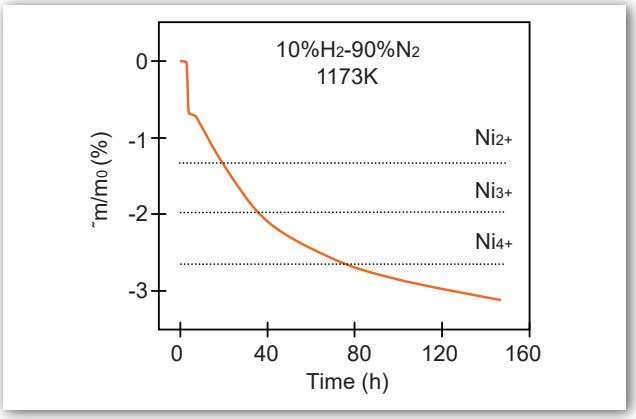
Oxygen stoichiometry of $LaGa_{0.65}Mg_{0.15}Ni_{0.20}O_{3-d}$

INTRODUCTION

$LaGaO_3$-based solid electrolytes and mixed ionic–electronic conductors attract significant attention during the last decade due to their potential application as materials of intermediate-temperature solid oxide fuel cells (ITSOFCs), electrochemical oxygen sensors, and membrane reactors for conversion of natural gas to synthesis gas. In particular, a very high level of ionic transport is observed for $La_{1-x}SrxGa_{1-y}MgyO_{3-d}$ (LSGM) solid solutions with x=0.10- 0.20 and y=0.15-0.20. The aim of this paper is to estimate oxygen stoichiometry from the weight changes by thermogravimetric analysis.



Example of reduction kinetics of $LaGa_{0.65}Mg_{0.15}Ni_{0.20}O_{3-d}$ in flowing 10%H_2–90%N_2 mixture at 1173 K. The sample was kept for 2 h in air, 1 h in argon, and then 144 h in the H_2-containing mixture.

Dashed lines correspond to the theoretical weight changes upon reduction into metallic nickel and binary oxides, calculated assuming that there is no gallium oxide volatilization and that all nickel cations in air are in 2+, 3+ or 4+ oxidation states.

EXPERIMENT

Estimation of oxygen stoichiometry of $LaGa_{0.65}Mg_{0.15}Ni_{0.20}O_{3-d}$ ceramic was carried out in a Setsys TGA.

The following program is used:
- Heating at 3K/min in flowing air with equilibration steps at 1073, 1123 and 1173K for 2h at each temperature;
- Flushing of the apparatus with argon for 1h;
- Reduction at 1173K in flowing 10%H_2 90%N_2 mixture (cf. figure);

RESULTS AND CONCLUSION

The values of oxygen nonstoichiometric in air at 10731173K, calculated from the TG data, are listed in the table below:

T (K)	δ	Average Ni oxidation state
1173	0.080	2.95
1123	0.070	3.05
1073	0.062	3.13

The average oxidation state of nickel cations is +2.95 at 1173 K, and increases up to +3.13 on cooling down to 1073K. This indicates coexistence of Ni2+, Ni3+ and Ni4+ states in the lattice of $LaGa_{0.65}Mg_{0.15}Ni_{0.20}O_{3-d}$ under oxidizing conditions. The formation of tetravalent nickel should still be understood as a hypothesis and requires additional experimental confirmation, particularly to verify exact location of the electron holes formed due to oxygen incorporation.

INSTRUMENT

THEMYS TGA

HIGH ACCURACY & VERSATILITY
hang-down symmetrical beam balance, specifically designed for TGA application.

ULTRA-HIGH TEMPERATURE CAPABILITY
to 2400°C with a single furnace.

MODULAR ADAPTIONS ALLOWING
TGA only, DTA only, TG-DTA, and TMA up to 2400°C, DSC only and TG-DSC up to 1600°C all in one instrument

EXTERNAL COUPLING CAPABILITY
designed for evolved gas analyzers (FTIR, MS, GCMS, MSFTIR, or FTIR-GCMS)

REFERENCE

Mixed conductivity, stability and thermomechanical properties of Ni-doped La(Ga,Mg)$O_{3-d'}$ A.A. Yaremchenko, V.V. Kharton, E.N. Naumovich, D.I. Shestakov, V.F. Chukharev, A.V. Kovalevsky, A.L. Shaula, M.V. Patrakeev, J.R. Frade, F.M.B. Marques, Solid State Ionics 177 (2006) 549-558