

## Optical properties

Spectral ellipsometry measurements were used to characterize the optical properties of the YSZ coatings such as thickness ( $d$ ) and refractive index ( $n$ ) which are summarizing in table IV (please, see the article).

The three coatings measured are *nano*-films which their thickness depends on both parameters: the deposition time and the sintered temperature. For the green coatings, (15min-green and 60 min green) the thickness increases with the deposition time due to the increment of the deposited nanoparticles. When the coatings are thermally treated, 60 min-sintered at 500°C, the thickness decreases due to sinterization facilities consolidation processes leading to a lower porosity nanostructure, as has been showed above in Figure 11. The refractive index of the coatings is also related with their porosity. Green coatings (15min-green and 60 min green), which have high porosity (~70%) lead to low refractive indexes, 1.03 and 1.13, respectively. But, the sintered coating, which is a consolidated nanostructure, has a refractive index of 1.85. This high value obtained is in the same range that the theoretical value measured for the YSZ,  $n=2.01$ .<sup>1</sup>

Figure 12 illustrates the effect of the EPD conditions and the resulting microstructural characteristics on the UV-visible transmittance spectra for the YSZ films.

The as- deposit films (15 min, red squares, and 60min, green squares) as well as the film annealed at 500° C ( blue squares) exhibit a high degree of transparency. The transparency of the films decreased with the deposition and the annealing times due to the increasing of the film thickness and the grain size. The YSZ films reveal the development of a broad shoulder of reduced transmittance in the spectral region 200-500 nm for the green bodies and from 200nm to 600 nm for the sintered film. The attenuation of the incident light can be caused by absorption and/ or scattering mainly at grain boundaries.

The high values measured for the linear absorption coefficients  $\alpha$  of the YSZ films (Figure 13) which are the order of  $10^5 - 10^6 \text{ cm}^{-1}$ , evidence the high cristallinity of the deposited films.

Values of  $\alpha$  of  $10^5 - 10^6 \text{ cm}^{-1}$  are typical for interband transitions. Analysis of the functional dependence of the absorption coefficient on the photon energy in the region of the valence band (VB) – (conduction band) CB transition allows a determination of the band gap energy ( $E_g$ ) according to Eq. 1 by extrapolation of the linear section of a plot  $(\alpha h\nu)^2$  vs.  $h\nu$  to the abscissa.

$$\alpha \sim \frac{(h\nu - E_g)^q}{h\nu} \quad (1)$$

The value of the parameter  $q$  depends on the type of transition, with  $q=2$  for an indirect band gap and  $q=0.5$  for direct band gap material such as zirconia.

This is shown in Figure 14 for the as deposited films during 15min and 60 min and for the film sintered at 500 °C. The  $E_g$  determined for the films are  $2.97 \pm 0.03\text{eV}$ ,  $3.49 \pm 0.03\text{eV}$  and  $2.69 \pm 0.03\text{eV}$ , respectively. The large discrepancy among published optical band gap data for YSZ, which cover a range of  $\sim 4\text{-}6\text{eV}$ , can be originated from a frequent misinterpretation of the rise in the absorption at sub-band gap photon energies in the range 2-4eV in terms of an interband transition.

The notable absorption detected and the linear dependence between  $\alpha$  and the  $E$  (Figure 13) suggests Urbach – type behavior, which have been found previously for YSZ.<sup>2, 3</sup> Urbach type behavior is attributed to a structural or thermal disorder causing a decaying density of localized states at the band edges (“band tailing”). Structural disorder is induced by the  $\text{Y}_2\text{O}_3$  stabilizer. The Y 4p and the Y 4d states, which are introduced by the  $\text{Y}^{3+}$  ions, lie energetically well below the O 2p valence band and above the Zr 4d conduction band as UV-Vis spectroscopy results indicate. On the other hand, oxygen vacancies introduce defect bands in the valence band as well as localized states in the vicinity of the conduction band edge.<sup>4</sup> The anion vacancies detected are the primary species in both solid-state conduction and heterogeneous electrocatalysis of solid oxide electrolytes, hence, the films developed in this work by the eco-one pot method would be suitable for these applications.

## References

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