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Oxy-apatite reaction sintering of colloidal and classic ceramic processed powders

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Abstract

Oxy-apatites are promising electrolyte materials for intermediate-temperature solid oxide fuel cells, IT–SOFC. However the requirements of electrolytes make necessary the preparation of dense films with the appropriated composition to show good electrical properties; in this way, colloidal processing is a key issue.

This work involves the application of colloidal processing for four oxygen-excess oxy-apatites, $La_{9.67}(Si_6O_{24})O_{2.5}$, $La_{10}(Si_6O_{24})O_3$, $La_{10}(Si_{5.5}Al_{0.5}O_{24})O_{2.75}$ and $La_{10}(Si_5Al_1O_{24})O_{2.5}$ and their characterization (phases, microstructure and electrical properties). The results have been compared with those obtained by classical ceramic method to assure the same composition without loosing properties. Samples with the desired compositions were obtained by reaction sintering of La_2O_3, SiO_2 and Al_2O_3. $La_{10}(Si_{5.5}Al_{0.5}O_{24})O_{2.75}$ prepared by colloidal processing and heated at 1923 K showed the highest conductivity value, 3.0×10^{-2} S cm^{-1} at 973 K. Furthermore, its residual porosity was very low. On the other hand, $La_{10}(Si_6O_{24})O_3$ stoichiometry was tried by colloidal and ceramic methods under several experimental conditions. Unfortunately, the obtained oxy-apatite seems to have slightly lower lanthanum content. In spite of previous reports claiming the preparation of stoichiometric $La_{10}(Si_6O_{24})O_3$, this study cannot support these findings.

Keywords: A. Suspensions; A. Powders: solid state reaction; C. Electrical conductivity; D. Apatite; E. Fuel cells

1. Introduction

Solid oxide fuel cells (SOFC) are one of the most promising types of fuel cell for large scale power generation and combined heat and power applications. SOFC offers many advantages over classical combustion-based power generation technologies and has been intensively studied for many years [1–4]. Yttria-stabilized zirconia, YSZ, is the oxide-conducting electrolyte used in the commercial systems. One significant disadvantage with the ZrO_2-based SOFCs is the temperature of operation at which ionic conductivity is sufficiently high for practical applications, usually 1073–1273 K, depending upon the thickness of the electrolyte. To increase the durability of the components, lower operating temperatures are required. Furthermore, to increase performance due to lower overall electrical resistance, thinner (dense) electrolyte films are needed. Hence, developing of new electrolyte materials with higher oxide-conductivities at intermediate temperatures (773–973 K) and the developing of procedures for the preparation and deposition of layers of those electrolytes on porous electrodes is a very important challenge.

Oxy-apatites have high potential to be used as oxide ion conductors working at moderate temperatures, ~973 K [4–8]. They adopt the general formula $A_{10-x}(M_6O_{24})O_{2\pm\delta}$, where A is a rare earth or alkaline earth cation and M is usually a p-block element such as Si, Al, Ge or P. Its structure consists of isolated MO_4 tetrahedra forming channels running parallel to the *c*-axis where the loosely bounded oxide-conducting anions are located. Recent computational studies [9,10] indicated that an unusually broad range of dopant ions (in terms of size and charge state) can substitute for La and Si in the $La_{9.33}(Si_6O_{24})O_2$ parent structure. The observed conductivity is very sensitive to the doping regime and cation–anion non-stoichiometry. The highest conductivities are found for oxygen-excess samples [11], with oxide-ion conduction occurring mainly, but not only, along the oxide-ion channels.

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One of the main limitation of oxy-apatite materials is related to their poor sinterability [5]. Many researchers have focused their efforts in this key subject by obtaining apatite materials through different routes, such as solid-state reaction [12–15], sol–gel [16–18], hot-pressing techniques [19], initial mechanosyntheses [20,21] facilitating further processing (i.e., colloidal [22]), or precipitate method combined with an azeotropic-distillation process [23]. In addition, electrolytes to be used in SOFCs have to show high densities and low thicknesses. In this way, oxy-apatite tapes and coatings have been recently prepared by tape casting [22,24,25], plasma spraying [26,27] and sputtering [28].

This work is a continuation of our research efforts devoted of the colloidal processing of oxy-apatites with the final goal of obtaining dense thin films of optimum composition(s). Our previous works [29,30] were focused on $La_{10}(Si_5Al_1O_{24})O_{2.5}$. Here, we expand this methodology to improve the processing for $La_{10}(Si_{5.5}Al_{0.5}O_{24})O_{2.75}$, $La_{9.67}(Si_6O_{24})O_{2.5}$ and $La_{10}(Si_6O_{24})O_3$. It is worth noting that we have tried the preparation of the contentious $La_{10}(Si_6O_{24})O_3$. Some groups reported that the preparation of non-doped lanthanum silicon oxy-apatites with very high La-contents by solid state reaction led to the segregation of La_2SiO_5 and the formation of a lanthanum deficient stoichiometry [10,31,32]. On the other hand, other groups assure to be achieved the $La_{10}(Si_6O_{24})O_3$ stoichiometry by classical methods [33,34]. In addition, there are several articles reporting the preparation of this composition by sol–gel [35,36] and precipitation methods [37,38].

2. Experimental

2.1. Synthesis and processing

$La_{9.67}(Si_6O_{24})O_{2.5}$, $La_{10}(Si_6O_{24})O_3$, $La_{10}(Si_{5.5}Al_{0.5}O_{24})O_{2.75}$ and $La_{10}(Si_5Al_1O_{24})O_{2.5}$ were prepared by reaction sintering using high purity oxides: micron powders of La_2O_3 (99.999%, Sigma–Aldrich), γ-Al_2O_3 (99.997%, Alfa Aesar) and SiO_2 (quartz, 99.8%, ABCR). Lanthanum oxide was precalcined at 1000 °C for 2 h for decarbonation. Each composition was prepared by two different synthesis-sintering procedures: the first one, consisting of a colloidal processing of the reagents followed by a reaction sintering step; and a second one, in which was used a single ceramic reaction sintering step. Both of them are described just below.

2.1.1. Colloidal processing

Suspensions with the stoichiometric mixtures of oxides were prepared at a solid loading of 5 wt% (1 vol%) in absolute ethanol by magnetic stirring for 15 min with the addition of the optimum amount of a polymeric dispersant that is soluble in ethanol (Hypermer KD6, Uniqema, Wirrall, UK). The best stabilization was obtained after the addition of 2.0, 2.0 and 3.0 wt% surfactant in dry solid based for La_2O_3, SiO_2 and Al_2O_3 powders, respectively [29]. The apparent pH of these diluted suspensions lies between 8 and 10. The so-prepared suspensions (50 mL) were ultrasonically homogenized using a 400 W sonication probe (UP400s Hielscher Ultrasonics GmbH) for 2 min. Suspensions were cooled in an ice-water bath during ultrasonication in order to avoid excessive heating. Then, the ethanol was evaporated for 24 h in an oven at 338 K. The dried powder was sieved through a 100 μm mesh, and pressed at 640 MPa into 10 mm diameter and 1 mm thickness pellets. After this treatment, samples were heated (heating/cooling rates of 5 K/min) to an intermediate temperature of 1393 K and held for 2 h [30], then the furnace was heated up to the final target temperature, ranged between 1873 and 1923 K (see Table 1) and held at that temperature for 10 h.

Table 1
Temperature of synthesis, theoretical density, secondary phases and electrical conductivity at 973 K for the reported samples.

Composition	Method	T (K)[a]	Density (%) TD	Secondary phases		V/Z (Å^3)	σ_{973} (mS cm^{-1})
				La_2SiO_5 (wt%)	$LaAlO_3$ (wt%)		
$La_{9.67}(Si_6O_{24})O_{2.5}$	Ceramic	1923	85	–	–	588.43(1)	9.5
	Colloidal	1873	68	–	–	588.83(8)	–
		1898	81	–	–	589.26(4)	0.7
		1923	80	–	–	589.17(3)	0.4
$La_{10}(Si_6O_{24})O_3$	Ceramic	1923	80	20.0(1)	–	588.72(1)	–
	Colloidal	1873	84	–	–	588.84(2)	6
		1898	80	7.0(8)	–	588.46(3)	9
		1923	80	Amorphous	–	589.44(4)	
$La_{10}(Si_{5.5}Al_{0.5}O_{24})O_{2.75}$	Ceramic	1873	90	–	–	590.91(1)	24
	Colloidal	1873	80	9.9(2)	1.7(2)	588.96(5)	6
		1898	85	–	–	590.61(4)	25
		1923	88	–	–	591.63(6)	30
$La_{10}(Si_5Al_1O_{24})O_{2.5}$	Ceramic	1873	89	–	–	592.71(1)	21
	Colloidal	1873	84	–	–	Two apatites	17
		1898	84	–	1.6(1)	592.16(5)	17
		1923	94	–	2.0(1)	592.51(6)	12

[a] The dwelling time was always 10 h.