

Thermodynamic Study of Some Micro and Nanostructured Perovskite-Type Compounds by a Solid State Electrochemical Technique  
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The perovskite-type oxides based on doped and undoped lanthanum manganites are receiving considerable attention due to their special electric, magnetic and catalytic properties. In order to evaluate and optimize the properties for utilization in different applications a thorough knowledge of the thermodynamics of the new materials is very important.

It is recognized that their physical and thermochemical properties are strongly affected by the nature and the content of the dopant, as well as by the oxygen stoichiometry. In the present study new measurements have been made by a solid state electrochemical technique in order to evidence the influence of the micro- and nanostructure, respectively on the thermodynamic data of some doped lanthanum manganites of general formula  $\text{La}_{1-x}\text{M}_x\text{Mn}_{1-y}\text{Me}_y\text{O}_3$  (where  $\text{M}=\text{Ca}$ ;  $\text{Me}=\text{Al}$ ;  $x=0-0.4$ ;  $y=0; 0.05$ ). The thermodynamic properties represented by the relative partial molar free energies, enthalpies and entropies of oxygen dissolution in the perovskite phase, as well as the equilibrium partial pressures of oxygen have been obtained as a function of temperature (873-1273 K temperature range) and composition.

For the compounds with the same composition, but obtained by different preparation procedures (sol-gel method and solid state reactions, respectively) the obtained data evidence the modifications in the thermodynamic properties connected with the nanocrystalline state (Fig. 1). Between 1073 and 1123 K the partial molar energy of oxygen dissolution is found to be markedly enhanced in nanocrystalline solids. At 1173 and 1273 K the energies values of the nano- and microcrystalline samples are closest, suggesting the increasing of the nano-grains size with the temperature. The results obtained for the nanocrystalline ceramics are discussed being related with the significant changes in the overall defect concentrations.

The influence of the oxygen stoichiometry change on the thermodynamic properties was examined using the data obtained by a coulometric titration technique coupled with EMF measurements (Fig. 2 and Table I). At the same deviation of the oxygen stoichiometry ( $\delta=0.02$ ), the energy values increase with temperature (Fig. 2). The results obtained for the nanocrystalline ceramics are discussed being related with the significant changes in the overall defect concentration, suggesting a reduced formation energy of oxygen vacancies.

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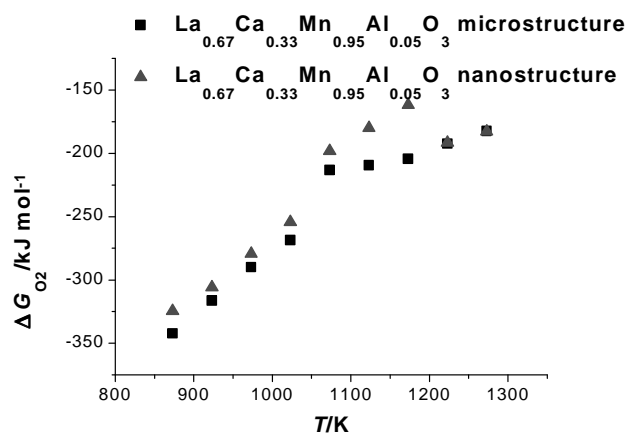


Fig. 1. The variation of the  $\Delta\bar{G}_{\text{O}_2}$  with the temperature for the doped lanthanum manganites prepared by ■ Solid state reactions and ▲ Sol-gel method

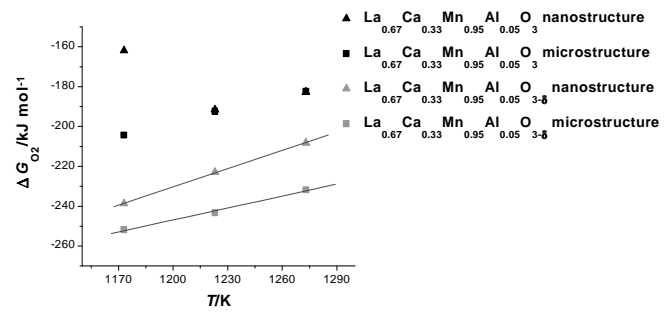


Fig. 2. The variation of the  $\Delta\bar{G}_{\text{O}_2}$  with the temperature and the oxygen stoichiometry change for nano- and microstructured lanthanum manganites.

Table I. Comparative results of the relative partial molar thermodynamic data of oxygen after titration in the nonstoichiometric compound  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.95}\text{Al}_{0.05}\text{O}_{3-\delta}$  ( $\delta=0.02$ ) (1173-1273 K)

	$\Delta\bar{H}_{\text{O}_2}$ (kJ mol <sup>-1</sup> )	$\Delta\bar{S}_{\text{O}_2}$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )
Nanostructure	$-595.662 \pm 8.167$	$-0.304 \pm 0.006$
Microstructure	$-487.244 \pm 21.83$	$-0.200 \pm 0.017$