# (P-4.38) EFFECTS OF CATION SIZE ON TRANSPORT PROPERTIES AND OXYGEN NONSTOICHIOMETRY OF $Ln_{0.5}A_{0.5}FeO_{3-\delta}$ (Ln = La-Sm, A = Sr, Ba)

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Ferrite-based mixed conductors with perovskite structure exhibit an attractive combination of transport properties and stability, and are hence considered for numerous electrochemical applications, such as dense ceramic membranes and SOFC cathodes. The present work is focused on the comparative analysis of oxygen nonstoichiometry, ionic transport and electronic conductivity in perovskite-type $Ln_{0.5}A_{0.5}FeO_{3-\delta}$ (Ln = La-Sm; A = Sr, Ba). Increasing the difference of $Ln^{3+}$ and $A^{2+}$ cation radii results in higher δ and lower ionic and *p*-type electronic conductivities. These trends are attributed to lattice strains, which promote $Fe^{4+}$ localization, decrease the average metal-oxygen bonding strength, and induce clustering of acceptor-type dopant cations and oxygen vacancies. No correlations with tolerance factors, lattice symmetry and unit cell volume were identified. The relationships between the anion transport and cation size mismatch remain essentially similar in air and under reducing conditions when most iron becomes trivalent, thus confirming critical influence of vacancy trapping. At low temperatures, analogous correlation is also observed for quadrupole splittings derived from the Mössbauer spectra of stoichiometric $Ln_{0.5}A_{0.5}FeO_3$. Contrary to the ionic conductivity variations, the role of surface exchange as a permeation-limiting factor tends to decrease on $Ba^{2+}$ doping and on decreasing $Ln^{3+}$ size, again correlating with the lattice strains. The *n*-type electronic conduction and low-$p(O_2)$ stability of the perovskite-like phases at 1223 K are substantially unaffected by the cation radius mismatch.

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