

CRYSTAL STRUCTURE AND PHASE TRANSITIONS OF THE PEROVSKITE-LIKE RARE-EARTH COMPLEX OXIDES

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The high-temperature behavior of the lanthanum and praseodymium complex oxides was established using XRD analysis. The calculations of the configurational entropy and fixation factor of the entropy-stabilized materials were performed.

Solid Oxide Fuel Cells (SOFCs) are a more efficient and environmentally friendly way to produce energy than burning natural fossil fuels [1]. The main problem with existing SOFCs is their high operating temperature range, which results in high operating costs and rapid degradation. Reducing the operating range has led to a reduction in the electrochemical activity of the electrode materials, with the cathode material being the main contributor to the increase in polarization resistance [2]. Therefore, there is a strong need to develop new cathode materials with improved electrochemical performance. Complex oxides with the perovskite structure $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ [3] and the perovskite-like Ruddlesden-Popper structure $\text{Ln}_2\text{NiO}_{4+\delta}$ (Ln = rare-earth element) [4] are the main candidates for the design of new materials with enhance functional properties. Especially, it is actual with the using of medium- and high-entropy doping strategy [5].

In the present study the synthesis of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8-y}\text{Mn}_y\text{O}_{3-\delta}$ at $0.0 \leq y \leq 0.8$ (LSCFM), $\text{La}_{1.7}\text{Ca}_{0.3}\text{Ni}_{1-y}\text{Cu}_y\text{O}_{4+\delta}$ at $0.0 \leq y \leq 0.4$ (LCNCO), $\text{Pr}_{1.6}\text{Ca}_{0.4}\text{Ni}_{1-y}\text{Cu}_y\text{O}_{4+\delta}$ at $0.0 \leq y \leq 0.4$ (PCNCO) samples was carried out by a pyrolysis of organic-salt compositions. The powder samples were heated in air in three stages, with a final annealing temperature of 1000 °C. The powders synthesized were X-ray tested at room temperature and at temperatures up to 1100 °C.

Calculations of the configurational entropy (or S_{mix}) for the studied compounds have shown that the LSCFM series has the values of S_{conf} in the range of $0.8 \leq S_{\text{conf}} \leq 1.05$, LCNCO and PCNCO have the values of S_{conf} in the range of $0.32 \leq S_{\text{conf}} \leq 0.67$. Thus, the LSCFM complex oxides can be considered as medium-entropy materials, the LCNCO and PCNCO complex oxides as the low-entropy oxides. Calculations of the fixation factor of the entropy-stabilized material, δ , have demonstrated, that all LSCFM oxides met the requirements up to the maximum value δ of 6 %.

XRD analysis indicated that the samples obtained were single-phase. Refinement of the crystal structure using a Rietveld full-profile method showed that LSCFM had a rhombohedral structure and was described within space group R-3c, LCNCO had a tetragonal syngony with space group I4/mmm, PCNCO had an orthorhombic structure with space group Bmab. It was found, that the LSCFM solid solutions converged by phase transition with temperature increasing to a cubic structure (Pm3m), and PCNCO

to a tetragonal structure (I4/mmm). No high-temperature phase transition was observed for LCNCO.

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