Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 27 (2007) 3619–3623

www.elsevier.com/locate/jeurceramsoc

Synthesis of ceria-based electrolyte nanometric powders by urea-combustion technique

E. Chinarro, J.R. Jurado, M.T. Colomer *

Instituto de Cerámica y Vidrio, ICV-CSIC, C/Kelsen no 5, 28049 Madrid, Spain

Abstract

Ceria-doped electrolytes have been extensively studied because they are promising candidates for intermediate temperature solid oxide fuel cells (ITSOFCs). In this work, the powder synthesis by the urea-combustion technique is used. The combustion synthesis is a really suitable synthesis route to achieve, at low temperatures, finely, homogeneous, and reactive powders for ceria-based electrolytes. This work describes the combustion synthesis of binary and ternary compositions of the $(CeO_2)_{0.92}(Ln_2O_3)_{0.04}(CaO)_{0.04}$ systems, being Ln = Y, Gd and Sm. The characterisation of the as-prepared combustion products showed that the combustion synthesis provides a straightforward method for the achievement of solid solutions of these materials as nanometric powder.

Keywords: Powders-chemical preparation; Combustion synthesis; Fuel cells

1. Introduction

Most of the effort in SOFCs is nowadays focussed on intermediate temperature solid oxide fuel cells (IT-SOFCs). For this purpose, relatively high ionic conductivity for suitable solid electrolytes is required at intermediate temperatures, and ceria-based materials could have sufficient high ionic conductivity at temperatures so low as 600 °C, which is appropriate electrolyte candidates in such as devices. Actually, doped-ceria-based materials are considered the most promising conducting solid electrolytes for IT-SOFC applications.

Taking into account pure ceria-powder is a key factor to reduce the grain boundaries electrical resistant, one of the research fields in the CeO_2-based ceramics is the synthesis of pure ceria-powders. Several synthesis routes have been developed to produced nanocrystalline CeO_2-based powders.[1–7] As is well-known, the wet-chemical synthesis methods produce ceramics single or multioxide powders with high sinterability, high surface area, well-defined chemical compositions and homogeneous distribution of the elements. In spite of the quality of the powders produced and although powder synthesis can be achieved at low temperature, many solution processes are complicated and lengthy procedures which limit their applicability. In the past few years, combustion synthesis of multicomponent ceramic oxides has been gaining reputation as a straightforward preparation process to produce homogeneous, very fine, crystalline and unagglomerated powders, without the intermediate decomposition and or calcining step.[8–10] The basis of the combustion synthesis technique comes from the thermochemical concepts used in the field of propellants and explosives.[11]

CeO_2-based powders have been synthesized successfully by the combustion synthesis, as is mentioned above, using different fuels such as glycine,[7,12–14] oxalyldihydrazide[15] and carbohydrazide.[16]

Up to now, CeO_2-based oxides prepared by combustion synthesis, to our best knowledge, were binary oxides.[2] Only one ternary oxide: $(CeO_2)_{0.92}(Y_2O_3)_{0.04}(CaO)_{0.04}$ has been prepared by combustion synthesis.[17] In this study, the combustion synthesis of binary and ternary compositions of the $(CeO_2)_{0.92}(Ln_2O_3)_{0.04}(CaO)_{0.04}$ systems, being Ln = Y, Gd and Sm, was used. The urea is employed as fuel and the nitrates as oxidizers.

2. Experimental

The ceria-based ceramics were synthesized by combustion reactions by employed Aldrich hydrate nitrate salts, $Ce(NO_3)_3{\cdot}6H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$, $Gd(NO_3)_3{\cdot}6H_2O$, $Sm(NO_3)_3{\cdot}6H_2O$ and $Y(NO_3)_3{\cdot}6H_2O$ as cation precursors, and Aldrich urea, $CO(NH_2)_2$, used as fuel. Batches were calculated

---

* Corresponding author. Tel.: +34 91 735 58 58; fax: +34 91 735 58 43.
E-mail address: tcolomer@icv.csic.es (M.T. Colomer).

0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.02.007

Table 1
Compositions prepared

Binary compositions	Ternary compositions
CeO_2–8 mol% Gd_2O_3 (CGd)	CeO_2–4 mol% Gd_2O_3–4 mol% CaO (CGdCa)
CeO_2–8 mol% CaO (CCa)	CeO_2–4 mol% CaO–4 mol% Y_2O_3 (CCaY)
CeO_2–8 mol% Sm_2O_3 (CSm)	CeO_2–4 mol% Sm_2O_3–4 mol% Gd_2O_3 (CSmGd)
CeO_2–8 mol% Y_2O_3 (CY)	CeO_2–4 mol% Gd_2O_3–4 mol% Y_2O_3 (CGdY)

on a basis of 5 g of cerium nitrate. The compositions prepared are indicated in Table 1. The stoichiometric composition of each mixture was calculated based on the total oxidising and reducing valences of the oxidiser and the fuel, in order to release the maximum energy for the reaction. The reactants were first melted in a wide-mouth vitreous silica basin (300 cm^3) by heating up to 300 °C on a hot-plate inside a fume cupboard, under ventilation. Soon after the thickened liquid began frothing, ignition took place rapid increase in temperature, appearance of a central point of incandescence that propagate in swift ripples to the walls of the basin, and evolution of a large quantity of gases. The reaction lasted for less than 5 min and produced a dry, mostly white and very fragile foam, that readily crumbled into powders, accompanied by a great volume increase when compared to the original volume of liquid. The final treatments were a calcination at 800 °C/12 h in air in order to increase the powder crystallinity and attrition-milling for 3 h using 1 mm diameter zirconia balls (purchased from Tosoh, Japan) in ethanol. A final sieve through 100 μm before compaction was performed. Differential thermal and thermogravimetric analysis (DTA/TG) in air of the as-prepared powder was carried out on a NETZSCH STA-409 Thermoanalyser, utilising alumina as the reference material, in the temperature range of 20–1500 °C with a heating rate of 3 °C/min. Phase identification was performed by X-ray Diffraction on a Siemens Powder diffractometer D-5000 operating at 50 kV and 30 mA using Cu Kα radiation and a Ni-filter in the range of $2\theta = 10°–80°$. The scanning step was 0.05°, the time/step 1.5 s and the rotation speed 30 rpm. X-ray patterns were collected on the as-prepared powders and at 800 °C for 12 h and 1500 °C (sintering temperature) for 4 h. The average agglomerate size was measured by means of a particle-size laser analyser provided by Malvern Instruments, model Mastersizer. BET specific surface area of the powders was determined using a Monosorb Analyzer MS-13 QuantaChrome. Agglomerate morphology was observed by scanning electron microscopy and chemical analysed by Energy Dispersive X-ray Spectroscopy (SEM-EDS) on a Zeiss DSM 950 microscope. Crystallite size and morphology of the as-prepared powders were also estimated by transmission electron microscopy and chemical analysed by Energy Dispersive X-ray Spectroscopy (TEM-EDS), using a JEM-2000FX microscope.

3. Results and discussion

The combustion reaction was fast and intense and the resulting dry foam was observed to grow larger and be more homogeneous. The reaction was so efficient that to achieve single phase (binary or ternary solid solutions) it was simply necessary to use a hot plate.

The combustion reaction of urea is described by the following equation (R1):

$$CO(NH_2)_2(c) + 1.5O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + N_2(g),$$
$$\Delta H^\circ = -129.90\,\text{kcal/mol} \tag{R1}$$

which is exothermic and should supply the heat needed for the synthesis reaction, and the nitrates should be mixed in the proportion mentioned (Table 1).

The combustion reaction to obtain ceria (R2), and the overall reaction to achieve the desired compositions (RT) are the following:

$$Ce(NO_3)_3{\cdot}6H_2O(c) + mCO(NH_2)_2(c) + (1.5m - 3.5)O_2(g)$$
$$\rightarrow CeO_2(c) + (1.5 + m)N_2(g) + mCO_2(g)$$
$$+ (2m + 6)H_2O(g) \quad \Delta H^\circ(m = 2.5) = -201.30\,\text{kcal/mol} \tag{R2}$$

Table 2
Relevant thermodynamic data[22]

Compounds	ΔH_f° (25 °C) (kcal mol^{-1})	ΔG_f° (25 °C) (kcal mol^{-1})	S (25 °C) (cal mol^{-1} K^{-1})	C_p (cal mol^{-1} K^{-1})
$Ce(NO_3)_3{\cdot}6H_2O(c)$	−729.14			
$Sm(NO_3)_3(c)$	−289.70			
$Ca(NO_3)_2{\cdot}4H_2O(c)$	−509.64	−409.53	89.70	
$CO(NH_2)_2(c)$	−79.71	−47.04	25.00	22.26
$CeO_2(c)$	−258.80	−244.9	14.89	14.73
$Gd_2O_3(c)$	−434.90			25.50
$Sm_2O_3(c)$	−435.70	−414.60	36.10	27.37
$Y_2O_3(c)$	−455.38	−434.19	23.68	24.50
CaO(c)	−151.80	−144.25	9.13	$6.44 + 0.0182T$
$H_2O(g)$	−57.796	−54.634	45.104	$7.20 + 0.00360T$
$CO_2(g)$	−94.051	−94.26	51.07	$10.34 + 0.00274T$
$N_2(g)$	0	0	45.77	$6.50 + 0.00100T$
$O_2(g)$	0	0	49.003	$5.92 + 0.00367T$
NO(g)	21.57	20.69	50.347	$6.46 + 0.00179T$
$N_2O_5(g)$	2.70	28.13	82.98	$5.13 + 0.0817T$

$$\begin{aligned}&0.92\mathrm{Ce(NO_3)_3{\cdot}6H_2O(c)} + 0.08\mathrm{M,N(NO_3)_2{\cdot}4H_2O(c)}\\&\quad + m\mathrm{CO(NH_2)_2(c)} + (1.5m - 3.38)\mathrm{O_2(g)}\\&\quad \rightarrow \mathrm{Ce_{0.92}(M,N_{0.08})O_2(c)} + (5.84 + 2m)\mathrm{H_2O(g)}\\&\quad + (1.46 + \mathrm{m})\mathrm{N_2(g)} + \mathrm{mCO_2(g)}\end{aligned} \qquad \text{(RT)}$$

being M: divalent cation and N: trivalent cation.

The thermochemical concepts from propellant chemistry applied to this synthesis mean that the total oxidisers and reducers valencies in the mixtures of salts should be zero. In this case, the valence of the oxidisers is −14.6 or −15 for binary or ternary compositions, respectively. These valences should be balanced by the total "valencies" of the fuel, which add up to +6. Thus, the stoichiometric composition of the redox mixture, in order to release the maximum energy for the reaction, demands that $-15\ (-14.6) + 6n = 0$ or $n = 2.5$ (2.43) mole of urea used. In other words, 0.92:0.08:2.5 (2.43) should be the ratio of the used raw materials, i.e., $\mathrm{Ce(NO_3)_3{\cdot}6H_2O}$, ($\mathrm{Ln(NO_3)_2{\cdot}6H_2O}$) and $\mathrm{CO(NH_2)_2}$, respectively.

The heat of combustion of urea at 298 °C calculated from the thermodynamic data listed in Table 2 is $\Delta H(\mathrm{R1}) = -129.90$ kcal/mol, for the $\mathrm{CeO_2}$ obtained by combustion with stoichiometric urea (2.5 mol), calculated by propellant chemistry, reaction (R2), $\Delta H(\mathrm{R2}) = -201.30$ kcal/mol. Thus, if $\mathrm{CeLnO_2ss}$ synthesis were to occur at 298 °C, on the basis of enthalpy change solely, excess of urea would be not needed, something expected knowing that only 0.95 moles of the urea are necessary for a thermodynamic stoichiometric reaction. The heat generated by the combustion of the stoichiometric moles of urea, specified by the propellant chemistry calculations, $n = 2.5$, will be absorbed for the development of the oxides and the rest of the combustion reaction products (i.e. $11\mathrm{H_2O(g)} + 2.5\mathrm{N_2(g)} + 2.5\mathrm{CO_2(g)}$), and for raising the reaction temperature. Using the relevant heat capacities listed in Table 2 and the $\Delta H(\mathrm{R2})$ calculated above, the temperature reached by the final products is 1096 °C. Of course, the gases produced in the combustion will dissipate some of this heat and the other part of it will be spent in the synthesis of the CeLnO2ss from the oxides. Therefore, the temperature reached in practice is expected to be lower than the calculated value.

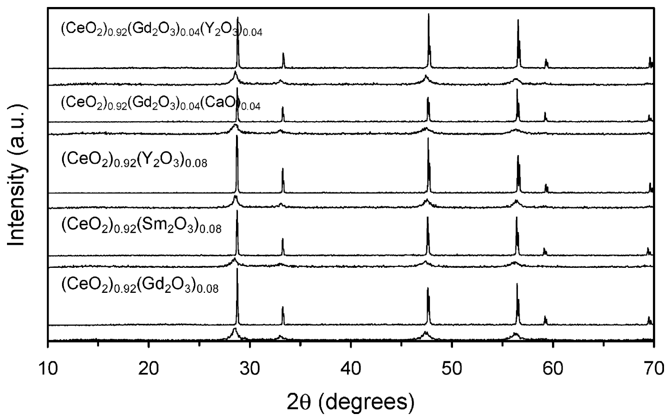

Fig. 1. X ray diffraction patterns of powders as-prepared (bottom) and at 1500 °C for 4 h (top) of some compositions.

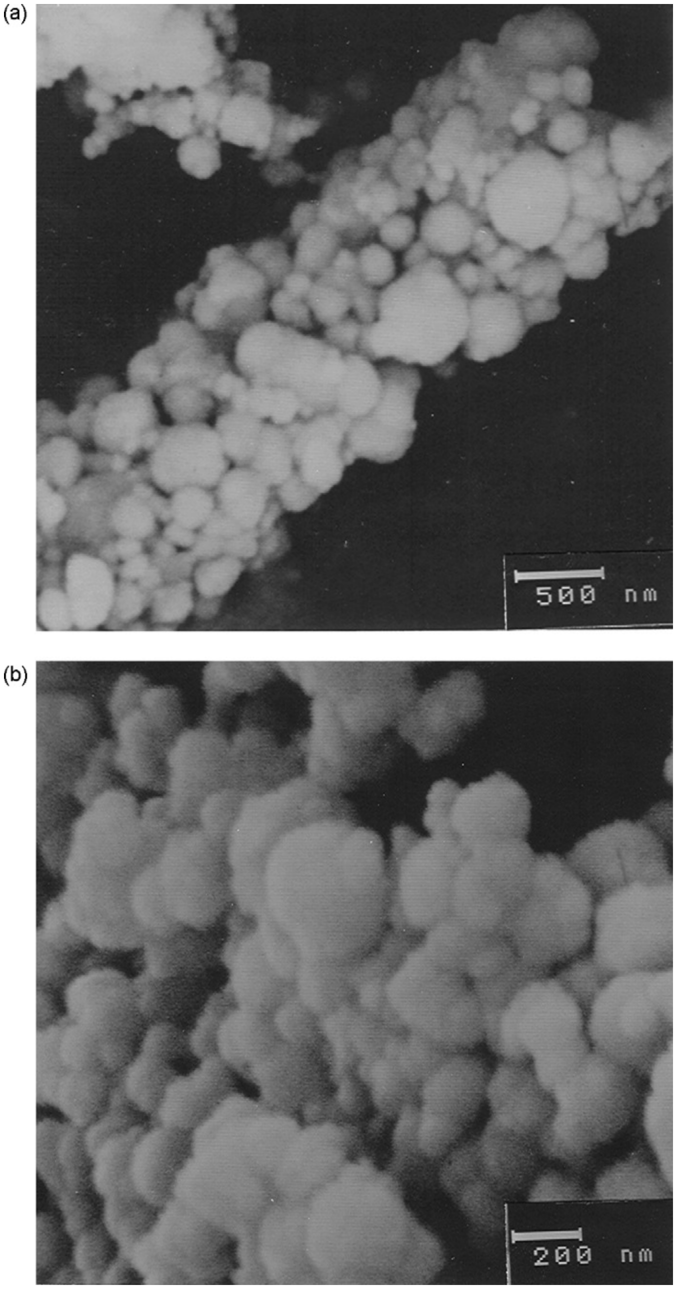

Fig. 2. SEM micrographs of the as-prepared powder of $\mathrm{CeO_2}$–$\mathrm{Gd_2O_3}$–CaO (a) and $\mathrm{CeO_2}$–$\mathrm{Gd_2O_3}$–$\mathrm{Y_2O_3}$ (b).

In view of the foregoing analysis, the temperature at which the reactions present the same free energy change is the same range of that experimentally observed for the ignition of the combustion. The estimated maximum theoretical temperatures of the reaction products (≈1100 °C) agree with observed experimental results of other authors[10] and suggest that the assumptions behind the calculations are reasonably valid.

An extensive study carried out on the urea-combustion synthesis of Lanthanum-Chromite perovskite powders,[18] indicated that the maximum temperature measured by optical pyrometry was ≈1100 °C; resulting in the rapid formation (≈20 s) of a dry

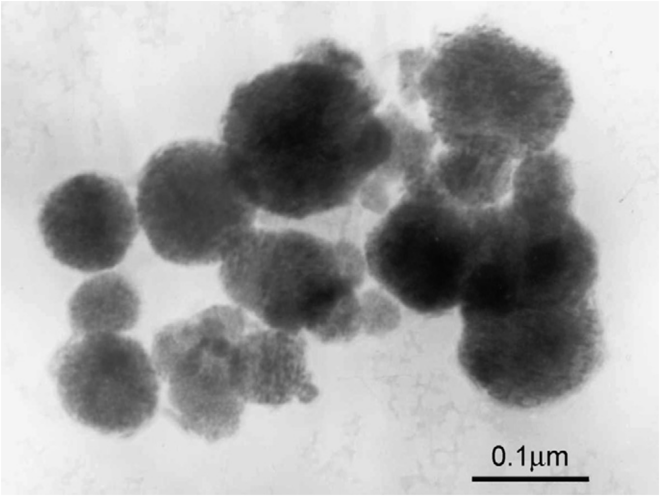

Fig. 3. TEM micrograph of the CeO_2-8 mol% of Gd_2O_3 as-prepared powders, showing typical particle agglomerates.

oxide powder, which reached incandescence and quickly cooled down, with a foamy macrostructure made of soft agglomerates of submicron particles with a considerable degree of crystallinity and the desired stoichiometry. Other authors[19–21] have measured the maximum temperature reached during the combustion synthesis of different oxides and obtained figures always in excess of 1000 °C.

Fig. 1 shows the various X-ray diffraction spectra for the prepared powders. In spite of the short reaction time, X-ray diffraction of the as-prepared powders showed, respectively, well crystallised CeLnO2ss fluorite single phase (full conversion) as the only phase present. The amount of urea satisfies the enthalpy requirements for complete decomposition at 25 °C and release of all the corresponding gases. In this case the temperature is high enough to promote the synthesis of the ceria fluorite structure. A higher crystallinity is observed for the samples sintered at 1500 °C for 4 h.

The as-prepared powders were observed by SEM and TEM (Figs. 2 and 3, respectively). The SEM pictures show agglomerates up to 500 nm with a spherical geometry. TEM picture shows spongy agglomerates of very fine crystals (ca. ∼10 nm or lesser).

Table 3 collects the specific surface area and the particle size distribution for the as-prepared powders of some compositions. The values of the SSA range between 15 and 30 m^2/g. They are in good agreement with the attained by Rocha and Muccillo,[2] for gadolinia doped ceria powders, prepared by a similar combustion synthesis.

Table 3
Specific surface area and agglomerate size distribution of the compositions prepared. The agglomerate size distributions show bimodal patterns; The two ranges of each bimodal distribution are collected

Material	SSA (m^2/g)	Agglomerate size distribution (µm)
CGd	22.0	
CGdSm	30.0	0.3–0.9/17–40
CGdY	15.0	0.25–1/10–35
CGdCa	15.0	0.3–1/6–50
CYCa	17.5	0.3–1/6–50
CY	17.6	0.3–1/6–50

4. Conclusions

Our work shows that the combustion synthesis technique is reliable and can be successfully used to produce pure, 100% crystalline powders of $CeLnO_2$ss with a good compositional control of the powder produced in a one single step. The valency-based molar proportions of reactants proposed by the propellant chemistry criterion were found to be in agreement with those predicted by thermodynamic calculations and can, therefore, be used as a valid simplification of an otherwise elaborate calculation.

References

1. Li, J.-G., Ikegami, T., Wang, Y. and Mori, T., Reactive ceria nanopowders via carbonate precipitation. *J. Am. Ceram. Soc.*, 2002, **85**, 2376–2378.
2. Rocha, R. A. and Muccillo, E. N. S., Preparation of nanocrystalline gadolinia doped ceria powders by combustion synthesis. *J. Eur. Ceram. Soc.*, 2004, **24**, 1287–1290.
3. Tsuzuki, T. and McCormick, P. G., Synthesis of ultrafine ceria powders by mechanochemical processing. *J. Am. Ceram. Soc.*, 2001, **84**, 1453–1458.
4. Sin, A., Dubitsky, Y., Zaopo, A., Aricò, A. S., Gullo, L., La Rosa, D. *et al.*, Preparation and sintering of $Ce_{1-x}Gd_xO_{2-x/2}$ nanopowders and their electrochemical and EPR characterization. *Solid State Ionics*, 2004, **175**, 361–366.
5. Purohit, R. D., Saha, S. and Tyagi, A. K., Powder characteristics and sinterability of ceria powders prepared through different routes. *Ceram. Int.*, 2006, **32**, 143–146.
6. Kang, H. S., Sohn, J. R., Kang, Y. C., Jung, K. Y. and Park, S. B., The characteristics of nano-sized Gd-doped CeO_2 particles prepared by spray pyrolysis. *J. Alloys Comp.*, 2005, **398**, 240–244.
7. Bianchetti, M. F., Juárez, R. E., Lamas, D. G., Walsöe de Reca, N. E., Pérez, L. and Cabanillas, E., Synthesis of nanocrystalline CeO_2–Y_2O_3 powders by a nitrate–glycine gel-combustion process. *J. Mater. Res.*, 2002, **17**, 2185–2188.
8. Fumo, D. A., Morelli, M. R. and Segadaes, A. M., Combustion synthesis of calcium aluminates. *Mater. Res. Bull.*, 1996, **31**, 1243–1255.
9. Fumo, D. A., Jurado, J. R., Segadaes, A. M. and Frade, J. R., Combustion synthesis of iron-substituted strontium titanate perovskites. *Mater. Res. Bull.*, 1997, **32**, 1459–1470.
10. Colomer, M. T., Fumo, D. A., Jurado, J. R. and Segadaes, A. M., Non-stoichiometric $La_{1-x}NiO_{3-\delta}$ perovskites produced by combustion synthesis. *J. Mater. Chem.*, 1999, **9**, 2505–2510.
11. Jain, J. R., Adiga, K. C. and Verneker, V. R. P., A new approach to thermochemical calculations of condensed fuel-oxidizer mixtures. *Comb. Flame*, 1981, **40**, 71–79.
12. Purohit, R. D., Sharma, B. P., Pillai, K. T. and Tyagi, A. K., Ultrafine ceria powders via glycine–nitrate combustion. *Mater. Res. Bull.*, 2001, **36**, 2711–2721.
13. Peng, R., Xia, C., Fu, Q., Meng, G. and Peng, D., Sintering and electrical properties of $(CeO_2)_{0.8}(Sm_2O_3)_{0.1}$ powders prepared by glycine–nitrate process. *Mater. Lett.*, 2002, **56**, 1043–1047.
14. Mokkelbost, T., Kaus, I., Grande, T. and Einarsrud, M., Combustion synthesis and characterization of nanocrystalline CeO_2-based powders. *Chem. Mater.*, 2004, **16**, 5489–5494.
15. Aruna, S. T. and Patil, K. C., Combustion synthesis and properties of nanostructured ceria–zirconia solid solutions. *Nanostruct. Mater.*, 1998, **10**, 955–964.

16. Aruna, S. T., Ghosh, S. and Patil, K. C., Combustion synthesis and properties of $Ce_{1-x}Pr_xO_{2-\delta}$ red ceramic pigments. *Int. J. Inorg. Mater.*, 2001, **3**, 387–392.
17. Jurado, J. R., Present several items on ceria-based ceramic electrolytes: synthesis, additive effects, reactivity and electrochemical behaviour. *J. Mater. Sci.*, 2001, **36**, 1133–1139.
18. Morelli, M. R., D. Phil. Thesis. University of Oxford, UK, 1995.
19. Manoharan, S. S. and Patil, K. C., Combustion synthesis of metal chromite powders. *J. Am. Ceram. Soc.*, 1992, **75**(4), 1012–1015.
20. Sekar, M. A. and Patil, K. C., Combustion synthesis and properties of fine-particle dielectric oxide materials. *J. Mater. Chem.*, 1992, **2**(7), 739–743.
21. Zhang, Y. and Stangle, G. C., Preparation of fine multicomponent oxide ceramic powder by a combustion synthesis process. *J. Mater. Res.*, 1994, **9**(8), 1997–2004.
22. Lide, D. R., ed., *CRC Handbook of Chemistry and Physics*. 84th ed. CRC Press, Boca Raton, Florida, USA, 2003–2004. pp. 5-1/5-106.