

Defect Formation and Thermal Expansion of Perovskites on the Basis of LaCrO_3 for Solid Oxide Fuel Cells (SOFC)

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LaCrO_3 base perovskites are of interest as ceramic interconnect materials for the development of Solid Oxide Fuel Cells (SOFCs). The interconnects are exposed to oxidising and reducing atmospheres under operating conditions.

By annealing in reducing atmosphere the LaCrO_3 base perovskites loose oxygen and form oxygen vacancies. The charge neutrality is maintained by changes in the valence state. The change in valence and the change of oxygen vacancy concentration in reducing environments leads to volume expansion, which can result in residual stresses in the interconnects of SOFCs under operating conditions. However, it should be noted that compositional changes allow to suppress at least to a certain extent the volume expansion.

The main goal of the work is to determine the oxygen vacancy formation and to provide a better understanding of the structural changes in LaCrO_3 base perovskites related with a reduction of oxygen partial pressure. In this respect, also the correlation between defect formation and isothermal volume expansion is elaborated. The compositions shown in Table 1 are investigated.

Oxygen vacancy formation in nine LaCrO_3 base perovskites of different composition (Table 1) was determined and correlated with data on the isothermal expansion (1).

Table 1. Sample compositions and labels

Doped on A site (Label)	Doped on A and B site (Label)
$\text{La}_{0.90}\text{Ca}_{0.10}\text{CrO}_{3-\delta}$ (LCC10)	$\text{La}_{0.80}\text{Sr}_{0.20}\text{Cr}_{0.97}\text{V}_{0.03}\text{O}_{3-\delta}$ (LSCV)
$\text{La}_{0.80}\text{Ca}_{0.20}\text{CrO}_{3-\delta}$ (LCC20)	$\text{La}_{0.95}\text{Ca}_{0.05}\text{Cr}_{0.84}\text{Al}_{0.16}\text{O}_{3-\delta}$ (LCCA)
$\text{La}_{0.80}\text{Sr}_{0.20}\text{CrO}_{3-\delta}$ (LSC20)	$\text{LaCr}_{0.79}\text{Mg}_{0.05}\text{Al}_{0.16}\text{O}_{3-\delta}$ (LCMA)
	$\text{LaCr}_{0.79}\text{Cu}_{0.05}\text{Al}_{0.16}\text{O}_{3-\delta}$ (LCCuA)
	$\text{LaCr}_{0.79}\text{Co}_{0.05}\text{Al}_{0.16}\text{O}_{3-\delta}$ (LCCoA)

Oxygen vacancy formation was determined at temperatures between 900 and 1100 °C and oxygen partial pressures between 1 bar and 10^{-22} bar using thermogravimetric measurements (see e.g. Fig1). Defect models were developed which describe the oxygen vacancy formation in the different perovskites. Enthalpy and entropy changes were evaluated for the reactions of the defect formation. The perovskites investigated can be divided into two groups. The chromites containing Ca, Sr or Mg (first group) essentially release oxygen by the

transition Cr^{+4} to Cr^{+3} according to the “small polaron” reaction. The composition LSCV may additionally show the transition V^{+4} to V^{+3} at very low oxygen partial pressures. The chromites with no addition of alkaline earth metals but Co or Cu (second group) lead to significant changes in the defect structures since Co and especially Cu tend to reduce their oxidation state. The results obtained on oxygen non-stoichiometry of doped

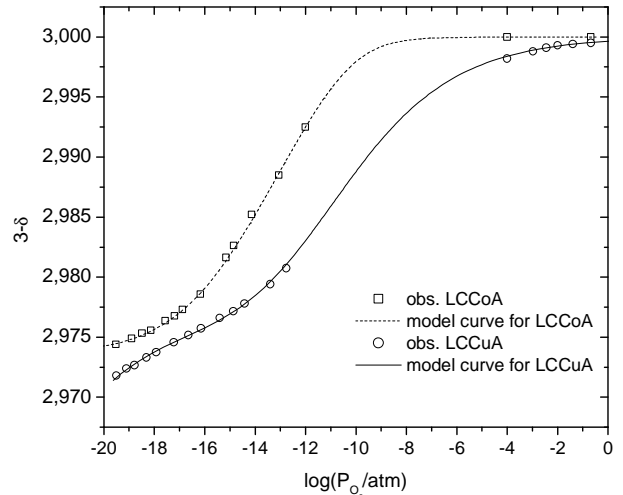


Fig.1. Nonstoichiometry of $\text{LaCr}_{0.79}\text{Co}_{0.05}\text{Al}_{0.16}\text{O}_{3-\delta}$ (LCCoA) and $\text{LaCr}_{0.79}\text{Cu}_{0.05}\text{Al}_{0.16}\text{O}_{3-\delta}$ (LCCuA) at 1000 °C. Fitted curves results on the basis of defect models chromite compositions showed the large impact of the nature of the dopants on the defect structure of these chromites.

The correlation between the oxygen non-stoichiometry and the isothermal expansion reveals that the latter can be understood by the change of the average B site cation

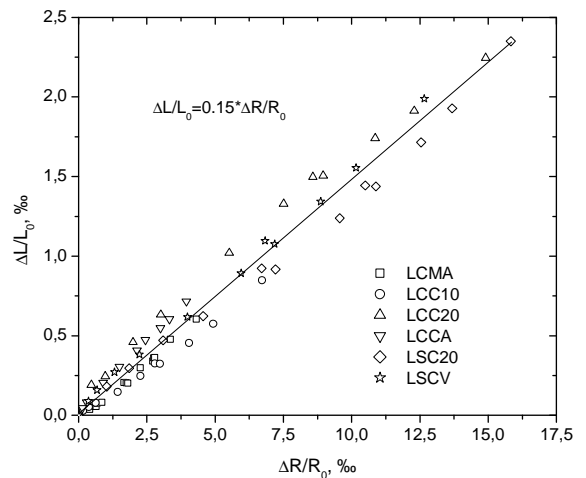


Fig.2. Linear isothermal expansion as function of the relative change of the average radius of the B site cations for different perovskite compositions (cf. Table 1) at 1000 °C

defect structure (see e.g. Fig.2). The figure reveals that in spite of the scatter which may be caused by experimental errors there is a linear trend in the expansion function of the average radius of the B site cations for different perovskite compositions (cf. Table 1). This relation can be used to predict the linear expansion.

1. H. Bausinger, PhD thesis, University Tübingen, Germany, 2000.

