We have studied the structure and conductivity of perovskite-type La_{0.8}Sr_{0.2}Ca_{0.5}Mg_{0.5}O_{3-δ}, the new, superior oxygen ion conductor (1, 2) for use as electrolyte in high temperature solid oxide fuel cells. Since the transport properties of substitutionally disordered and oxygen deficient materials are largely determined by their local structure, which may differ in symmetry from the average long range crystalline symmetry, we studied the local and average structures of La_{0.8}Sr_{0.2}Ca_{0.5}Mg_{0.5}O_{3-δ} using powder neutron and electron diffraction and high resolution lattice imaging in TEM. Despite the macroscopic cubic symmetry revealed by neutron powder diffraction, La_{0.8}Sr_{0.2}Ca_{0.5}Mg_{0.5}O_{3-δ} exhibits a lower symmetry short range order evidenced by, firstly, weak and sharp superstructure reflections and, secondly, streaks of diffuse scattering in the electron diffraction pattern. Neutron powder profile refinement shows that the oxygen nuclei are displaced from the sites of cubic symmetry in a manner similar to that in perovskite-related layered structure of brownmillerite. Thermal stability of the local structures was studied by high temperature electron microscopy and will be discussed in relation with the conductivity measurements. Modeling of the oxygen mobility was performed using the bond valence method (3).

References

Pyrochlore oxides can exhibit high ionic conductivity or high electronic conductivity or both. They therefore have potential as Solid Oxide Fuel Cell (SOFC) materials. For the electrolyte materials of the SOFC a high ionic and a low electronic conductivity is a necessity while the cathodes require a mixed ionic and electronic conductivity. Service of the same structure in both functions would avoid materials compatibility problems.

The pyrochlore structure, A_2B_2O_7, is a superstructure of the fluorite type, (A,B)_2O_3, having twice the lattice parameter a=2a_f , spacegroup Fd3m. It was earlier suggested that the ratio r_A/r_B of the larger A cation and the smaller B cation is the governing parameter for the order in these systems. The pyrochlore structure can exhibit mainly two types of disorder: anti-site disorder of the cations and a Frenkellike disorder on the oxygen-ion array. Neutron Rietveld analyses of the Y_2(Zr_{1.5}Ti_{0.5})_2O_7 (Y2ZT) system have shown that substitution of zirconium for the smaller titanium ions causes disordering of both the cation and anion arrays to a non-stoichiometric fluorite-type structure. As a consequence, the ionic conductivity increases. However, for a similar series of compounds, Y_2(Sn_{1.5}Ti_{0.5})_2O_7, where Y is chosen to match the average radius of the B site in the Y2ZT series, no disordering is observed. Although the cations partially disorder for the end member Y_2SnO_3, no anion disorder is observed. A parameter very sensitive to the degree of disorder seems to be the positional coordinate (r=0.375) of the oxygen occupying the 48f position, which in a completely disordered structure becomes 0.357. The effect of the change in the state of disorder with composition has been used to interpret the variation in measurements of ionic conductivity obtained through impedance spectroscopy.

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