Journal of the European Ceramic Society 20 (2000) 1289–1295

Chemical synthesis and structural characterization of nanocrystalline powders of pure zirconia and yttria stabilized zirconia (YSZ)

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Received 5 July 1999; received in revised form 15 October 1999; accepted 27 October 1999

Abstract

Nanocrystals of pure zirconia and yttria stabilized zirconia (YSZ) are obtained by a simple chemical synthesis route using sucrose, polyvinyl alcohol (PVA) and metal nitrates. The reaction mixture on pyrolysis and calcination gives nanocrystals. These are characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The size of the nanocrystallites for pure zirconia is in the range of about 7.0–45.0 nm and for yttria stabilized zirconia, is in the range of about 5.0–24.0 nm at 200°C and above, according to the preparative condition. At 200°C, pure zirconia forms cubic phase and this cubic phase is stable up to 600°C and then slowly transformed into monoclinic form. For yttria stabilized zirconia, the crystals are tetragonal in the temperature range from 200 to 1200°C.

Keywords: Electron microscopy; Phase transformation; Powders–chemical preparation; X-ray methods; ZrO_2; YSZ

1. Introduction

The importance of zirconia in various technical applications makes the compound an interesting subject for research work. Over the past years, there has been an increasing interest in nanostructured ceramics for their lower sintering temperature and improved mechanical properties. Zirconia exists in three polymorphic modifications, these are monoclinic (m) tetragonal (t) and cubic (c). Among them tetragonal and cubic phases are metastable forms but monoclinic is the stable form at room temperature. Stabilization of cubic and tetragonal forms are gaining importance because of its excellent thermal stability, chemical resistance, mechanical properties and oxygen conductivity. In the literature many hypotheses have been proposed regarding the factors which control the stabilization of the tetragonal and cubic phase relative to the thermodynamically stable monoclinic phase at room temperature. Among the factors, type and amount of stabilizing agent, particle size, heat treatment temperatures are important. Stabilization of metastable phases depends on crystallite size[19,20] and on the process of preparing the powders.[16] There are various techniques for the preparation of nano particles. By the gas condensation method (originally proposed by Gleiter) nano structured monoclinic zirconia particles (dia. ranging from 4 to 8 nm) have been synthesized and at high pressure tetragonal structure is obtained depending on size.[1] In spray pyrolysis process,[2] at 550°C pure zirconia forms cubic phase and at 1000°C, it forms only monoclinic phase, via a small amount of tetragonal phase. At 500°C, YSZ forms cubic phase and maintains this form as a major phase upto 1000°C. By solid state reaction,[3] at 500°C tetragonal zirconia is prepared of crystallite size 9 to 25 nm and agglomerated average particle size 2–4 μm. It is reported[6] that m-ZrO_2 transforms into the tetragonal form at ~1000°C and then to the fluorite type structure at ~2370°C. The high temperature forms can not be retained at room temperature, because both of these transformations are reversible. However, it has been found that the high temperature forms can be partially or fully stabilized at room temperature by the addition of a small amount of oxides (e.g. MgO, CaO, and certain rare earth oxides).[9] Moreover, thermal decomposition of amorphous hydrous ZrO_2,[4] zirconium alkoxides[21] and zirconium salt;[7] ball milling of m-zirconia, vapor phase reactions, and hydrothermal treatments of amorphous

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0955-2219/00/$ - see front matter
PII: S0955-2219(99)00293-9

hydrated ZrO_2 are known to produce cubic ZrO_2(c). Srinivasan et al.[12] claimed that a pure cubic phase is originated at 500°C starting from a precursor precipitated at pH = 13.5 using a solution of NaOH. Nishizawa and co-workers[13,14] succeeded in stabilizing (at room temperature), the cubic form of zirconia by inserting Na^+ (or Ca^{+2}) ions in to the initial zirconia gel by means of suitable hydrothermal reaction. Our preparative route is based on pyrolysis of polymer base precursor solution.[5] This polymeric precursor plays a crucial role in designing the final product and is also better and less cumbersome method for the production of fine grained oxide powder. In this process metastable cubic phase of pure zirconia is obtained with crystallite size of about 7nm at 200°C (heated on a hot plate) which is stable up to 600°C, in which the crystallite size increases up to 11nm. At 600°C, the monoclinic phase transformation starts and at 1000°C major phase is monoclinic with crystallite size up to 26 nm. For YSZ, tetragonal phase is obtained at 200°C with crystallite size of about 5.0 nm and this phase is stable at 1200°C and above, with the crystallite size upto 24.0 nm.

2. Experimental procedure

Zirconium oxychloride (Aldrich Chemicals) is dissolved in a minimum quantity of distilled water, from this solution zirconium hydroxide is precipitated by the addition of ammonium hydroxide, which is washed several times. Then the precursor nitrate solution is formed by the reaction of nitric acid and hydroxide. To prepare pure zirconia, a predetermined proportion of sucrose (Aldrich Chemicals) and PVA (MW 125000, Aldrich Chemicals) are added to the nitrate solution and the resulting mixture is evaporated to a viscose mixture on a water bath to avoid frothing in subsequent heat treatment. Then the mixture is heated to about 200°C (hot plate) to make black porous mass, and in some cases a white fluffy powder was obtained for uniform heating. This mass is ground to powder for calcination. The resulting powder was calcined at various temperatures to make the nano crystallites of pure zirconia. To prepare yttria stabilized zirconia, yttria (99.9% Aldrich chemicals) was dissolved in nitric acid to form a yttrium nitrate solution, which was mixed with zirconium nitrate

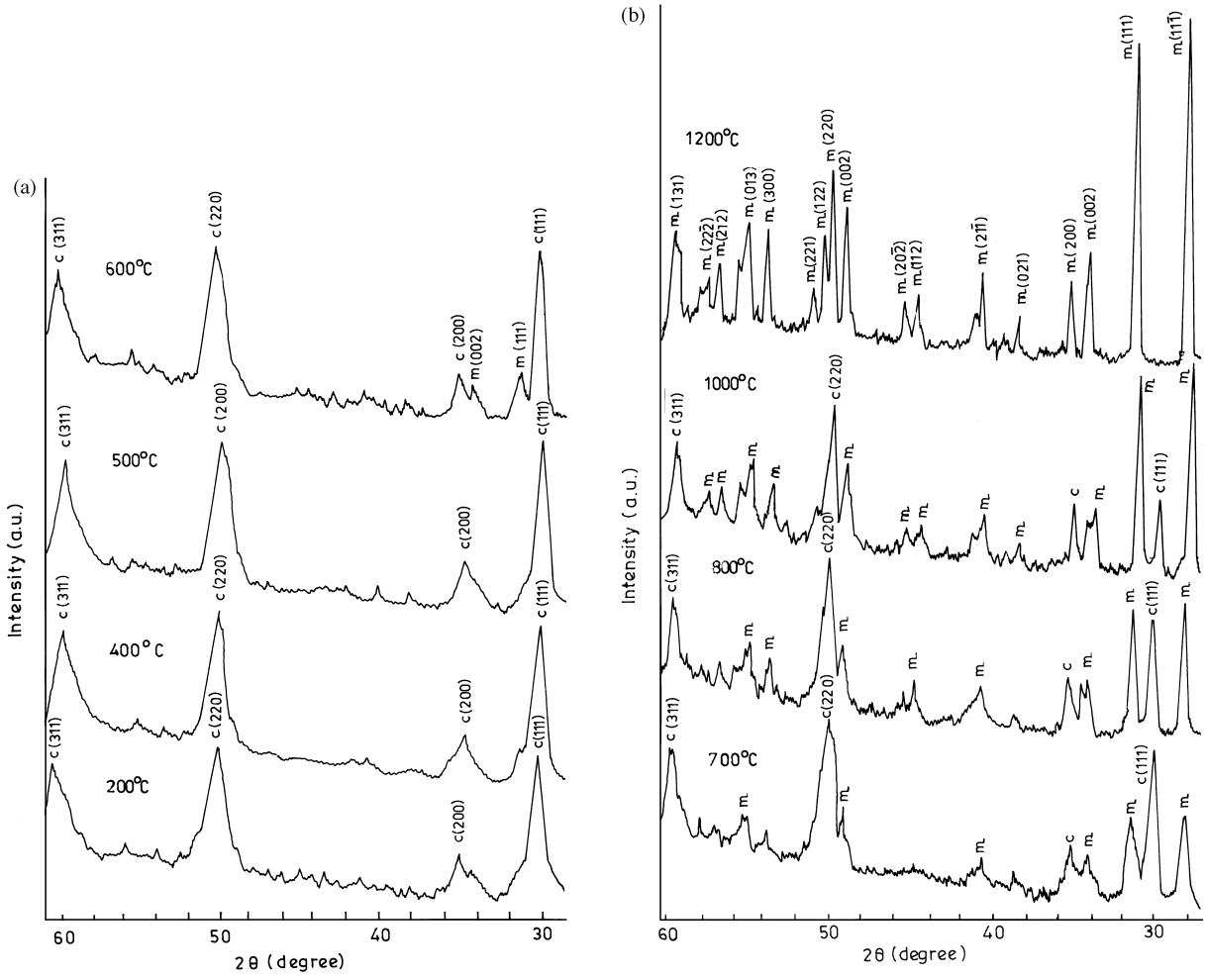


Fig. 1(a and b). Room temperature X-ray diffractogram (using CuK_α radiation, $\lambda = 0.1541$ nm) of pure zirconia calcined at various temperatures.

solution in the proper proportion. The resulting solution was mixed with sucrose (Aldrich chemicals) and PVA (MW 125000, Aldrich chemicals). This mixture was then evaporated, pyrolysed and calcined as before. For preparation of pure zirconia, Zr^{+4}: sucrose molar ratio used are 1:1, 1:2, 1:4, 1:6, which are denoted as samples P_1, P_2, P_3 and P_4 respectively. The amount of 10%(w/v) solution of PVA used in each experiment is 5 mol% (with respect to monomer unit). For preparation of YSZ, the same ratio of sucrose and metal ion, as before, is used. In this case the samples are denoted as S_1, S_2, S_3 and S_4. Here Y^{+3} used is 7 mol%. The pyrolysis and the calcination temperatures are 200, 300, 400, 600, 700, 800, 1000 and 1200°C and the time used in each case is 2 h, except 200°C, where the time used is 6 h.

Table 1
Optical spectroscopic analysis of powder ZrO_2 calcined at 600°C

Elements present	wt%
A1	0.01–0.02
B	n.d.
Cu	n.d
Fe	0.008–0.01
K	0.005–0.03
Mg	0.005–0.008
Hf	0.3–0.8
Na	0.03–0.5
Si	0.01–0.03
Ti	.003–0.008

3. Characterization

Pure zirconia and yttria stabilized zirconia powders are characterized by XRD by Philips X-ray powder diffractometer PW1804 using Ni filtered CuK_α radiation and transmission electron microscopy using Philips TM 300 electron microscope and Hitachi H-600 electron microscope. The interplaner spacing (d) of the crystallites are determined by using Bragg's equation and the crystallite size (D) is determined by using Scherrers' equation.[15] By comparing the "d" values with the standard "d" values from powder diffraction file, the structure of the crystallites are predicted. Particle size and distribution are measured by transmission electron microscopy (TEM) for 800, 600 and 1200°C calcined powder. The monoclinic and the cubic phase contents in pure zirconia powder are calculated with the integral intensities of the monoclinic peaks ($11\bar{1}$) and (111) versus the cubic peak(111) using the following relationship[8,11]

$$X_m = \frac{I_{(11\bar{1})\mathrm{m}} + I_{(111)\mathrm{m}}}{I_{(11\bar{1})\mathrm{m}} + I_{(111)\mathrm{m}} + I_{(111)\mathrm{c}}}$$

4. Results and discussions

In the synthesis of nano phase zirconia, the sugar is used as fuel and also to make a mesoporous carbonaceous phase with PVA, which is evident from the large surface area of the mesoporous carbonaceous material

Table 1A
(Sample No-P_3) pure zirconia[a]

Temp °C	d_{111}Å	D nm	d_{220} Å	D nm	d_{311} Å	d_{200}Å	d_{111} Å	d_{002} Å	Average D nm	Phase
200/6 h	2.93	9.0	1.81	6.0	1.53	2.54	—	—	7.0	c
400/2 h	2.93	10.0	1.81	8.0	1.53	2.54	—	—	9.0	c
500/2 h	2.93	11.0	1.81	8.0	1.53	2.54	—	—	9.0	c
600/2 h	2.93	15.0	1.81	8.0	1.53	2.54	2.84	2.61	11.0	c, m 10%

[a] Where: d = interplaner distance of the corresponding hkl values in angstrom, D = crystallite size in nm calculated from higher intensity peaks, c = cubic phase and m = monoclinic phase.

Table 1B
(Sample No-P_3) pure zirconia[a]

Temp °C	$d_{11\bar{1}}$ Å	d_{111} Å	d_{111} Å	d_{311} Å	d_{002} Å	$d_{21\bar{1}}$ Å	d_{022} Å	d_{200} Å	d_{300} Å	d_{013} Å	$d_{21\bar{1}}$ Å	d_{220} Å	Average D nm	Phases
700/2 h	3.16	2.93	2.83	1.53	2.60	2.21	1.84	2.52	1.69	1.65	2.21	1.81	16.5	c = 50% m = 50%
800/2 h	3.16	2.93	2.83	1.53	2.61	2.21	1.84	2.53	1.69	1.65	2.21	1.81	20.5	c = 30% m = 70%
1000/2 h	3.16	2.93	2.83	1.53	2.60	2.21	1.84	2.53	1.69	1.65	2.21	1.81	26.0	c = 10% m = 90%
1200/2 h	3.16	—	2.83	1.53	2.60	2.21	1.84	2.53	1.69	1.65	2.21	1.81	45.0	m = 100%

[a] Where: d = interplaner distance of the corresponding hkl values in angstrom, D = crystallite size in nm calculated from higher intensity monoclinic peaks, c = cubic phase and m = monoclinic phase.

(160 m^2/g). This phase is responsible for making the small clusters of zirconia. It is observed that only sugar is not sufficient for making nanophasic material. Addition of excess sugar introduces a problem in the removal of carbon from the material, which requires higher temperature and longer time. This facilitates the growth of the nano crystallites. Hence the optimum amount of sugar is essential. Among the various ratio of the metal ion and sucrose used, in the case of YSZ, the optimum ratio is 1:4, sample No. S_3, (i.e. 4 mol of sucrose per mol of metal ion) and for pure zirconia, the ratio of the metal ion and sucrose is also 1:4 (sample No. P_3). The XRD experiment shows (Fig. 1a and b) that pure zirconia forms a cubic phase at 200°C (heating on hot plate) having the average crystallite size of about 6 nm. The cubic phase is stable above 600°C. As the calcination temperature increases, the size of the crystallite increases, but the rate of increase is slow between 200 and 600°C, which is shown in Table 1A. It is important to note that without using any stabilizing agent, like calcia, Na^+, yttria, metastable cubic phase is stabilized in the temperature range from 200 to 600°C, by this chemical method. It shows that the crystal structure of nano crystal is highly dependent on the chemical preparation condition.[10,16,17] The particle size of cubic zirconia is 30 nm and below, which is shown in the TEM photograph (Fig. 5) and diffraction pattern of the particles is shown in Fig. 7. An optical spectroscopic analysis (Table 1) is performed to test the presence of any impurities, which may cause the stabilization of the cubic form. It is seen that there is no stabilization. Here the formation of cubic form is process and size dependent.[16,20] At 600°C phase transformation from cubic to monoclinic starts and at 700°C cubic and monoclinic phases are equal in amount. This transformation is in accordance with critical size effect[18,19] as has been suggested by R.C. Garvie and M.F. Goss. At 800°C, the amount of monoclinic phase becomes greater than the cubic phase. At 1000°C, the monoclinic phase predominates and at 1200°C, only the monoclinic phase is present. At this temperature, the TEM photograph shows that the particle size is in the range of 100–150 nm (Fig. 6) and their diffraction pattern is shown in Fig. 8. There is no sharp line of demarcation of phase transition and it is gradual in nature. As the temperature increases, the main XRD peak of cubic phase ($d = 2.93$)

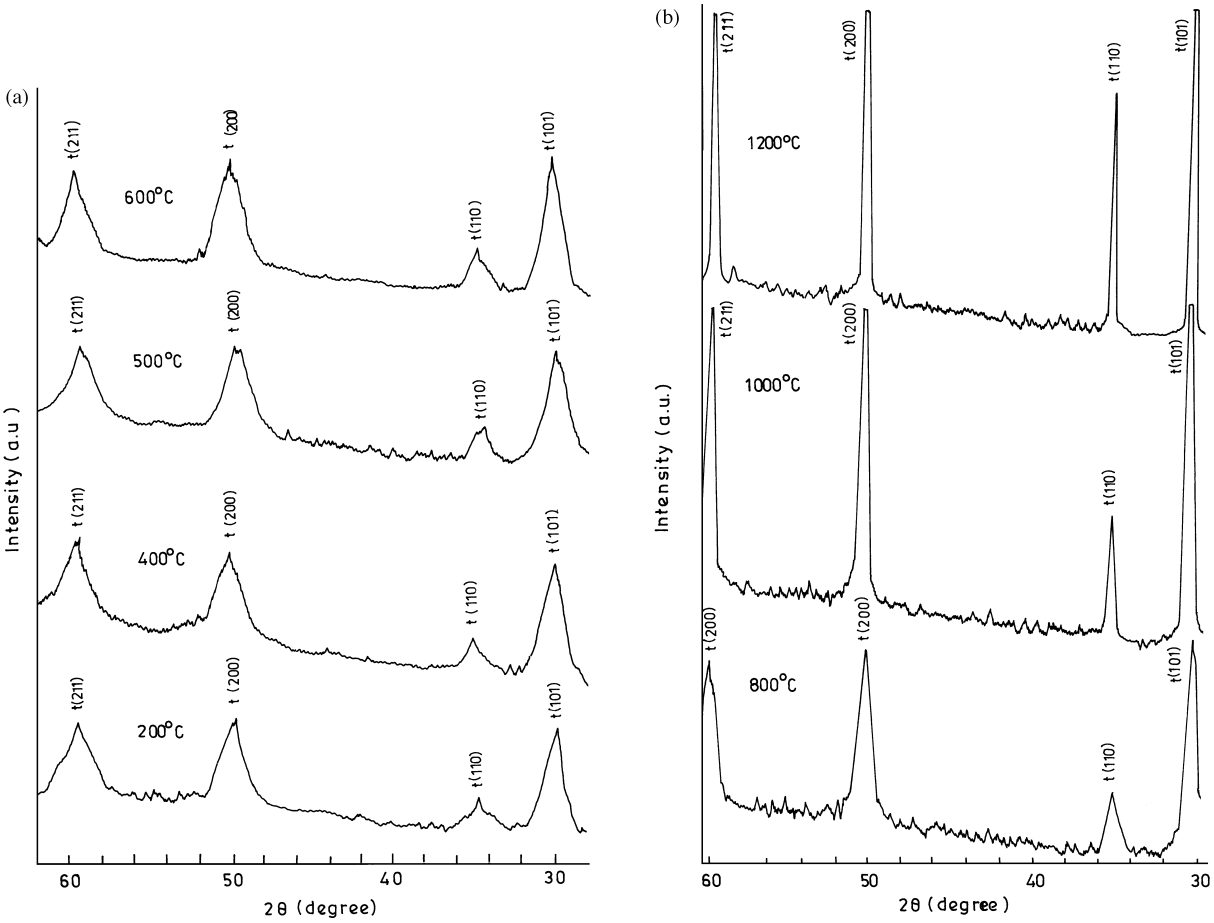


Fig. 2 (a and b). Room temperature X-ray diffractogram (using CuK_α radiation, $\lambda = 0.1541$ nm) of yttria stabilized zirconia (YSZ) calcined at various temperatures.

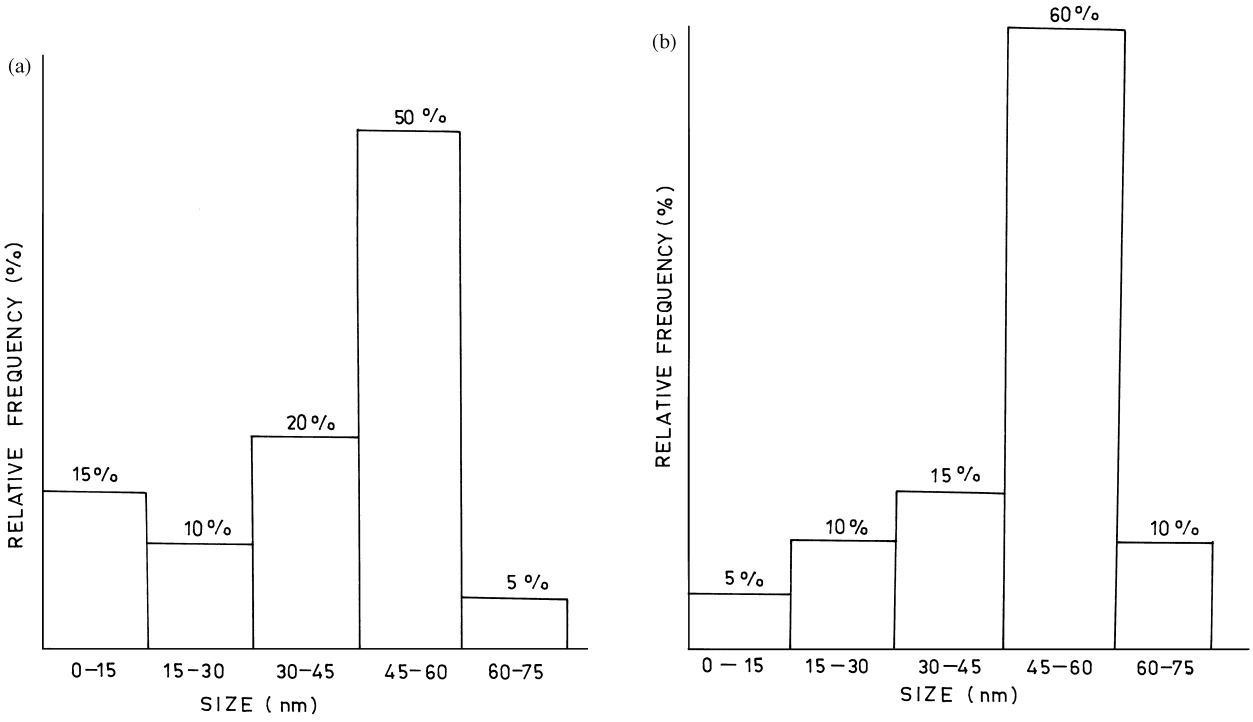
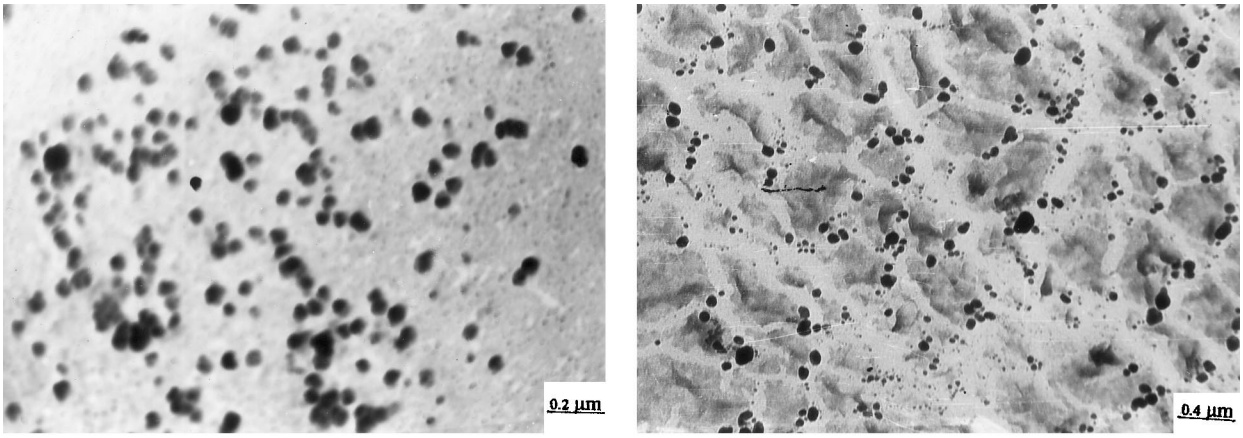


Fig. 3 (a and b). Histograms for particle size distribution of pure zirconia and YSZ powder calcimined at 800°C.



(a) (b)

Fig. 4 (a). Bright field TEM micrograph of pure zirconia powder calcined at 800°C. (using Philips TM 300 electron microscope). (b) Bright field TEM micrograph of yttria stabilized zirconia (YSZ) powder calcined at 800°C. (using Philips TM 300 electron microscope).

decreases and the monoclinic XRD peak ($d=3.16$, $d=2.83$) increases. At 1200°C, principal XRD peak of the cubic phase disappears and only monoclinic peaks are present. The rate of increase of crystallite size is high from 600°C and onward for pure zirconia but for YSZ, the rate is slow. At 1200°C for pure zirconia, the crystallite size reaches up to 45 nm. This is shown in Table 1B. In the case of YSZ, X-ray diffractogram shows (Fig. 2a and b) that tetragonal phase is formed at 200°C (heated in hot plate) with average crystallite size of about 5.0 nm. As the temperature increases, the crystallite size increases very slowly up to 800°C but the phase remains unchanged up to 1200°C as shown in Table 2. The rate of increase of crystallite size is higher above 800°C. The average crystallite size at 1000°C is about 18 nm. and at 1200°C, it is about 24 nm, TEM examination shows that the average particle sizes for 800°C calcined powder in both the cases are similar (for pure zirconia and YSZ). The particle size distribution for 800°C calcined powder is given in two histograms (Fig. 3a and b). The size ranges for 800°C calcined powder from 30–50 nm for pure zirconia (Fig. 4a) and 40–70 nm. for YSZ (Fig. 4b). For pure zirconia the particle size is similar to crystallite size obtained from

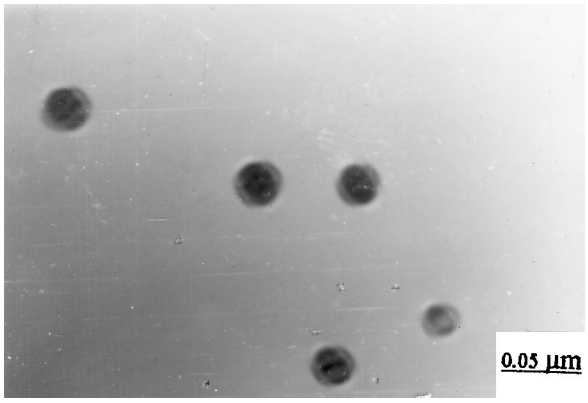


Fig. 5. Bright field TEM micrograph of pure zirconia powder calcined at 600°C. (using Hitachi H-600 electron microscope).

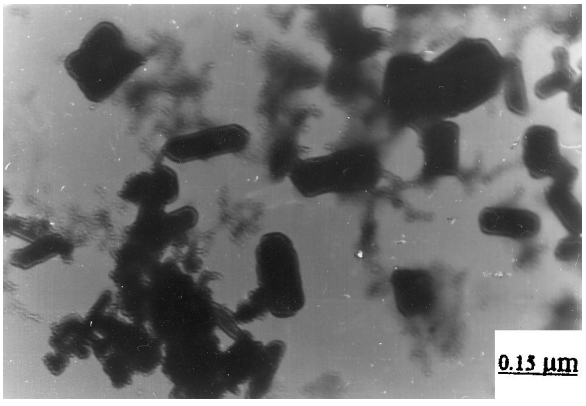


Fig. 6. Bright field TEM micrograph of pure zirconia powder calcined at 1200°C. (using Hitachi H-600 electron microscope).

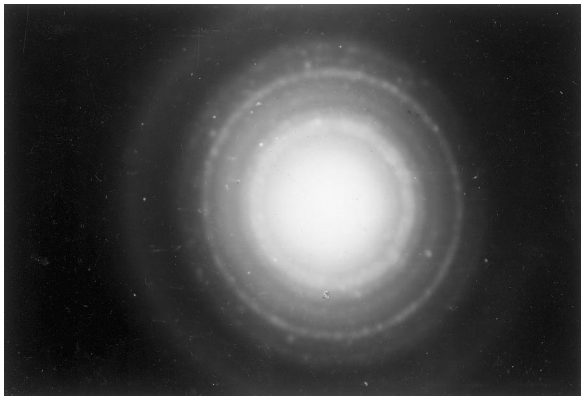


Fig. 7. Diffraction pattern of pure zirconia powder calcined at 600°C (using Hitachi H-600 electron microscope).

XRD with few (2 of 3 crystallites) agglomeration (crystallite size at 800°C is 18 nm). But for YSZ, the particle size is much higher than the crystallite size due to higher (4–7 crystallites) agglomeration (crystallite size at 800°C is 10 nm). This higher physical agglomeration of crystallites originates from higher surface energy of smaller crystallites. According to the phase diagram of the system ZrO_2–Y_2O_3, when the temperature is between 500 and 1000°C,

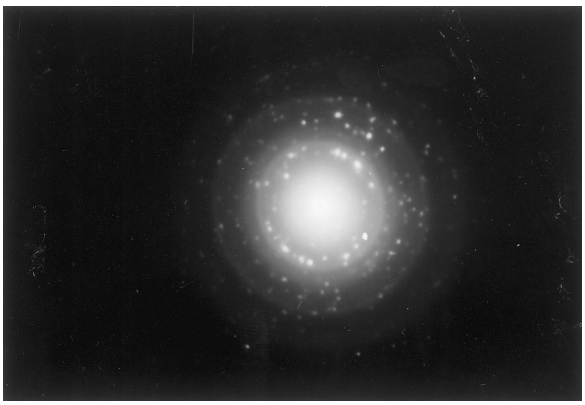


Fig. 8. Diffraction pattern of pure zirconia powder calcined at 1200°C (using Hitachi H-600 electron microscope).

Table 2
(Sample No S_3) yttria stabilized zirconia[a]

Temp °C	d_{101} Å	D nm	d_{200} Å	D nm	d_{211} Å	d_{110} Å	Average D nm	Phase
200/6 h	2.98	6.0	1.82	5.0	1.55	2.56	5.5	t
300/2 h	2.98	6.0	1.82	6.0	1.55	2.56	6.0	t
400/2 h	2.98	6.0	1.82	6.0	1.55	2.56	6.0	t
600/2 h	2.98	7.0	1.82	7.0	1.55	2.56	7.0	t
800/2 h	2.98	10.0	1.82	10.0	1.55	2.56	10.0	t
1000/2 h	2.98	18.0	1.82	19.0	1.55	2.56	18.5	t
1200/2 h	2.98	23.0	1.82	24.0	1.55	2.56	23.5	t

[a] Where: d = interplaner distance of the corresponding hkl values in angstrom, D = crystallite size in mm calculated from higher intensity peaks and t = tetragonal.

the stable phase for the pure zirconia is m-ZrO_2 and for 1.5 mol% Y_2O_3–ZrO_2, it is monoclinic or a combination of the monoclinic and the tetragonal phase.[2] However, in this method, tetragonal phase of YSZ and low temperature cubic phase of pure zirconia is obtained. In this process the fuel (sucrose) provides the heat of crystallization through its combustion, which reduces the external formation temperature. In the absence of PVA, the segregation of nano particles is very frequent. It is probably due to absence of a polymeric net work, which grows during simultaneous decomposition of sucrose and PVA. Only PVA works well but it has a tendency to grow graphite particles, whose removal is difficult and the optimum ratio of metal ion and sucrose is 1:4. To ensure proper synthetic condition, the amount of sucrose and PVA in the starting solution have been optimized with respect to metal ion for obtaining nanosized zirconia powder.

5. Conclusion

This chemical synthesis through polymer matrix comprising of sucrose and PVA, is convenient and cost effective compared to those of other processes, for the preparation of nano sized zirconium oxide. In this process,

the pure zirconium oxide produced in cubic form, having the particle size 30 nm and below and corresponding crystallite size is 11 nm at 600°C. At 1200°C, the monoclinic zirconia acquires the particle size from 100–150 nm, having the crystallite size 45 nm and YSZ has the particle sizes ranging between 40 to 70 nm having average crystallite size of 10 nm at 800°C calcined powder. In both the cases, the particles are physical agglomerates of a few crystallites. Here low temperature synthesis and stabilization of nanocrystalline pure cubic zirconia and tetragonal yttria stabilized zirconia are achieved.

Acknowledgements

The authors wish to acknowledge the valuable contributions made by Mr. R. N. Das, and Dr. A. Pathak towards this research work. This investigation is funded by DST, CSIR and ICCR, New Delhi, Government of India.

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