A COMPARATIVE ANALYSIS OF OXYGEN VACANCY DIFFUSION IN LSCF AND BSCF PEROVSKITE SOLID SOLUTIONS: *AB INITIO* MODELING

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Complex ABO_3-type perovskite solid solutions with oxygen deficiency exhibit a perceptible ionic conductivity, leading to their promising use as electrolytes $((La,Sr)(Ga,Mg)O_{3-\delta})$, oxygen permeation membranes, and solid oxide fuel cell (SOFC) cathodes $((La,Sr,Ba)(Mn,Fe,Co)O_{3-\delta})$. Oxygen stoichiometry strongly affects transport properties of the materials, which, in turn, defines suitability of the material for targeted applications.

The oxygen migration in those perovskites occurs via the vacancy mechanism in which the vacancy moves through a bottleneck formed by the "critical triangle" of one *B* site cation and two *A* site cations. In addition to their influence on bulk transport properties, the concentration and mobility of oxygen vacancies are two major factors determining the surface oxygen incorporation rate. Although oxygen vacancies are being extensively studied in perovskites, our understanding of their effects on behavior of the materials and the corresponding performance of practical devices is far from complete.

By using first principles parallel GGA-level calculations (VASP computer code) combined with large (40-320 atoms) supercells, we simulated migration of oxygen vacancies in $(La,Sr)(Co,Fe)O_{3-\delta}$ (LSCF) and $(Ba,Sr)(Co,Fe)O_{3-\delta}$ (BSCF) perovskites. The atomic relaxation, charge redistribution, migration barrier, and the structure of transition states for oxygen ion migration are obtained. We explore differences between BSCF perovskites [1,2], which exhibit considerably lower migration barriers for oxygen than other perovskites, and LSCF [3]. We discuss relevant implications for the oxygen surface and bulk reaction and hence for energy conversion in practical devices, first of all SOFC [4-6].

References
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