

Low Thermal Conductivity and Enhanced Charge Transport in Nb⁵⁺-Substituted High-Entropy Perovskite Ceramics

Asif Ali¹, Monika Tatarková¹, Vladimir V. Srdić², Nikola Kanas³, Ondrej Hanzel¹, Peter Tatarko¹

¹*Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dubravská cesta 9, 845 36 Bratislava, Slovakia*

²*Department of Materials Engineering, Faculty of Technology Novi Sad, University of Novi Sad, Bul. Cara Lazara 1, 21000, Novi Sad, Serbia*

³*TEGMATICA Ltd, Karlovacki drum 32, 23300, Kikinda, Serbia*

ABSTRACT

Novel stabilized high-entropy perovskite oxides, $\text{Sr}_{0.25}\text{Ba}_{0.25}\text{Ca}_{0.25}\text{La}_{0.25}\text{Ti}_{1-x}\text{Nb}_x\text{O}_3$, with varying Nb⁵⁺ concentrations were synthesized via the conventional solid-state route and sintered using field-assisted sintering technology at temperatures ranging from 1200 to 1400 °C. The compositions were rationally designed based on theoretical predictions considering the tolerance factor, polarizability, electronegativity, configurational entropy, and global instability index (GII*) calculated using the Structure Prediction Diagnostic Software (SPuDS). X-ray diffraction analysis confirmed the formation of a single-phase cubic perovskite structure with the $\text{Pm}\bar{3}\text{m}$ space group. Scanning electron microscopy and energy-dispersive X-ray spectroscopy revealed dense microstructures with relative densities exceeding 95% and confirmed the compositional homogeneity of the sintered ceramics. Fourier-transform infrared spectroscopy further confirmed the formation of metal–oxygen bonds characteristic of the perovskite structure. UV–visible diffuse reflectance measurements revealed a gradual increase in the optical band gap with increasing Nb⁵⁺ concentration. The high configurational entropy and Nb⁵⁺ substitution significantly influenced the thermoelectric properties of the ceramics. All compositions exhibited large negative Seebeck coefficients, confirming their n-type semiconducting behavior. Furthermore, the ceramics demonstrated low thermal diffusivity ($<1 \text{ mm}^2 \text{ s}^{-1}$), low thermal conductivity ($<3 \text{ W m}^{-1} \text{ K}^{-1}$), and moderate electrical conductivity, reaching 1.26 S cm^{-1} for $x = 0.05$. The combination of these transport properties resulted in an enhanced dimensionless thermoelectric figure of merit, with a maximum ZT of 0.06 for $x = 0.05$. These results demonstrate a compositional design strategy for stabilizing high-entropy perovskite oxides while suppressing thermal transport and improving their thermoelectric performance.