

# Synthesis of Monoclinic and Cubic ZrO<sub>2</sub> Nanoparticles from Zircon

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Zirconia (ZrO<sub>2</sub>) nanoparticles with nonstabilized monoclinic and sodium-stabilized cubic phase were produced from zircon sand using the ball mill-aided precipitation route. Characterization and a comprehensive study of nanocrystalline ZrO<sub>2</sub> particles were expressed by X-ray diffraction, particle size distribution (PSD), Fourier transform infrared spectroscopy, thermal analysis, Brunauer-Emmett-Teller surface area and pore size analysis, X-ray fluorescence spectrometry, scanning electron microscopy, and transmission electron microscopy. In this article, the influence of the processing parameters on the crystalline phase, particle size, PSD, aggregation, and morphology are reported. The experimental results prove that the precipitation leads to aggregated particles, which are disaggregated by the ball-milling process. The ball-milling process strongly influences the formation of uniform-sized spherical particles with a high surface area. Fully crystalline monoclinic ZrO<sub>2</sub> nanoparticles with an average particle size of 64 nm ( $d_{50}$ ) and the specific surface area of 126  $m^2/g$  were obtained. In addition, the sodiumstabilized cubic ZrO<sub>2</sub> nanoparticles with an average particle size of 39 nm ( $d_{50}$ ) and the specific surface area of 227 m<sup>2</sup>/g were obtained with the help of the ball-milling process. In the present process, a simple reaction scheme is developed for the largescale production of stabilized and nonstabilized ZrO<sub>2</sub> nanoparticles using inexpensive precursor obtained from zircon sand.

#### I. Introduction

ZIRCONIA-BASED advanced ceramics are immensely attractive because of their outstanding thermal stability, chemical resistance, mechanical characteristics, and ionic conductivity.<sup>1-3</sup> The ceramics system established with zirconia has been applied to wide range of applications such as catalysis,<sup>4-6</sup> chromatographic materials,<sup>7,8</sup> fuel cell technology,<sup>9,10</sup> and gas sensors.<sup>6,11–13</sup> Owing to their excellent properties such as high strength, toughness, hardness, wear resistance, and thermal shock resistance, zirconia-based materials are used in many engineering applications including automobile engine parts, wire-drawing dies, and cutting tools.  $ZrO_2$  is an attractive oxide ceramic for thermal barrier coatings on metals and metallic alloys due to its low thermal conductivity and relatively high coefficient of thermal expansion.<sup>14,15</sup> The developments of functional ceramics require the nanoscale oxide powders with uniform shapes and narrow PSD. The production of nanoparticles has attracted considerable attention due to their potential applications in the densifi-

Manuscript No. 28062. Received May 29, 2010; approved October 28, 2010. This work was financially supported by the Department of Science and Technology, New Delhi, India to carry out this research project (SR/S5/NM-40/2005 dated, June 26, 2007). cation of ceramics at lower sintering temperature and ultrafinegrained ceramics.<sup>16</sup> Dispersion of nanoscale particles into the ceramic matrix is used to improve the mechanical properties of a ceramic-based nanocomposite system. The incorporation of nanoparticles in the ceramics matrix facilitates considerable modification of the behavior of the ceramics, which exposes new functions such as superplasticity or high machinability like metal.<sup>17</sup>

In recent years, ZrO<sub>2</sub> nanoparticles have attracted wide attention due to their size-dependent properties and significant technological applications.  $^{18-20}$  ZrO<sub>2</sub> nanoparticles with a high refractive index are used as fillers in transparent coatings such as anticorrosive, antireflection, and scratch-proof coatings.<sup>1</sup> In addition, there is a high level of interest in zirconia nanocoatings have because of high-performance applications, such as wearresistant insulating coatings, sensors and thermal barrier coatings.<sup>21,22</sup> It is suitable for powder phosphorization and is used to produce proton-conductive zirconium phosphate particles. Phosphorized zirconium oxide nanoparticles are used for the preparation of composite polymer membranes.<sup>23</sup> Nanocrystalline  $ZrO_2$  ceramics, with an average grain size of <100 nm, has attracted more attention due to its exotic properties such as sintering ability, mechanical toughness, and superplastic behavior.<sup>24</sup> Owing to their chemical inertness, thermal stability, high hardness, and refractive index, they are used as an ideal inorganic material for the fabrication of organic–inorganic nanocomposites.<sup>25</sup> Zirconia nanoparticles having 1–10 nm pore size distributions are used in membrane applications and this is often considered because of their stability in the aqueous environment in a wide pH window.<sup>26</sup> The addition of nanoscale zirconia (ZrO<sub>2</sub>) particles into alumina matrix is used to enhance the mechanical properties of Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> composite system.<sup>2</sup>

Pure  $ZrO_2$  has three stable crystal forms, namely P21/cmonoclinic (m), P42/nmc tetragonal (t) and Fm3 m cubic fluorite (c) at different temperatures.<sup>22</sup> An orthorhombic polymorph is also possible,<sup>28</sup> but only occurs at room temperature in pure zirconia under metastable conditions due to constraint.<sup>29</sup> Zirconia has a monoclinic phase at room temperature and it transforms into tetragonal and cubic phase at 1170° and 2370°C, respectively.<sup>24</sup> The tetragonal and cubic phases are unstable in bulk forms at ambient temperature. Unfortunately, these two high-temperature phases of zirconia are more valuable for the technological applications mentioned above than at the room temperature monoclinic phase. In particular, it has received much attention due to their specific applications such as thermal barrier coatings, high-fracture toughness and electro-chemical devices.<sup>30,31</sup> To stabilize the cubic and tetragonal phases at room temperature, many divalent and trivalent cationic species, such as  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Y^{3+}$ , and  $Ce^{4+}$ , are embedded in ZrO<sub>2</sub> by doping with MgO, CaO,  $Y_2O_3$ , and CeO<sub>2</sub> during their synthesis.<sup>30,32</sup> However, the cubic phase can also be stabilized at room temperature by doping with Na.<sup>33</sup>

The development of inexpensive methods for producing mass quantities of highly crystalline and monodispersed nano- $ZrO_2$ 

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particles, remains an area of extensive interest. A variety of synthesis methods are being explored and developed for the production of stabilized and nonstabilized nanoscale zirconia particles, such as thermal decomposition,<sup>16,20</sup> sol-gel,<sup>34,35</sup> precipitation, <sup>35,36</sup> emulsion precipitation, <sup>37</sup> hydrothermal, <sup>38</sup> reverse microemulsion, <sup>39</sup> solvothermal synthesis, <sup>31</sup> gel combustion, <sup>30</sup> plasma synthesis, <sup>40</sup> freeze drying, <sup>32</sup> sonication, <sup>41</sup> and mechanical milling.<sup>42</sup> Reliable, high-quality nanometer-sized particles are readily available using precipitation technologies. These powders have high chemical purity but are relatively expensive. Early work showed that zircon ore could be fused at 600°C using NaOH and mixed with water to form a hydrolyzed zirconate, which was further treated with HCl to form a zirconium oxychloride before precipitation.<sup>43</sup> This is an inexpensive process and has not been exploited to the authors' knowledge. The purpose of this paper is to use a slight variation on this process and use nitric acid to form a zirconyl nitrate, which can be precipitated. The use of ball milling as a means for breaking down loose agglomerates is also explored. It was hypothesized that this route may be less expensive than hydrothermal<sup>44</sup> or other industrial processes currently in use<sup>45</sup> and may be suitable for applications requiring high-surface area where sodium impurities can be tolerated. The objective of the present paper is to demonstrate a process for making soft, nonagglomerated, and inexpensive nanometer-sized zirconia powder.

#### **II. Experimental Procedure**

#### (1) Extraction of Zirconyl Nitrate from Zircon Sand

Zircon sand (ZrSiO<sub>4</sub>) obtained from the Kanyakumari region, a coastal part of Tamil Nadu, India, was used as a starting material for precursor synthesis without further purification. Physical and chemical analysis of zircon sand is given in Table I. Twenty-five grams of zircon sand that was obtained was powdered and roasted at 150°C for 1 h to remove the moisture content followed by boiling with 25 mL of concentrated hydrochloric acid (35%, Merck GR, Mumbai, India) at 50°C for 1 h on a hot plate. The water-soluble metal chlorides that were present in the acid-treated sand were removed by washing with double-distilled water. The residue was further fused with about four times its weight (100 g) of sodium hydroxide (98%, Merck GR) at 600°C for 3 h. The fused mass was cooled to room temperature and then the hot cake that was formed was leached with water and filtered. The insoluble residue consisted of zirconium hydroxide, which was dissolved in 250 mL of 6M nitric acid (69%, Merck GR) and then filtered. The clear filtrate that was obtained was repeatedly evaporated to dryness and the residue was extracted using 250 mL of DD water. The extracted zirconyl nitrate was used as the precursor for the synthesis of nano-ZrO<sub>2</sub> particles. The chemical reactions, which took place during precursor extraction and synthesis of nano-ZrO<sub>2</sub> particles, are shown in Scheme 1.

#### (2) Synthesis of Zirconia (ZrO<sub>2</sub>) Nanoparticles

Two-hundred and fifty milliliter of the extracted zirconyl nitrate  $(ZrO(NO_3)_2)$  precursor was hydrolyzed by the drop-wise addition of 4*M* NaOH (98%, Merck GR) solution while being constantly stirred and an amorphous hydrated zirconium oxide was

Table I. Physical and Chemical Analysis of Zircon Sand

Physical analysis	XRF chemical analysis		
Property	Proportion	Component	Weight (%)
Apparent porosity (%)	0.20	$ZrO_2$	$62.9 \pm 0.1$
Bulk density $(g/cm^3)$	4.65	$SiO_2$	$35.2\pm0.1$
Apparent specific gravity	4.20	$Na_2 \tilde{O}$	$0.3 \pm 0.1$
Particle size (µm)	12.50	CaO	$0.08 \pm 0.01$
Surface area $(m^2/g)$	5.00	Hf	$1.50 \pm 0.1$
Loss on Ignition (%)	0.10	—	_

precipitated at pH 7. At this stage of the reaction, a characteristic white precipitate of  $ZrO(OH)_2 \cdot xH_2O$  was appeared. The resultant precipitate was aged in the mother liquor at a temperature of 25°C for 24 h in a bath at constant temperature. After the completion of the ageing period, the precipitate was filtered and washed several times in double-distilled water until the precipitate was free from sodium nitrate and unreacted components. Then, the precipitate was dried in a hot air oven at a temperature of 120°C for 1 h. The synthesis of nanozirconia particles was performed at three different pH values such as 7, 10, and 13±0.1. The above process was repeated for pH 10 and 13±0.1. All the synthesized samples were calcined at different temperatures ranging from 500° to 800°C for 6 h in a static air atmosphere with a heating rate of 5°C/min and were then cooled to room temperature inside the oven.

#### (A) Ball Milling

Ball milling of soft aggregates of calcined (at  $500^{\circ}$ C) samples were performed by mean of a planetary ball mill (PM100; Retsch Corporation, Haan, Germany) in a dry medium at 500 rpm for 3 h. Milling parameters such as ball to charge ratio (20:1) and rotational speed (500 rpm) as well as grinding time (3 h) were optimized. Milling was done in a 250 mL of zirconia grinding jar with protective jacket of zirconium oxide. Zirconium oxide balls of 10 mm were utilized for millings. The samples calcined at 500°C were placed in the jar at room temperature and atmospheric pressure then sealed and imposed to milling. After grinding period, the jar was allowed to be cooled down to room temperature. The particles were collected from grinding jar and stored under nitrogen atmosphere to prevent particles agglomeration. The overall yield of present process is 84 %, i.e., 5.2 g out of 10 g of zircon (63 wt% ZrO<sub>2</sub>).

### (4) Powder Characterization

(A) X-ray Powder Diffraction (XRD): Crystallinity and the crystalline phase of synthesized zirconia samples were determined by XRD (X'Pert Pro, PANalytical, Almelo, the Netherlands) using CuK $\alpha$  as a radiation source ( $\lambda = 0.15406$  Å). The samples were scanned in the 2 $\theta$  range from 10° to 80° at a scanning rate of 24°/min. The average crystallite size of all the zirconia samples was calculated using the Scherrer's formula.<sup>31</sup>

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{1}$$

where *D* is the crystal size, *k* the Scherrer's constant (k = 0.9),  $\lambda$  the wavelength of the X-ray,  $\beta$  the full-peak width at half of the maximum intensity after correction for instrument-broadening contributions and  $\theta$  the peak position. The percentage composition of each phase was calculated from the integral peak intensity ratio.<sup>46,47</sup>

(B) Particle Size Distribution (PSD): The PSD was determined with a submicrometer particle size analyzer (Nanophox, Sympatec, Clausthal-Zellerfeld, Germany) according to the dynamic light scattering technique. The particle size of all the samples was measured in the range of 1-1000 nm at the scattering angle of 90°. The three-dimensional photon cross-correlation technique was used for the simultaneous measurement of particle size and stability. The He-Ne Laser with 10 mW maximum intensity was used as a light source at a wavelength of 632.8 nm. As synthesized ZrO<sub>2</sub> nanoparticles were dispersed in an aqueous solution, which contains 5 mM 4,5-dihydroxy-m-benzenedisulfonic acid disodium salt (99%, Loba GR, Mumbai, India) under sonication. To achieve stable dispersion, the pH of ZrO<sub>2</sub> colloidal solution was adjusted to pH 12 by adding a 0.1 N NaOH (98%, Merck GR) solution. The sonochemically dispersed stable ZrO<sub>2</sub> colloidal solution was used to obtain particles size distribution.

(C) Fourier Transform Infrared (FT-IR) Spectrometry: An FT-IR spectrum of as-synthesized zirconia samples was obtained on a PerkinElmer infrared spectrometer (spectrum 100, PerkinElmer, Waltham, MA) using KBr pellets. The KBr

## **Precursor extraction:**

$ZrSiO_4 + 4NaOH$ Zircon sand	Alkali fusion →	$Na_2ZrO_3 + Na_2SiO_3 + 2H_2O$ Fussed mass
$2Na_2ZrO_3 + 4H_2O$	Hydrolysis	4NaOH + $2$ ZrO(OH) <sub>2</sub>
ZrO(OH) <sub>2</sub> + 2HNO <sub>3</sub>	Extraction	$ZrO(NO_3)_2 + 2H_2O$ Zirconyl nitrate
Precipitation synthesis:		
$ZrO(NO_3)_2 + 2NaOH$ Zirconyl nitrate	Precipitation	$ZrO(OH)_2 + 2NaNO_3$ Precipitate
ZrO(OH) <sub>2</sub> Wet	Dried at 120 ℃	$ZrO(OH)_2 + H_2O$ Dry
ZrO(OH) <sub>2</sub>	Calcined at 500 °C	$ZrO_2 + H_2O$

Scheme 1. Schematic representation of the synthesis of nano zirconia particles from zircon sand using the conventional precipitation route.

discs were made by pressing the mixture, which contained 10 mg of zirconia nanoparticles with 100 mg of KBr at a pressure of  $125 \text{ kg/cm}^2$ .

Dry

(D) Thermal Analysis: Thermogravimetric (TG) and differential thermal analysis (DTA) measurements were carried out using thermal gravimetric/differential thermal analyzers (Diamond TG/DTA, PerkinElmer). The samples were heated continuously with a rate of 10°C/min from 40 to 1200°C in a static air atmosphere.

(E) Brunauer-Emmett-Teller (BET) Surface Area Analysis: The specific surface areas of all the samples were calculated according to the BET method<sup>48</sup> using the BET surface area analyzer (Autosorb AS-1MP, Quantachrome, Boynton Beach, FL). The samples were degassed under vacuum at 295°C for 3 h to remove the physisorbed moisture. The physisorption analysis was done with N2 adsorption-desorption measurements at liquid nitrogen temperature ( $-196^{\circ}$ C). Very low temperature is used to avoid any thermally induced changes on the surface of the particles. The average pore diameter and total pore volume were calculated according to the Barret-Joyner-Halenda method.<sup>49</sup>

(F) X-ray Fluorescence Spectrometry (XRF): Qualitative and quantitative elemental analysis of zircon and zirconia samples was performed using XRF (EDX-720, Shimadzu, Kyoto, Japan). The powder samples can be analyzed directly without any preparation on it.

(G) Chemical Analysis: The chemical purity of the assynthesized samples was determined through wet chemical analysis using EDTA titration method.<sup>50</sup> A weighted sample (0.25 g) of zirconia was fused with a 1:1 borax and sodium carbonate fusion mixture, dissolved in 2 N HNO<sub>3</sub> and filtered. The filtrate was made up to 250 mL by using a 2 N HNO<sub>3</sub> solution in a standard measuring flask (SMF). An SMF solution (50 mL) was added into a conical flask, which contained 60 mL of water, and was boiled for 5 min; then it was titrated against a 0.02 N EDTA solution using xylenol, an orange indicator in a hot condition (60°C). The end point was marked as the disappearance of pink color.

(H) Electron Microscopic Analysis: The surface morphology of the samples was inspected using an SEM (JSM-6390LV, JEOL, Tokyo, Japan) with an accelerating voltage of 25 KV. Transmission electron microscope (TEM) pictures of the samples were obtained using a TEM (CM200, Philips, Hillsboro, OR) operating at 120 kV.

#### III. Results and Discussion

### (1) TG/DTA Observation

Figures 1(a) and (b) displays the DTA and TGA curves of the hydrous zirconia synthesized at pH 7 after being dried at 120°C. TGA results indicate that the samples obtained by the wet methods are hydrous samples. The controlled thermal decomposition of hydrous zirconia  $(ZrO(OH)_2 \cdot xH_2O)$  and its crystallization temperature are established with the help of TG/DTA



In the DTA curve, the broad endothermic peak centered at 220°C is attributed to a loss of the physically adsorbed water and the weight loss on heating is equal to 10.6% at 148°C and 12.8% at 183°C. The endothermic effect occurring at 431°C is assigned to a loss of chemically coordinated (chemisorbed) water molecules present in hydrous zirconia and the weight loss on heating is equal to 23.7% at 431°C. The total 24.3% weight loss on heating to 480°C results from the molecular decomposition of  $ZrO(OH)_2 \cdot H_2O$  into  $ZrO_2$  and  $2H_2O$ .

It is noted that hydrous zirconia is progressively decomposed into amorphous zirconia due to dehydroxylation with increasing temperature (431°C). A sharp exothermic peak that appeared at 480°C is associated with the enthalpy of the transformation of the amorphous zirconia into crystalline zirconia. The kinetic process of dehydration and crystallization of hydrous zirconia appeared, respectively, at 431° and 480°C. The above thermal decomposition behavior of hydrous zirconia is in good agreement with the data obtained for undoped-zirconia nanoparticles synthesized by other methods.<sup>24,51</sup>

#### (2) FT-IR Measurements

Figure 2 displays the FT-IR spectra of zirconia samples precipitated at pH values of 7, 10, and 13 after calcination at 500°C. The IR active modes, between 490 and 1030 cm<sup>-1</sup>, correspond to the asymmetric and symmetric stretching frequencies of Zr– O–Zr vibrational bands.<sup>52</sup> The absorption peaks obtained at 1360 and 1630 cm<sup>-1</sup> show, respectively, the O–H stretching and bending vibrations of ZrO<sub>2</sub> · xH<sub>2</sub>O and H<sub>2</sub>O molecules. The OH group is distinguished easily in the H<sub>2</sub>O molecule by its bending vibrations that appear in a single band at ~1630 cm<sup>-1</sup>. Further, the O–H bending vibration of the hydroxyl group of ZrO<sub>2</sub> · xH<sub>2</sub>O molecule appears at ~1360 cm<sup>-1</sup>. The above



**Fig. 1.** (a) DTA and (b) TGA curves of the hydrous zirconia precipitated at pH 7 after dried at 120°C.

results summarize the finding that the  $ZrO_2$  powder consists of chemisorbed hydroxyl groups and adsorbed water molecules.

## (3) XRD Studies

Three samples of zirconia were synthesized at three different pH levels, respectively, pH 7, 10, and  $13\pm0.1$  to investigate the effect of pH on crystalline phase. The crystalline phase, phase fraction and average crystallite size of all zirconia samples are presented in Table II. Figures 3(a–d) shows the XRD patterns of the zirconia sample precipitated at pH  $7\pm0.1$  after calcinations at (a) 500°, (b) 600°, (c) 700°, and (d) 800°C for 6 h. Figure 4 displays XRD data of ZrO<sub>2</sub> synthesized at pH  $10\pm0.1$  after being calcined at 500°C for 6 h. Figures 5(a–d) shows the XRD patterns of the zirconia sample precipitated at pH  $13\pm0.1$  after calcinations at (a) 500°, (b) 600°, (c) 700°, and (d) 800°C for 6 h. The diffraction peaks of all the samples were identified and assigned with standard powder diffraction data using the JCPDS Files 81–1314 (monoclinic), 87–2105 (orthorhombic), 49–1746 (orthorhombic), 50–1089 (tetragonal), and 65–0461(cubic).

From the XRD pattern (Fig. 3(a)), it is found that the  $ZrO_2$ particles synthesized at pH  $7\pm0.1$  yield a predominantly monoclinic (90%) phase along with some fraction of orthorhombic (10%) zirconia. The XRD pattern (Fig. 4) of the sample synthesized at pH  $10\pm0.1$  results a monoclinic structure (86%) coexisting with some fraction of cubic zirconia (14%), whereas the XRD pattern (Fig. 5(a)) of the sample synthesized at pH  $13\pm0.1$ exhibits a cubic phase (96%) along with some fraction of tetragonal (4%) zirconia. It can be seen from the XRD results that the phase transformation of zirconia is influenced by the pH of precipitation. A greater quantity (90%) of monoclinic zirconia  $(m-ZrO_2)$  is noticed at pH 7, which is reduced (86%) in the sample synthesized at pH 10. In contrast, the minor orthorhombic phase (10%) obtained at pH 7 disappeared at pH 10. The minor orthorhombic zirconia obtained at pH 7 was transformed into cubic zirconia (14%) at pH 10, while both the monoclinic and orthorhombic structures disappeared in the sample synthesized at pH 13. Instead of both monoclinic and orthorhombic structures, cubic (96%) and tetragonal (4%) zirconia is detected at pH 13.

## (4) Effect of Precipitation pH

The above structural transitions are explained in terms of the nonstabilized monoclinic and sodium-stabilized cubic zirconia.<sup>6</sup> In an effort to understand the effect of pH and sodium ions on the crystal structure of zirconia, the samples synthesized at pH 7 and 13 were examined by qualitative elemental analysis.



**Fig. 2.** FT-IR spectra of  $ZrO_2$  samples precipitated at (a) pH 7, (b) pH 10, and (c) pH 13 after calcination at 500°C and after ball milling for 3 h at 500 rpm.

Precipitation pH $(\pm 0.1)$	Calcinations temperature (°C)	Crystalline phase	Phase fraction % $(\pm 1)$	Average particle size (nm)	
7	500	Monoclinic	90	22	
		Orthorhombic	10		
	600	Monoclinic	92	27	
		Orthorhombic	08		
	700	Monoclinic	93	32	
		Orthorhombic	07		
	800	Monoclinic	95	38	
		Orthorhombic	05		
10	500	Monoclinic	86	18	
		Cubic	14		
13	500	Cubic	96	11	
		Tetragonal	04		
	600	Cubic	96	16	
		Tetragonal	04		
	700	Cubic	95	19	
		Tetragonal	05		
	800	Cubic	92	22	
		Tetragonal	08		

Table II. Crystalline Phase, Phase Composition, and Average Grain Size of ZrO<sub>2</sub> Samples Precipitated at pH 7, 10, and 13

Table III shows that the chemical composition of  $ZrO_2$  samples precipitated at pH 7 and 13 after calcinations at 500°C. It can be observed from Table III that the major components present in the sample precipitated at pH 7±0.1 are 97.8 wt% ZrO<sub>2</sub>, 0.2 wt% Na<sub>2</sub>O, 0.4 wt% SiO<sub>2</sub>, 0.012 wt% CaO, and 1.5 wt% Hf, whereas the samples precipitated at pH 13±0.1 are 95.3 wt% ZrO<sub>2</sub>, 2.6 wt% Na<sub>2</sub>O, 0.5 wt% SiO<sub>2</sub>, 0.016 wt% CaO, and 1.5 wt% Hf. It is obvious that the sample synthesized at pH 13±0.1 has 2.6 wt% of sodium in its composition whereas the sample synthesized at pH 7±0.1 has 0.2 wt% sodium in its composition. When compared with pH 7±0.1, pH 13±0.1 has 13 times higher sodium content in its composition.

It is used to frame the discussion that the presence of sodium in the crystal structure is influenced by the phase formation of zirconia. The above result agrees with the known fact that a fraction of Na<sup>+</sup> cations present in the mother liquor after the precipitation at pH  $13\pm0.1$  is electrostatically chemisorbed on the surface of  $ZrO(OH)_2 \cdot xH_2O$ . At basic pH 13±0.1, it is noteworthy that the strong negative surface potential of  $ZrO(OH)_2 \cdot xH_2O$  facilitates the chemisorptions of Na<sup>+</sup> cation on the precipitate surface. The chemisorbed sodium ions enter the structure of zirconia during the crystallization to form sodium-stabilized cubic zirconia. Formation of sodium-stabilized cubic zirconia under basic pH is studied experimentally in detail by other methods developed from chemical precursors.<sup>6</sup> At neutral pH 7±0.1, the surface potential of  $ZrO(OH)_2 \cdot xH_2O$  is equal to zero, i.e. electro kinetically uncharged.<sup>53</sup> In this case,

Na<sup>+</sup> cations are not chemisorbed on the uncharged surface of  $ZrO(OH)_2 \cdot xH_2O$  and lead to monoclinic zirconia. The monoclinic-to-cubic phase transformation is clearly established by varying the pH from 7 to 10 and 10 to 13. It is evident from XRD results that the neutral pH 7±0.1 has no cubic phase whereas the pH 10 and 13±0.1 yields, respectively, 14% and 96% cubic phases. In conclusion, the pH of the medium is higher than the pH of the isoelectric point, i.e. pH 7, the negative charge developed on the surface of hydrous zirconia and chemisorptions of sodium ions take place. An increase in pH during precipitation results in an increase in the interaction between the sodium ions and hydrous zirconia, which leads to increased sodium ion chemisorptions and formation of cubic zirconia.

The XRD patterns of zirconia samples synthesized at pH  $7\pm0.1$  (Figs. 3(a–d)) and pH  $13\pm0.1$  (Figs. 5(a–d)) indicate the influence of calcination temperature on the crystalline phase and size of zirconia in the temperature range of  $500^{\circ}-800^{\circ}$ C. It can be seen from Table II that the calcination temperature of the sample that is synthesized at pH  $7\pm0.1$  increases from  $500^{\circ}$  to  $800^{\circ}$ C, the percentage of monoclinic phase increases from 90% to 95% while decreasing the percentage of the orthorhombic phase from 10% to 5% (Figs. 3(a–d)). A complete (>98\%) transformation of the orthorhombic to the monoclinic phase was observed after calcination at  $1000^{\circ}$ C. As shown in Fig. 3(a), after calcination at  $500^{\circ}$ C for 6h, the average crystallite size of monoclinic zirconia is about 22 nm, which increases to 27 nm at



Fig. 3. XRD patterns of  $ZrO_2$  samples precipitated at pH 7 after calcination at (a) 500°C, (b) 600°C, (c) 700°C, and (d) 800°C and after ball milling for 3 h at 500 rpm.



Fig. 4. XRD patterns of  $ZrO_2$  sample precipitated at pH 10 after calcination at 500°C and after ball milling for 3 h at 500 rpm.

600°C, 32 nm at 700°C and 38 nm at 800°C (Table II). Table II indicates that crystallite size and orthorhombic-to-monoclinic phase transformation are inter-related. When increasing the calcinations temperature, the monoclinic phase fraction starts to increase significantly with an increase in the crystallite size. The major monoclinic zirconia appears only in the samples synthesized at pH 7, but even at pH 13, cubic zirconia is predominant in the sample. The enhanced durability of the cubic phase in this case can be explained by partial incorporation of sodium into the zirconia structure.<sup>6</sup> When the calcination temperature of the sample synthesized at pH  $13\pm0.1$  from 500° to 800°C (Figs. 5(a-d) is increased, the percentage of the cubic phase decreases from 96% to 92%, whereas the percentage of the tetragonal phase increases from 4% to 8%. A complete (>96%) transformation of the cubic to the monoclinic phase was observed after calcinations at 1200°C.

Table II shows that the average crystallite size of cubic zirconia is 11 nm at 500°C, 16 nm at 600°, 19 nm at 700°, and 22 nm at 800°C. The above results indicate that the grain size of cubic zirconia is increased considerably with an increase in the calcination temperature, which notably induces the cubic-to-tetragonal phase transformation. In general, the results that are observed show that the degree of crystallinity and the crystallite size of both monoclinic and cubic zirconia increase with increasing calcination temperature. Further, the temperature seems to be the dominant factor for the grain size and phase contents. The results that are obtained in accordance with earlier reports<sup>6,35</sup> are that the increase in calcination temperature is

accompanied by an increase in crystallite size, which induced the phase transformation of zirconia. The present work shows close agreement with early studies<sup>54,33</sup> that cubic zirconia has been stabilized by incorporation of sodium in zirconia gel during the precipitation of hydrous zirconia under alkaline conditions. Conversely, Chang et al.<sup>55</sup> showed that the monoclinic phase with increased crystallite size was formed at 1000°C while increasing the sodium content. However, our results indicated that increasing the sodium content is detrimental to the stabilization of cubic zirconia with decreased crystalline size at 500°C. This is due to effect of high-energy ball milling which leads to incorporation of sodium in zirconia crystal structure and form cubic zirconia with reduced crystalline size. Further, the present work shows that the sodium stabilized cubic zirconia has been destabilized at higher calcination temperature (>1000°C) to form monoclinic zirconia with increased crystallite size. It is in line with early work<sup>56</sup> that the sodium destabilizes the metastable, i.e., tetragonal zirconia and lead to the formation of monoclinic phase at higher sintering temperature.

## (4) Chemical Purity

It is evident from the chemical analysis that the sample synthesized at pH  $7\pm0.1$  contains 97.6% of ZrO<sub>2</sub>, whereas the sample synthesized at pH  $13\pm0.1$  contains 92.5% of ZrO<sub>2</sub>. It can be seen from XRF (Table III) results that the samples synthesized at pH 7 $\pm$ 0.1 contains 97.8% of ZrO<sub>2</sub>, whereas the sample synthesized at pH  $13\pm0.1$  contains 95.3% of ZrO<sub>2</sub>. The results obtained from quantitative elemental analysis (XRF) are in close agreement with the results obtained from the chemical analysis. From the above studies, it was concluded that the nonstabilized monoclinic zirconia synthesized at pH  $7\pm0.1$  shows 97.6%chemical purity whereas the sodium-stabilized cubic zirconia synthesized at pH  $13\pm0.1$  shows 92.5% chemical purity. Commercial high-purity zirconia powders have Na contents, which are <0.05 wt%. Not only do high sodium contents impede densification<sup>56</sup> but they are detrimental to strength and ionic conductivity, which are important properties of zirconia-based materials. While zirconia-containing sodium would still be useful for thermal barrier coatings, it is clear that the sodium contents in the present powders are too high to be acceptable. Keeping the pH low and lowering the sodium content is therefore critical issues to address if this method is to be pursued.

#### (5) **PSD**

Figure 6 presents the PSD of  $ZrO_2$  samples after calcination at 500°C, (a) pH 7 and (b) pH 13 samples before milling, (c) pH 7 and (d) pH 13 after milling for 3 h at 500 rpm. It can be seen from Figs. 6(a) and (c) that the monoclinic zirconia before ball milling yields a particle size in the range of 269–444 nm (Fig. 6(a)), whereas the ball-milled monoclinic zirconia yields a



Fig. 5. XRD patterns of  $ZrO_2$  samples precipitated at pH 13 after calcination at (a) 500°C, (b) 600°C, (c) 700°C, and (d) 800°C and after ball milling for 3 h at 500 rpm.

Table III. Chemical Compositions of ZrO<sub>2</sub> Samples Precipitated at pH 7 and 13

		XRF chemical composition (wt%)				
Precipitation pH $(\pm 0.1)$	$ZrO_2$	Na <sub>2</sub> O	SiO <sub>2</sub>	CaO	Hf	
7 13	$97.8 \pm 0.1$ $95.3 \pm 0.1$	$0.2 \pm 0.1$ 2.6 $\pm 0.1$	$0.4 \pm 0.1 \\ 0.5 \pm 0.1$	$\begin{array}{c} 0.012 \pm 0.01 \\ 0.016 \pm 0.01 \end{array}$	$1.5 \pm 0.1$ $1.5 \pm 0.1$	

particle size in the range of 5-193 nm (Fig. 6(c)). Before ball milling, the mean diameter of monoclinic zirconia is about 327 nm, which decreases to 64 nm after ball milling (Figs. 6(a) and (c)). Hence, it is evident that precipitation followed by calcination yields aggregated zirconia particles, which are further disaggregated by ball milling. Four to five times reduction of the mean diameter of zirconia particles results with the aid of the ball-milling process. It can be seen from Fig. 6(b), before ball milling the calcined cubic zirconia yields a particle size in the range of 122-300 nm with an average diameter of 193 nm, whereas the ball-milled cubic zirconia (Fig. 6(d)) yields a particle size in the range of 26-54 nm with an average diameter of 39 nm. From the above observations it is clear that the calcined cubic zirconia yields highly aggregated particles (193 nm), which are disaggregated (39 nm) by the ball-milling process. From the above results, it can be understood that the ball-milling process helps the diminution of the particle size of the aggregated zirconia by four to five times. The effect of ball milling on the PSD and average diameter was studied with help of PSD analysis. In addition, the width of the PSD can be directly derived from the scattering parameters obtained from the PSD results. Figure 6 show that calcined zirconia has a wide PSD width when compared with the ball-milled samples. From the PSD results, we conclude that the precipitation, drying and calcination steps lead to aggregated particles that are further disaggregated by a subsequent ball-milling process. While planetary mixing at a high ball to charge ratio was effective in increasing the surface area, two problems are obvious: (1) as the process is scaled up from a laboratory process to a commercially viable process it is not possible to keep the ball to charge ratio as high as in this process, and (2) high surface areas mean that particle packing is difficult. Commercial powders are typically having surface areas on the order of 5–20 m<sup>2</sup>/g. The important point from the present study is that it shows that this process results in soft agglomerates, which are easy to break down.

## (6) Effect of Calcinations Temperature

Figure 7 presents the effect of calcinations temperature on the particle size of  $ZrO_2$  samples synthesized at (a) pH 7, (b) pH 10,



**Fig. 6.** Particle size distribution of  $ZrO_2$  after calcination at 500°C, (a) pH 7 and (b) pH 13 samples before ball milling, (c) pH 7 and (d) pH 13 samples after ball milling for 3 h at 500 rpm.



Fig. 7. Effect of calcination temperature on the particle size of  $ZrO_2$  samples, (a) pH 7, (b) pH 10, and (c) pH 13.

and (c) pH 13. Figure 7 shows a steady progression toward larger particle size as the temperature increases. It is noted (Fig. 7) that the variation in the calcination temperature from 500° to 800°C leads to variations in average particle size, which is in the range of 64–135, 56–110, and 39–86 nm, respectively, for the samples synthesized at pH values of 7, 10, and 13. The above result indicates that the powders that are obtained by high-temperature calcination are aggregated because the aggregates will be hard, which will be difficult to break efficiently by a subsequent ball-milling process. To obtain a well-dispersed nanosized particle product, the processing temperature must be kept as low as possible and high-temperature calcination should be avoided.

### (7) SEM and TEM Observation

It is interesting to note that the PSD results are in good agreement with SEM studies. The influence of ball milling on particles size and morphology is also well established with SEM observations. Figure 8 displays the SEM images of  $ZrO_2$  samples after calcination at 500°C, (a) pH 7 and (b) pH 13 samples before milling, (c) pH 7 and (d) pH 13 after milling for 3 h at 500 rpm. Similarity with PSD (Fig. 6(a)), the SEM micrograph of monoclinic zirconia before ball milling (Fig. 8(a)) is shows a highly aggregated surface. Particle aggregation is apparent, suggesting the formation of a continuous particulate network in the suspension structure, whereas the SEM micrograph of the



**Fig. 8.** SEM images of  $ZrO_2$  after calcination at 500°C, (a) pH 7 and (b) pH 13 samples before ball milling, (c) pH 7 and (d) pH 13 samples after ball milling for 3 h at 500 rpm.



Fig. 9. Transmission electron microscopic images of ZrO<sub>2</sub> samples precipitated at (a) pH 7 and (b) pH 13 calcined at 500°C after ball milling for 3 h at 500 rpm.

ball-milled monoclinic zirconia (Fig. 8(c)) shows the disaggregated particles with almost spherical morphology. It can be seen from Fig. 8(b) that synthesized cubic zirconia has an aggregated surface with higher particles size, whereas the ball-milled (Fig. 8(d)) cubic zirconia gets disaggregated particles with quite reduced particles size and highly shaped spherical morphology. Aggregated and nonaggregated zirconia could be well distinguished from the SEM results. The SEM findings not only justify the aggregation of the particles but also show the particle morphology. Figure 9 displays the TEM images of ZrO<sub>2</sub> samples precipitated at pH 7 and pH 13 calcined at 500°C after ball milling for 3 h at 500 rpm. It can be seen from the TEM images that cubic zirconia (pH 13) has predominantly spherical particles with a slightly agglomerated surface, whereas monoclinic zirconia (pH 7) shows almost spherical morphology with some rectangular-shaped particles. The above results are in good agreement with PSD and SEM observations, which are presented in Figs. 6 and 7.

#### (8) Textural Properties and Particle Size

Table IV summarises BET surface area, mean aggregate, and particle size of  $ZrO_2$  samples before and after ball milling for 3 h at 500 rpm. Before ball milling, the mean aggregate size of zirconia is 327, 220, and 193 nm, respectively, for the samples precipitated pH 7, 10, and 13. After ball milling, the mean particle size of zirconia is 64, 56, and 39 nm, respectively, for the samples precipitated with pH 7, 10, and 13 (Table IV). Whereas the average crystalline size decreases from 22 to 18 and 18 to 11 nm with an increase in the pH value of precipitation from 7 to 10 and 10 to 13 (Table II). It can be noticed from Table IV that the surface area of aggregated particles are 18, 26, and 35 m<sup>2</sup>/g, respectively, for the samples precipitated pH 7, 10, and 13 (Table IV). After milling, the surface area of the disaggregated particles

are 126, 190, and 227  $m^2/g$ , respectively, with increasing the pH value of precipitation from 7 to 10 and 10 to 13 (Table IV). Disaggregated particles have six to seven times higher specific surface area than the aggregated particles. Aggregated and non-aggregated particles are well distinguished from the observed surface area of the zirconia samples. When increasing the pH (7–13) values of precipitation, a decrease in the mean aggregate and particle size and an increase in the surface area of the zirconia samples are noticed. The above results conclude that the monoclinic-to-cubic phase transformation leads to higher surface area and lower particle size.

The particle size of zirconia depends on the nucleation of hydrous zirconia sols during the precipitation process. Further, the nucleation of hydrous zirconia depends on the experimental conditions, including pH, temperature, concentration of reactants, nature of anions, and stirring and ageing time.<sup>57</sup> It is used to frame the discussion that the pH value of precipitation affects the size distribution of the zirconia particles. In a neutral value of pH, the surface potential of hydrous zirconia is almost zero, i.e., near iso-electric,<sup>53</sup> which induce surface aggregation of hydrous zirconia sols because of hydrogen bonding caused by van der Waals attraction between the hydrolyzed hydrous zirconia molecules. At the basic pH value of 10 and 13, the surface of hydrous zirconia has a negative  $\zeta$  potential, which, in turn, reduces the surface aggregation of hydrous zirconia sols because of the strong electrostatic repulsion between the negatively charged hydrous zirconia molecules. Thus, the aggregation behavior of hydrous zirconia is strongly dependent on the pH value according to the Derjaguin and Landau, Verwey and Overbeek theory.<sup>58</sup> In addition, above a pH value of 7, i.e., basic pH value of 10 and 13, the present process has free sodium ions in the mother liquor, which protects the coalescence of hydrous zirconia molecules because of the chemisorption of sodium ions on the negative surface of hydrous zirconia. The

Table IV.	BET Surface Area. M	lean Aggregate, ai	nd Particle Size of ZrO <sub>2</sub>	Samples Before and A	fter Ball Milling	for 3 h at 500 rpm

Precipitation pH (±0.1)		Before n	nilling	After milling	
	Calcination temperature (°C)	Mean aggregate size (nm)	BET surface area (m <sup>2</sup> /g)	Mean particle size (nm)	BET surface area $(m^2/g)$
7	500	327	18	64	126
10	500	220	26	56	190
13	500	193	35	39	227

justification of the above argument shows that the basic pH value of 13 has a positive effect on particle size reduction.

#### Summary

Nonstabilized monoclinic and sodium stabilized cubic zirconia are synthesized from raw zircon sand using a chemical extraction process followed by a ball mill-aided precipitation route. Detailed characterization using XRD and EDS revealed that the sample synthesized at pH 7 affords nonstabilized monoclinic zirconia, whereas pH 13 affords sodium-stabilized cubic zirconia. This method yields monoclinic zirconia with chemical purity of 97.6% and cubic zirconia with a chemical purity of 92.5%. The pH value of precipitation is the key controlling factor for the crystalline phase and particle size of the product. Although increasing calcination temperature can induce growth of crystals, which leads to higher particle size. The stable m-ZrO<sub>2</sub> and c-ZrO<sub>2</sub> can be synthesized in a large quantity under neutral and strong basic conditions with an average size of  $64 \pm 3$  and  $39 \pm 3$  nm, respectively. The specific surface area of m- $ZrO_2$  was 126 m<sup>2</sup>/g for the powder synthesized at a pH value of 7, whereas the powder synthesized at pH 13 yields c-ZrO<sub>2</sub> of a specific surface area of 227  $m^2/g$ . It is observed that precipitation yields aggregated particles that are disaggregated by a ballmilling process. It is worth noticing that the ball mill process develops reduced particle size with spherical morphology. The results are useful for understanding the surface chemistry and properties of hydrous zirconia precipitated at different pH values and its design for the synthesis of nonstabilized m-ZrO<sub>2</sub> and sodium stabilized c- $ZrO_2$  nanoparticles. The effect of planetary ball milling on particle size, surface area, and morphology has been addressed. It may be noted that this method has some advantages such as quite simple to conduct and easy scaling-up the process to commercial production rates than many of the other commercially available methods. This process has the potential to be inexpensive when this reaction scheme is developed for large-scale tonnage production of nanosized zirconia particles. The major limitation of this process, at present, is the residual sodium in the material.

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