

Ionic conductivity of directionally solidified zirconia–mullite eutectics



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ABSTRACT

The properties of directionally solidified eutectic (DSE) zirconia–mullite composites are presented. These materials combine two oxide ion conductors in eutectic microstructures stable over broad temperature (570–1415 °C) and pO_2 (10^{-20} to 10^5 Pa) ranges, which are pertinent for their application as high temperature (>1200 °C) solid electrolytes, e.g. in Nernstian sensors. X-ray diffraction and scanning electron microscopy/energy dispersive spectroscopy results reveal a composite structure comprising eutectic crystals of mullite and zirconia, and an intergranular amorphous phase rich in Al–Y–Si–O. The amorphous phase is crystallised upon annealing at 1400 °C, and the resulting composites have a composition close to the nominal eutectic consisting of 79 vol.% mullite and 21 vol.% zirconia. The electrical conductivity of these materials is rationalized in terms of percolation, fraction and properties of each phase, attaining values in excess of 0.01 S/cm at 1370 °C and displaying Arrhenius behaviour with activation energy of 70 kJ/mol. The broad electrolytic domain of these solid electrolytes is demonstrated by conductivity measurements carried out from 600 °C to 1370 °C in O_2 , air, Ar and 10% H_2 + 90% N_2 atmospheres.

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1. Introduction

Directionally solidified eutectic (DSE) oxide composites are characterized by very particular microstructures displaying textured and homogeneous fine mixtures of the components. These microstructures can be tailored as rod-like, lamellar or fibrous by a relatively simple control of the processing conditions [1–5]. These features are attractive to the design of electroceramics with low percolation threshold volumes [2–4]. Most of the investigations have been carried out in oxide DSE composite fibres grown by the laser floating zone (LFZ) method [1], with the composites of alumina and an ionic conductor such as yttria-stabilized zirconia being a good example where higher bending strength is expected when compared to pure zirconia [6–8].

Yttria-stabilized zirconia (YSZ, $(Zr,Y)O_2$) is an excellent oxide ion conductor with high thermo-mechanical and chemical stabilities. YSZ is by far the most studied and used solid electrolyte for high temperature electrochemical applications, from promising technologies such as solid oxide fuel cells and electrolyzers, to well-established mass-produced oxygen sensors [9,10]. The ionic conductivity of zirconia is (besides a minor contribution from intrinsic anti-Frenkel defects) mainly due to the extrinsic oxide vacancies (V_O^\bullet) formed to balance the partial substitution of Zr^{4+} with lower valence Y^{3+} according to the equilibrium $Y_2O_3 \xrightarrow{ZrO_2} 2Y_{Zr}' + 3O_O^\bullet + V_O^\bullet$ expressed in Kröger–Vink notation [9].

Mullite is an aluminosilicate with excellent chemical and thermo-mechanical stability that is widely employed in structural applications [11,12], having also been suggested as a possible substitute for zirconia electrolytes in potentiometric sensors able to operate in reducing conditions at very high temperatures (1400–1600 °C) [13–15]. The oxide conductivity of mullite is due to the oxide vacancies created by the substitution of Si^{4+} for Al^{3+} ($Al_2O_3 \xrightarrow{SiO_2} 2Al_{Si}' + V_O^\bullet + 3O_O^\bullet$). However, the concentration of free vacancies is low and so is the conductivity, e.g. 3.2×10^{-5} S/cm at 800 °C for $3Al_2O_3-2SiO_2$ [16,17]. As desired for a solid electrolyte, the electronic conductivity is negligible, with ionic transference numbers higher than 0.99 at oxygen partial pressure (pO_2) higher than 10^{-5} Pa at 1400 °C, or 1 Pa at 1600 °C [13].

Zirconia–mullite composites are potentially interesting high temperature solid electrolytes because they combine the high ionic conductivity and broad electrolytic domain of zirconia with the good creep resistance, excellent chemical stability and strength of mullite at high-temperature [18]. Moreover, zirconia may improve the fracture toughness. Such composites were indeed proposed as oxygen sensors to work under the thermally and chemically harsh environment of steel making [18,19]. As expected, the ionic conductivity increases with increasing zirconia fraction, with major changes near the percolation limit (2.0×10^{-5} S/cm and 1.4×10^{-4} S/cm for 20 vol.% and 30 vol.% zirconia, respectively, at 700 °C) [16,18].

It was previously shown by some of the authors that zirconia–mullite DSE composites obtained by LFZ may display various microstructures (planar coupled eutectic, faceted mullite crystals enclosing a dispersion of fine zirconia fibrils or mullite columnar growth with

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coarse zirconia inclusions), depending on the pulling rate [20]. In the present work, the study of the ZrO_2 - SiO_2 - Al_2O_3 eutectic composition is refined in order to explore the potential of zirconia–mullite DSEs with low zirconia content (21 vol.%) as a dual-phase solid oxide electrolyte for application at temperatures higher than 1300 °C.

2. Experimental

Feed and seed rods were prepared from commercial powders with a composition of 50 wt.% γ - Al_2O_3 (Merck, anhydrous, >99.9%), 20 wt.% SiO_2 (Sigma, 99%) and 30 wt.% ZrO_2 stabilized with 8 mol% Y_2O_3 (Tosoh Co., 99.9% with approximately 2% HfO_2). The powders were mixed during 90 min at 500 rpm in a planetary ball-mill (Retsch, PM100). Green rods were then processed by extrusion with the help of a polyvinyl alcohol (PVA 0.1 g/ml) binder. A LFZ apparatus described elsewhere [20] was used to grow fibres in air using pulling rates of 10, 100 and 500 mm/h. Typical fibres are ~1.5 mm in diameter and ~30 mm in length. Selected fibres were subjected to a post-synthesis annealing for 10 h at 1400 °C in air.

The structural analysis of powdered fibres was carried out by X-ray diffraction (XRD, X'Pert MPD Philips, $Cu-K\alpha$ radiation) with a step width of 0.01° and a scan rate of 3°/min. Variable temperature X-ray diffraction patterns (HTXRD) were collected between 300 °C and 1000 °C in the same apparatus, using a step width of 0.02°. The system is equipped with a Anton-Parr GmbH HTK16 chamber, containing a platinum filament and a Pt–Pt/Rh(10%) thermocouple. Rietveld analysis of the XRD patterns collected at each temperature was performed with FullProf [21] refining the scale factor, background, lattice parameters, sample displacement, and peak profile parameters.

The microstructural characterization was carried out in a scanning electron microscope (SEM Hitachi S4100) equipped with an energy dispersive X-ray spectrometer (EDS). The fractional area occupied by each phase was estimated based on SEM images, using ImageJ 1.45s [22], and assumed as equivalent to the volume fraction of each phase. At least 10 images for each sample were analysed in order to obtain an average value and the associated dispersion.

The electrical conductivity was measured by impedance spectroscopy along the growth direction of samples with ~4.5 mm in length, which were cut from the original fibres. Platinum electrodes were applied at the tips and thermally treated at 1000 °C for 1 h to provide good electrical contacts. The impedance spectra were acquired with a Hewlett Packard 4984a LCR metre in the frequency range 20–10⁶ Hz and using a test signal amplitude of 1 V. The measurements were carried out during cooling under flows (50 mL/min) of air, argon, oxygen or a mixture of 90% N_2 + 10% H_2 (pO_2 monitored in situ using a YSZ Nernstian sensor) and as a function of temperature in the range 570 °C–1415 °C. Two experimental set-ups were used, one covering the high temperature range from ~900 °C up to ~1400 °C where only air, argon and oxygen atmospheres could be used (hydrogen is avoided for security reasons), and another specified for a low temperature range (under 1000 °C) which is compatible with hydrogen containing gas mixtures, offering in addition the possibility to humidify the gases. The sample holders have the same design in both set-ups.

3. Results and discussion

3.1. Microstructural characterization and phase analysis

The room temperature XRD pattern of the fibre pulled at 100 mm/h (Fig. 1, thick line) shows the presence of three phases: orthorhombic mullite (M, space group $Pb\bar{a}m$ [23]), and tetragonal (Z^t , space group $P4_2/nmc$ [24]) and monoclinic (Z^m , space group $P2_1/c$ [25]) zirconias. The HTXRD data in Fig. 2 show the expected decrease of the intensity of the mullite reflections upon heating, due to the temperature factor. They also clearly depict the progressive transformation of Z^m into Z^t with increasing temperature, suggesting that the $YO_{1.5}$ content in ZrO_2

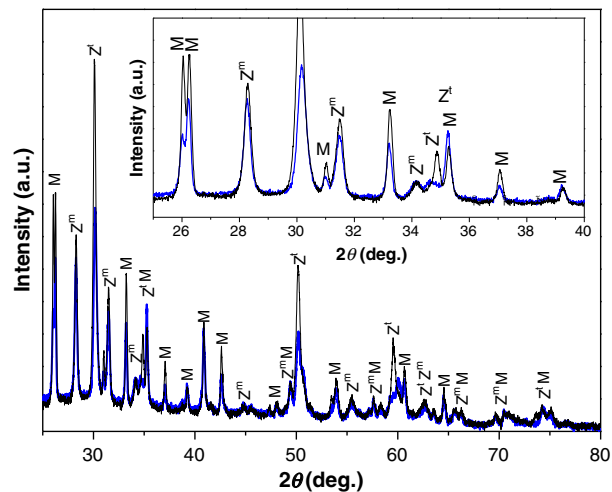


Fig. 1. Powder XRD patterns of a zirconia–mullite eutectic fibre obtained at 100 mm/h (thick blue line) and of the same fibre annealed at 1400 °C in air for 10 h (thin black line). M is mullite (JCPDS card no. 01-074-4146), Z^m is monoclinic zirconia (JCPDS card no. 00-007-0343) and Z^t is tetragonal zirconia (JCPDS card no. 04-016-2094).

is lower than ~6 mol%, and thus that the existing Z^t lies on the category of the transformable tetragonal zirconia [26,27]. One may thus obtain an estimate of the yttria content as a function of temperature from the ratio between the intensities of the Z^m ($\bar{1}11$) and Z^t (101) reflections. The HTXRD patterns did not support refinement of the fractional coordinates and thermal parameters for each independent atom of the three phases, but these restrictions are expected to have a minimal influence on the estimated weight fractions. The full list of the refined lattice

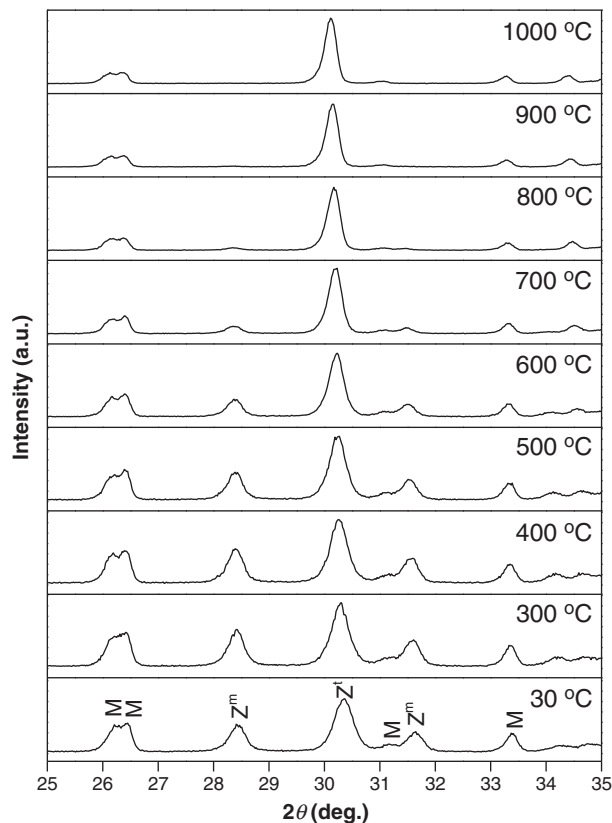


Fig. 2. Powder HTXRD patterns of a fresh zirconia–mullite eutectic fibre grown at 100 mm/h.

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