

Computationally Guided Design and Experimental Synthesis of p-Type High-Entropy Perovskite Oxides for High-Temperature Thermoelectric Applications

Muhammad Saad Ur Rahman¹, Peter Tatarko¹

¹Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovak Republic

High-entropy perovskite oxides (HEPOs) are emerging as promising thermoelectric materials for high-temperature waste-heat recovery (800–1500 K). Their compositional disorder, particularly on the B-site, is expected to suppress lattice thermal conductivity through enhanced phonon scattering while retaining considerable flexibility for tuning electronic transport properties. Identifying viable p-type compositions within this materials family remains challenging, as the B-site chemistry must simultaneously provide appropriate carrier generation and a suitable electronic band structure.

In this work, density functional theory and Boltzmann transport modelling were used to screen a broad range of A- and B-site chemistries. Initial candidates combining Ca-, La-, or Sr-containing A-sites with Cr, Fe, Co, Ni, and Mn on the B-site showed key limitations: strong 3d orbital overlap led to metallic behaviour, Fe³⁺-related polaron trapping was worsened by A-site size mismatch in Ca²⁺-containing systems, and Co³⁺ oxidation-state ambiguity narrowed the band gap and promoted early bipolar conduction. As full lattice thermal conductivity calculations are computationally demanding, screening was instead based on the predicted power factor, with detailed thermal conductivity and ZT calculations reserved for the most promising compositions. This approach identified La_{0.5}Sr_{0.5}(Ti,Zr,Sn,Mn,Ni)O₃ as the best-performing candidate, in which closed-shell d⁰ cations (Ti⁴⁺, Zr⁴⁺, Sn⁴⁺) maintain a semiconducting band structure while Mn/Ni mixed-valence pairs generate p-type carriers through oxidation-state changes, giving the most favourable predicted power factor trend across 800–1200 K.

Based on these results, the selected composition was synthesized experimentally via solid-state calcination, high-energy ball milling, and Spark Plasma Sintering (SPS) to obtain dense ceramic pellets. Preliminary XRD data indicate formation of a predominantly single-phase cubic perovskite after sintering. Ongoing optimisation focuses on sintering conditions to maximise densification and phase purity while ensuring reproducibility. X-ray photoelectron spectroscopy (XPS) is being employed to further verify the oxidation states of the constituent cations. Comprehensive thermoelectric characterisation (Seebeck coefficient, electrical conductivity, and thermal conductivity) will subsequently be performed on the optimised dense ceramics.