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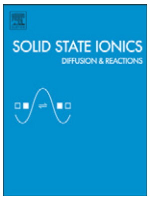

Microstructural and electrical characterizations of chemically prepared $Ce_{0.8}Gd_{0.2-x}(Ag, Sr)_xO_{1.9}$ $(0 \leq x \leq 0.02)$

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ABSTRACT

Gadolinia-doped ceria with co-additions of Sr and Ag were prepared by the cation complexation technique. The influence of co-additives on the densification, microstructure and electrical conductivity of the matrix were investigated by dilatometry, scanning electron microscopy and impedance spectroscopy, respectively. Both co-additives promoted changes on the densification behavior of the matrix. Strontium promoted densification and grain growth, whereas silver did not change the mean grain size but slowed down the densification of gadolinia-doped ceria. The grain conductivity of samples containing silver is considerably higher than that of pure gadolinia-doped ceria. The effect of strontium addition is predominant on the grain boundary by reducing the blocking effect. The apparent activation energy for grain conduction is lower for samples containing co-additives.

1. Introduction

To date, one of the great challenges in the development of electrochemical energy conversion devices, namely solid oxide fuel cells (SOFCs), is the optimization of requirements such as durability, efficiency and cost per kWh to become competitive with traditional energy conversion systems [1]. In this context, there is a current trend towards the development of solid electrolytes allowing for lowering the working temperature (<970 K), which would avoid problems related to mechanical instability, premature aging of materials and undesirable interface reactions among the cell components [2].

Ceria-based solid solutions, especially gadolinia-doped ceria (CGO) and samaria-doped ceria are the most promising candidates for solid electrolyte in intermediate-temperature SOFCs, since their ionic conductivity is higher than that of yttria-stabilized zirconia [3]. In addition, these doped-cerias are able to be used in composite anodes and as protection layers to avoid detrimental reactions at the electrode-electrolyte interface [2].

High densification of ceria-based solid electrolytes, prepared by the conventional mixing of oxides, are attained only for sintering temperatures exceeding 1400 °C [4]. Solution methods for preparation of ultrafine powders are preferred, even if the same sintering temperature is used, because they allow for obtaining better cation distribution and overall microstructure homogeneity. The amorphous citrate, or simply citrate method precludes an optimized homogeneity in the final product with advantages like low cost and simplicity [5]. In effect, solid solutions of gadolinia-doped ceria with excellent densities, >99% and >96% of the theoretical density, were obtained with this method after sintering at 1773 K for 3 h [6] and 1573 K for 30 h [7], respectively.

Another challenge in the development of materials for SOFCs is related to the ionic conductivity, which should be sufficiently high. This is generally obtained by a suitable choice of the aliovalent cation type and content. A recent approach to enhance the ionic conductivity of ceria-based solid electrolytes has been the introduction of a second additive. This approach has allowed for obtaining higher grain or grain boundary conductivity, depending on the type and content of the second additive [8,9].

The co-additive, whether being used as a sintering aid or as an additive to promote a special property, like phase stabilizer or increasing the ionic conductivity, will be able to modify several characteristics of the powder compact, thereby acting on both the kinetics and the thermodynamics of sintering [10]. Dissolution and/or segregation of the co-additive will influence mass transport due to possible changes in the diffusion coefficients (bulk, surface and grain boundary diffusion and vapor phase). Segregation of additives can also modify the interface (solid–solid and solid–gas) energies and the mobility of grain boundaries [10]. Therefore, a thorough investigation on the effects of additives during sintering of ceramic materials is highly desirable.

Chen and Chen [11] investigated a series of oxide additives to ceria in contents of 0.1% and 1.0%. In that work the effects of the additives on the grain boundary mobility was investigated, but no information concerning the type of solid solution formed (interstitial or substitutional) was given They concluded that additives with cation radius smaller than that of the host cation promoted grain growth, but this effect was influenced by the cation valence.

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No other systematic study relating the cation radius of the additives and their valences are presently known. Particularly, when the additive is used to promote the ionic conductivity, the valence is of relevance because it may change the charge carrier concentration.

The influence of Sr addition to CGO has been studied by Lane [12] and Kim [13]. In these studies, specific amounts of SiO_2 and SrO were intentionally added to $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ and mitigation of the blocking effect of silica was demonstrated by electrical conductivity measurements. To the best of our knowledge there are no reports on the effects of Ag addition to CGO, although its effects have been studied in a number of oxide systems as shown in the following examples. Taninouchi et al. reported increase of the electrical conductivity of $Bi_2VO_{5.5}$ below 570 °C, which was attributed to improvement of the subcell symmetry and stabilization of the γ-phase at a lower temperature due to Ag doping [14]. In ZnO, Fan and Freer [15] found that Ag occupies interstitial sites in specimens prepared by the conventional mixing of oxides route. In contrast, Yan et al. [16] have shown by first principles calculation that the formation energies are very low for doping elements of group IB on the substitutional sites, but rather high at the interstitial sites under oxygen-rich growth conditions.

This work aims to investigate the effects of partial substitutions of gadolinium and strontium or gadolinium and silver for cerium on densification and electrical conductivity of pellets prepared with nanopowders. The co-additives possess different stable valence (Sr^{2+}, Ag^{+}), but similar cation radius ($r_{Sr}^{2+} = 1.26$ Å, $r_{Ag}^{+} = 1.28$ Å [17]) in 8-fold coordination. Thus, the lattice strain produced by the partial substitution of the co-additives is expected to be also similar.

2. Experimental

2.1. Materials and method of synthesis

Solid solutions of $Ce_{0.8}Gd_{0.2-x}(Ag, Sr)_xO_{1.9}$ with $0 \leq x \leq 0.02$ were chemically prepared by the cation complexation technique using citric acid as complexant agent.

Cerium nitrate hexahydrate ($(CeNO_3)_3 \cdot 6H_2O$, 99.99%, Aldrich), gadolinium oxide (Gd_2O_3, 99.9%, Aldrich), and strontium carbonate (reagent grade) and silver nitrate (reagent grade) were used as starting materials. Other chemicals were anhydrous citric acid (99.5%) and nitric acid (65%). Experimental details of this technique may be found elsewhere [6]. The precursor resins were heat treated at 523 K for 1 h and subsequently calcined at 1073 K for 1 h for complete decomposition. The calcined nanopowders were pressed in a stainless steel dye at 20 MPa followed by isostatic pressing at 100 MPa. Sintering of the green compacts was carried out at 1773 K for 3 h.

The solid solutions will be denoted as CGO*MX* where *M* (=Ag, Sr) and *X* (=1 for 0.01 and 2 for 0.02) stand for the type and content of the second additive, respectively.

2.2. Characterization methods

The linear shrinkage of selected compositions was followed in a dilatometer (Anter, Unitherm™ model 1161) heating at a rate of 8 K min^{-1} up to 1773 K. Scanning electron microscopy, SEM (Philips, XL30) was used to observe microstructural features in sintered pellets after polishing and thermal etching. The mean grain size was determined by digital image analysis using NIH Image J public domain software. This routine is described in detail elsewhere [18]. The ionic conductivity was determined by impedance spectroscopy measurements using a low-frequency impedance analyzer (4192A Hewlett Packard) in the 5 Hz to 13 MHz frequency range. Silver paste was used as electrode material.

3. Results and discussion

3.1. Thermal and microstructure characterizations

Fig. 1 shows the linear shrinkage of CGO, CGOAg2 and CGOSr2 compacts up to 1773 K.

Similar features in theses plots are the temperature for initial shrinkage (~1083 K) and the change of slope at about 1370 K. This change of slope is associated with agglomerates formed during synthesis. The main differences in the linear shrinkage curves are due to specific effects produced by the second additive. Silver slowed down the densification of CGO, whereas strontium has the opposite effect. At 1773 K the total shrinkage is 15% (CGO), 8.6% (CGOAg2) and 17.5% (CGOSr2).

Fig. 2 shows representative scanning electron microscopy micrographs of (a) CGOAg1 and (b) CGOSr1 sintered pellets. The grain size of CGO determined by digital image analysis (~1.4 μm) does not change with silver addition. For samples containing strontium, the grain size is 1.5 (CGOSr1) and 2.8 μm (CGOSr2). A full description of the microstructure features in powders and sintered pellets of co-doped ceria was reported previously [18].

3.2. Impedance spectroscopy

Fig. 3 shows impedance spectroscopy diagrams of the studied compositions recorded at 533 K. All samples display two well-resolved semicircles in the frequency (5 Hz–13 MHz) and temperature (450–580 K) ranges of measurement. These semicircles attributed, in decreasing frequency, to the grain resistivity and blocking effect at grain boundaries present different contributions to the overall electrolyte conductivity. CGO, CGOAg1 and CGOAg2 samples, for example, exhibit a huge grain boundary blocking effect (Fig. 3a), which could not be resolved. In contrast, for samples containing strontium (CGOSr1 and CGOSr2) the two semicircles (Fig. 3b) were deconvoluted and the blocking effect was analyzed.

These results evidence that silver (Fig. 3a) seems to be soluble, at least at the levels studied in this work, in the ceria matrix, hence acting on the bulk of the electrolyte. Furthermore, its action favors to increase the ionic conductivity of CGO. Therefore, in a first approach, its influence on the blocking effect should be negligible. Increase of the electrical conductivity of Bi2VO5.5 oxygen-ion conductor with Ag (5 and 10 mol%) addition was also recently reported [14]. In that case, the improvement of the electrical conduction was attributed to the γ-phase stabilization at lower temperatures than usual.

The impedance spectroscopy diagrams of samples containing strontium (Fig. 3b) shows clearly that this additive acts primarily on

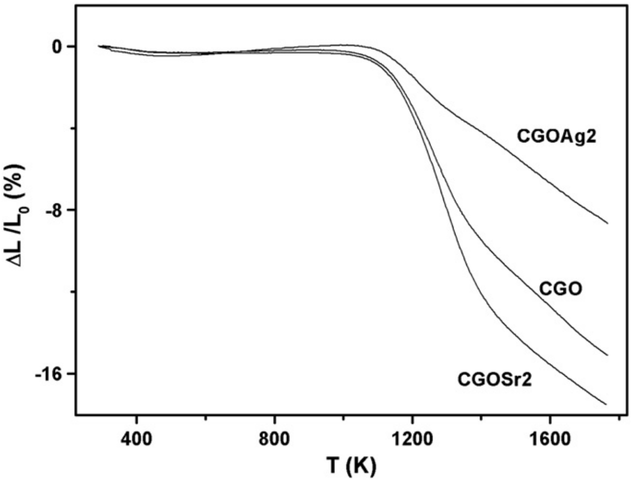

Fig. 1. Linear shrinkage curves of CGO, CGOAg2 and CGOSr2 compacts.

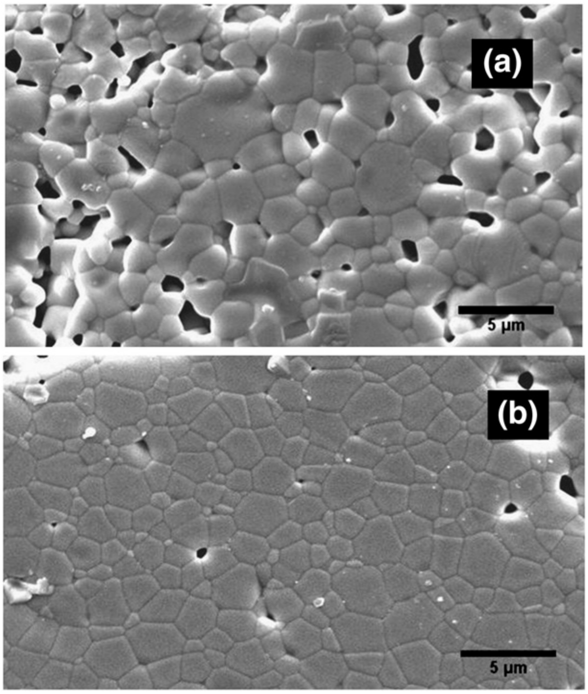

Fig. 2. Scanning electron microscopy micrographs of (a) CGOAg1 and (b) CGOSr1 sintered pellets.

the grain boundaries in such way that increasing the additive content, the blocking effect is gradually reduced.

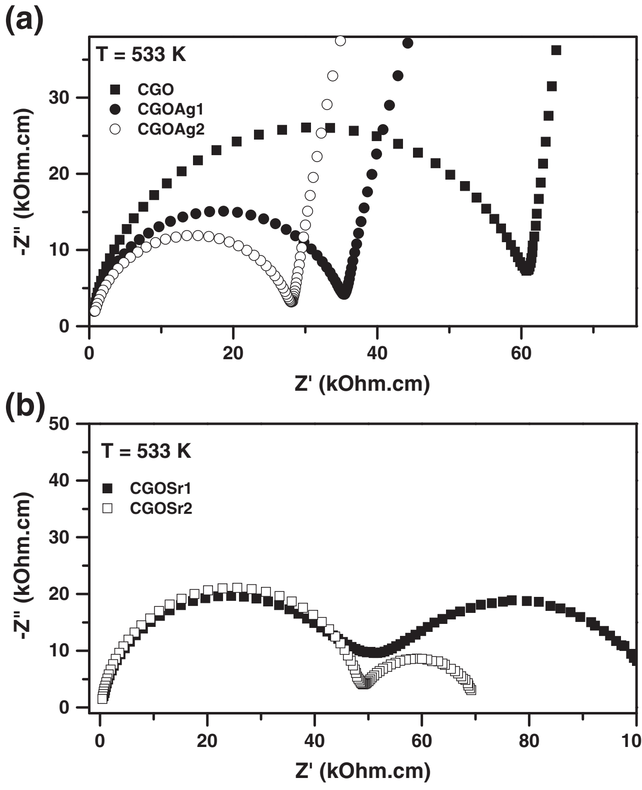

Fig. 3. Impedance spectroscopy diagrams at 533 K of (a) CGO, CGOAg1 and CGOAg2, and (b) CGOSr1 and CGOSr2 samples.

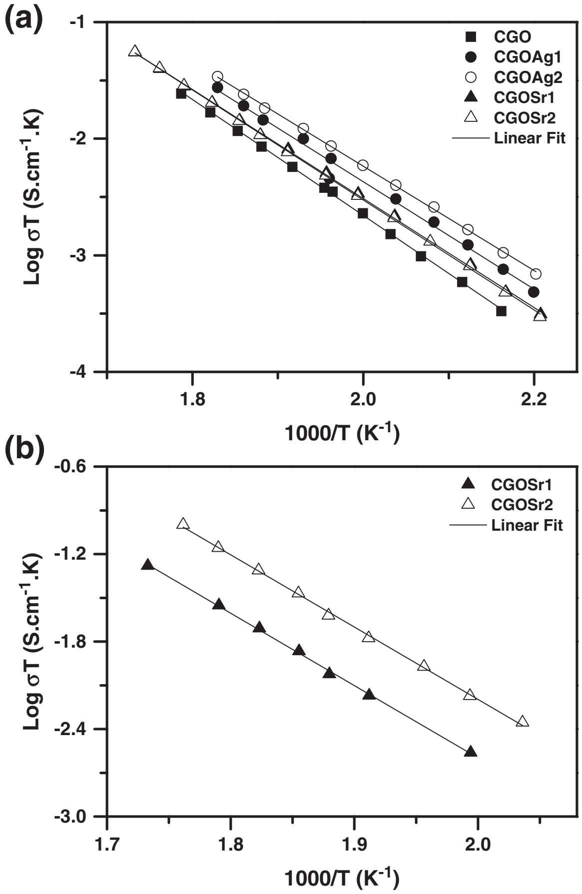

Fig. 4. Arrhenius plots of (a) grain conductivity of gadolinia-doped ceria containing co-additives and (b) grain boundary conductivities of samples containing strontium.

The Arrhenius plots of the electrical conductivity are shown in Fig. 4. The grain conductivity (Fig. 4a) is enhanced in pellets with co-additives. The influence of strontium addition is independent on its content, whereas increasing the silver content the grain conductivity increases gradually. The grain conductivity of CGOAg2, for example, is half order of magnitude higher than that of CGO. Additional experiments are necessary to clarify why this occur. This effect is probably related to an increased concentration of oxygen vacancy due to Ag^+ introduction in the ceria matrix. The apparent activation energy for grain conductivity is 0.98 (CGO), 0.91 (CGOAg1), 0.89 (CGOAg2), 0.93 (CGOSr1) and 0.93 eV (CGOSr2).

The temperature dependence of the electrical conductivity of grain boundaries (Fig. 4b) for CGOSr1 and CGOSr2 evidences the action of strontium on the grain boundary blocking effect. The apparent activation energy is 0.98 eV for both samples.

The beneficial effect of strontium on the grain boundary component of the overall electrolyte conductivity may be related to the grain size, *G*. It is generally known that the increase of the grain size results in the decrease of the grain boundary area and then decrease of the blocking effect. Fig. 5a shows the Arrhenius plots of the electrical conductivity of grain boundaries normalized for the grain size.

It is worth to note that the difference between the two straight lines has decreased (see Fig. 4b). However, the reduction of the grain boundary area is not the only reason for the enhancement of the grain boundary conduction behavior of CGO containing strontium. It has been shown [15] that this additive improved the grain boundary conductivity of CGO containing 500 ppm of SiO_2. The same effect might have occurred in this case, because although the starting materials are of relatively high purity, minor amounts of silica are sufficient to produce a large effect on the grain boundary conductivity of ceria-based ceramics [19].

The blocking effect may be estimated from the relation between the grain (g) and grain boundary (gb) resistances, *R*, by $\alpha_R = R_{gb}/(R_g + R_{gb})$

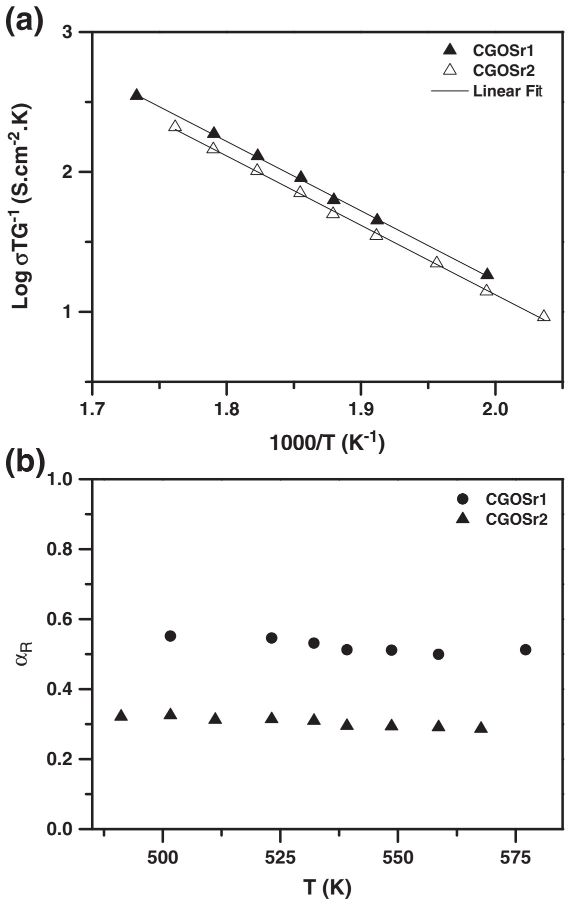

Fig. 5. (a) Arrhenius plots of the grain boundary conductivity of CGOSr1 and CGOSr2 normalized for the mean grain size; (b) temperature-dependence of the blocking factor for samples CGOSr1 and CGOSr2.

[20], α_R is the blocking factor. The variation of the blocking factor with temperature for samples CGOSr1 and CGOSr2 is shown in Fig. 5b.

The blocking of charge carriers is almost constant over the temperature range of measurements and amounts ~55% and ~32% for CGOSr1 and CGOSr2, respectively.

Based on the above results, it may be proposed a relationship involving the cation radius, solubility and the cation valence. Additives of higher cation radius, with full or partial solubility and lower valence than that of the host cation tend to increase the grain conductivity. When the solubility is partial, the fraction of the additive at the grain boundaries enhances also the grain boundary conductivity. The mean grain size depends on the difference between the additive and host cation valences.

4. Conclusions

Additions of small amounts of silver to gadolinia-doped ceria do not influence significantly the microstructure of sintered pellets. The densification process of the ceria matrix is slowed down, and the total shrinkage reached 8.6% upon heating up to 1773 K. The electrical conductivity of grains is considerably improved evidencing the solubility of silver in the ceria matrix. Strontium addition to gadolinia-doped ceria resulted in higher shrinkage (~17.5%) at the same temperature. The grain conductivity is slightly higher than that of pure CGO. Both co-additives reduced the apparent activation energy for grain conduction in gadolina-doped ceria. The major effect of strontium is on the grain boundaries. This additive enhances grain growth and contributes to the decrease of the blocking effect of charge carriers. This improvement is attributed to the decrease of grain boundary surface area along with possible scavenger of silica.

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