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Mobility Driven Thermoelectric and Optical Properties of Two-Dimensional Halide-based Hybrid Perovskites: Impact of Organic Cation Rotation

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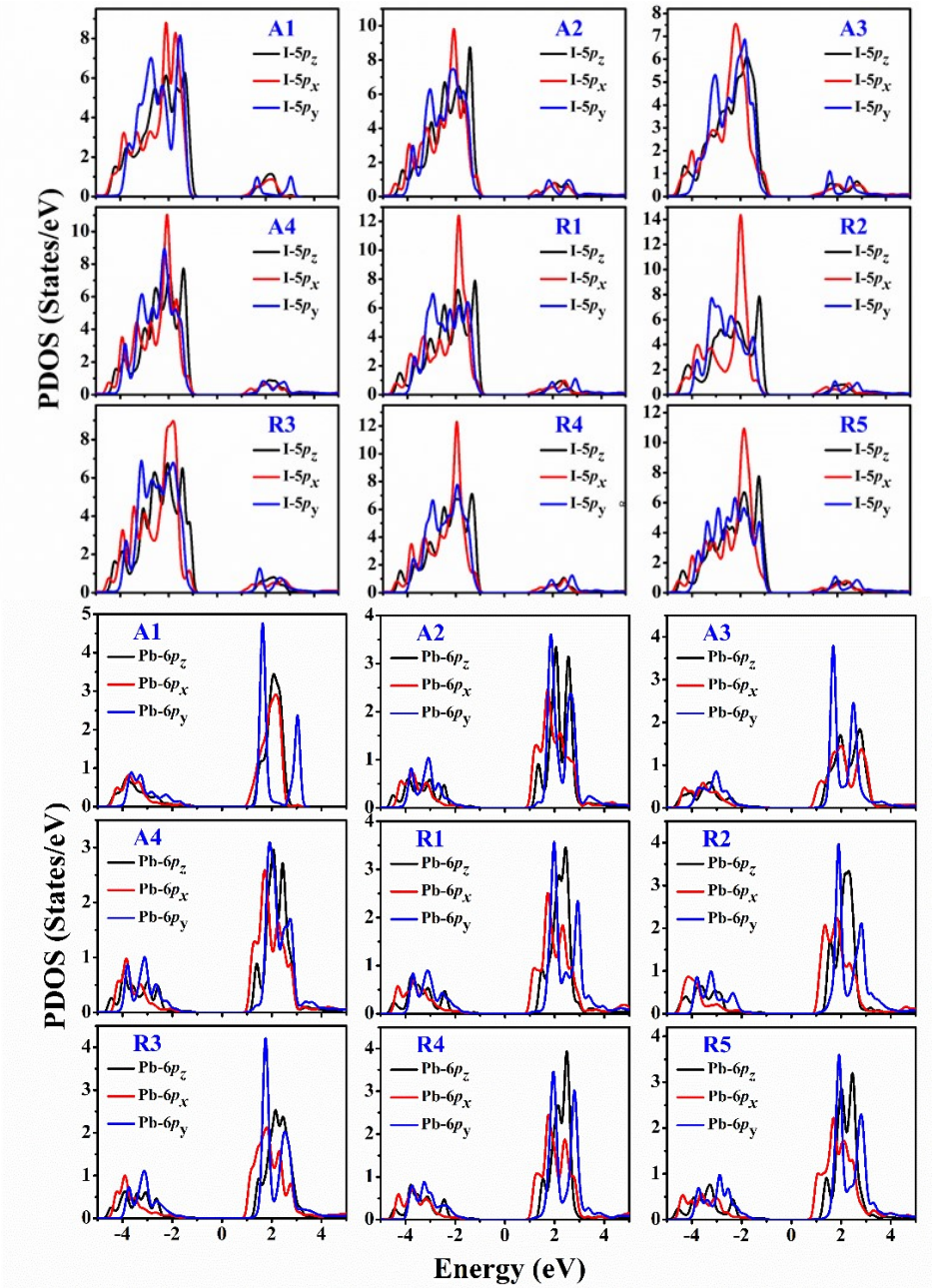

Figure S1. Projected density of states (PDOS) with the projection of I-5(p_x, p_y and p_z) and Pb-6(p_x, p_y and p_z) orbitals for each MA cation rotation in Pb-I network. Fermi level located at 0 eV.

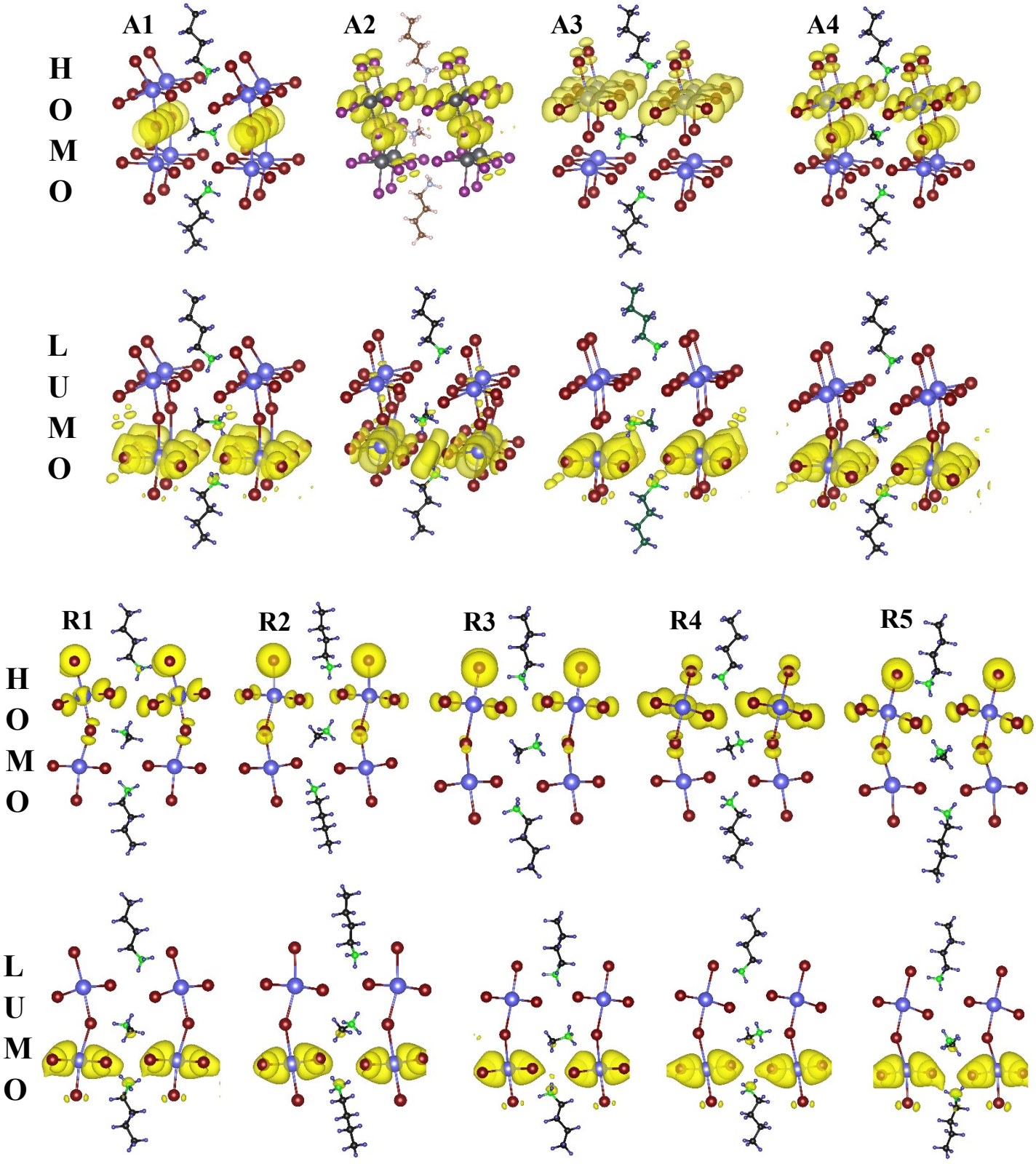

Figure S2. Charge density iso-surfaces (for HOMO and LUMO level) (without SOC) with MA cation rotation.

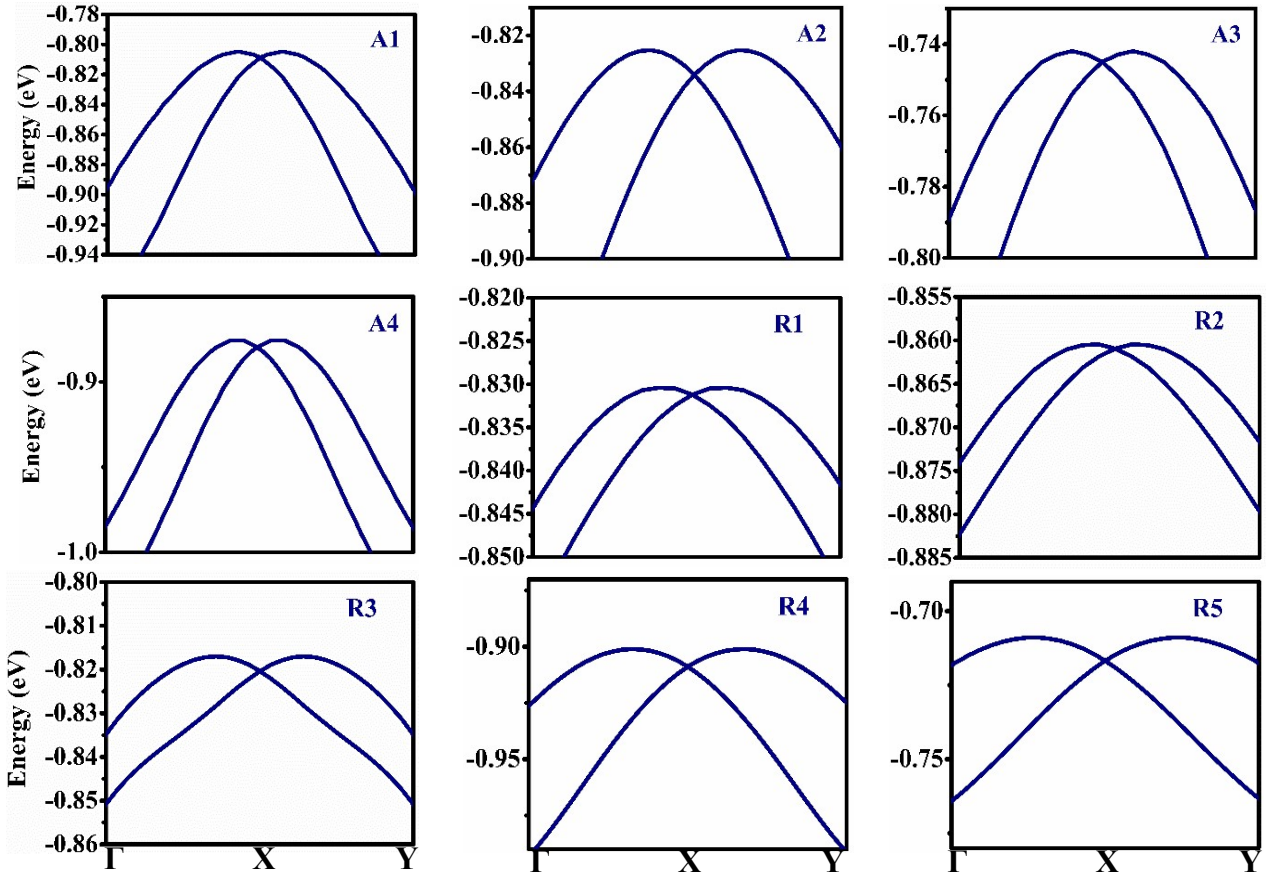

Figure S3. Part of the valence band structure (along the **Γ-X-Y** high symmetry direction of BZ for A1-A4 and R1-R5 structures) calculated with spin-orbit coupling (SOC) effects for visualization of Rashba splitting with the rotation of MA cation.

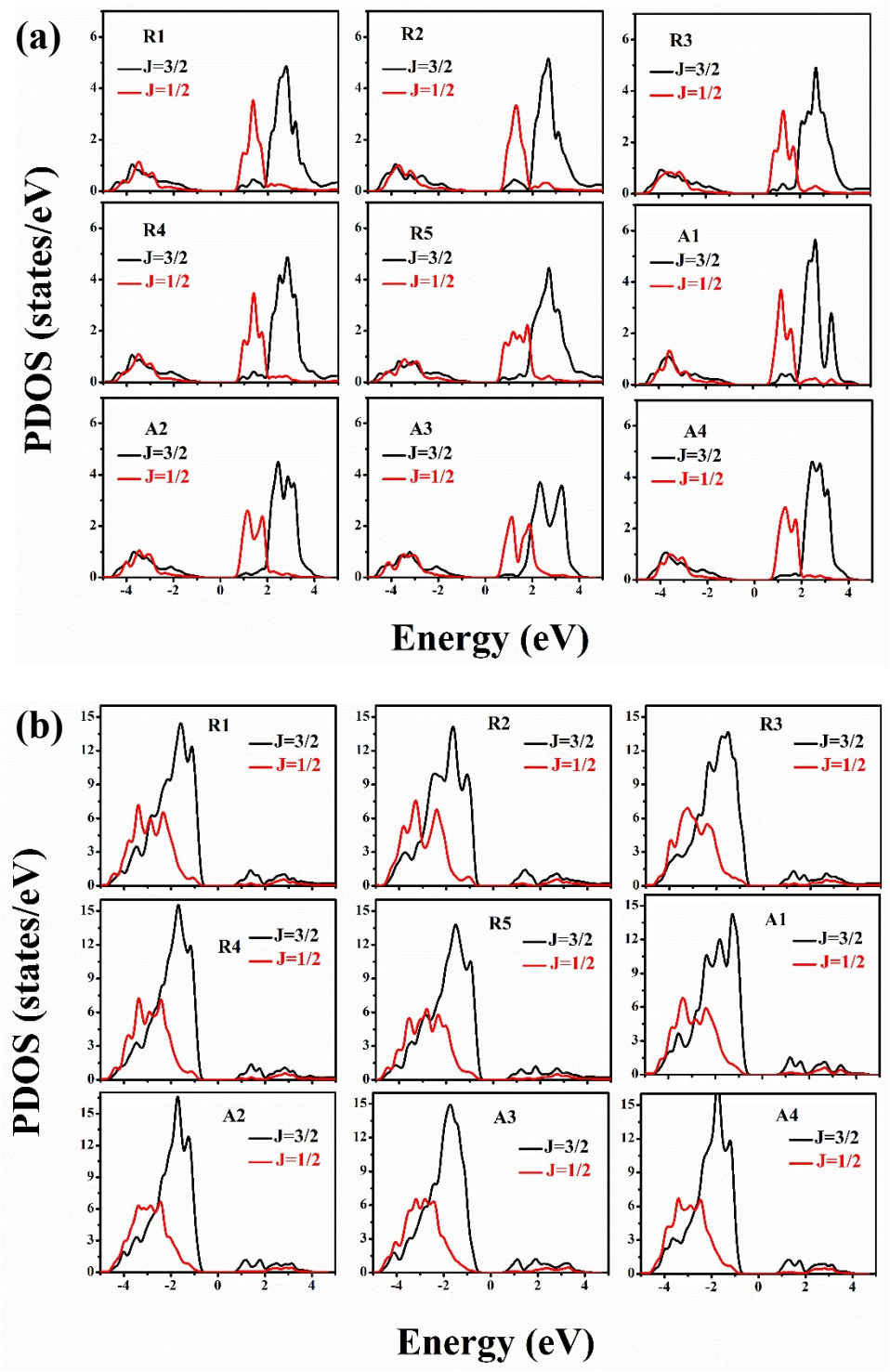

Figure S4. SOC-Projected density of states (PDOS) (a) Pb-6p and (b) I-5p orbitals including spin orbit coupling effects for A1-A4 structures (symmetric rotation of MA cation) and R1-R5 (Random rotation of MA cation). Fermi level located at 0 eV.

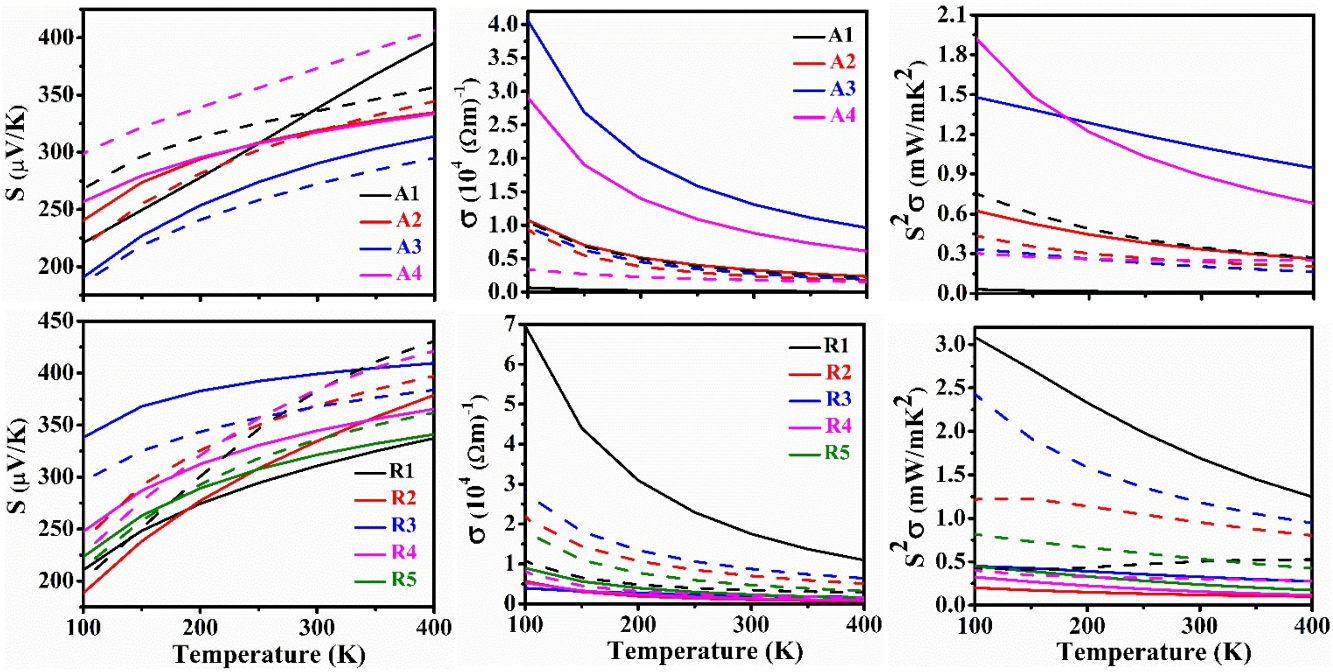

Figure S5. Anisotropic transport coefficients (for holes) Seebeck coefficients (S), electrical conductivity (σ) and thermoelectric power factor ($S^2\sigma$) for rotation A1-A4 (upper panel) and R1-R5 (lower panel) respectively. Here solid and dashed lines determine the respective transport properties along x and z-axis of structure, respectively.

The electrical conductivity and Seebeck coefficients have been calculated using BoltzTrap code through following expressions[1,2]:

$$S_{\alpha\beta}(\varepsilon, T, \mu_c) = \frac{\int_{-\infty}^{\infty} g(\varepsilon)(\varepsilon - \mu_c)\left[\frac{-\partial f(T,\ \varepsilon, \mu_c)}{\partial \varepsilon}\right] d\varepsilon}{T\int_{-\infty}^{\infty} g(\varepsilon)\left[\frac{-\partial f(T, \varepsilon, \mu_c)}{\partial \varepsilon}\right] d\varepsilon} \quad (1)$$

$$\sigma_{\alpha\beta} = \frac{1}{\Omega}\int \sigma_{\alpha\beta}(\varepsilon)\left[-\frac{\partial f_{\mu_c}(T;\varepsilon)}{\partial \varepsilon}\right]\partial\varepsilon \quad (2)$$

Where $\sigma_{\alpha\beta}(\varepsilon_{i,k}) = e^2\tau_{i,k}v_\alpha(i,k)v_\beta(i,k)$, while $g(\varepsilon)$ determines the transport function. Here, $\varepsilon_{i,k}$ represents the band energy for i^{th} band at k wavevector. α and β are the components of the conductivity tensor, while μ_c, T and Ω depicts the chemical potential, temperature and volume of cell.

References

1. D. Parker and D. J. Singh, Thermoelectric Properties of $AgGaTe_2$ and Related Chalcopyrite Structure Materials. Phys. Rev. B., (2012) **85,** 125209.

2. G. K. H. Madsen and D. J. Singh, BoltzTraP: A Code for Calculating Band-Structure Dependent Quantities. *Comput. Phys. Commun.* 2006, **175,** 67−71.