ACADEMIC PRESS

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Solid State Chemistry 177 (2004) 126–133

JOURNAL OF SOLID STATE CHEMISTRY

http://elsevier.com/locate/jssc

Energetics of magnesium, strontium, and barium doped lanthanum gallate perovskites

Jihong Cheng and Alexandra Navrotsky*

Department of Chemical Engineering & Material Sciences, Thermochemistry Facility and NEAT ORU, University of California at Davis, 1 Shields Avenue, Davis, CA 95616, USA

Received 10 April 2003; received in revised form 2 June 2003; accepted 6 June 2003

Abstract

$LaGaO_3$ perovskites doped with Sr or Ba at the La site and Mg at the Ga site were prepared by solid-state reaction or sol–gel method and characterized. Enthalpies of formation from constituent oxides at 298 K were determined by high-temperature oxide melt solution calorimetry. Energetic trends are discussed in terms of defect chemistry. As oxygen deficiency increases, formation enthalpies define three trends, $LaGa_{1-y}Mg_yO_{3-\delta}$ (LGM), $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ (LSGM), and $La_{1-x}Ba_xGa_{1-y}Mg_yO_{3-\delta}$ (LBGM). They become less exothermic with increasing doping, suggesting a dominant destabilization effect from oxygen vacancies. The endothermic enthalpy of vacancy formation is 275 ± 37, 166 ± 18 and 138 ± 12 kJ/mol of $V_O^{\cdot\cdot}$ for LGM, LBGM and LSGM, respectively. Tolerance factor and ion size mismatch also affect enthalpies. In terms of energetics, Sr is the best dopant for the La site and Mg for the Ga site, supporting earlier studies, including oxygen ion conductivity and computer modeling.

Keywords: Enthalpy of formation; Doped lanthanum gallate; Perovskites; Oxygen vacancies; Tolerance factor; Solid oxide fuel cells; Thermodynamics; Solid electrolyte