\frac{\varepsilon-\mu}{k_BT}\Xi(\varepsilon)d\varepsilon$$

$$\sigma = e^2\int\left(-\frac{\partial f_0}{\partial \varepsilon}\right)\Xi(\varepsilon)d\varepsilon$$

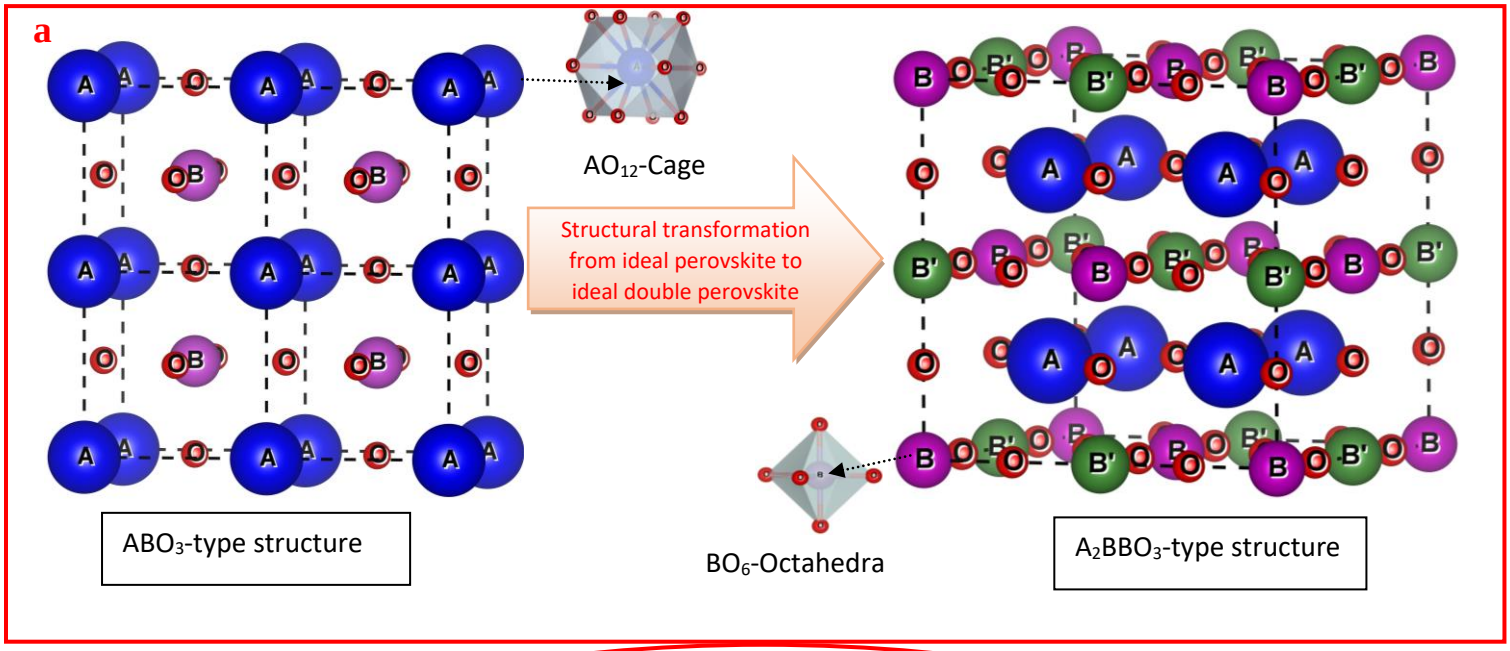
,

$$\kappa_e = k_B{}^2 T \int \left(-\frac{\partial f_0}{\partial \varepsilon} \right) \left(\frac{\varepsilon - \mu}{k_B T} \right)^2 \Xi(\varepsilon) d\varepsilon$$

.

Here, $\Xi(\varepsilon)$ is a transport distribution function given by $\Xi^{\alpha,\beta}(\varepsilon) = \sum_k \delta(\varepsilon - \varepsilon_k) v_k^{\alpha} v_k^{\beta} \tau_k$ where, v_k^{α} depict α^{th} component of the group velocity having wave vector *k*. the K-mesh was increased to 100000-k points to have better output.

Structural Properties



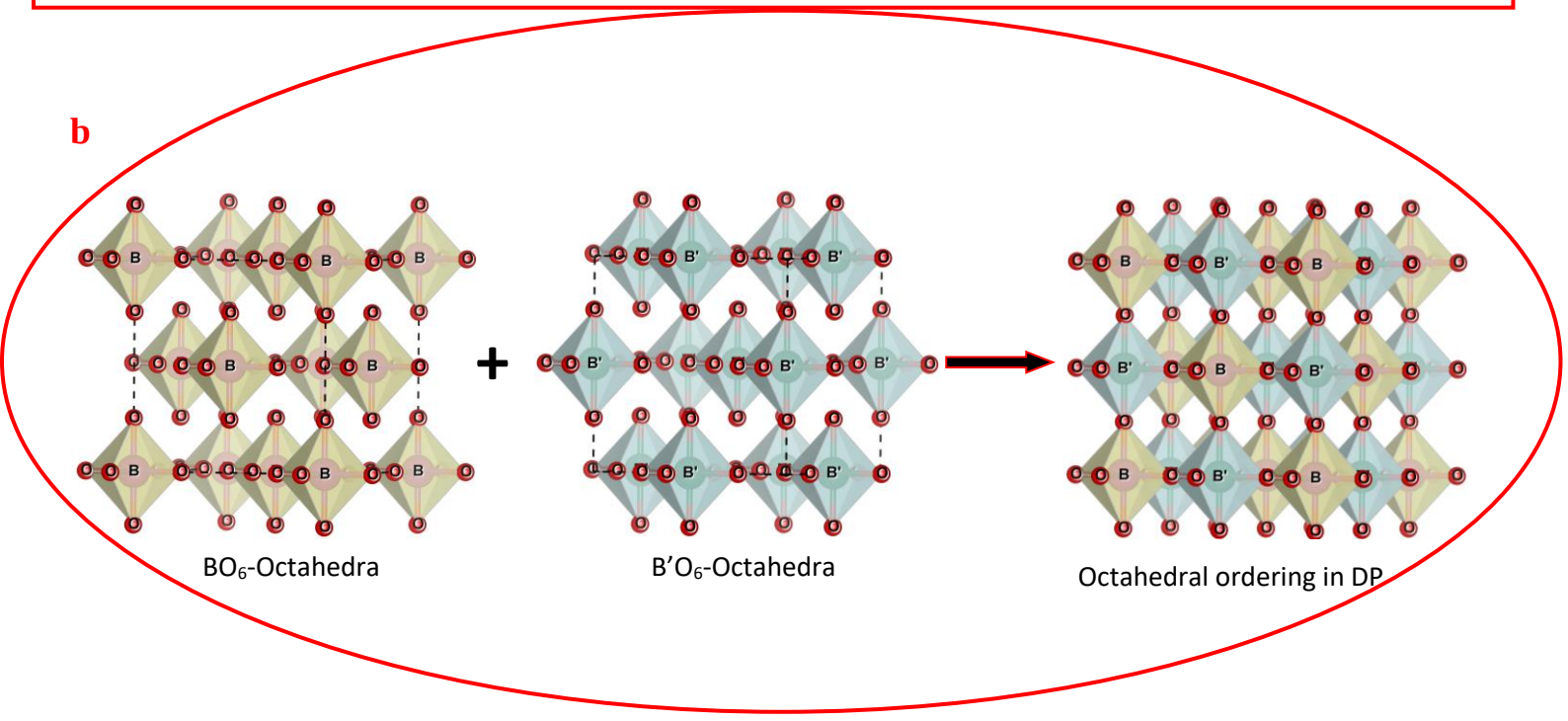


Fig. S1: (a) Ideal crystal structure of simple perovskites and double perovskites within the structure B (B') is filled inside the octahedra and A-is surrounded by 12-oxygen atoms. (b) The crystal structure of $A_2BB'O_6$ is composed of two ordered sub-structure BO_6 and $B'O_6$ extending over 3D with A-occupying inter-octahedral voids.

Thermodynamic Properties

The Grüneisen parameter (γ) and Debye temperature variations are to measure the anharmonicity in the crystal. The plot is shown in **Fig. S2(b)** with temperature suggests that anharmonicity increases with the temperature although the variation is sluggish. The atomic vibrations increase vigorously with temperature due to which γ-parameter also increases. Debye temperature (θ_D) is one of the important thermo-elastic parameters of solids. It is a good indicator of the hardness; materials with high θ_D exhibit high are comparatively rigid over materials with low θ_D. The θ_D as a function of temperature is shown in **Fig. S2(c)**, it is clear that θ_D decrease with temperature. At the low temperature the thermal expansion, as well as anharmonicity, is small resulting in almost constant Debye temperature. Even the high-frequency modes can be considered to be frozen at low temperatures. The high value of Debye temperature suggests the perovskites can be used even at higher temperatures for application purposes.

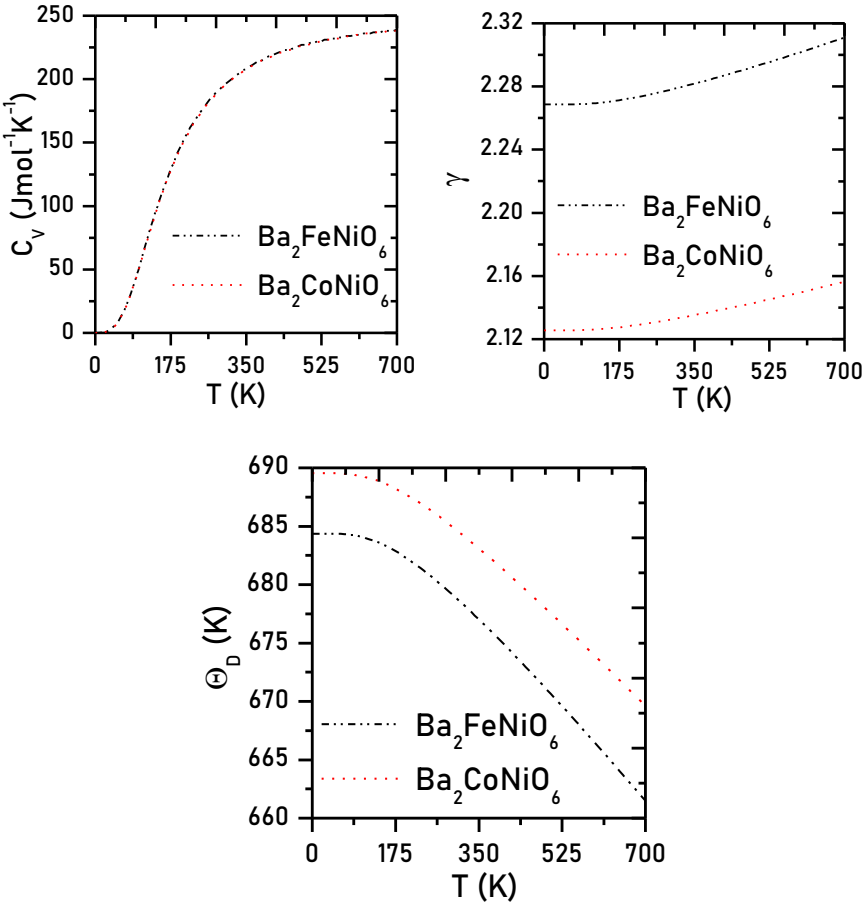


Fig. S2: Variation in thermodynamic properties with temperature (a) Specific heat at constant volume; (b) Grüneisen parameter; and (c) Debye temperature

Electronic Properties

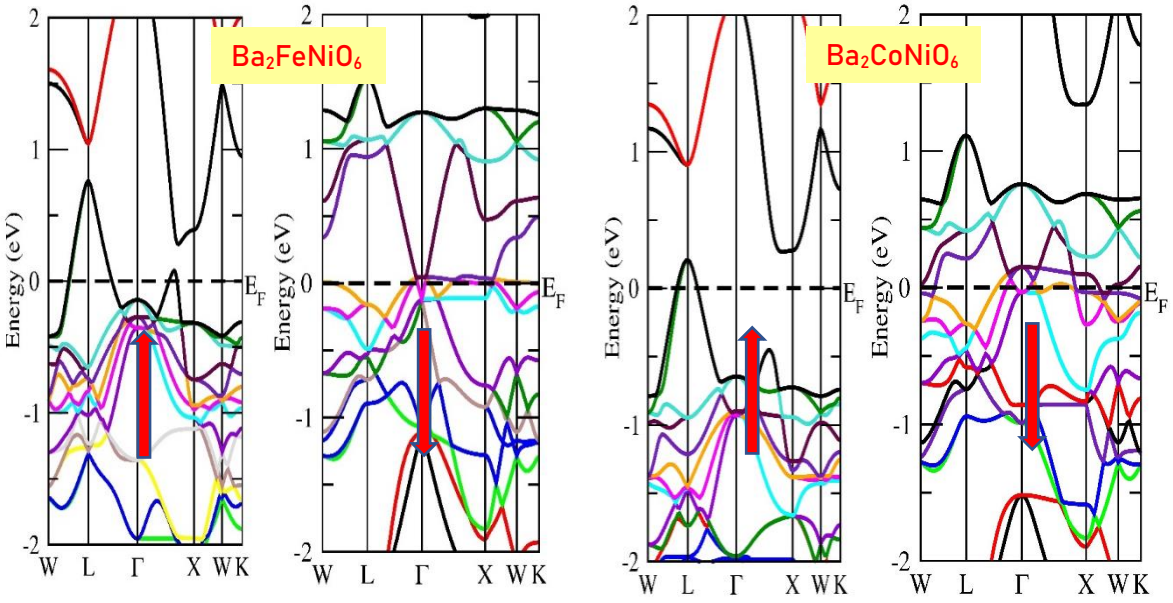


Fig. S3: Band Structure of Ba_2MNiO_6 computed by applying GGA approximation passing of Fermi level in-between of bands reflects metallic character (the arrows are used to designate spin channels).

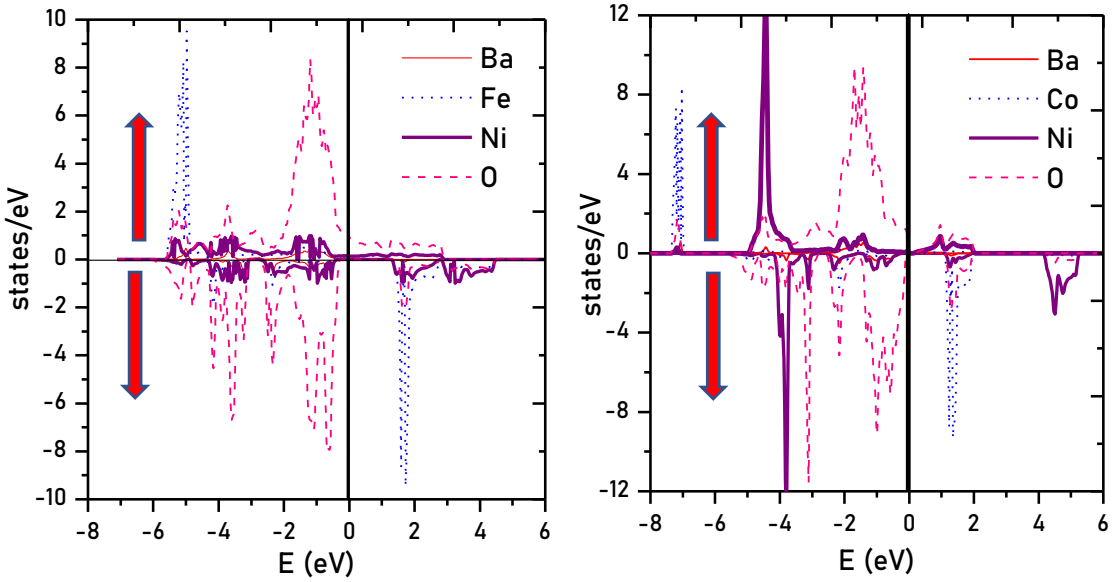


Fig. S4: Atomic states contribution towards band formation; The transition-metal d-states with O-p states are more prominent in characterizing the electronic bandstructure

Thermoelectric Properties

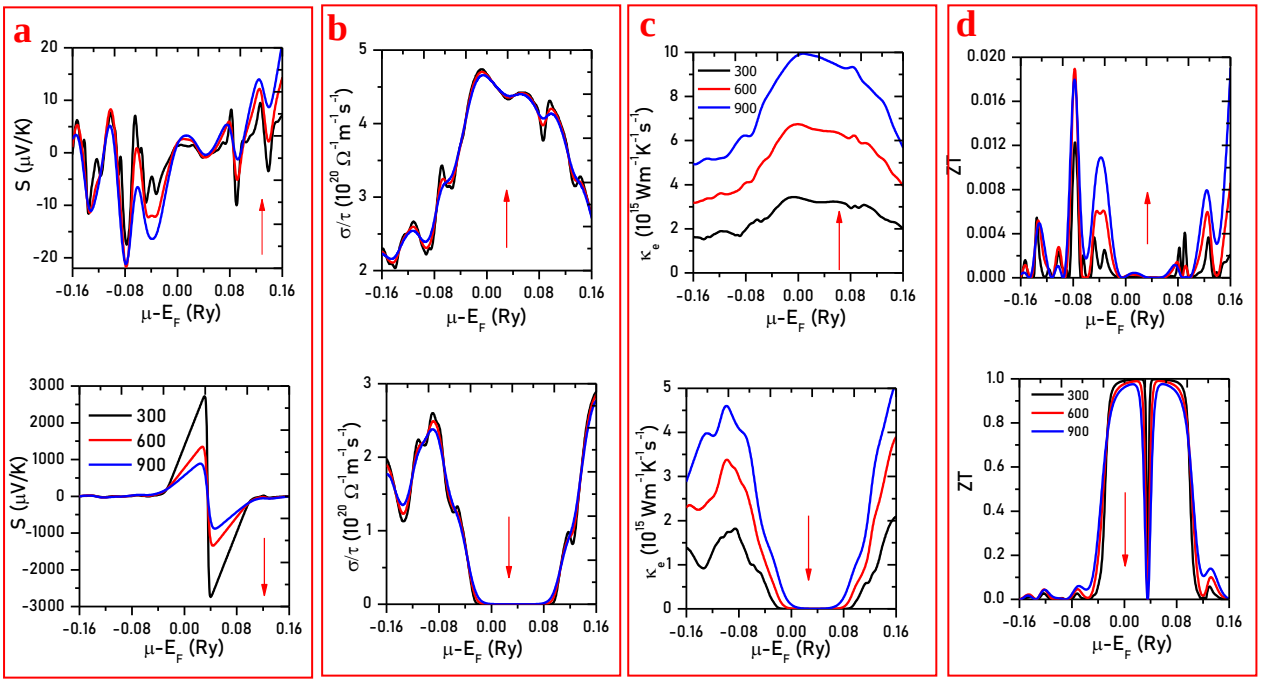


Fig. S5: The variation in the designated thermoelectric parameters (a) Seebeck coefficient; (b) Electrical conductivity; (c) Thermal conductivity; (d) Figure of merit of Ba_2FeNiO_6. (Arrows are used to represent spin up and spin down channels; different colors for the line are used to distinguish temperature Black-300K, Red-600K, and Blue-900K)

The drastic variation in the transport properties from spin up to spin down channel is expected due to metallic behavior in the spin-up channel and the semiconducting nature in the spin-down channel. The figure of merit (ZT) varies inversely with thermal conductivity. Due to the metallic nature of the spin-up channel, the thermal conductivity is high thereby ZT is very low. However, in the spin-down channel, there is vanishing thermal conductivity around the Fermi level, which overturns the ZT ~1. However, the total thermal conductivity, as well as electrical conductivity, is the sum of two channels, due to which the metallic channel remains more dominant in characterizing the overall thermoelectric behavior of the materials.

Ba_2CoNiO_6 is a ferromagnetic semiconductor with a small bandgap in the spin-up channel compared to spin down the channel. The e_g-states of transition metals are filled in spin up-channel lie beneath fermi level gives rise to a small bandgap. However, due to the semiconducting nature, the thermal conductivity is low compared to the Fe-based counter partner **Fig. S6**. Because of that ZT in both spin channels as well as total ZT turns to be very high. However, with the rise in temperature bands smear give a metallic effect in the spin channel, so ZT decreases drastically.

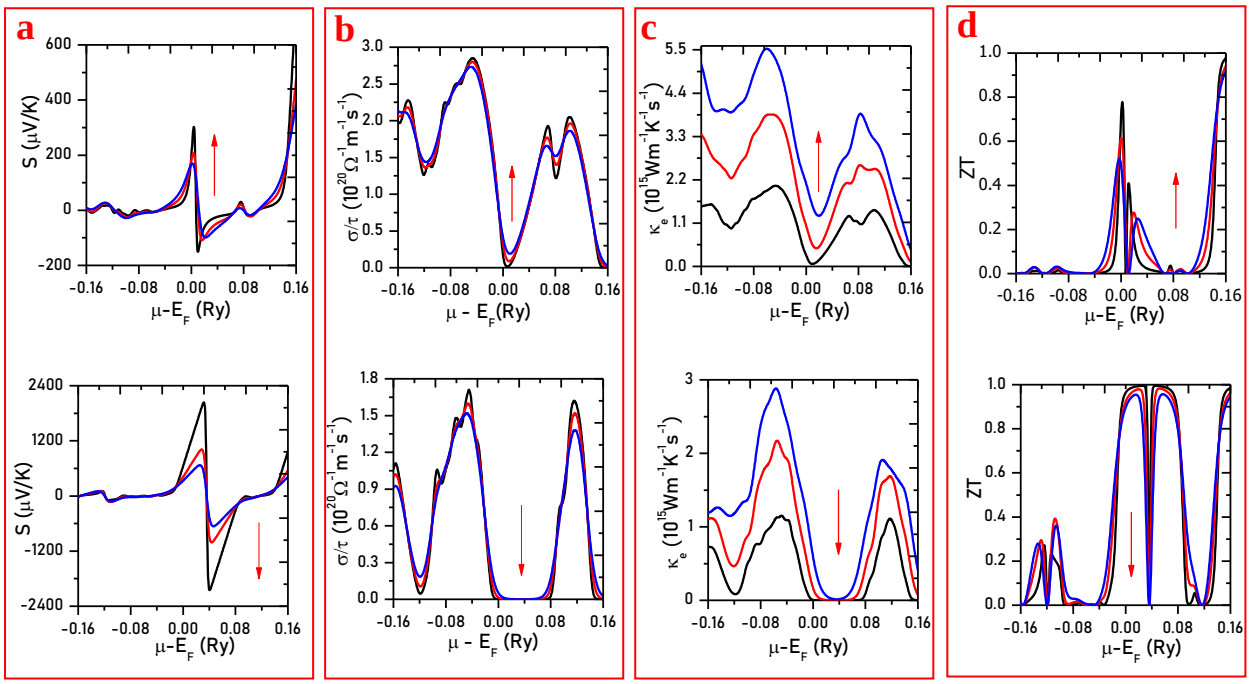


Fig. S6: The variation in the designated thermoelectric parameters (a) Seebeck coefficient; (b) Electrical conductivity; (c) Thermal conductivity; (d) Figure of merit of Ba_2CoNiO_6. (Arrows are used to represent spin up and spin down channels; different colors for the line are used to distinguish temperature Black-300K, Red-600K, and Blue-900K)