

## Hole doping mechanism and electrochemical behaviour of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+\delta}$ ( $0 \leq x \leq 0.2$ ) manganites

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### Abstract

The influence of hole doping mechanism on the electrochemical behaviour of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+\delta}$  manganites ( $0 \leq x \leq 0.2$ ) with the maximum degree of oxygen non-stoichiometry ( $\delta = \delta_{\text{max}}$ ) has been studied by voltammetry using carbon-paste electroactive electrode. In the interval  $0.1 < x < 0.12$ , a structural phase transition ortho-rhombo occurs and also the predominance of hole doping mechanism due to oxygen content (the vacancy mechanism) is replaced by the predominance of the formation of holes localized on  $\text{Mn}^{\text{IV}}$  ions due to cation substitution (the concentration mechanism). The regularities (the number, nature and sequence of stages) of cathodic reduction of the oxides has been found to not depend on the nature of hole doping. At the same time, a sharp change in the character of the concentration dependence of the electrochemical reactions rates in the phase transformation region takes place. In the composition range where the holes formation due to oxygen content prevails, an anomaly is observed with increasing parameter  $x$ : acceleration of reactions with decreasing concentration of charge carriers. The intensity of cathodic response is in direct correlation with the charge carriers concentration in the region where the concentration mechanism of hole doping is predominant. Based on the experimental facts cited in the literature we have suggested that the anomalous effect is due to increase in the charge mobility with increasing parameter  $x$ .