

SSI - 17

17TH INTERNATIONAL CONFERENCE ON SOLID STATE IONICS
28 JUNE - 3 JULY, 2009
TORONTO, CANADA

Poster Abstracts



ORGANIZED BY

Alfred University

UNDER THE AUSPICES OF

ISSI INTERNATIONAL SOCIETY
FOR SOLID STATE IONICS

OXYGEN NONSTOICHIOMETRY AND TRANSPORT PROPERTIES OF $\text{Ln}_{0.5}\text{A}_{0.5}\text{FeO}_{3-\delta}$ (Ln = La-Sm, A = Sr, Ba): EFFECTS OF CATION SIZE

V.V. Kharton¹, A.V. Kovalevsky^{1,2}, M.V. Patrakeev³, E.V. Tsipis⁴, A.P. Viskup⁵, V.A. Kolotygin¹, A.L. Shaula^{1,6}, J.C. Waerenborgh⁴

¹ Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

² Materials Department, Flemish Institute for Technological Research (VITO), 2400 Mol, Belgium

³ Institute of Solid State Chemistry, Ural Division of RAS, 91 Pervomayskaya Str., Ekaterinburg 620219, Russia

⁴ Chemistry Department, Instituto Tecnológico e Nuclear, CFMC-UL, EN 10, 2686-953 Sacavém, Portugal

⁵ Institute of Physicochemical Problems, Belarus State University, 14 Leningradskaya Str., 220050 Minsk, Belarus

⁶ Department of Mechanical Engineering, SEG-CEMUC, University of Coimbra, P-3030-788 Coimbra, Portugal

Email: kharton@ua.pt

Keywords: perovskite, mixed conductor, ionic conductivity, lattice strain, oxygen nonstoichiometry, Mössbauer spectroscopy

Introduction

Ferrite-based mixed conductors with ABO_3 perovskite structure exhibit an attractive combination of transport properties and stability, and are hence considered for numerous electrochemical applications, such as dense ceramic membranes and SOFC cathodes. The present work is focused on the comparative analysis of oxygen nonstoichiometry, ionic transport and electronic conductivity in perovskite-type $\text{Ln}_{0.5}\text{A}_{0.5}\text{FeO}_{3-\delta}$ (Ln = La-Sm; A = Sr, Ba).

Experimental

Single-phase $(\text{Ln,A})\text{FeO}_{3-\delta}$ ceramics were prepared by the glycine-nitrate synthesis and sintering at 1530-1790 K in air. The materials were characterized by XRD, Mössbauer spectroscopy, and measurements of the oxygen partial pressure dependencies of total conductivity. The oxygen deficiency was determined by coulometric titration in the $p(\text{O}_2)$ range from 10^{-20} to 0.7 atm at 973-1223 K. The partial ionic conductivity was derived from the steady-state oxygen permeability and total conductivity data. The permeation flux vs. membrane thickness dependencies were also used to assess relative role of the surface exchange kinetics.

Results and Discussion

Increasing the difference of the Ln^{3+} and A^{2+} cation radii in $\text{Ln}_{0.5}\text{A}_{0.5}\text{FeO}_{3-\delta}$ (Ln = La, Pr, Nd, Sm; A = Sr, Ba) results in higher oxygen deficiency and lower oxygen-ionic and p-type electronic conductivities. These trends are attributed to lattice strains caused by the A-site cation size mismatch, which promote Fe^{4+} localization, decrease the average metal-oxygen bonding strength, and induce clustering of acceptor-type dopant cations and oxygen vacancies. No correlations with tolerance factors, lattice symmetry and unit cell volume were identified. The relationships between the anion transport and cation size mismatch remain essentially similar in air and under reducing conditions when most iron becomes trivalent, thus confirming critical influence of vacancy trapping. At low temperatures, analogous correlation is also observed for quadrupole splittings derived from the Mössbauer spectra of oxygen-

stoichiometric $\text{Ln}_{0.5}\text{A}_{0.5}\text{FeO}_3$. Contrary to the ionic conductivity variations, the role of surface exchange as a permeation-limiting factor tends to decrease on Ba^{2+} doping and on decreasing Ln^{3+} size, again correlating with the lattice strains. The n-type electronic conduction and low- $p(\text{O}_2)$ stability of the perovskite-like phases at 1223 K are substantially unaffected by the cation radius mismatch.

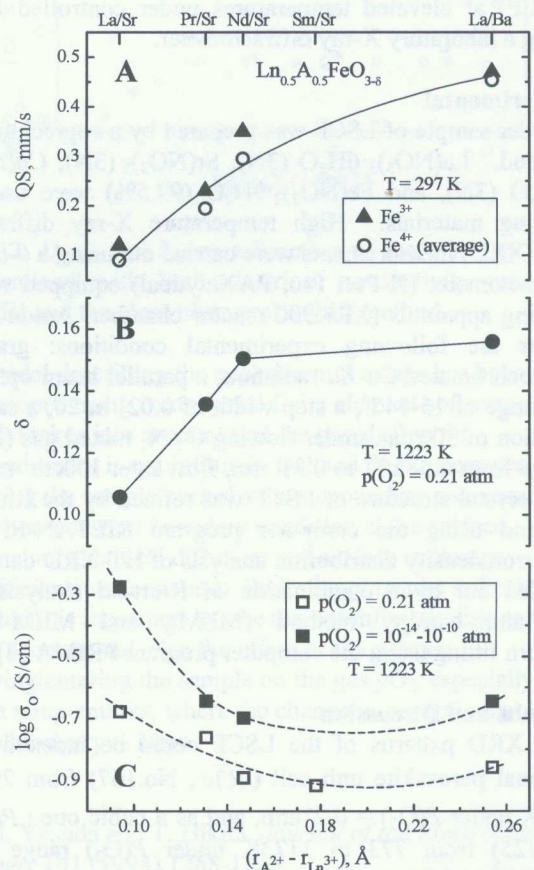


Fig. 1. Room-temperature quadrupole splittings of Fe^{3+} and Fe^{4+} signals (A), oxygen nonstoichiometry at 1223 K and atmospheric oxygen pressure (B), and ionic conductivity values at 1223 K in air and in reducing atmospheres (C) vs. the difference between A^{2+} and Ln^{3+} cation radii.