Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of the European Ceramic Society 23 (2003) 3043–3047

www.elsevier.com/locate/jeurceramsoc

Thorium (IV) or titanium (IV) stabilized tetragonal zirconia nanocrystalline powders processed by chemical synthesis

A.B. Panda, J.C. Roy, P. Pramanik*

Department of Chemistry, Indian Institute of Technology, Kharagpur-721302, West Bengal, India

Received 8 September 2002; received in revised form 13 January 2003; accepted 24 January 2003

Abstract

Stabilized tetragonal zirconia nanocrystalline powders have been prepared through a chemical synthesis method using thorium (IV) or titanium (IV) salts. In this method, the precursor solution prepared from zirconyl nitrate, thorium nitrate or titanium tartarate and TEA (triethanolamine), which are evaporated, pyrolysed and calcined to nanocrystalline powders. Stabilizing ability of thorium (IV) is better than that of titanium (IV). In both the cases pure t-ZrO_2 is formed initially at the calcination temperature of 650 °C but their thermal stabilities are different. The crystallite sizes of the powders are in the range of 10–30 nm and the particle size is in the range of 30–70 nm within the range of calcination temperature of 650–1100 °C.

Keywords: Nanocrystals; Powders-chemical preparation; Th-TZP; Ti-TZP; TZP; ZrO_2

1. Introduction

Zirconia (ZrO_2) has three polymorphs: monoclinic (m), tetragonal (t) and cubic (c).[1] Among them c- and t-ZrO_2 are metastable high temperature polymorphs. The transition between the first two (t→m) is displacive in nature and involves a large volume expansion of ~4% at ~950 °C on cooling and on heating the transformation (m↔t) occurs at ~1150 °C in pure ZrO_2. This volume change prevents its use in refractory.[2,3] The problems of phase transformation may be avoided by adapting the principles of phase stabilization. The t-phase is a very important engineering material because of its tunable martensitic transformation, which is responsible for transformation toughening in zirconia ceramics.[4,5]

The stabilization of t- and c-phases of ZrO_2 by using the aliovalent dopants, such as Y^{3+}, Ca^{2+}, and Na^{+} was elaborately studied and the oxygen vacancies, introduced by these dopants for charge compensation, was shown to play an important role for the stabilization.[6,7] Tetravalent dopants like Si^{4+}, Ce^{4+}, Ge^{4+} etc. were also found to be effective agents to stabilize t-ZrO_2 forming cationic network and high-energy surface layer.[8–10] In cases of aliovalent dopants and tetravalent dopants, it was suggested that the larger size of dopant had the higher stabilizing effect. Aliovalent dopants like $Na^{=}$, Ca^{2+}, Y^{3+} etc. has been used successfully to stabilize the t- and c-phase of ZrO_2. But the stabilizing ability of the tetravalent ions is not fully explored. Some reports of the stabilization with Si^{4+}, Ce^{4+}, Sn^{4+} etc. are available, where the stabilization of t-ZrO_2 by Si^{4+} is achieved by strong surface interaction[11] and the stabilization of c- and t-ZrO_2 by Ce^{4+} is achieved by its larger size with higher coordination number.[12] But the stabilization of the metastable states of ZrO_2 with Th^{4+} or Ti^{4+} not so explored in the literature is the subject of the paper.

2. Experimental

The starting materials are zirconium oxychloride ($ZrOCl_2$. $8H_2O$) (Aldirich Chemical, 99.99%), thorium nitrate [Th $(NO_3)_4$] (Aldrich Chemical, 99.99%), titanium oxide (E. Merk. India 99.0%)., tarataric acid (E. Merk. India 99.0%), hydrofluoric acid (E. Merk. India 99.0%) and Triethanolamine (TEA) (E. Merk. India 99.0%). Other materials are common laboratory reagents.

---

* Corresponding author. Fax: +91-3222-55303.
E-mail address: asitp@chem.iitkgp.ernet.in (P. Pramanik).

0955-2219/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00091-8

2.1. Preparation of the precursor solution

Zirconium oxychloride is converted into zirconyl nitrate solution via zirconyl hydroxide and mixed with thorium nitrate solution with proper mole ratio to form 1.0, 2.50, 5.0, 10.0 at.% Th^{4+} containing ZrO_2 in the final product (samples are denoted as ZT-1, ZT-2.5, ZT-5, ZT-10). With the above mixed solution 6 M. TEA is added per mole of total metal ion to form the precursor solution. In the similar way Ti^{4+} containing precursor solution is prepared. In this case Ti^{4+} is entered into the precursor solution as its tartarate, which is synthesized chemically.[13] In the latter case, the samples are designated as ZTi-1, ZTi-2.5, ZTi-5, ZTi-10.

2.2. Preparation of precursor material and nanopowders

The precursor solutions are evaporated and pyrolyzed over a hot plate for about 4 h at bed temperature ~250 °C to form the precursor material. These are calcined at different temperatures (650–1200 °C) to form the nanocrystalline powders.

2.3. Characterization

Thermal decomposition/combustion of precursor material into ThO_2–ZrO_2 and TiO_2–ZrO_2 ceramic powders are studied with thermogravimetry and differential thermal analysis (TG–DTA) using a thermal analyzer (Model DT-40, Shimadzu Co. Kyoto, Japan). The data are obtained by heating the sample at 5 °C/min. Phase analysis of samples calcined at various temperatures is carried out with X-ray powder diffraction. The diffraction patterns are recorded with the help of a Philips PW-1817 X-ray powder diffractometer using Ni-filtered CuK_α radiation of wavelength, $\lambda = 0.15418$ nm. Crystallite sizes are calculated from peak broadening of principal peaks with the Scherrer formula.[14] The finer details of the powder are determined by transmission electron microscopy (TEM) using Hitachi H-600 electron microscope.

3. Result and discussion

3.1. Synthesis method producing nanocrystals

In this synthesis method, zirconyl nitrate, thorium nitrate or titanium tartarate and TEA form the precursor solution in water. This, on evaporation, gives a highly porous and fluffy carbonaceous mass, where the metal oxides are embedded in amorphous carbon matrix termed as precursor material, which on calcination at lower temperatures results in nanocrystals with controlled crystallite size. Here the role of TEA is dual: **(i)** It forms stable co-ordinate complexes with the metal ions in solution. **(ii)** It forms mesoporous carbonaceous mass which acts as a host to accommodate nano-sized oxides, forms during pyrolysis of precursor solution.

The amount of TEA is optimized with respect to metal ions to get the smallest particles. The optimum ratio of metal ion to TEA is 1:6.

3.2. Thermal analysis

Fig. 1 shows DTA and TG curves in thermal decomposition/combustion during heating 6.5 mg of a precursor (ZTi-5) at a heating rate 5 °C/min. DTA curve initially shows a small endothermic effect (A–B) probably due to desorption of water and then it shows a monotonically increase of heat output due to slow combustion (B–C) of the precursor. An exothermic peak at 505 °C indicates the peak point of mass combustion of carbonaceous material along with crystallization of Ti^{4+} doped ZrO_2. The coincidence of the two processes indicates clearly that sensible heat of combustion helps to form nanocrystals. The TG curve shows a slow mass loss up to up to D and a sharp loss up to point E. The total mass loss is up to ~35% of the initial weight of the precursor at a temperature of about 600 °C. At this temperature, the sample becomes carbon free. All the precursor materials show similar thermal effects. The data of two representative samples are given in Table 1.

3.3. Phase analysis

The phase analysis and the calculation of the crystallite sizes of the calcined powders are determined from the X-ray diffraction patterns obtained in the 2θ range 20–70° in the CuK_α radiation of wavelength $\lambda = 0.15418$ nm. Fig. 2 shows the X-ray diffraction patterns of the sample ZT-5 calcined at (a) 650 °C, (b) 950 °C and (c)

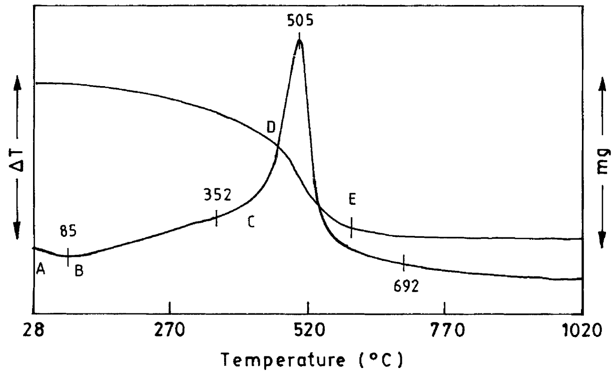


Fig. 1. DTA–TG diagram of the precursor mass of the sample ZTi-5. The data are obtained with the heating at 5 °C/min using a thermal analyzer (Model DT- 40, Shimadzu Co. Kyoto, Japan).

Table 1
Comparison of the thermal effects of the precursor materials

Sample	Peak temp. (°C)	Complete combustion temp. (°C)	Mass loss (%)
ZTi-5	505	600	35
ZT-5	465	620	33

Peak temperature is the temperature of the exothermic peak in DTA curve and complete combustion temperature is the temperature at which no mass loss occurs in TG curve.

1200 °C. The phase formed at the calcination temperature of 650 °C (Fig. 2a) is t-ZrO_2 with the average crystallite size of ~10 nm. As the calcination temperature increases, the peak splitting occurs characteristic to t-phase. Though this splitting is absent in Fig. 2a, the asymmetric broadening of the peaks clearly indicates the overlapping of the split peaks. The t-phase is stable up to 950 °C with some m-phase (Fig. 2b). Beyond this temperature, transformation of t-phase into m-phase starts and at 1200 °C, complete transformation occurs [Fig. 2(c)]. The average crystallite sizes at these temperatures are 20 and 35 nm respectively. Other details of phase analysis of ZT-5 are given in Table 2. Lower concentration of Th^{4+}also can stabilize the t-ZrO_2, but its thermal stability is lower than ZT-5. Even 1 mol% Th^{4+} can stabilize t-ZrO_2. However, higher concentration of Th^{4+} does not improve the thermal stability of t-phase. Therefore, ZT-5 is the optimum composition for the stabilization.

Stabilization characteristics of t-ZrO_2 using Ti^{4+} is displayed in Fig. 3 for the sample ZTi-5. It is almost similar to ZT-5 except the lower thermal stability. At the calcination temperature of 1000 °C, total transformation into m-phase occurs in case of Ti^{4+} stabilized t-ZrO_2. At 900 °C, about 8% m-phase appears for the sample ZTi-5, but in the case of sample ZT-5 about 3% m-phase is present even at the calcination temperature of 950 °C. Therefore, it can be concluded that the stabilizing ability of Th^{4+} is better than Ti^{4+} with respect to thermal stability. This observation gives an insight of

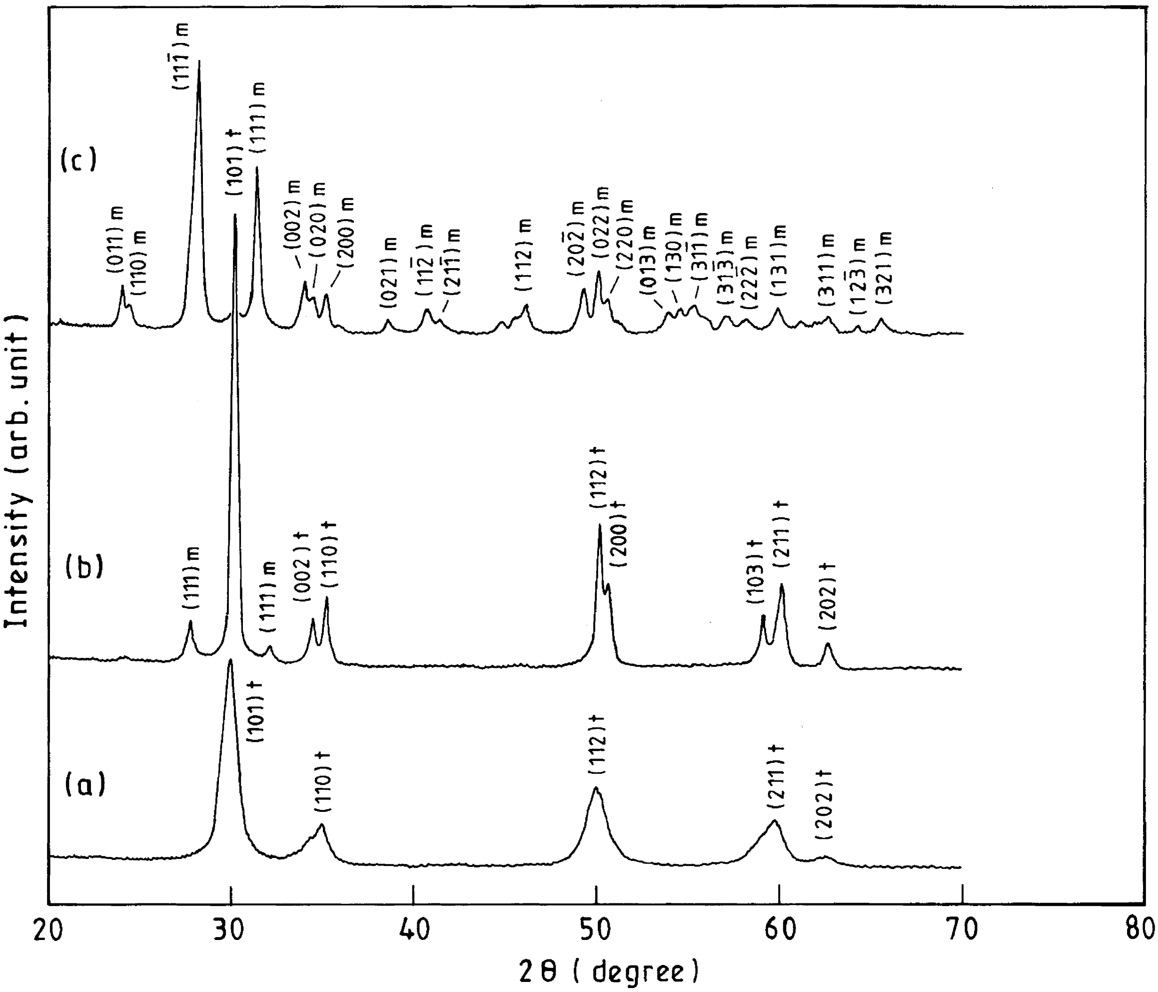


Fig. 2. X-ray diffraction patterns of the sample ZT-5 calcined at (a) 650 °C, and (b) 950 °C and (c) 1200 °C (using Philips PW1710 X-ray powder diffractometer, Ni-filtered CuK_α radiation of wavelength, λ = 0.15418 nm).

Table 2
Crystallite size, particle size and phases with corresponding d_{hkl} values of the principal peaks at different calcining temperatures of the sample ZT-5

Calcining temp. (°C)	d_{hkl} values (Å) of principal peaks (observed)				Av. crystallite size (nm)	Av. particle size (nm)	Phases[a]
650	2.99_{101}	1.84_{112}	1.82_{200}	1.55_{211}	10.0	30	t
1000	2.98_{101}	1.83_{112}	1.82_{200}	1.55_{211}	15.0	35	t
1200	$3.15_{11\bar{1}}$	2.98_{101}	2.83_{111}	1.82_{200}	35.0	50	m

[a] t and m denote tetragonal and monoclinic phases respectively, *hkl* values are given as subscripts of the corresponding '*d*' values, crystallite sizes are determined by Scherrer equation from full width at half intensity of the principal peaks with correction of instrumental broadening and the particle sizes are determined by TEM.

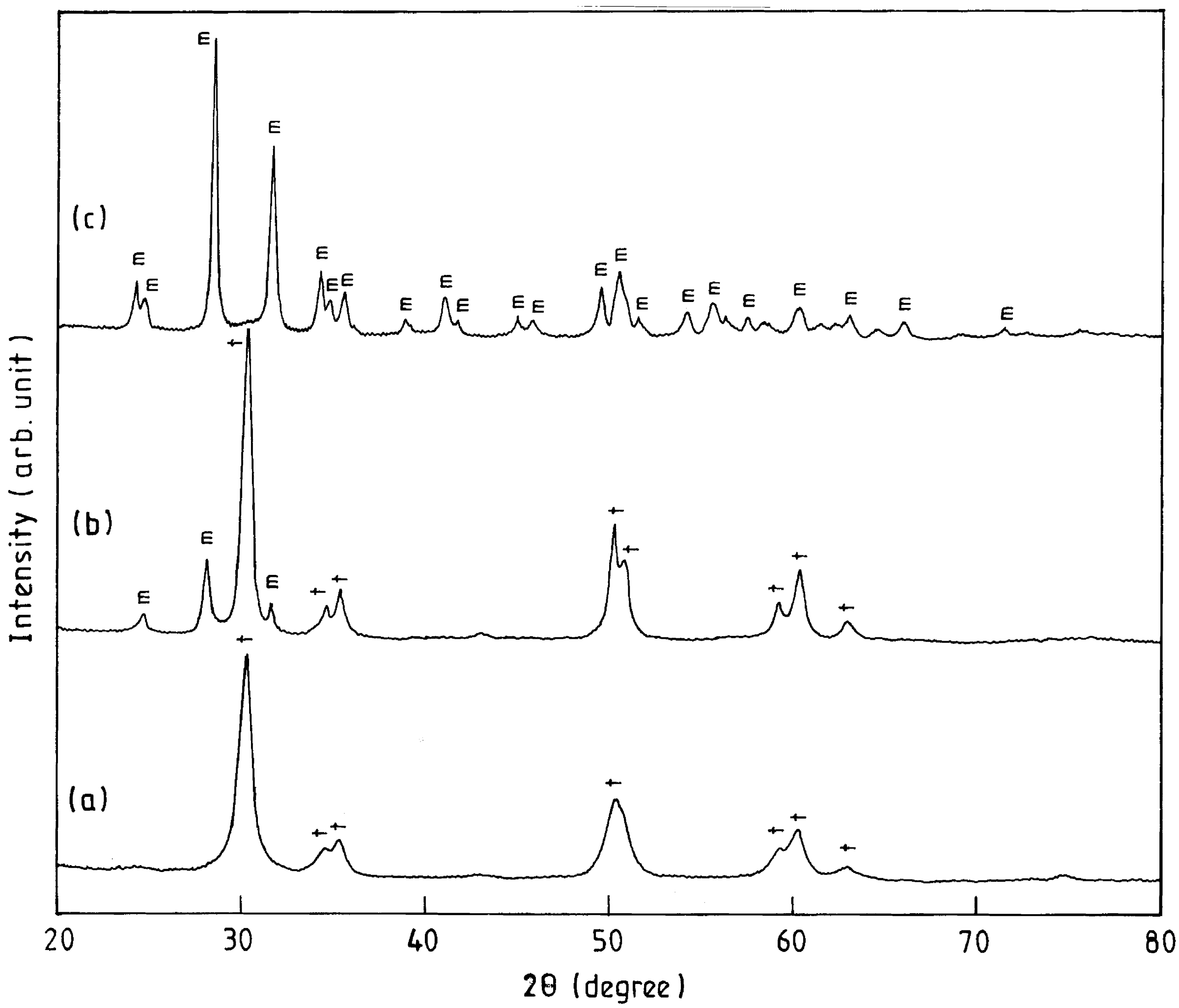
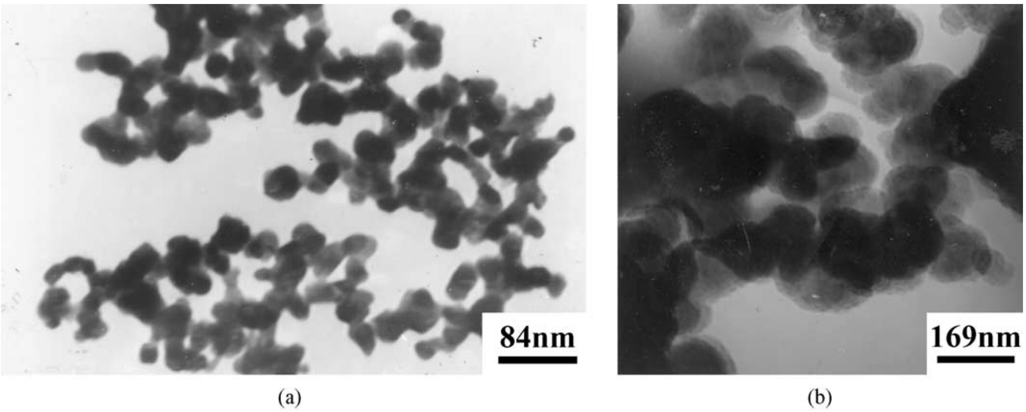


Fig. 3. X-ray diffraction patterns of the sample ZTi-5 calcined at (a) 6500 °C, and (b) 900 °C and (c) 1000 °C (using Philips PW1710 X-ray powder diffractometer, Ni-filtered CuK_α radiation of wavelength, λ =0.15418 nm).

the stabilization mechanism of ZrO_2. The cationic radius of Th^{4+} (0.95Å) is greater than Ti^{4+} (0.64 Å), which is probably the reason of different stabilizing ability. This again proves the dopant size effect for stabilization.[12] Ionicity of Th^{4+} and Ti^{4+} is not very different, so it may not play an important role for making any difference in ability of stabilization.

The stabilization of t-ZrO_2 with ThO_2 is similar to effect with SiO_2 as reported by del Monte et al.[15] and superior to the stabilization of t-ZrO_2 with SnO_2 as reported by Ray et al.[16] Here again ionic charges of Si^{4+}, Sn^{4+} and Th^{4+} are same. The effect of Si^{4+} will be different from the other because its higher covalent character of the Si–O bond. In general it shows that



(a) (b)

Fig. 4. (a) TEM micrograph of ZT-5 calcined at 600 °C (using Hitachi H-600 electron microscope). (b) A magnified TEM micrograph of (a).

with an increase of size of ion the stabilization effect from metal ion increases.

3.4. Transmission electron microscopy studies (TEM)

The nanocrystalline nature of the powders is observed in the TEM experiment. One representative pattern of the particles is displayed in Fig. 4a of the sample ZT-5, calcined at 650 °C. The particles are hexagonal in shape having size ranges 30±5 nm. Fig. 4b shows the magnified pattern of the selected area of Fig. 4a, which clearly indicates the narrow size distribution of the particles. As the calcination temperature increases, the particle size increases with their crystallite sizes that are shown in Table 2.

4. Conclusions

The chemical synthesis process using TEA is a very useful process to prepare stabilized nanocrystalline powders of ZrO_2. Both Th^{4+} and Ti^{4+} is effective agent to stabilize t-ZrO_2 at low calcination temperature but the former is more effective. In stabilizing the metastable states of ZrO_2 with tetravalent dopants, size effect is more important, particularly when the covalence between M–O is weak.

Acknowledgements

The authors are grateful for financial assistance for this study from Council of Scientific and Industrial Research (CSIR), Government of India.

References

1. Garvie, R. C., Hannink, R. H., Pascoe, R. T., Ceramic steel? *Nature*, 1975, **258**, 703–704.
2. Hannink, R. H. J., Kelly, P. M. and Muddle, B. C., Transformation toughening in zirconia-containing ceramics. *J. Am. Ceram. Soc.*, 2000, **83**(3), 461–487.
3. Garvie, R. C., *Zirconium Dioxide and Some of Its Binary Systems*. Academic Press, New York, 1970.
4. Lin, J.-D. and Duh, J. G., Crystallite size and microstrain of thermally aged low-ceria- and low-yttria-doped zirconia. *J. Am. Ceram. Soc.*, 1998, **81**(4), 853–860.
5. Heuer, A. H., Transformarion toughening in ZrO_2 containing ceramics. *J. Am. Ceram. Soc.*, 1987, **70**(10), 689–698.
6. Ho, S.-M., On the structural chemistry of zirconium oxide. *Mater. Sci. Eng.*, 1982, **54**, 23–29.
7. Benedetti, A., Fagherazzi, G. and Pinna, F., Preparation and structural characterization of ultrafine zirconia powders. *J. Am. Ceram. Soc.*, 1989, **72**(3), 467–469.
8. del Monte, F., Larsen, W. and Mackenzie, J. D., Stabilization of tetragonal ZrO_2 in ZrO_2–SiO_2 binary oxides. *J. Am. Ceram. Soc.*, 2000, **83**(3), 628–634.
9. Zhou, E., Bhaduri, S., Bhaduri, S. B., Lewis, I. R. and Griffiths, P. R., Auto ignition processing of nanocrystalline zirconia. In *Processing and Properties of Nanocrystalline Materials*, ed. C. Suryanarayana, J. Sing and F. H. Froes. The Minerals, Metals & Materials Society, 1996, pp. 123–133.
10. Chen, Li.I.-W. and Penner-Hahn, J. E., Effect of dopants on zirconia stabilization—an X-ray absorption study: I. Trivalent dopants. *J. Am. Ceram. Soc.*, 1994, **77**(1), 118–128.
11. del Monte, F., Larsen, W. and Mackenzie, J. D., Chemical interaction promoting the tetragonal ZrO_2 stabilization in ZrO_2–SiO_2 binary oxides. *J. Am. Ceram. Soc.*, 2000, **83**(6), 1506–1512.
12. Chen, P.Li.I.-W. and Penner-Hahn, J. E., Effect of dopants on zirconia stabilization—an X-ray absorption study: II. Tetravalent dopants. *J. Am. Ceram. Soc.*, 1994, **77**(5), 1281–1288.
13. Das, R. N. and Pramanik, P., Low temperature chemical synthesis of nabosized ceramic powders. *British Ceramic Transaction*, 2000, **99**(4), 153–158.
14. Klug, M. P. and Alexander, L. E., *X-ray Diffraction Procedure for Polycrystalline and Amorphous Materials*. Wiley, New York, 1974.
15. del Monte, F., Larsen, W. and Mackenzie, J. D., Stabilization of tetragonal ZrO_2 in ZrO_2–SiO_2 binary oxides. *J. Am. Ceram. Soc.*, 2000, **83**(6), 628–634.
16. Ray, J. C., Saha, C. R. and Pramanik, P. Chemical synthesis of nanocrystalline tin doped cubic ZrO_2 powders. *Mater. Lett.*, 2003, **57**, 2140.