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Synthesis of nanocrystalline zirconia powders for TZP ceramics by a nitrate–citrate combustion route

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Abstract

A nitrate–citrate combustion route to synthesise nanocrystalline yttria-doped zirconia powders for tetragonal zirconia polycrystal (TZP) ceramics is presented. This route is based on the gelling of nitrate solutions by the addition of citric acid and ammonium hydroxide, followed by an intense combustion process due to an exothermic redox reaction between nitrate and citrate ions. X-ray diffraction characterisation of powders showed the stabilisation of the tetragonal phase at room temperature because of their small crystallite size (about 10 nm). Dense ceramic samples prepared by uniaxial pressing and sintering in air were also studied. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Tetragonal zirconia polycrystal (TZP) ceramics are widely studied because of their mechanical and electrical properties. They are tough, wear resistant and show a low thermal conductivity, so these materials are useful from the structural point of view.[1,2] In addition, they are applied in electrochemical cells (fuel cells, oxygen sensors, oxygen pumps, etc.) due to their high oxygen-ion conductivity at elevated temperatures.[3]

Although the monoclinic phase is the stable one at room temperature, the high-temperature tetragonal phase can also be retained by the addition of yttria, scandia, calcia or several rare-earth oxides provided the grain size is smaller than a critical value.[4–6] For example, Lange studied yttria-doped zirconia ceramics and found that the critical grain size varies from 0.2 to 1 μm for compositions ranging between 2 and 3 mol% Y_2O_3.[5] Recently, our research group showed that this phase can also be stabilised by the addition of calcia (with a composition of ZrO_2–4 mol% CaO), with a critical grain size of 150 nm.[6] These small grain sizes can only be achieved by starting from nanocrystalline powders. A wide variety of methods have been used for the production of nanocrystalline zirconia-based powders, such as co-precipitation,[7–9] amorphous citrate process,[8] polymerised complex process,[9,10] sol–gel,[11,12] and gel-combustion process.[6,13–19]

Of all the above mentioned processes, gel-combustion methods show some advantages due mainly to its relatively low cost compared to alkoxide-based sol–gel methods and better control of stoichiometry in comparison with co-precipitation ones, while producing powders in the nanometer range. Gel-combustion routes are based on the gelling and subsequent combustion of an aqueous solution containing salts of the desired metals (usually nitrates) and some organic fuel, such as urea,[15,16] carbo-hydrazide,[17,18] oxalic dihydrazide,[19] citric acid,[6,13,14,20–22] glycine,[23,24] alanine,[25] etc. The combustion process is due to an exothermic redox reaction between nitrate ions and the fuel. The large volume of gases produced during the reaction promotes the disintegration of the over-inflated precursor gel yielding nanocrystalline particles after calcination.

The aim of this paper is to present the synthesis of nanocrystalline ZrO_2–2.8 mol% Y_2O_3 powders for TZP ceramics by means of a nitrate–citrate gel-combustion route, which has already been presented by the authors

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in previous papers for other zirconia-based materials.[6,13,14] This method is similar to the amorphous citrate[8,26,27] and polymerised complex processes,[9,10] but an intense redox reaction between nitrate and citrate ions takes place. Similar nitrate-citrate combustion routes have been applied by other researchers for the synthesis of different oxides.[20-22]

2. Experimental procedure

Zirconium oxychloride and yttrium oxide were dissolved in an excess of nitric acid in a ratio corresponding to a final composition of ZrO_2–2.8 mol% Y_2O_3 and this nitrate solution was thermally concentrated in order to eliminate chlorine. Citric acid was then mixed in a proportion of 2 mols per mol of metal atom and the pH of the solution was adjusted to pH = 7 by adding ammonium hydroxide. The resulting translucent solution was heated on a hot plate (at about 200–250°C) until it turned into a black viscous gel, which on continued heating burned due to a vigorous exothermic reaction. The system was homogeneous during the whole process and no precipitation was observed. All the chemicals used were of analytical reagent grade.

Grey ashes obtained after combustion were treated at 350°C in air for 1 h to eliminate the carbonaceous residues and calcined at 600°C for 2 h resulting in a white, foamy powder. It was then milled at 110 rpm in a non-contaminating plastic container with zirconia pellets in an ethanol medium.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out in order to study the combustion process using a TA Instruments (DuPont) 910 calorimeter and a 951 analyser, respectively. Temperature ranges of analysis were from room temperature to 500 and 700°C, respectively, both with a heating rate of 20°C min^{-1}.

The as-synthesised (obtained after calcination) and milled powders were characterised by X-ray diffraction (XRD) employing a PW 3710-Philips diffractometer with Cu-K_α radiation in order to identify the existing phases. Data in the angular region of $2\theta = 71$–$77°$ were carefully collected in order to observe the splitting of $(400)_t$ and $(004)_t$ peaks of the tetragonal phase and to calculate its lattice parameters, a and c. The region $2\theta = 26$–$33°$ was also studied in order to determine the volume fraction of the monoclinic phase, V_m, by means of the method of Toraya et al.:[28]

$$V_m = \frac{1.311X_m}{1 + 0.311X_m} \tag{1}$$

$$X_m = \frac{I_{(\bar{1}11)m} + I_{(111)m}}{I_{(111)t} + I_{(\bar{1}11)m} + I_{(111)m}} \tag{2}$$

where X_m is the integrated intensity ratio (the subscripts m and t represent the monoclinic and tetragonal phases, respectively). For a precise measurement of the above integrated intensities, fitting procedures were used. The crystallite size was determined by means of the X-ray line broadening method[29] using the Scherrer equation:

$$D = \frac{0.9\lambda}{\beta \sin\theta} \tag{3}$$

where D is the crystallite size, λ is the wavelength of the radiation (1.4518 Å for Cu-K_α radiation), β is the corrected peak width at half-maximum intensity, and θ is the peak position. α-Al_2O_3 powder with a mean particle diameter of 25 μm was used to measure the instrumental broadening in order to correct the value of β.

The specific surface area of the milled powder was measured with a Flow Sorb 2300-Micromeritics equipment by determining the amount of nitrogen gas absorbed as a monomolecular layer on the sample. From this value, the average particle size was calculated assuming the presence of spherical particles, by means of the equation:

$$d = \frac{6}{\rho A} \tag{4}$$

where d is the particle size, ρ is the theoretical density of the material and A is of the specific surface area of the sample. The milled powder was also studied by means of a Philips-ElectroScan 2010 environmental scanning electron microscope (ESEM) and the observed average particle size was compared with the value obtained from Eq. (4).

Cylindrical specimens of 8 mm diameter and 1–2 mm height were uniaxially pressed at 200–300 MPa by using polyethylene glycol 4000 as a binder and sintered in air at 1400–1500°C for 2–4 h with a heating rate of 2°C/min and cooled together with the furnace. XRD spectra of the sintered materials were studied to verify the retention of the tetragonal phase. Polished and thermally etched samples (treated at 1300–1400°C for 15 min depending on sintering conditions) were used for the measurement of the average grain size by analysing ESEM micrographs with the linear intercept method. Density was evaluated by the Archimedes method using de-ionised water and Vickers microhardness was measured by means of a Leco H-400-G microhardness tester at a load of 1 kgf.

3. Results and discussion

The proposed method for the synthesis of nanocrystalline yttria-doped zirconia powders involves the combustion of a nitrate–citrate gel. As the starting solution is thermally concentrated, the system evolves with no lack of homogeneity until a viscous consistence is reached. If this process is carried out slowly and carefully, it is possible to stop it retaining the system at a clear gel stage. If this gel is fused and subsequently heated, it darkens, turns into a foamy consistence, and finally burns out with vivid flames. The combustion process occurs when the gel loses essentially all the free water. In Fig. 1, a photograph of the combustion process is shown.

Fig. 2 shows DSC and TGA plots obtained for the dark gel. As can be seen in the DSC plot, an exothermic reaction takes place at about 285°C. This combustion reaction involves nitrate and citrate ions releasing a great amount of gases, and such a vigorous process desegregates the precursor gel yielding nanocrystalline particles in the resulting final product. The abrupt fall between 150 and 300°C in the TGA plot is another evidence of the main decomposition of the gel during the combustion, while a subsidiary weight loss at a lower rate between 300 and 500°C is presumably due to the oxidation to CO_2 of some carbonaceous residues.

Fig. 3 shows typical XRD spectra of the as-synthesised (a) and milled (b) powders. The as-synthesised powder only presented the metastable tetragonal phase, with the typical high-angle splitting of $(400)_t$ and $(004)_t$ peaks, while a small amount of the monoclinic phase was found in the milled one, probably due to the mechanical stresses generated during milling process. By applying the Toraya method (after fitting the angular region $2\theta = 26$–$33°$ of the spectrum), it was found that the volume fraction of the monoclinic phase was about 20%. The crystallite size of the as-synthesised powder determined by the X-ray line broadening method was of (10.5 ± 0.5) nm. The error is due to the different values found from one synthesis process to another. The high-angle region of the

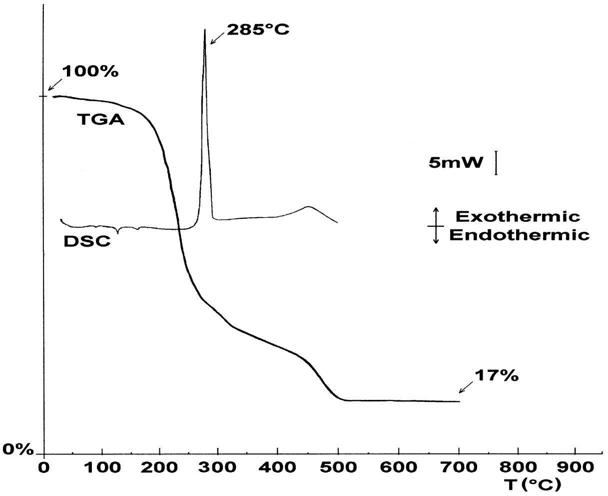

Fig. 2. DSC and TGA plots of the nitrate–citrate precursor gel.

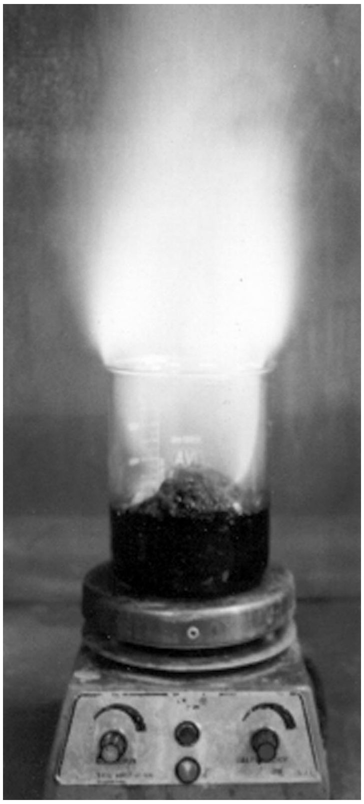

Fig. 1. Photograph of a typical nitrate–citrate combustion process for nanocrystalline yttria-doped zirconia powders.

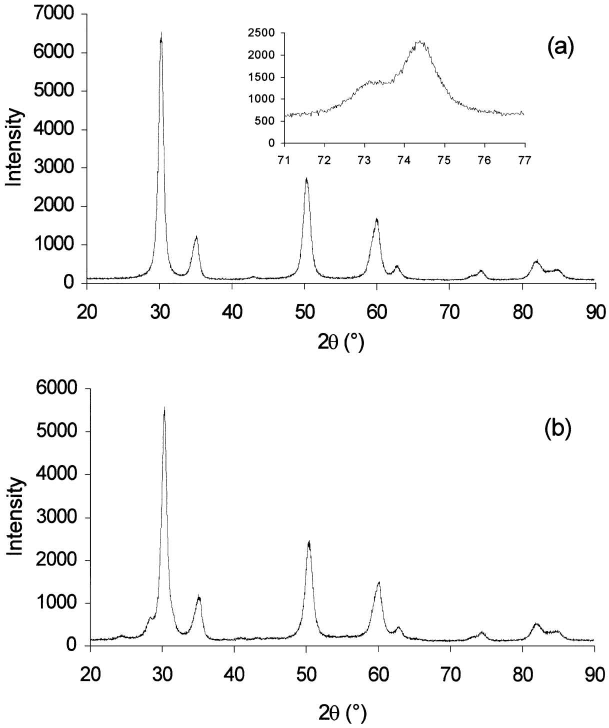

Fig. 3. Typical XRD spectra of nanocrystalline yttria-doped zirconia powders: (a) as-synthesised; (b) after milling. The high-angle region of as-synthesised powders is shown in detail.

spectrum of the as-synthesised powder was used to determine the lattice parameters a and c of the tetragonal phase, by accurately measuring the 2θ position of $(400)_t$ and $(004)_t$ peaks. The following values were obtained:

$$a = (0.5099 \pm 0.0003)\,\text{nm}$$

$$c = (0.5177 \pm 0.0003)\,\text{nm}$$

with an axial ratio of $c/a = 1.015 \pm 0.001$, in agreement with published data.[2]

The as-synthesised powder presented large aggregates with a foamy aspect, as can be observed in Fig. 4. These aggregates were voluminous and very light. Typical sizes were about 50–100 μm. After milling, these aggregates were broken into small spherical particles with diameters of about 100–150 nm (Fig. 5). The specific surface area of the milled powder was of 8.0 m^2/g, giving a particle size of 125 nm, in agreement with ESEM study. By comparing crystallite and particle sizes, it can be seen that the milled powder still exhibited an important degree of agglomeration.

The metastable tetragonal phase could also be retained in the ceramics obtained after uniaxial pressing and sintering. Fig. 6 is a typical XRD spectrum of a

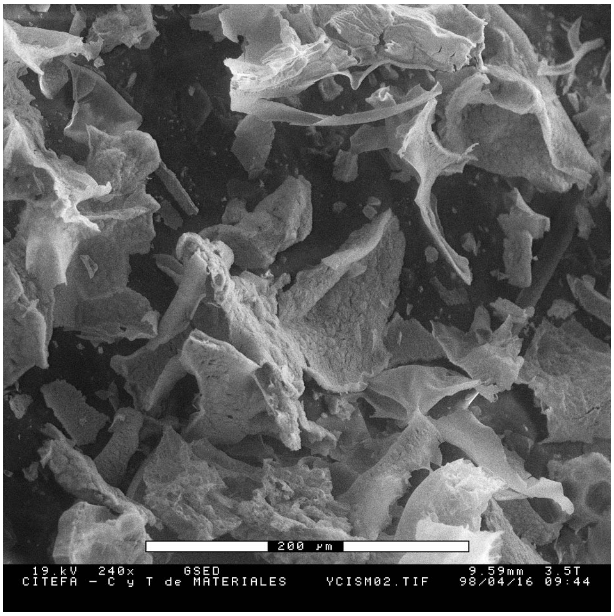

Fig. 4. ESEM micrograph showing the large aggregates presented in as-synthesised powders.

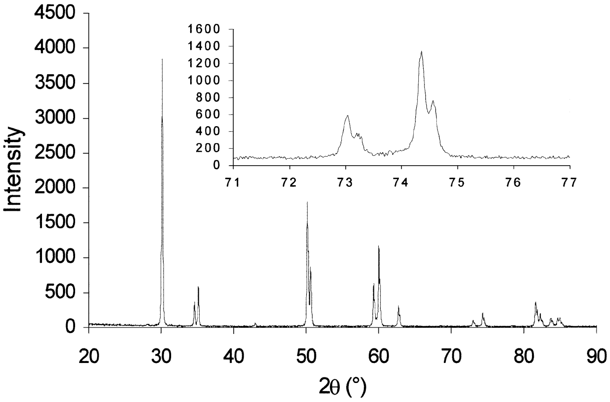

Fig. 6. XRD spectrum of a TZP ceramic obtained from the nitrate–citrate combustion route powder and sintered at 1450°C for 4 h.

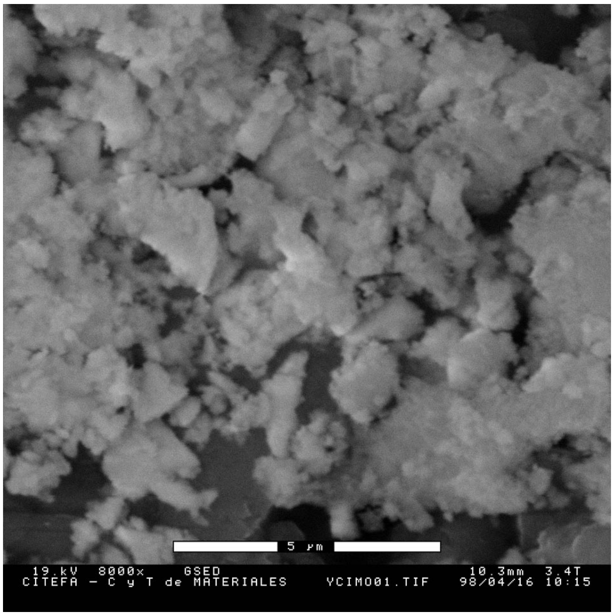

Fig. 5. Typical ESEM micrograph of milled powders.

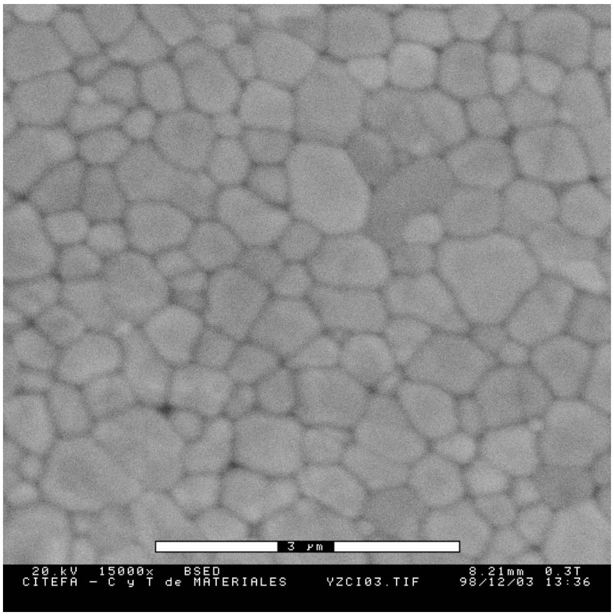

Fig. 7. Typical ESEM micrograph of a TZP ceramic sintered at 1500°C for 4 h.

ceramic sintered at 1450°C for 4 h. In this spectrum, the presence of the tetragonal phase can be verified by the splitting of several peaks. The high-angle region is shown in detail, where the K_{α_1}–K_{α_2} splitting is also present. The lattice parameters of these ceramics were in agreement with those calculated for powders, considering their errors.

Fig. 7 shows the microstructure of a TZP ceramics sintered at 1500°C for 4 h. It presented an average grain size of 0.4 μm and low porosity. These ceramics presented the highest relative density, which was of 97%, while those sintered at 1450°C have a relative density of 95%. Vickers microhardness of samples sintered at 1500°C was of (11.6 ± 0.4) GPa. This high hardness coincides with the best values reported for TZP ceramics.[2] The microcracks produced by the charges available for the indenter were too low to be used in a reliable calculation of the fracture toughness coefficient.

4. Conclusions

A nitrate–citrate combustion route to synthesise nanocrystalline yttria-doped zirconia powders for tetragonal zirconia polycrystal (TZP) ceramics has been investigated. This route is based on the combustion of nitrate–citrate gels due to an exothermic redox reaction between nitrate and citrate ions. This method is inexpensive and easy to implement, while producing nanocrystalline, compositionally homogeneous powders.

The as-synthesised powder exhibited the tetragonal phase at room temperature because of their small crystallite size (about 10 nm), while the milled powder presented a small amount of the monoclinic phase (a volume fraction of about 20%). Specific area measurements and ESEM observations showed that the milled power presented a particle size of about 125 nm, which showed that an important degree of agglomeration was present in this powder. TZP ceramics prepared by uniaxial pressing and sintering in air did not contain the monoclinic phase and showed high values of density and hardness.

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References

1. Garvie, R. C., Hannink, R. H. J. and Pascoe, R. T., Ceramic Steel? *Nature*, 1975, **258**, 703–704.
2. Lee, W. E. and Rainforth, W. M., *Ceramic microstructures, property control by processing*. Chapman and Hall, London, 1994. pp. 317–387, 509–570.
3. Novotny, J. (ed.), *Science of ceramic interfaces II*. Elsevier Science, Amsterdam, 1994, pp. 71–111.
4. Yoshimura, M., Phase stability of zirconia. *Ceram. Bull.*, 1988, **67**, 1950–1955.
5. Lange, F. F., Transformation toughening, part 3: experimental observations in the ZrO_2–Y_2O_3 system. *J. Mater. Sci.*, 1982, **17**, 240–246.
6. Lamas, D. G., Juárez, R. E., Caneiro, A. and Walsöe de Reca, N. E., Preparation of novel calcia stabilized TZP ceramics.. *NanoStruct. Mater.*, 1998, **10**, 1199–1207.
7. Hernández, M. T., Jurado, J. R., Durán, P., Abrantes, J. C. C. and Marques, F. M. B., Evaluation of ionic transport number of CeO_2 doped Y-TZP and PSZ ceramics with alumina additions. *Solid State Ionics*, 1992, **50**, 167–173.
8. Yashima, M., Kakihana, M., Ishii, K., Ikuma, Y. and Yoshimura, M., Synthesis of metastable tetragonal (t′) zirconia–calcia by pyrolisis of organic solutions and coprecipitation route. *J. Mater. Res.*, 1996, **11**, 1410–1420.
9. Yashima, M., Ohtake, K., Kakihana, M. and Yoshimura, M., Zirconia ∼13 mol% calcia solid solution synthesis by the polymerized complex and coprecipitation routes. *J. Mater. Sci. Lett.*, 1994, **13**, 1564–1566.
10. Yashima, M., Ohtake, K., Kakihana, M. and Yoshimura, M., Synthesis of metastable tetragonal (t′) zirconia–ceria solid solutions by the polymerized complex method. *J. Am. Ceram. Soc.*, 1994, **77**, 2773–2776.
11. Caruso, R., Benavídez, E., de Sanctis, O., Caracoche, M. C., Rivas, P. C., Cervera, M., Caneiro, A. and Serquis, A., Phase structured and thermal evolution in coating films and powders obtained by sol–gel process: part II. ZrO_2–2.5 mol% Y_2O_3. *J. Mater. Res.*, 1997, **12**, 2594–2601.
12. Chatterjee, M., Chatterjee, A. and Ganguli, D., Preparation of ZrO_2–CaO and ZrO_2–MgO fibres by alkoxide sol–gel processing. *Ceramics International*, 1992, **18**, 43–49.
13. Juárez, R. E., Lamas, D. G., Lascalea, G. E. and Walsöe de Reca, N. E., Síntesis y caracterización de electrolitos sólidos de ZrO_2–Y_2O_3 (Synthesis and characterisation of ZrO_2–Y_2O_3 solid electrolytes). *Anales de la Asociación Física Argentina*, 1994, **6**, 307–310 (in Spanish).
14. Lamas, D. G., Lascalea, G. E. and Walsöe de Reca, N. E., Synthesis and characterization of nanocrystalline powders for partially stabilized zirconia ceramics. *J. Eur. Ceram. Soc.*, 1998, **18**, 1217–1221.
15. Zhou, E., Bhaduri, S. and Bhaduri, S. B., Development of phases in combustion synthesized nanocrystalline-ZrO_2. *Ceram. Eng. Sci. Proc.*, 1997, **18**, 653–660.
16. Badhuri, S. and Bhaduri, S. B., Enhanced low temperature toughness of Al_2O_3–ZrO_2 nano/nano composites. *NanoStruct. Mater.*, 1997, **8**, 755–763.
17. Arul Dhas, N. and Patil, K. C., Properties of magnesia-stabilized zirconia powders prepared by a combustion route. *J. Mater. Sci. Lett.*, 1993, **12**, 1844–1847.
18. Shulka, A. K., Sharma, V., Arul Dhas, N. and Patil, K. C., Oxide-ion conductivity of calcia- and yttria-stabilized zirconias prepared by a rapid-combustion route. *Mater. Sci. Eng.*, 1996, **B40**, 153–157.
19. Venkatachari, K. R., Huang, D., Ostrander, S. P., Shulze, W. A. and Stangle, G. C., Preparation of nanocrystalline yttria-stabilized zirconia. *J. Mater. Res.*, 1995, **10**, 756–761.

20. Roy, S., Das Sharma, A., Roy, S. N. and Maiti, H. S., Synthesis of $YBa_2Cu_3O_{7-x}$ powder by autoignition of citrate–nitrate gel. *J. Mater. Res.*, 1993, **8**, 2761–2766.
21. Shaji Kumar, M. D., Srinivasan, T. M., Ramasamy, P. and Subramaniam, C., Synthesis of lanthanum aluminate by a citrate-combustion route. *Mater. Lett.*, 1995, **25**, 171–174.
22. Schäfer, J., Sigmund, W., Roy, S. and Aldinger, F., Low temperature synthesis of ultrafine $Pb(Zr,Ti)O_3$ powder by sol–gel combustion. *J. Mater. Res.*, 1997, **12**, 2518–2521.
23. Chick, L. A., Pederson, L. R., Maupin, G. D., Bates, J. L., Thomas, L. E. and Exarhos, G. J., Glycine–nitrate combustion synthesis of oxide ceramic powders. *Mater. Lett.*, 1990, **10**, 6–12.
24. Pederson, L. R., Maupin, G. D., Weber, W. J., McReady, D. J. and Stephens, R. W., Combustion synthesis of $YBa_2Cu_3O_{7-x}$: glycine/metal nitrate method. *Mater. Lett.*, 1990, **10**, 437–443.
25. Zhong, Z. and Gallagher, Combustion synthesis and characterization of $BaTiO_3$. *J. Mater. Res.*, 1995, **10**, 945–952.
26. Marcilly, C., Courty, P. and Delmon, B., Preparation of highly dispersed mixed oxides and oxide solid solutions by pyrolysis of amorphous organic precursors. *J. Am. Ceram. Soc.*, 1970, **53**, 56–57.
27. Anderson, D. J. and Sale, F. R., Production of conducting oxide powders by amorphous citrate process. *Powder Metall.*, 1979, **1**, 14–21.
28. Toraya, H., Yoshimura, M. and Somiya, S., Calibration curve for quantitative analysis of the monoclinic-tetragonal ZrO_2 system by X-ray diffraction. *J. Am. Ceram. Soc.* 1984; **67**, C-119–121.
29. Klug, H. and Alexander, L., *X-ray diffraction procedures for polycrystalline and amorphous materials*. John Wiley and Sons, New York, 1974, pp. 618–708.