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Ionic and electronic conductivities, stability and thermal expansion of $La_{10-x}(Si,Al)_6O_{26\pm\delta}$ solid electrolytes

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Abstract

Apatite-type $La_{10-x}Si_{6-y}Al_yO_{27-3x/2-y/2}$ ($x=0-0.33$; $y=0.5-1.5$) exhibit predominant oxygen ionic conductivity in a wide range of oxygen partial pressures. The conductivity of silicates containing 26.50–26.75 oxygen atoms per formula unit is comparable to that of gadolinia-doped ceria at 770–870 K. The average thermal expansion coefficients are $(8.7-10.8)\times10^{-6}$ K^{-1} at 373–1273 K. At temperatures above 1100 K, silicon oxide volatilization from the surface layers of apatite ceramics and a moderate degradation of the ionic transport with time are observed under reducing conditions, thus limiting the operation temperature of Si-containing solid electrolytes.

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Keywords: Apatite; Lanthanum silicate; Ionic conductivity; Electronic transport; Thermal expansion

1. Introduction

Commercialization of solid oxide fuel cells (SOFCs) requires developments of new economically feasible materials, with a special attention to solid electrolytes as key components of SOFCs [1]. High oxygen ionic conductivity was recently reported for apatite-type $A_{10-x}(MO_4)_6O_{2\pm\delta}$ (M = Si, Ge) phases where A corresponds to rare- and alkaline-earth cations [2–5]. The apatite lattice can be described as "hybrid" structure consisting of covalent SiO_4 tetrahedra and ionic-like La/O channels. The oxygen transport in $Re_{10-x}Si_6O_{26+\delta}$ (Re = La–Yb; $x=0-0.67$) increases with increasing Re^{3+} radius, whereas the activation energy decreases [2]. Germanate-based apatites possess a higher conductivity compared to silicates, but suffer from Ge volatility, transformation into La_2GeO_5 and high activation energies for ionic transport [4]. The apatite lattice can tolerate considerable A-site deficiency and extensive doping, thus providing an important tool for further optimization. This work was focused on the study of Al-substituted $La_{10-x}Si_6O_{27-\delta}$ apatites and their comparison with common solid oxide electrolytes [6–10].

2. Experimental

Single-phase $La_{10-x}Si_{6-y}Al_yO_{27-3x/2-y/2}$ ($x=0$, 0.17 and 0.33; $y=0.5$, 1.0 and 1.5) were synthesized by the standard solid-state technique from high-purity La_2O_3, SiO_2 and $Al(NO_3)_3{\cdot}9H_2O$. Gas-tight ceramics were sintered at 1923–1973 K during 10 h in air. The materials were characterized by X-ray diffraction (XRD, Rigaku D/Max-B diffractometer), scanning electron microscopy (SEM, Hitachi S-4100 microscope), dilatometry (Linseis L75 dilatometer), and impedance spectroscopy (HP4284A precision LCR meter). The oxygen ionic transference numbers were determined by the modified Faradaic efficiency technique and confirmed by the e.m.f. measurements of oxygen concentration cells; description of the experimental procedures was published earlier (see [5] and references cited).

3. Results and discussion

The silicate-based materials prepared in this work were single phase, although minor secondary peaks may be visible

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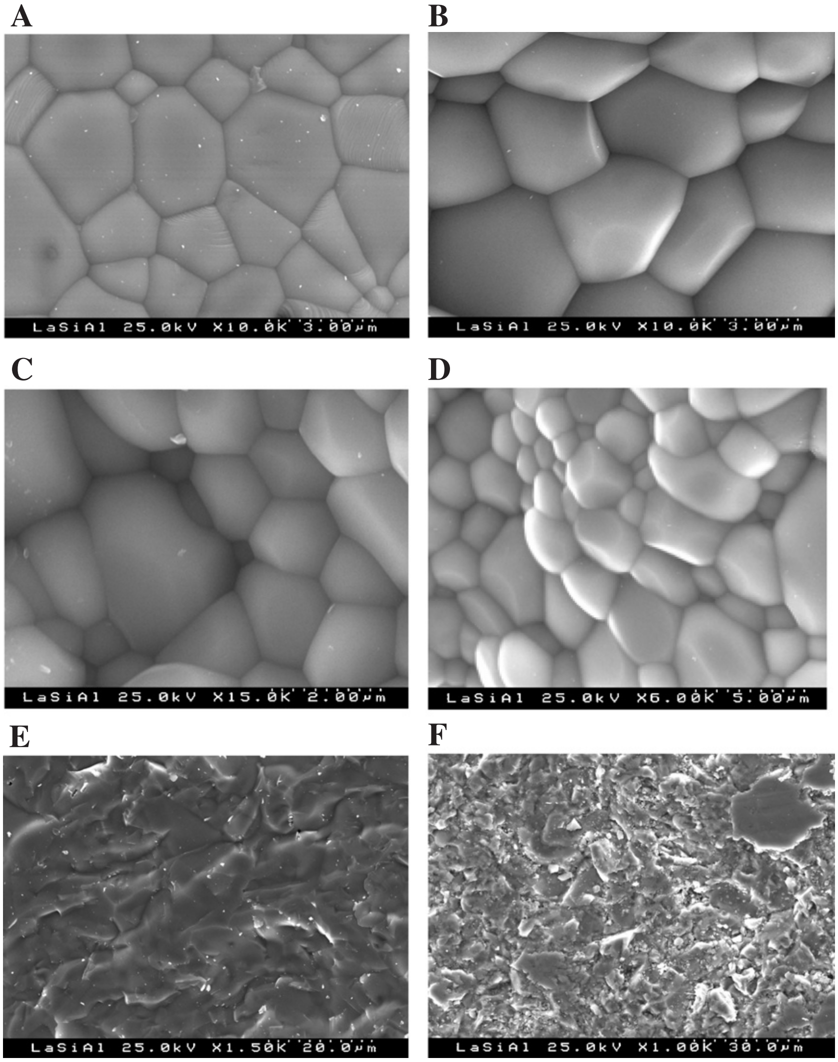

Fig. 1. SEM micrographs of as-prepared $La_{9.67}Si_{5.5}Al_{0.5}O_{26.25}$ (A), $La_{9.67}Si_{4.5}Al_{1.5}O_{25.75}$ (B), $La_{9.67}Si_5AlO_{26}$ (C), $La_{9.83}Si_{4.5}Al_{1.5}O_{26}$ (D), and fractured bulk (E) and surface (F) of $La_{10}Si_5AlO_{26.5}$ ceramics after long-term annealing in H_2–H_2O–N_2 mixture at 1173 K.

for the phases with highest oxygen content. The identification of the phase impurities, if any, is impossible due to very low intensity of these peaks. The apatite-type unit cells expand on the incorporation of Al^{3+} having a larger radius with respect to Si^{4+}. As for $La_{7-x}Sr_3Si_6O_{26-\delta}$ and $La_{10-y}Si_5FeO_{26\pm\delta}$ systems [5], increasing A-site deficiency at fixed B-site composition has an opposite effect. The density of sintered ceramics was higher than 91% of theoretical. SEM inspection showed a relatively good quality of the ceramic materials (Fig.1, A–D). The impedance spectra also indicated no significant grain-boundary contribution to the total resistivity, at least at temperatures above 873 K. The average grain size for all materials was 2–4 μm. The thermal expansion of $La_{10-x}Si_{6-y}Al_yO_{27-3x/2-y/2}$ at 373–1273 K is approximately linear. The average thermal expansion coefficients (TECs) calculated from the dilatometric data are relatively low, $(8.7–10.8)\times10^{-6}$ K^{-1}, and close to those of common solid electrolytes (Table 1).

The Faradaic efficiency and e.m.f. measurements showed that all title materials are solid electrolytes. The ion transference numbers at 973–1223 K vary in the range 0.9949–0.9997 in air and increase on reducing oxygen partial pressure due to decreasing p-type electronic conduction. The ionic conduction

Table 1
Average thermal expansion coefficients of solid electrolyte ceramics

Composition	T (K)	$\alpha\times10^6$ (K^{-1})	Reference
$La_{9.67}Si_{4.5}Al_{1.5}O_{25.75}$	373–1173	10.0	This work
$La_{9.67}Si_5AlO_{26}$	373–1173	9.9	
$La_{9.67}Si_{5.5}Al_{0.5}O_{26.25}$	373–1273	9.4	
$La_{9.83}Si_{4.5}Al_{1.5}O_{26}$	373–1173	8.9	
$La_{9.83}Si_{5.5}Al_{0.5}O_{26.5}$	373–1273	10.8	
$La_{10}Si_5AlO_{26.5}$	473–1173	9.1	
$La_{10}Si_{5.5}Al_{0.5}O_{26.75}$	373–1273	8.7	
8 mol% Y_2O_3–ZrO_2 (8YSZ)	300–1273	10.0	[6]
8YSZ–10 wt.% Al_2O_3	300–1273	9.7	
$Ce_{0.8}Gd_{0.2}O_{2-\delta}$	300–1100	11.8	[7]
$La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$	300–1073	10.4	[8]
$La_{0.9}Sr_{0.1}Al_{0.9}Mg_{0.1}O_{3-\delta}$	300–1223	11.2	[9]
$Gd_{1.86}Ca_{0.14}Ti_2O_{7-\delta}$	400–1300	10.4	[7]
$La_{1.7}Bi_{0.3}Mo_2O_{9\pm\delta}$	373–1073	16.0	
$(Bi_{0.95}Zr_{0.05})_{1.7}Y_{0.3}O_{3+\delta}$	710–1120	16.6	