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Conductivity and structure of sub-micrometric SrTiO₃ -YSZ composites

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Abstract

Sub-micrometric composites of SrTiO₃-YSZ (1:1 volume) and samples of SrTiO₃ were prepared by high temperature consolidation of precursors obtained by precipitation with NaOH. The structure development and morphology of the precursors were studied by XRD and SEM. The perovskite and fluorite phases in the composites are clearly formed at 600 °C with no signs of reaction up to 1100 °C; the nominally pure SrTiO₃ can be formed at temperatures as low as 400 °C. Composites with sub-micrometric grain sizes can be prepared successfully without reaction between the components, although a change in the cell parameter of the SrTiO₃ is attributed to the presence of Na.

The consolidated composites were studied by impedance spectroscopy between 200-400 °C and at a fixed temperature of 600 °C with a scan in the partial pressure of oxygen. The composites did not exhibit high levels of ionic conductivity in the grain boundary nor the bulk. The conductivity of Na-free composites shows lower levels of conductivity than pure YSZ, while samples with Na showed increased conductivity. The conductivity of SrTiO₃ exhibited an enhancement attributed to p-type conductivity, although contributions from protons cannot be disregarded as some Na doping is present.

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Keywords

SrTiO₃/YSZ composites, Na-doped SrTiO₃, conductivity in composites

1. Introduction

An unprecedented increase in oxygen ion conductivity in intercalated structures of 8% Y₂O₃ doped ZrO₂ (YSZ) and SrTiO₃ was reported a few years ago by Garcia-Barriocanal et al [1]. If the conductivity of one of these heterostructures is extrapolated to room temperature a difference of ca. 8 orders of magnitude compared to standard YSZ is found. These findings were followed by serious criticism [2,3,4]: one of the main objections being that SrTiO₃ can exhibit p-type conductivity.

Conductivity enhancement has been reported before in heterolayers of CaF₂/BaF₂ very much in accord with space charge theory [5]. The possibility of conductivity enhancement in YSZ/Ln₂O₃ interfaces has been discussed in [3] where the authors argue that the strain at the interface, dilative or compressive, can lead to enhancement or decrease of the oxygen mobility, respectively. On the other hand, other groups have found no indication of oxygen mobility in similar systems [6] or even indicated that the conductivity is dominated by SrTiO₃ [7].

Despite the current disagreement on the nature of the conductivity in SrTiO₃-YSZ interfaces there is further interest on composites of these two materials as they represent alternative anodes for fuel cells: SrTiO₃ can exhibit high electronic conductivity achieved by suitable doping and high temperature reduction treatment (>1300°C) [8, 9, 10].

The objectives of this work are then: To present a novel fabrication method for composites of SrTiO₃ and YSZ and to study the electrical properties of samples with a large interfacial contact between the two phases. Should a large effect exist as reported in [1], then it might be possible to detect it in 3-dimensional systems where a large number of SrTiO₃-YSZ interfaces exist.

2. Experimental

2.1 Synthesis of nanocrystalline SrTiO₃ and YSZ

A batch of SrTiO₃ and several batches of SrTiO₃/YSZ (1:1 volume unless otherwise indicated) were prepared. Stoichiometric amounts of Sr(NO₃)₂ (> 99.0% Aldrich) and Y(NO₃)₃.6H₂O (99.8%) were dissolved in 20 ml of de-ionised water under constant stirring in nitrogen atmosphere. This was followed by addition of TiCl₃ solution 10 w% in 30% HCl (Aldrich) and ZrOCl₂ solution 30 w% in HCl (Aldrich). This mixture was added to a 2M solution of NaOH. The precipitation was immediate and a clear separation between liquid and solids occurs within 1 hour. The crystal clear liquid was removed with a pipette and the precipitate centrifuged. To avoid re-dissolution of Sr(OH)₂, the precipitate was then washed with a mixture of concentrated NH₄OH and absolute ethanol and centrifuged again; this rinsing process was repeated five times.

To essay the possible re-dissolution of Sr in the rinsate concentrated NaOH was added to confirm that no precipitate was formed; CO₂ was also bubbled into the rinsate to check for SrCO₃ precipitation. The precipitate was further processed by drying in nitrogen atmosphere in a hot plate to eliminate the excess water.

The evolution of this precipitate was followed by thermogravimetry (TG) in air with a heating rate of 5 °C min⁻¹. Several batches of the powder were annealed at different temperature (T = 400-1100 °C) for 1 hour and each sample was analysed by XRD (STOE Theta-Theta diffractometer) to observe the formation of the perovskite and the fluorite phases as well as to detect any possible reaction between them. The crystallite size was determined using Scherrer's formula and the lattice parameter with the

embedded refinement in the Xwin XPOW software. The microstructure was studied with a scanning electron microscope (Zeiss, SUPRA 35 or LEO 1525).

2.2 Consolidated samples

The washed precipitate was calcined at 400 °C for 1 hour, uniaxially pelletised and then isostatically compressed (195 MPa) at room temperature. The pellets were then heated (300 °C h⁻¹) in air up to 1100 °C for 1 hour. The density of pellets was measured with the Archimedes' method using de-ionised water as the immersion fluid. The structure development and microstructure were followed as a function of temperature by XRD and SEM, respectively.

A reference composite was prepared from commercial powders SrTiO₃ (American Elements 99.9%, < 100 nm) and YSZ (Fuel Cell materials, 5-10 nm). The powders were milled overnight using zirconia balls and absolute ethanol. The dried powders were then treated exactly as the precipitated powders to obtain a consolidated body.

2.3 Conductivity measurements

An impedance analyser (Solartron 1260) was used to perform most of the measurements within the frequency range 0.1 Hz - 1 MHz. Silver paint was applied on both faces of the pellets and baked at 400 °C in air for 1 hour before the measurements. The first set of measurements took place between 200 and 400 °C in air.

A second set of measurements was taken on a dense sample at a fixed temperature of 600 °C at different partial pressures of oxygen. A mixture of H₂O and H₂ was used to control the low pO₂ region while for the high pO₂ region, a mixture of air, N₂ and oxygen was used. All the gases were controlled with flow meters while the p_{H₂O} was controlled by bubbling the gases in de-ionised water at T = 14

°C. In most cases the partial pressure of oxygen was tested ex-situ with a zirconia sensor at $T = 997$ °C.

The impedance spectra were fitted using the routine embedded in the software ZsimpWin 3.21. The equivalent circuits selected are discussed in the corresponding section.

3. Results and discussion

3.1. *Strontium titanate*

3.1.1 Microstructure

Figure 1a shows the room temperature XRD patterns of powders and a pellet of SrTiO₃ prepared by precipitation of metal hydroxides. SrTiO₃ was obtained as a nanocrystalline phase at 400 °C; SrCO₃ traces were observed but these were eliminated completely after 800 °C. No other phase was detected.

The microstructure of SrTiO₃ nano-powders annealed at 400 °C and at 800 °C for 1 hour is seen in Figures 1b and 1c, respectively. The powder in both cases consisted of spherical particles of ca. 200 nm in diameter. The crystallite size of all the annealed samples stayed around 37 nm. At 800 °C the surface of the particles became smoother due to the decomposition of SrCO₃, as observed comparing Figures 1b and 1c, detected in the XRD (Figure 1a) and determined by the weight change in the TG experiments.

Figure 1d shows a micrograph of fractured pieces of SrTiO₃ sintered at 1100 °C. The individual grains have a more faceted shape and did not undergo a large grain growth as can be seen by comparing the images in Figure 1. Na was observed by Energy-dispersive X-ray spectroscopy (EDS) to be distributed inhomogeneously with some regions reaching up to 3% in weight. It can be assumed that

part of the excess Na substituted into the Sr sites, since their ionic radii are very similar: Sr²⁺, 12-coordinated is 1.44 Å while Na⁺, 12-coordinated is 1.39 Å); Ti⁴⁺ is too small to be substituted by ions such as Na⁺. Na then constituted an acceptor dopant and also led to a contraction of the lattice parameter of SrTiO₃.

3.1.2 Conductivity

Figure 2a shows the impedance spectrum of a SrTiO₃ pellet at 300 °C. One clear semicircle was visible and fitted to a single Resistance-Constant Phase Element (R-CPE) parallel circuit corresponding to the bulk. The spectrum for SrTiO₃ was similar to that reported for nanocrystalline un-doped SrTiO₃ [11]. The conductivity σ was thermally activated with an Arrhenius behaviour described by

$$\sigma T = 1.17 \times 10^7 \exp(-0.95\text{eV} / k_b T) \text{ S cm}^{-1} \text{ K} \quad \text{Eq. 1}$$

Where T is temperature in Kelvin, and k_b is the Boltzmann constant. The increased conductivity found in SrTiO₃ in comparison with un-doped SrTiO₃ must be related to the excess Na doping and the subsequent creation of oxygen vacancies, electron holes, or protons as compensating defects. These generation can be written respectively as:



The conductivity of SrTiO₃ can be greatly modified by small amounts of doping [12]. Protons are potential charge carriers due to the hydrophilic nature of Na [13] and the known capability of the

SrTiO₃ perovskite to incorporate water into its lattice [14, 15, 16, 17]. Hole conductivity or oxygen ions are also expected to transport charge in SrTiO₃ [12,18,19].

3.2 Composites

3.2.1 Microstructure

XRD patterns of the composite SrTiO₃/YSZ powders annealed at different temperatures are shown in Figure 3a. Three main observations are:

1.- The dry precipitate obtained from the synthesis was mainly amorphous as seen at 400 °C. The first compound to crystallise was SrCO₃ but it disappeared completely at 800 °C according to TG and XRD.

2.- Complete crystallisation of the fluorite YSZ and the perovskite SrTiO₃ took place between 500 °C and 600 °C. No reaction between YSZ and SrTiO₃ was observed up to 1100 °C. This was also confirmed by the XRD of the reference sample i.e., the mixture of commercial powders, and seems in accord with the literature [8, 9, 10].

3.- The lattice parameters of SrTiO₃ and of YSZ change slightly in the presence of Na. See table 1. As observed by EDS there was Na in this batch, most likely incorporated into the SrTiO₃ lattice at high temperature. Due to ionic radius mismatch in the sites of Y³⁺ (1.019 Å, 8-coordinated), Ti⁴⁺ (0.605 Å, six-coordinated) and Zr⁴⁺ (0.84 Å, 8-coordinated), other doping sites were not considered, although Ti⁴⁺ can be incorporated into the Zr site in YSZ. Na⁺ ionic radii are 1.19 Å for 8-coordination and 1.02 Å for 6-coordination.

Table 1 shows the crystallite sizes, cell parameters, and relative densities of the different composites prepared here. The data of the IPDF files are included as a reference as well as the reference sample prepared from commercial nanopowders.

No extra peaks were observed in the XRD pattern as seen in Figure 3a but according to the EDS some regions had up to 3% weight in Na. The effect of the excess Na was observed in the XRD pattern as a change in the lattice parameter of SrTiO₃ and not as a secondary phase. Samples with Na levels below the detection level of the EDS were prepared but did not achieve a good density.

Figure 3b shows a micrograph of a precipitate treated at 800 °C for 1 hour. The powder consisted of spherical particles of up to 200 nm in size. All particles seemed to show the same shape, topography, and contrast; at this stage there was no clear distinction between the fluorite and the perovskite phases.

Figure 3c and 3d show the structure of a composite with 88 % of the theoretical density, the highest achieved for the composite pellets annealed at 1100 °C. There was a clear microstructural characteristic: particles of ca. 0.7-0.8 μm in diameter and small particles < 50 nm. Considering the low grain growth exhibited by SrTiO₃ (see Figure 1d) and the calculation of the crystallite size (Table 1), the large particles can be assigned to YSZ and the small particles to SrTiO₃. A relevant observation is the very good contact that exists between the grains and the consequent large interfaces between the YSZ and the SrTiO₃, despite the presence of pores. Due to our interest in the interfacial transport, the conductivity of this sample was further studied in this work.

3.2.2 Conductivity

A typical impedance spectrum for a tested composite in air at 300 °C is shown in Figure 2b. It consisted of two signals with the highest frequency semicircle clearly defined. The symmetric Bruggeman model for inter-percolating phases in a composite was used to model the bulk conductivity [20]. The conductivity of the composite Ψ_m is

$$\Psi_m = \frac{1}{4} \left\{ q + (q^2 + 8\Psi_1\Psi_2)^{\frac{1}{2}} \right\} \quad \text{Eq. 5}$$

where

$$q = (3x_1 - 1)\Psi_1 + (3x_2 - 1)\Psi_2 \quad \text{Eq. 6}$$

And x is the volume fraction and the subindices indicate the phase.

A good fit to the experimental data is obtained only if the conductivity of each phase is smaller in the composite: a value of $\sigma = 5 \times 10^{-7} \text{ S cm}^{-1}$ was used for YSZ, as it decreases by ca. an order of magnitude when doped with Ti [21,22,23] and for a lightly acceptor doped SrTiO_3 , $\sigma = 1 \times 10^{-7} \text{ S cm}^{-1}$ was used [24].

The bulk conductivities obtained from the high frequency semicircle for different samples are shown in Figure 4 as an Arrhenius plot. The results can be summarised as:

- 1.- The reference composite presented lower bulk conductivity than YSZ and high activation energy (E_a), too high to be due to YSZ. There was no evidence of improved conductivity although the conductivity may be low because the sample was not very dense or YSZ was doped with Ti.
- 2.- The Na-doped composite presented a higher conductivity than the reference composite, a phenomenon associated with defect formation and transport (see Eq. 2-4).
- 3.- SrTiO_3 showed the highest conductivity and could be clearly associated with Na doping. Since the Na in SrTiO_3 is hygroscopic [13], this might suggest proton conduction. Proton conduction has been reported in Sc-doped SrTiO_3 [14-17].

Figure 5a shows an impedance plot of a tested composite in air at 600 °C. At this temperature a scan of partial pressures of oxygen was performed; all the spectra were fairly similar. Three CPE-R elements were used to fit the spectra as shown in Figure 5a. The impedance of a CPE element is given by

$$Z = \frac{1}{Y_0(j\omega)^n} \quad \text{Eq. 7}$$

Where Y_0 is the admittance and n the exponential value obtained from the fitting of the CPE element [25]. To help in the assignation of the three signals observed, the equivalent capacitance C was estimated using

$$C = \frac{(R_0 Y_0)^{1/n}}{R_0} \quad \text{Eq. 8}$$

Some information on the grain boundary can be obtained from the spectra measured at a fixed temperature of 600 °C and as a function of partial pressure of oxygen. The equivalent capacitances obtained from the three elements observed at 600 °C for all atmospheres are displayed in Figure 5b. The estimated equivalent capacitances can be used to identify the different elements in the impedance plots, namely bulk (ca 10^{-11} C F⁻¹), grain boundary, (ca 10^{-8} and 10^{-9} C F⁻¹) and electrode (ca 10^{-7} C F⁻¹).

Figure 5c shows a plot of the resistance of bulk, grain boundary and electrodes as a function of pO_2 for the YSZ/SrTiO₃ sample tested at 600 °C.

In general, the bulk and grain boundary resistances did not seem to change dramatically with partial pressure of oxygen, although in the air-oxygen mixtures their values hinted at p-type behaviour at high pO_2 and n-type at low pO_2 as expected for SrTiO₃ despite the scatter of data. The electrode response was clearly affected by the partial pressure of oxygen. No remarkable enhancement in the conductivity is seen in any of the fitted elements.

4. Conclusions

A method for the manufacture of sub-micrometric composites of SrTiO₃-YSZ (1:1 volume) and samples of SrTiO₃ was presented. No reaction between the components was seen but a change in the cell parameter of the SrTiO₃ is attributed to the presence of Na. There is good interfacial contact

between the phases in the consolidated composites SrTiO₃-YSZ although they did not exhibit high levels of ionic conductivity in the grain boundary, nor in the bulk. The conductivity of Na-free composites is lower than the conductivity of pure YSZ while the conductivity of Na-doped composite samples was higher than non-doped composites. The composites did not exhibit high levels of ionic conductivity in the grain boundary nor in the bulk. The conductivity of single phase SrTiO₃ exhibited an enhancement caused by Na doping. Charge transport is likely to be p-type, but it may be protonic in nature as in Sc-doped SrTiO₃ and due to the hygroscopic nature of Na in SrTiO₃.

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Table 1. Lattice parameters, crystallite size and percentage of theoretical densities. All composites were prepared at 1100 °C.

| | $SrTiO_3/\text{Å}$ | Crystallite size / nm | YSZ/ Å | Crystallite size / nm | % theo. density |
|---|--------------------|--------------------------|-----------------|--------------------------|--------------------|
| <i>IPDF file</i> | 3,905 | | 5,1390 | | |
| <i>Reference SrTiO₃/YSZ</i> | 3,8979 | 40 | 5,1206 | 38 | 57 |
| <i>SrTiO₃/YSZ (up to 3%w Na)</i> | 3,973 | 11 ^a | 5,134 | 44 | 88 |
| <i>SrTiO₃ (up to 1%w Na)</i> | 3,8894 | 37 | ----- | ----- | 66 |

^a *The crystallite of SrTiO₃ is unusually small. Apparent broadening of the peak may be due to the presence of two similar SrTiO₃ phases with different levels of Na.*

Figure captions

Figure 1. a) XRD of SrTiO₃ powders annealed at different temperatures. The sample at 1100 °C is a pellet. b). Micrograph of SrTiO₃ powder annealed at 400 °C for 1 hour. The small grains observed on the surface of the spheres are SrCO₃. c) Particles of SrTiO₃ annealed at 800 °C. SrCO₃ is not detectable by XRD. A small amount of Na is observed by EDS. Note the smooth surface of the spheres and compare with those of b. d) A crushed sintered pellet of SrTiO₃ with 66 % of the theoretical density

Figure 2. a) Impedance spectrum in air at 300 °C for SrTiO₃. b) Impedance plot in air for a composite with 88% density at T = 300 °C. Included is the result of the simulation using the symmetric Bruggeman model for a composite with inter-percolating materials [20].

Figure 3. a) XRD of SrTiO₃/YSZ powders calcined for 1 hour at the temperature indicated. All samples were powders except sample at 1100 °C which is a pellet. b) Micrograph of a precipitate calcined at 800 °C. c) SEM micrograph of a composite with 88% density. d). SEM Micrograph of the surface of a composite with excess Na (Some regions up to 3% according to the EDS but no extra peaks were observed in the XRD.

Figure 4. Arrhenius plot for 2 different composites and Na-doped SrTiO₃. The black line is the standard YSZ conductivity. Activation energy values: 1.19 eV for the composite with commercial powders, 0.95 for SrTiO₃ and 1 eV for composite YSZ/SrTiO₃.

Figure 5. a) Impedance plot of composite at log (pO₂/atm) = -27 at 600 °C b) Capacitances of the three different elements observed in the impedance spectra as a function of pO₂. From small to large equivalent capacitance the elements most likely represented are bulk, grain boundary and electrode respectively. c). Resistances of the 3 different elements observed in the impedance spectra.