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Thermoanalytical study of the YSZ precursors prepared by aqueous sol–gel synthesis route

K. Tõnsuaadu · A. Zalga · A. Beganskiene · A. Kareiva

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Abstract The Y-Zr-O precursors derived from an aqueous sol–gel synthesis have been applied for the preparation of yttria-stabilized zirconia (YSZ) powders and thin films on the corundum (Al_2O_3) substrate, using dip-coating technique. In this aqueous sol–gel synthesis route, citric acid as a complexing agent has been used for the preparation of stable Y-Zr-O nitrate–citrate sols and gels. Thermal decomposition of dried gels was studied by simultaneous TG/DTA/EGA-FTIR measurements in the dynamic 80%Ar + 20%O_2 atmosphere. FTIR and X-ray diffraction analyses were used for the determination of phase purity of the end products obtained at 700, 800 and 900 °C. The morphological features of the prepared YSZ coatings and powders were evaluated using scanning electron microscopy.

Keywords Sol–gel synthesis · TG/DTA/EGA-FTIR · Y-Zr-O nitrate–citrate complex

Introduction

Yttria-stabilized zirconia (YSZ) is used as electrolyte for electrode-supported solid oxide fuel cells (SOFCs) due to their high ionic conductivity [1, 2]. The negligible electronic conductivity even under reducing atmosphere, the electrochemical stability as well as the mechanical properties of YSZ facilitate the use this material in fuel-cell applications [3]. In order to increase the chemical stability of the SOFCs components and decrease the cell cost, it is necessary to decrease the working temperature to around 700–800 °C. The control of the microstructure and the thickness of the solid electrolyte may reduce the internal resistance of the YSZ electrolyte. Consequently, an improvement of the performance of the cell could then be reached [4–6]. Moreover, the synthesis of nanoscale materials, which could be used for the development of SOFC systems in the intermediate-temperature regime of 500 °C $< T <$ 750 °C, now is of substantial interest [7].

The synthesis of YSZ powders and thin films on various substrates with a number of different techniques was previously published [8–15]. For this purpose, the solid-state, spray pyrolysis, non-aqueous sol–gel, hydrothermal methods, electrochemical, chemical vapour, physical vapour deposition, tape casting, slurry coating, and other techniques have been applied to synthesize bulk YSZ and dense ceramic coatings on different substrates for solid oxide fuel cells (SOFCs). All the coating techniques, mentioned before, have some advantages and disadvantages. However, the commercialization of SOFC on a big scale until today does not occur [16].

The technological applications of an aqueous sol–gel technique range in a very wide field, because of the versatility and simplicity of the method [17–19]. Compared with other techniques, an aqueous sol–gel method has the advantages of a good control of the processing parameters. The use of sol–gel processing can eliminate major problems such as long diffusion paths, impurities and agglomeration, which will result in products with improved homogeneity.

In this paper, we report on the synthesis and characterization of YSZ powders and thin films on the corundum substrates obtained using dip-coating technique. For the preparation of stable sols, an aqueous sol–gel synthesis

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approach in which citric acid as a complexing agent was used. The impact of a concentration of starting chemicals used in gel preparation, gels thermal behaviour including the analysis of the evolved gases by FTIR spectroscopy, phase purity and crystallinity of the annealed samples is studied.

Experimental details

Sample preparation

The Y-Zr-O nitrate–citrate sol was prepared by an aqueous synthesis route. In this case, the appropriate amount of zirconium oxonitrate dihydrate ($ZrO(NO_3)_2{\cdot}2H_2O$, 99.9%) was first dissolved in concentrated nitric acid solution (65% HNO_3) by stirring at 70–80 °C. Three samples with different starting concentration of zirconium were prepared. The amount of $ZrO(NO_3)_2{\cdot}2H_2O$ selected was 0.0025 mol (sample 1), 0.005 mol (sample 2) and 0.01 mol (sample 3). Secondly, citric acid (CA) with a molar ratio of Zr/CA = 0.25, dissolved in a small amount of distilled water, was added with a continuous stirring at the same temperature. Next, after 5 h, the required amount of yttrium nitrate hexahydrate ($Y(NO_3)_3{\cdot}6H_2O$, 99.99%) dissolved in distilled water, was mixed with the previous solution. Finally, the same amount of the aqueous solution of the complexing agent CA was repeatedly added to the reaction mixture in order to prevent crystallization of metal salts during the gelation process. The beaker with the solution was closed with a watch glass and left for 1 h with continuous stirring. The obtained clear solution was concentrated by slow evaporation at 80 °C in an open beaker. A pale yellow, transparent, Y-Zr-O nitrate–citrate sol formed after nearly 60% of the water has been evaporated under continuous stirring. The synthesis scheme is shown in Fig. 1.

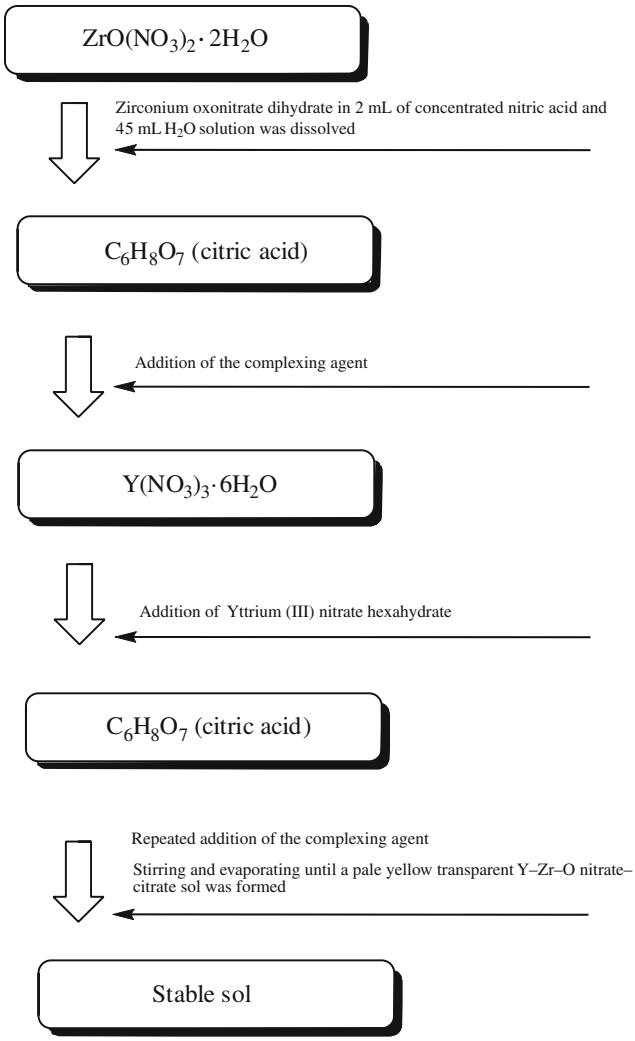

Fig. 1 Synthesis scheme of the sol–gel preparation of the Zr-Y-O nitrate–citrate sol

Y-Zr-O nitrate–citrate gel was prepared by continuous stirring of the stable Y-Zr-O nitrate–citrate sol in an open beaker. After the evaporation of residual solvent at the same 70-80 °C temperature, the porous brown Y-Zr-O gel was formed. The obtained gel was repeatedly dried in an oven at 110 °C temperature, and fine-grained powders were obtained.

The Y-Zr-O precursor gels were calcined for 5 h at 500 °C in alumina crucibles and reground carefully in an agate mortar. Since the gels are very combustible, slow heating (1 °C/min), especially between 150 and 300 °C, was found to be essential. After intermediate grinding, the obtained powders were repeatedly annealed for 5 h at 700, 800 and 900 °C temperatures in air at ambient pressure.

YSZ thin films were deposited onto commercial corundum (Al_2O_3; 1.5 × 1.5 cm) substrates by dip-coating technique from the stable Y-Zr-O nitrate–citrate sol. The films on corundum substrate were deposited at 5 mm/min immersion rate and were dried at room temperature for 24 h in air at ambient pressure in a horizontal position. Afterwards, the dried coated substrate was annealed at 800 °C temperature in air for 1 h. According to the previous studies [20, 21] at this temperature, the crystallization process begins, and a pure cubic phase of yttria-stabilized zirconia was obtained from the YSZ sol–gel film.

Characterization of samples

The thermal decomposition processes of Y-Zr-O precursor nitrate–citrate gels were examined by thermogravimetric and differential thermal analysis (TG/DTA) combined with Fourier-transform infrared spectroscopy coupled with the evolved gas analysis (FTIR/EGA). The measurements were taken on a SetSys-Evolution instrument connected to a Nicolet 380 FTIR spectrometer using a sample weight of about 10–12 mg in open Pt crucibles and a heating rate of

10 °C min^{-1} in flowing artificial (80%Ar + 20%O_2) air (60 cm^3 min^{-1}) atmosphere at ambient pressure from room temperature to 1000 °C. The gases evolved were led through a heated tube into a FTIR gas cell. The FTIR gas cell and the connecting tube were kept at 220 °C. The absorption spectra were recorded in the wavenumbers interval of 4,000–400 cm^{-1} with a resolution of 4 cm^{-1} and 60 scans averaged. The evolved gases were identified using the FTIR reference spectra in Thermo Scientific FTIR vapour phase and gases Database, Vol. 3. Powder X-ray diffraction (XRD) analysis was carried out using a Bruker D8 Advance powder X-ray diffractometer with CuKα source. The spectra were recorded at the standard rate of 1.5 2θ/min. After pressing the samples into the pellets with KBr (~1.5%), the Fourier-transform infrared (FTIR) spectra were recorded with a Perkin–Elmer FTIR Spectrum 1000 spectrometer. The scanning electron microscope (SEM) DSN 962 was used to study the surface morphology and microstructure of the obtained ceramic samples.

Results and discussion

Thermal analysis

In order to explain and better understand the possible thermal decomposition behaviour of precursors and crystallization process of the sol–gel materials, the thermal analysis (TG-DTA) with simultaneous FTIR analysis of evolved gases during (FTIR-EGA) decomposition could be successfully used [22–24]. The TG-DTA curves of the YSZ nitrate–citrate gels prepared using different concentrations of $ZrO(NO_3)_2{\cdot}2H_2O$ are displayed in Fig. 2. The impact of the initial concentration of the $ZrO(NO_3)_2{\cdot}2H_2O$ solution is manifested in the TG–DTA curves. The decomposition process of gels can be roughly divided into three intervals. The first weight loss observed in the TG curves between room temperature and 248 °C was 38, 67 and 72% for samples 1, 2 and 3, respectively. These differences could be explained by the possible loss of some nitrate during dehydration [25] or different composition of complexes formed in gelation process due to different concentrations. In the DTA curve of sample 1 (of the lowest concentrations of $ZrO(NO_3)_2{\cdot}2H_2O$ used in the sol–gel processing (Fig. 2), only one broad endothermic peak with top at 217 °C was observed. In the DTA curves of samples 2 and 3, additional endothermic effect with peak top at 155 °C appeared. This additional effect is complemented with the bigger mass loss at these temperatures and could be related to melting of the precursor [26] before decomposition of gel complexes.

At the second, from 250 to 330 °C, and third, from 330 to 480 °C, decomposition steps, the mass loss values of the studied samples equalized and achieved the values from 88 to 94 %. At these temperatures, the decomposition process was strongly exothermic (Fig. 2) with peak top at 365–370 ° characteristic for oxidation process of organic compounds.

With the temperature increase of up to 1,000 °C, the weight remains almost constant, which indicates that the decomposition and combustion of all organic components in the precursor gel were completed at below 450 °C. However, the negligible exothermic peak in the DTA curve (sample 2) at ~530 °C is also detected with a mass loss of 2%. These TG/DTA results of synthesized YSZ nitrate–citrate precursor gels show that for the preparation of bulk YSZ or thin films from Y-Zr-O nitrate–citrate sols with higher concentrations of starting materials, at least the temperature of 550 °C is needed to complete solid-state reaction.

The citrate–nitrate mixture combustion is often explained by simplified reactions with the release of CO_2, H_2O, CO, NO and N_2 [26, 27], respectively:

$$aC_6H_8O_7 + bNO_3^- \rightarrow cC + dCO + eCO_2 + fH_2O + gOH^- + hNO \quad (1)$$

or

$$Zr(NO_3)_4 + 10/9C_6H_8O_7 \rightarrow ZrO_2 + 20/3CO_2 + 2N_2 + 40/9H_2O \quad (2)$$

The results obtained from TG/DTA analyses complemented by FTIR/EGA permitted to understand the process more

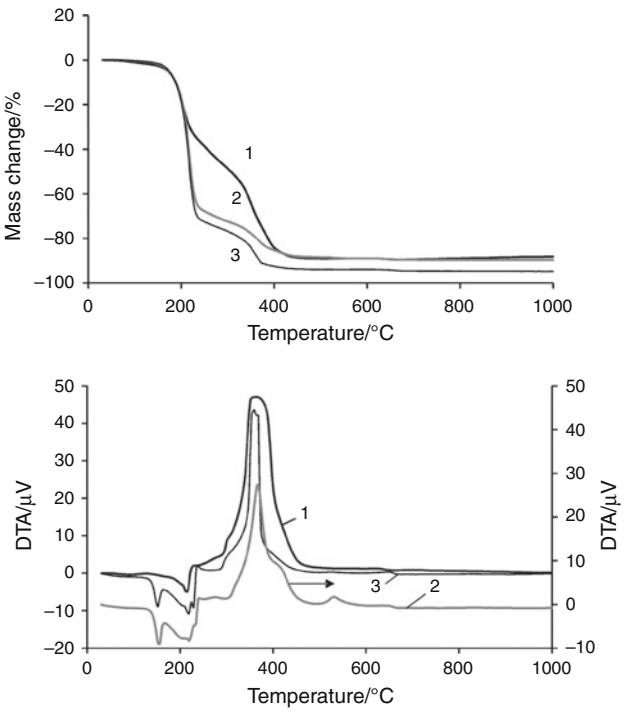

Fig. 2 TG/DTA curves of YSZ nitrate–citrate gels having lowest concentration (sample 1), intermediate concentration (sample 2) and highest concentration (sample 3) of starting materials

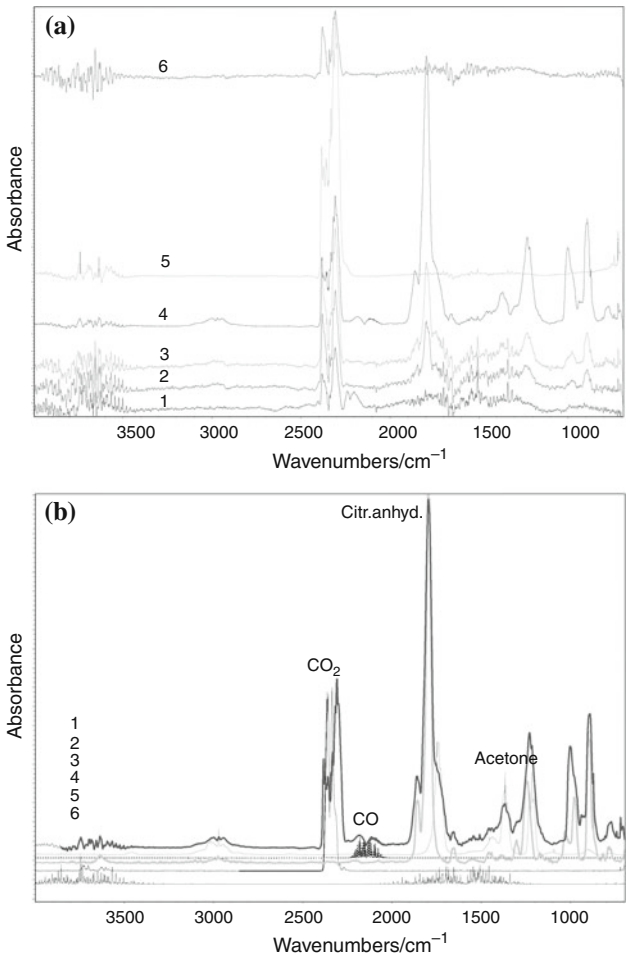

Fig. 3 FTIR spectra of the gaseous products (EGA) of thermal decomposition of YSZ nitrate–citrate gel (sample 2) at different temperatures **a** *1* 170 °C; *2* 180 °C; *3* 190 °C; *4* 220 °C; *5* 380 °C; *6* 500 °C and analysis of the FTIR spectra of the evolved gas **b** *1* gases from sample 2 at 210 °C; *2* ref. acetone; *3* ref. CO; *4* ref. citraconic anhydride; *5* ref. CO_2; *6* ref. H_2O

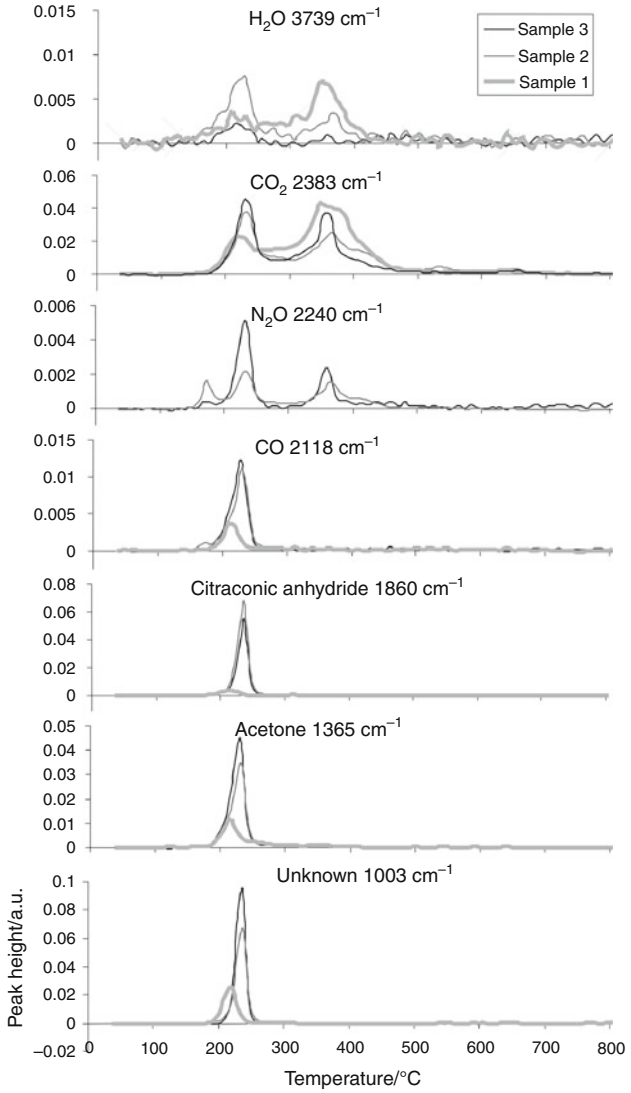

Fig. 4 Comparison of the evolution profiles of the detected gases, samples 1–3

deeply. At first, the composition of the evolved gases was analysed. The spectra of gases evolved at different temperatures are presented in Fig. 3. In accordance with TG curves (Fig. 2) at temperatures below 180 and above 670 °C, no remarkable gaseous products are evolved. Decomposition of the YSZ nitrate–citrate gels in the temperature region of 180–290 °C with evolvement of a complex mixture of different gases was followed. For all samples, the evolvement of H_2O, CO_2, CO, N_2O, acetone, and citraconic anhydride was detected (Fig. 3a, b). Recently, the formation of citraconic anhydride was found as a result of thermal decarboxylation of citric acid in inert atmosphere [28] that supports our result of thermal decomposition of the citric complexes before oxidation.

Using the height change of characteristic peaks of the components in the evolved mixture of gases (less overlapping one's), evolution profiles of the gases were obtained (Fig. 4). Peak positions used were as follows: 3,739 cm^{-1} (O–H symmetric and asymmetric stretching vibrations) for water vapour, 2,383 cm^{-1} (C=O asymmetric stretching vibrations) for CO_2, 2,240 cm^{-1} (O–N–N stretching vibrations) for N_2O, 2,118 cm^{-1} (C–O asymmetric stretching vibrations) for CO, 1,859 cm^{-1} (asymmetric and symmetric coupled C=O stretching vibrations) for citraconic anhydride, 1,365 cm^{-1} (C–O stretching vibrations) for acetone, and 1,002 cm^{-1} for unknown component.

The endothermic decomposition reaction of gels starts with the evolution of N_2O from samples 2 and 3 at about 160 °C. Species of partial decomposition of the citrate–nitrate complex together with H_2O, CO_2, CO and N_2O are followed at 190–270 C. In accordance with the TG results, this process is more intensive at heating samples 2 and 3. The evolution of CO, N_2O, acetone, citraconic anhydride and an unknown component was essentially lower from sample 1 (Fig. 4). An exothermic combustion of intermediate

pyrolysis products with evolvement of CO_2 and H_2O occurs from 250 to 500 °C, more intensively from sample 1. The decomposition of the residual carbonates or burning of some residual carbon [26] is followed at temperatures above 500 °C. According to the TG/DTA/EGA results, this combustion process ends up to 750 °C.

Therefore, the concentration of the initial $ZrO(NO_3)_2 \cdot 2H_2O$ influences the composition of the formed complexes and thereby their thermal decomposition characteristics. In case of using lower concentrations (sample 1) in gel preparation step, the evolvement of partially decomposed species (citraconic anhydride and acetone) is less and accordingly the main decomposition occurs at higher temperatures with evolvement of CO_2 and water vapour.

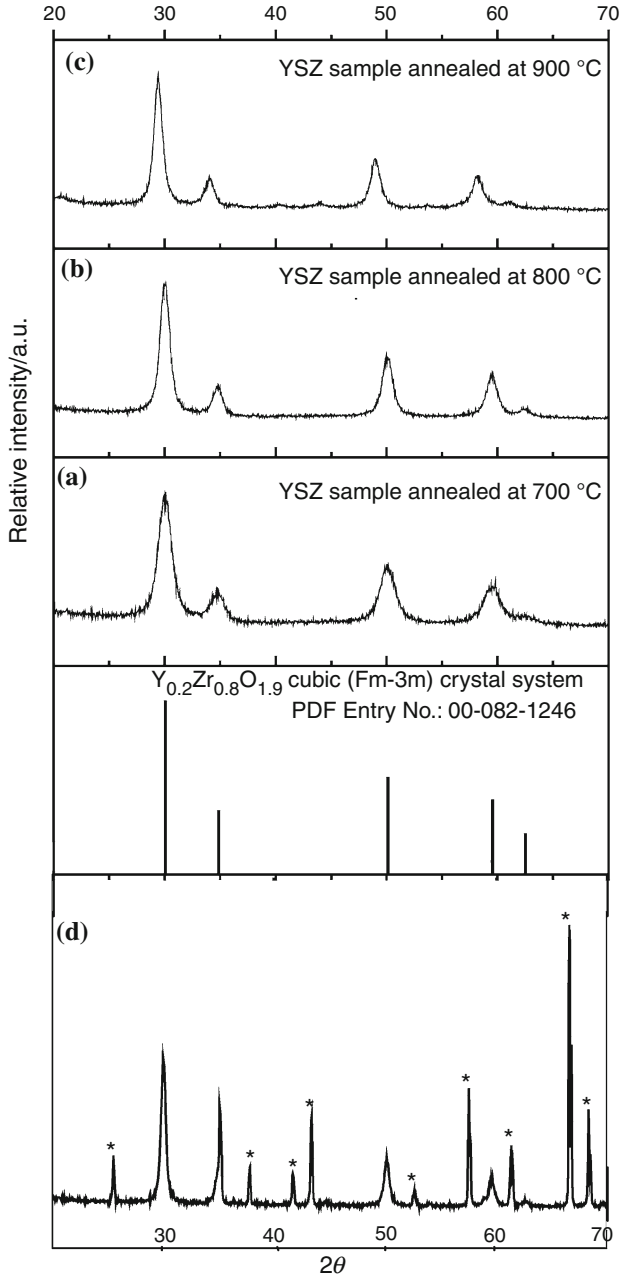

Fig. 5 X-ray diffraction patterns of sol–gel-derived YSZ annealed from 700 to 900 °C (**a**, **b**, **c**) and YSZ thin film on the Al_2O_3 (corundum) substrate obtained from the YSZ nitrate–citrate sol using dip-coating technique (**d**). *Peaks from Al_2O_3 substrate

X-ray diffraction

The XRD patterns of sol–gel-derived yttria-stabilized zirconia powders annealed at 700, 800 and 900 °C and YSZ thin film on the Al_2O_3 substrate are shown in Fig. 5. These spectra prove that even annealing of the synthesized gel precursors at 700 °C gave $Y_{0.2}Zr_{0.8}O_{1.9}$ compound of the cubic crystal structure (Fig. 5a). After calcination at 800 and 900 °C, the XRD pattern of YSZ powders (Fig. 5b, c) is almost identical to the previous one. XRD patterns show only small deviation of peaks width and intensity. These results are in a good agreement with the well-known tendency that at higher annealing temperatures, the crystallinity of mixed metal oxides increases. The XRD pattern of YSZ thin film obtained from YSZ nitrate–citrate sol dip-coating technique and annealed at 800 °C is shown in

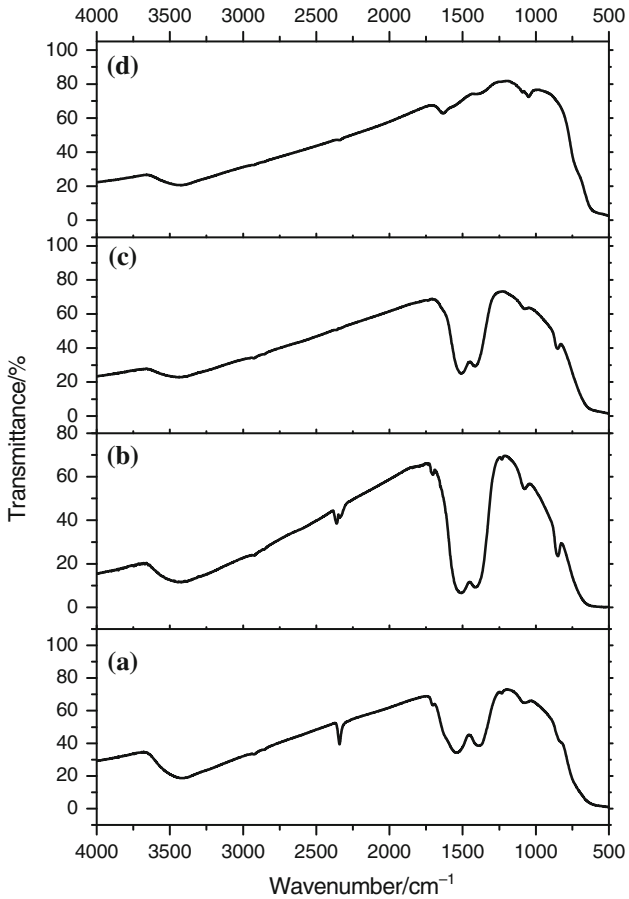

Fig. 6 FTIR spectra of YSZ powders calcined at **a** 500 °C, **b** 700 °C, **c** 800 °C and **d** 900 °C

Fig. 5d. This XRD pattern also indicates the formation of the cubic crystal structure YSZ on the corundum surface.

FTIR spectroscopy

The FTIR spectra of the YSZ powders obtained from the nitrate–citrate gels at calcination in the temperature range of 500–900 °C are shown in Fig. 6. The band clearly seen in the IR spectra at ~500 cm^{-1} is fundamental infrared frequency attributable to the cubic ZrO_2 crystal phase [29]. The broad band in the 3,500 cm^{-1} region may result from atmospheric moisture retained by the KBr pellet used in the measurement or from H–O characteristic vibrations from the water adsorbed by the final products during exposure in atmosphere. A sharp small peak at 2,345 cm^{-1} is attributed to the vibrational stretching of the C=O band, which is assigned to the CO_2 molecules from air. For the samples heated at 500–800 °C, the two bands in the 1,200–1,700 cm^{-1} region with maximum values at approximately 1,540 and 1,400 cm^{-1} could be attributed to the ionic carbonate or oxycarbonate groups [30] in accordance with the FTIR spectrum of the YSZ sample which was annealed at 900 °C and does not contain characteristic vibrational bands in the 1,200–1,700 cm^{-1} region.

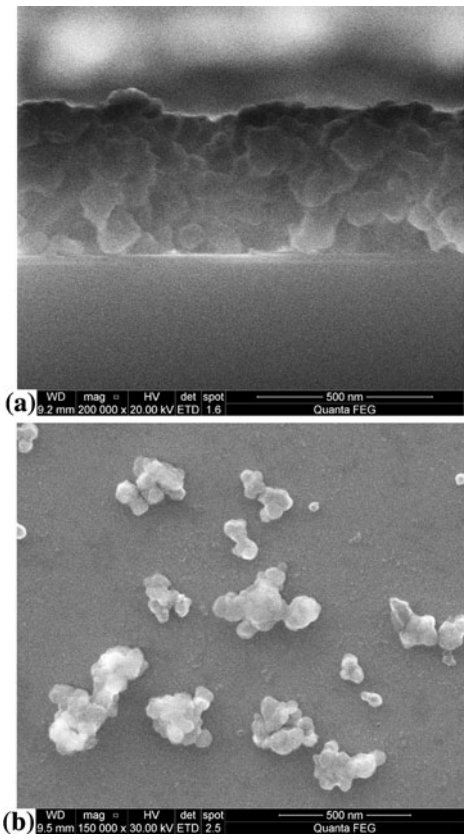

Fig. 7 SEM micrographs of the YSZ thin film cross-section on Al_2O_3 (corundum) substrate (**a**) and YSZ bulk powders (**b**), both annealed at 800 °C

SEM measurements

Figure 7 shows the SEM images of the yttria-stabilized zirconia thin film cross-section deposited from YSZ nitrate–citrate sol on the Al_2O_3 (corundum) substrate using dip-coating technique (Fig. 7a) and YSZ powders (Fig. 7b) obtained from YSZ nitrate–citrate gel after annealing both samples at 800 °C. These SEM images demonstrate that almost spherical YSZ particles 30–70 nm in size those tend to agglomerate to 100–150-nm crystallites have formed. The aggregation of YSZ nanoparticles has caused the formation of porous materials. Thin coating of about 500 nm is obtained after 30 immersion and annealing procedures as shown in Fig. 7a.

Conclusions

In conclusion, the simple, inexpensive and environmentally benign aqueous sol–gel synthesis methods have been developed for the preparation of yttria-stabilized zirconia (YSZ) bulk powders and thin films on the corundum (Al_2O_3) substrate using dip-coating technique. Regardless the impact of concentration of the $ZrO(NO_3)_2{\cdot}2H_2O$ on the composition of the formed complexes and thereby their thermal decomposition characteristics, particularly on the composition of the evolved gases, it has insignificant effect on the YSZ powders or thin films characteristics obtained after annealing. Monophasic YSZ particles 30–70 nm in size those tend to agglomerate to 100–150-nm crystallites of cubic crystal structure were obtained at 800 °C.

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