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The system Al_2O_3 and (Sr,Mg)-doped $LaGaO_3$: phase composition and electrical properties

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Abstract

Mixtures of α-Al_2O_3 and $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$, with α-$Al_2O_3$ concentrations ranging from 1 to 20 wt.%, were uniaxially and isostatically pressed and finally sintered at 1500 °C for 4 h. The phase composition and microstructure were investigated by X-ray powder diffraction and scanning electron microscopy techniques. The electrical properties were studied by complex impedance spectroscopy in a wide range of temperatures (200–800 °C) in air. In the sintered bodies pure α-Al_2O_3 was not detected; the partial substitution of Al for Ga was suggested entailing the formation of the solid solutions of perovskite-type $(La_{0.8}Sr_{0.2})(Ga_{1-x-y}Al_xMg_y)O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Ga_{1-x}Al_xO_{3-\delta}$. α-$Al_2O_3$ added to $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ inhibited the grain growth of the majority phase. Under isothermal conditions, the electrical conductivity decreases with increasing alumina content, while the activation energies increase.

Keywords: Lanthanum gallate; LSGM; Alumina; Perovskite; Solid electrolyte

1. Introduction

Present development of intermediate temperature solid oxide fuel cells (IT-SOFCs) follows two strategies: reduction of the thickness of the traditional Y_2O_3-stabilised ZrO_2 (YSZ) electrolyte layer to approximately 10 μm, and/or the use of alternative solid oxide electrolytes with an ionic conductivity higher than 10^{-2} S cm^{-1} below 750 °C.

The family of (Sr,Mg)-doped $LaGaO_3$ compounds, which exhibit high ionic conductivity at 600–800 °C over a wide range of oxygen partial pressures, appears to be promising as electrolyte for IT-SOFCs [1–4]. Partial substitution of La by Sr and Ga by Mg to the $LaGaO_3$ lattice produces an anion-deficient perovskite of the general formula $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$, generally indicated as LSGM. For $x=0.2$ and $y=0.2$, $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$ shows an oxygen-ion conductivity of approximately 10^{-1} S cm^{-1} at 750 °C, which exceeds the ionic conductivity of Y_2O_3-stabilised ZrO_2 at the same temperature.

A solid oxide electrolyte incorporated into an IT-SOFC stack must satisfy many requirements in addition to a high value of ionic conductivity. To achieve a good cell performance, the materials should be chosen so that chemical stability at high temperature is high, the reactivity among adjacent components is at minimum and the thermal expansion is matching. Nevertheless, when considering stacks of SOFCs with planar configuration, good mechanical properties of the electrolyte and the other main components (anode, cathode, interconnection material) are important selection criteria. The mechanical properties of LSGM materials are relatively poor and they may be improved by the addition of a secondary phase. For example, the bending strength of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ is about 150–160 MPa at room temperature and 55–100 MPa at 900 °C [5–7]. Yasuda et al. [8] found that the dispersion of a small amount of α-Al_2O_3 (around 2 wt.%) doubles the bending strength of

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LSGM, while the addition of >2 wt.% of alumina reduces the total conductivity.

A major disadvantage of LSGM is the high cost of Ga containing precursors; this obstacle would be reduced by dispersing an inexpensive phase in the LSGM powder. The present study was carried out to evaluate mixtures of α-Al_2O_3 and $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ as electrolyte for IT-SOFCs as well as to study the phase composition of the system. Al_2O_3–LSGM mixtures, with Al_2O_3 concentrations from 0 to 20 wt.%, were prepared and characterised.

Table 1
Composition and relative density ρ of LSGM and Al_2O_3–LSGM samples

Sample	LSGM (wt.%)	α-Al_2O_3 (wt.%)	α-Al_2O_3 (mol%)	ρ (%)
A0	100	–	–	95
A1	99	1	2.4	94
A2	98	2	4.7	93
A3	97	3	7.0	94
A5	95	5	11.3	94
A10	90	10	21.3	92
A20	80	20	37.8	85

2. Experimental

$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}(CO_3)$ powders (Anan Kasei, Japan) were calcined at 800 °C for 5 h in air, ground 15 min with an agate mortar and uniaxially pressed at 100 MPa for 20 s into pellets of 10 mm diameter. The pellets were sintered at 1400 °C for 3 h and re-ground; the X-ray diffraction (XRD) pattern of the $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (from now on denoted as LSGM) powder is reported in Fig. 1.

The mixtures of α-Al_2O_3 (99.9%, Alcoa) and LSGM were prepared by ball-milling (3 h treatment in a tungsten carbide jar using a Retsch S100 planetary ball mill), with Al_2O_3 concentrations of 1, 2, 3, 5, 10 and 20 wt.% as listed in Table 1. A low rotation speed (200 rev/min) was used for ball milling, in order to avoid tungsten contamination of the LSGM powder; in addition, the presence of tungsten in milled powders was investigated by EDX analysis, based on the $L_{\alpha 1}$ line at 8.3977 keV of the spectrum. The six series of mixed powders were uniaxially pressed (100 MPa, 20 s) into 2.5 g pellets of 12 mm diameter, and subsequently subjected to cold isostatic pressing at 200 MPa for 60 s. The pellets were sintered at 1500 °C for 4 h in air (10 °C/min ramp) and furnace cooled. Prior to each heating, the specimens were placed on a platinum sheet.

For each composition, phase analysis and structural parameters were determined by X-ray diffraction from ground pellets. The patterns were collected at room temperature, in the 2θ range 4–70°, using graphite monochromated Cu-K_α radiation; the step scan was 0.02° 2θ and the counting time of 1 s per step. The XRD data were refined by the Rietveld method using the GSAS program of Larson and Von Dreele.

Morphology and microstructure were investigated by scanning electron microscopy (SEM) of samples polished and thermally etched at 1350 °C in air for 1 h; EDX analysis was also carried out. Electrical conductivity measurements of the pellets were carried out by impedance spectroscopy (IS) in the temperature range from 300 to 800 °C in air. For the electrodes, Pt paste was painted onto both surfaces of the pellets and heated at 850 °C for 1 h.

The experimental density was measured by the Archimedes technique and the relative densities of all samples are

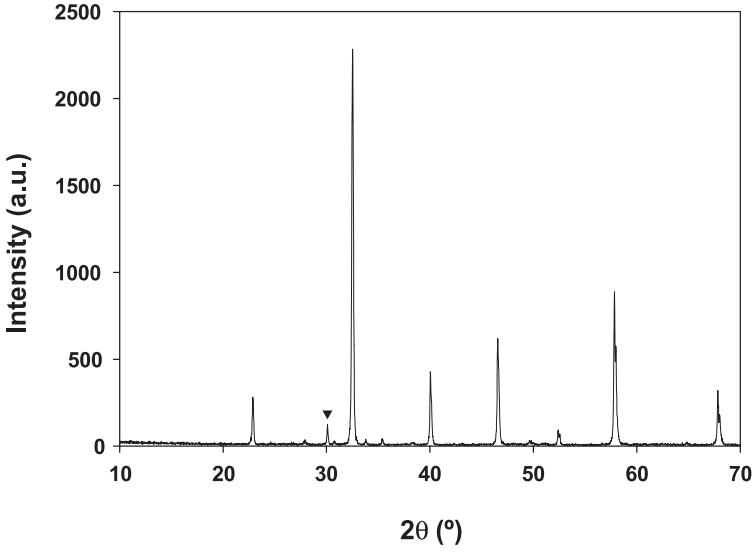

Fig. 1. XRD pattern of LSGM powder fired at 1400 °C; (▼) represents $LaSrGa_3O_7$ impurity phase strongest reflection.