

Roles of alumina, a base catalyst, a fine particle effect on the metastable phase Stabilization of the tetragonal zirconia at temperatures of 600-800 °C

Rifki Septawendar^{a,b,*}, Suhanda^a, Soesilowati^a and Bambang Sunendar Purwasasmita^b

^aDepartment of Advanced Ceramics, Glass, and Enamel, Center for Ceramics, Ministry of Industry of Indonesia, Akhmad Yani 392, Bandung 40272, West Java, Indonesia

^bLaboratory of Advanced Material Processing, Engineering Physics Department, Institute of Technology Bandung, Ganesa 10, Bandung, West Java, Indonesia

Nanoparticles of the tetragonal alumina-stabilized zirconia were synthesized from zirconium salt of $ZrOCl_2 \cdot 8H_2O$ and approximately 23 wt % alumina stabilizer with ammonia as a base catalyst and sucrose as a gelling agent at a room temperature. In the preparation process of nanoparticles of alumina-stabilized zirconia, the calcination was conducted at temperatures of 500-800 °C. The calcined powder was analyzed and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) studies. The tetragonal phase of ZrO_2 started to crystallize at a low temperature of 500 °C. Further phase transformation of the alumina-stabilized zirconia maintained the tetragonal ZrO_2 at 600 °C. Besides, the addition of sucrose by weight ratio of 1 : 6 to the total weight precursors produced nanoparticles of alumina-stabilized zirconia less than 20 nm in size at that temperature. The tetragonal phase of ZrO_2 was stable and no transition alumina was identified at 800 °C. It is suggested that alumina is in solid solution in the tetragonal zirconia polymorph at that temperature. The typical SEM images show high agglomeration of ultrafine microstructures of alumina-stabilized zirconia nanoparticles at that temperature. The results indicate that the method represents an effective methodology for the preparation of alumina-stabilized zirconia nanoparticles at a lower temperature than 800 °C.

Key words: Alumina, Ammonia catalyst, Sucrose, Nanoparticles effect, Tetragonal zirconia, Low calcination temperatures.

Introduction

Zirconia is one of the interesting oxide materials that frequently used in many applications. However, zirconia lacks of good properties in a pure form. Since zirconia is stabilized by lower-valence metal oxides, its properties significantly improve. Therefore, stabilized zirconia is one of the important materials that attracts great attention in material science due to their excellent properties including high fracture strength (~ 1500 MPa), high toughness (~ 13 MPa m^{1/2}) and high ionic conductivity at a high temperature [1, 2, 3, 4, 5]. It finds application in high temperature solid oxide fuel cells (SOFC), high temperature pH sensors, oxygen sensors, refractory materials, capacitors, catalyst substrates, and as abrasives [2, 6, 7, 8].

Yttrium oxide (Y_2O_3), cerium oxide (CeO_2), scandium oxide (Sc_2O_3), magnesium oxide (MgO), calcium oxide (CaO), and aluminum oxide (Al_2O_3) are commonly used to stabilize the metastable tetragonal phase (t-) and cubic phase (c-) of zirconia [2, 7, 9, 10, 11, 12, 13, 14, 15]. The crystallization of the metastable phases at a low temperature involves stabilization process due to the defects or atomic vacancies in the lattice created by the

presence of the lower valent doped metal ions [16]. However, the properties of the stabilized zirconia depend on the type and the concentration of the stabilizer [2, 12, 17]. Many researches focus on the study of the yttria, calcia, and magnesia stabilizers in stabilizing zirconia. However, several attempts have been made to study the alumina behavior in the binary system of Al_2O_3 - ZrO_2 .

Alumina is particularly added into zirconia to stabilize the tetragonal polymorph at a lower temperature than for pure zirconia [18, 19, 20]. Nevertheless, its solubility in zirconia is limited only to a few percent [19, 20]. Other studies reported substantially higher solubility of alumina in zirconia up to 40 wt% at the temperatures ranging from 800° to 1100 °C, resulting metastable supersaturated solid solutions which expel alumina to grain boundaries during long-term heating [15, 18, 21, 22]. The present work is to study the role of alumina on the stabilization of the tetragonal metastable phase of nanoparticle zirconia at low temperatures of 600-800 °C.

Many methods have been proposed to prepare stabilized zirconia micron powder or nano powder, such as molten salts [6], co-precipitation methods, thermal decomposition of metal alkoxides [7], sol-gel processing [8], hydrothermal processing [12], spray pyrolysis processing [15], chemical vapour synthesis [21], self-combustion methods [2, 23], and conventional methods such as powder mixing and ball milling [7, 24].

*Corresponding author:

Tel : +62-82-126-123-777

E-mail: rifkiseptawendar@gmail.com, purwa@tf.itb.ac.id

Our previous research successfully prepared alumina zirconia nanocomposites at low temperatures by means of using sucrose as a gelling agent and ammonia as a catalyst [25]. Besides, in another our previous work, it was clearly found that ammonia base catalyst and nanoparticle effects had assisted the stabilization process of the tetragonal to the cubic phases of zirconia during preparation of the cubic calcia stabilized zirconia [26]. Therefore, the tetragonal zirconia was prepared using alumina (23 weight %) as a stabilizer assisted by a base catalyst and sucrose during synthesis. Nevertheless, this work focused only on identification of the phase transformation of alumina stabilized zirconia (ASZ) at low temperatures of 500-800 °C. Further studies on the effect of alumina concentrations in the ASZ and the phase transformation of ASZ at temperatures above 1000 °C are going to be conducted.

Experimental Procedure

Materials and Instruments

Zirconium oxychloride octahydrates ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 99.9% purity), aluminum sulphate octadecahydrates ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, >99.9% purity) and 25% ammonia solution, were obtained from Merck Inc. Germany and were used as precursors and a catalyst respectively, and sucrose as a gelling agent. The instruments used were an IKA dual speed mixer model RW 20 DZM with the maximum speed of 2000 rpm, a pot mill, a Heraeus electrical furnace, an X-Ray Phillips PANalytical, a QUANTA FEG scanning electron microscope (SEM), and a JEM-1400 120 kV transmission electron microscope (TEM).

Synthesis of ASZ Precursors

The precursors for the preparation of ASZ were zirconium oxychloride octahydrates, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and aluminum sulphate octadecahydrates, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. A single component of zirconium and aluminum salt solutions was prepared separately from the respective precursor materials. About 30 grams of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ were dissolved in 150 ml of distilled water to give a Zr^{4+} aqueous solution. About 20 grams of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ were weighed and dissolved in distilled water to give an Al^{3+} aqueous solution. The aluminum salt weighed might produce approximately 23 weight % Al_2O_3 of zirconia. The pH of both aqueous solutions were adjusted at the ambient temperature by adding a 25% ammonia solution drop wise under vigorous stirring, producing $\text{Zr}(\text{OH})_4$ and $\text{Al}(\text{OH})_3$ sols; until the final pH both solutions recorded was 10 and 4, respectively. Both of $\text{Zr}(\text{OH})_4$ and $\text{Al}(\text{OH})_3$ sols were mixed under constant stirring at an approximately 800 rpm, until the final pH was 9. An appropriate amount of sucrose solution as a gelling agent was added slowly to the mixture such that the metal salts to sucrose weight ratio was maintained at

6 : 1; and stirred constantly at an approximately 800 rpm. The final pH of the gel solution was recorded 7. The mixture was constantly stirred and slowly heated until a concentrated yellowish brown gel was formed at 100 °C. The concentrated gel was continuously heated while simultaneously being stirred, until water completely evaporated and a brown gel formed. The gel was then dried in an oven at 200 °C and swollen to produce light black charcoal precursors. The precursors were milled in kerosene using a pot mill for 24 hours and successfully calcined at the temperatures of 600 °, 700 °, and 800 °C in an Heraeus electric furnace to give very fine powder.

Characterization

The calcined powder was then characterized by a PAN analytical X-ray instrument, a QUANTA FEG SEM, and a JEM-1400 120 kV TEM. The crystalline phase of as-synthesized TZP was identified by powder X-ray diffraction (XRD) instrument (XRD, PW 3710 MPD control, Philips, PAN analytical) at 40 Kv and 35 mA with Cu/K α ($\lambda = 1.54060 \text{ \AA}$) radiation source. The diffraction patterns were scanned from 4.010 to 64.950 (2θ) with angular step of 0.020. Crystallite sizes were estimated from XRD peak widths using the Scherrer equation [27].

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where D is the crystallite size, K is a shape factor with a value of 0.9-1.4, λ is the wavelength of the X-rays (1.54056 Å), q is Bragg's angle and β is the value of the *full width at half maximum* (FWHM). XRD patterns were identified using the PDF2 CD-ROM (JCPDS-International Centre for Diffraction Data).

Meanwhile, a TEM study was performed to ensure the crystal phase and particle sizes of the calcined ASZ at 600 °C using a JEM-1400 120 kV TEM. A QUANTA FEG SEM was also used to observe the morphology of the calcined ASZ at 800 °C.

Results and Discussion

X-Ray diffraction analysis on the zirconia phase transformation of ASZ

Fig. 1 shows the XRD patterns of ASZ calcined for 5 hrs at the different temperatures of 500 °C, 600 °C, 700 °C, and 800 °C [28].

According to Fig. 1, the as-prepared ASZ from the hydroxide precursors and sucrose started to transform and to crystallize at a low temperature of 500 °C with the broadening main peak of the t- ZrO_2 at a diffraction angle 2θ of 30.394 °, corresponding to the (1 1 1) crystal plane of the t- ZrO_2 structure (PDF2. 140534). By increasing temperature from 500 °C to 600 °C, the t- ZrO_2 peaks increased significantly at a diffraction angle 2θ of 30.394 ° (2θ -CuK α) corresponding to the (1 1 1)

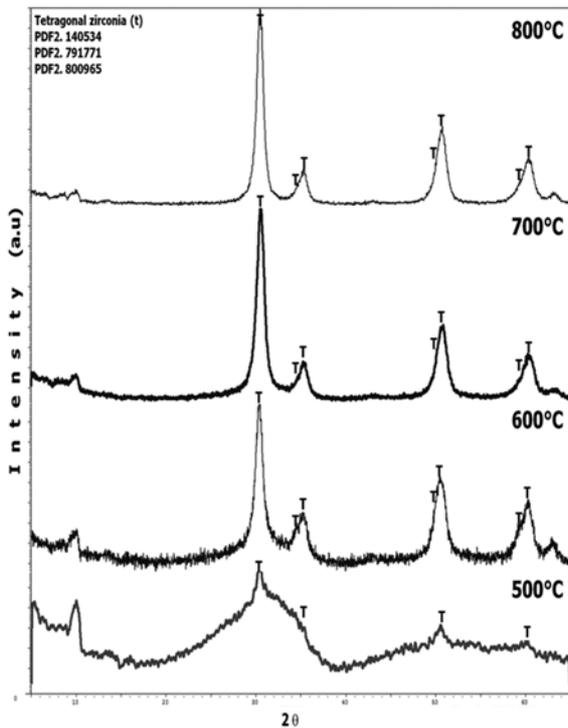
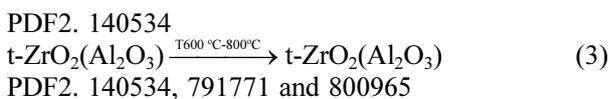
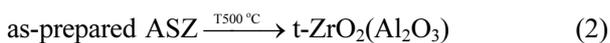


Fig. 1. XRD patterns of an as-heated sample at elevated calcination temperatures on the formation of ASZ [28].

and (1 0 1) crystal planes of the t-ZrO₂ structures, as referring to PDF2. 140534, 791771 and 800965 (see in Fig. 1). At the higher temperatures of 700° and 800°C, the t-ZrO₂ was the only zirconia phase in the ASZ whereas no other zirconia phases were identified at these temperatures. According to the X-ray diffraction analysis, no transition alumina phases was found in the ASZ during calcination treatment at the temperatures of 600°, 700°, and 800°C. It is suggested that alumina is in a solid solution of the tetragonal zirconia polymorph at those temperatures. In a case, the addition of 23 weight % of Al₂O₃ has stabilized zirconia into the tetragonal form at those temperatures. After calcination at the various temperatures from 500°C to 800°C, the direct phase transformation of the as-prepared ASZ during calcination treatment might be assumed as follows:

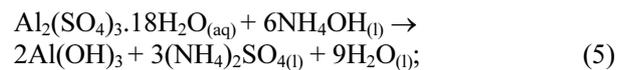
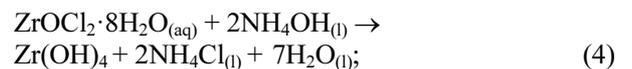


The peak patterns are broad in the diffractograms for the ASZ at the temperatures of 600°, 700°, and 800°C, thus indicating the calcined ASZ has very fine crystallite sizes. The existence of the main diffraction

peaks in certain crystal planes at certain diffraction angles emphasizes that the calcined ASZ are crystalline not amorphous.

Effect of pH in the stabilization process of the tetragonal phase of ASZ

Both zirconium oxychloride octahydrate, ZrOCl₂ · 8H₂O and aluminum sulphate octadecahydrates, Al₂(SO₄)₃ · 18H₂O are types of salts of strong acids and weak bases; hence, when the salts are hydrolyzed in water, they produce very acidic solutions. This phenomenon is in agreement with the experimental results, where the pH of both the zirconium and aluminum solutions measured was equal to 1. Besides, when the salts are dissolved in distilled water, the ion complex forms of aluminum hexaqua ion, [Al(H₂O)₆]³⁺ and tetrameric zirconium cation, [Zr₄(OH)₈(H₂O)₁₆]⁸⁺ were formed. The Zr⁴⁺ ion is stable only at low concentrations and high acidity because of the high valence of four. Further increase in pH results in gelation or precipitation [25, 29]. If the hydrolysis polymerization occurs rapidly, the tetrameric cation will not only be produced but the zirconium hydroxide will also be amorphous [30]. In addition, the aluminum hydroxide (Al(OH)₃) also formed. The addition of a NH₄OH catalyst on the ASZ preparation had accelerated the hydrolysis process of the zirconium solution, resulting zirconium hydroxide amorphous. In the case of the preparation of ASZ nanoparticles from the aqueous solutions of zirconium and aluminum with ammonia as a catalyst, the complete reaction was assumed to be as follows [31]:



Since ammonia was used as the hydrolysis catalyst, hence OH⁻ ions and Zr vacancies were produced in the crystalline structure of zirconia and stabilized the tetragonal zirconia nanophase [16]. Since the thermal treatment was conducted at the higher temperatures, it eliminated the bound OH groups and started the tetragonal-to-monoclinic phase transformation at the same time, which was followed by crystallite growth [16, 23, 32]. However, the structure transformation of the tetragonal to monoclinic phase was not occurred when ASZ samples were heated at the elevation temperatures, as shown by XRD patterns in Fig. 1. The tetragonal phase was stable at 600°C and even at higher temperatures of 700° and 800°C because of the reduction of the surface energy, which was probably caused by lower-sized crystallites and the presence of trivalent dopant Al³⁺ in the zirconia crystalline structure.

The effect of Al³⁺ dopant in the stabilization of metastable phase zirconia on the preparation of ASZ

The stabilizer aluminum hydroxide that added onto the zirconia structure, disintegrated into the respective aluminum oxide (Al_2O_3) and reacted with the metathetically formed ZrO_2 to give a solid solution, thus stabilizing the zirconia tetragonal polymorph after calcination treatments at 500 °-800 °C.

Stabilization of the t- ZrO_2 stabilization occurs through direct substitution of the trivalent metal cations to Zr^{4+} cations in the crystal lattice of zirconia. This replacement process, not only stabilizes the tetragonal structure, but also produces oxygen vacancy because of the charge compensation in zirconia lattice. The charge differences between Zr^{4+} and stabilizer cations or between oxygen anion and oxygen vacancy are to be considered, for Al^{3+} doping, two cations are accompanied with one oxygen vacancy [33]. The stabilization process can be written using the following Kroger-Vink notation:



The oxygen vacancies in zirconia can lower the phase transition temperatures, stabilize and enlarge tetragonal phase areas in the Zr- ZrO_2 binary system

[34].

In the preparation of ASZ, the addition of ammonia into the solution of zirconium and aluminum salts was to increase the concentration of oxygen vacancy (O^{2-}) by means of forming hydroxides of zirconium and aluminum, producing a symmetrical system of the crystal structure of stabilized-zirconia with 23 weight % Al_2O_3 solid solution [26].

In addition, according to the XRD results, no transition alumina phases was found in the ASZ at the temperatures of 600 °, 700 °, and 800 °C. However, based on the thermal behavior of synthetic alumina hydroxides, a high amount of alumina added onto zirconia as a stabilizer should be able to produce transition aluminas such as gamma or eta alumina phases at a temperature range of 500-800 °C [35]. By contrast, no transition alumina phases was found in the zirconia samples at those temperatures, so that alumina must be in a solid solution of the tetragonal zirconia polymorph.

Nanoparticle size effect on the stabilization process of the tetragonal zirconia phases

Tables 1-3 present the quantitative results of the ASZ

Table 1. Quantitative results from the Scherrer method on the zirconia phases in nanoparticles ASZ at 600 °C.

| Zirconia Phase | Average Crystallite Size (nm) | | | | | | |
|---|-------------------------------|-----|-----|-----|-----|-----|-----|
| (hkl) | 111 | 002 | 200 | 220 | 113 | 311 | |
| t- ZrO_2 PDF2-140534 | 8 | 7 | 8 | 7 | 5 | 5 | |
| (hkl) | 101 | 002 | 110 | 112 | 200 | 103 | 211 |
| t- ZrO_2 PDF2-791771 PDF2-800965 | 8 | 7 | 8 | 7 | 7 | 5 | 5 |

Table 2. Quantitative results from the Scherrer method on the zirconia phases in nanoparticles ASZ at 700 °C.

| Zirconia Phase | Average Crystallite Size (nm) | | | | | | |
|---|-------------------------------|-----|-----|-----|-----|-----|-----|
| (hkl) | 111 | 002 | 200 | 220 | 113 | 311 | |
| t- ZrO_2 PDF2-140534 | 7 | 6 | 7 | 7 | 5 | 5 | |
| (hkl) | 101 | 002 | 110 | 112 | 200 | 103 | 211 |
| t- ZrO_2 PDF2-791771 PDF2-800965 | 7 | 6 | 7 | 6 | 7 | 5 | 5 |

Table 3. Quantitative results from the Scherrer method on the zirconia phases in nanoparticles ASZ at 800 °C.

| Zirconia Phase | Average Crystallite Size (nm) | | | | | | |
|---|-------------------------------|-----|-----|-----|-----|-----|-----|
| (hkl) | 111 | 002 | 200 | 220 | 113 | 311 | |
| t- ZrO_2 PDF2-140534 | 7 | 5 | 6 | 5 | 4 | 5 | |
| (hkl) | 101 | 002 | 110 | 112 | 200 | 103 | 211 |
| t- ZrO_2 PDF2-791771 PDF2-800965 | 7 | 5 | 6 | 5 | 6 | 4 | 5 |

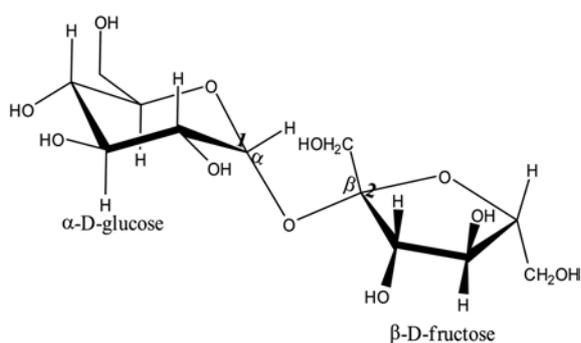


Fig. 2. The sucrose structure [38].

nanoparticles at the temperatures of 600 °, 700 °, and 800 °C, of any phases formed, using the Scherrer method. The method was apply to calculate the crystallite sizes of the certain t-zirconia crystal planes at every calcination temperature, based on the main peaks of the XRD patterns from Fig. 1, and assisted by using an XRD software. Tables 1, 2, and 3 show the average crystallite sizes of ASZ are less than 20 nm at the different elevated calcination temperatures.

As previously mentioned, the tetragonal phase was stable in ASZ sample at temperatures of 600, 700, and 800 °C because of the reduction of the surface energy, which was caused by very small-sized crystallites, as shown in Tables 1, 2, and 3. Since nanocrystalline powder has a very high specific surface area and more than 50% of the total atoms locate on the surface, hence a large amount of metal-oxygen bonds are fragile. Thus, resulting in desorption of the lattice oxygen ions, creating a greater number of oxygen ion vacancies, and stabilizing the metastable zirconia phases. This phenomenon is considered as a ‘nanoparticle size effect’ [16, 36]”.

The nanocrystallite sizes of ASZ may be produced by the addition of sucrose as a gelling agent in the preparation of as-synthesized ASZ. Sucrose has a disaccharide structure consisting of two monosaccharides of the six-carbon sucroses D-glucose and D-fructose joined covalently by an O-glycosidic bond [34, 37, 38] (see in Figure 2[38]). Each of them contains hydroxyl and ether groups, thus hydrogen bond may be created from the sucrose functional groups with the other hydroxyl groups. Therefore, sucrose is very soluble in water. When the sols of $Zr(OH)_4$ and $Al(OH)_3$ were mixed with sucrose solution, hydrogen bond was created fthe sucrose functional groups with the hydroxyl groups on the particle surfaces. functional groups with the hydroxyl groups on the particle surfaces. As a result, sucrose molecules coating on as-prepared alumina-stabilized zirconia particle surfaces results in reduced particle aggregation due to the steric hindrance of the sucrose structure [26]. The binding distance among zirconium and aluminum hydroxide molecules therefore will extend because sucrose restrains the grain contact among the nucleated ASZ and retards crystallite growth. Accordingly, the crystallite and the particle size

produced from the aluminum-zirconium hydroxides would be smaller with the presence of sucrose [25, 37].

When the mixture solution was constantly stirred and slowly heated until at the boiling point of water, some water molecules might evaporate and the solution became viscous forming gel. This gel form of sucrose masked or covered the as-prepared alumina-stabilized zirconia particles. When the mixture was constantly stirred and heated at 100 °C for a longer time, a concentrated yellowish brown gel was formed. Sucrose starts to decompose into glucose and fructose at 180 °C. Therefore, when the heating process was continuously carried out until water completely evaporated, a brown viscous gel formed and some aroma gases were produced. Since fructose and glucose begin to disintegrate into smaller during caramelization, more volatile compounds with different aroma are generated.

They are the furans, diacetyl, maltol, and ethyl acetate [39]. Almost all the compounds contain the -OH and -COOH groups promoting in binding the metal ions in the precursor mixture, reducing the chances of agglomeration in the as-prepared alumina-stabilized zirconia particles [40, 41, 42]. Furthermore, when the precursor of zirconium-aluminum-sucrose was heated at an approximately temperature of 200 °C, the precursor was being decomposed; leaving residual carbonaceous material, which undergone a combustion reaction with the lattice oxygen ions, below the crystallization temperature [37]. However, this combustion process eliminates the lattice oxygen ions and generates oxygen ion vacancies with trapped electrons, which stabilized the tetragonal phase at room temperature [23]. Besides, since a combustion reaction was generated in further heating and produced gases accompanied by a large amount of heat these outgoing gases prevent agglomeration and form fine particles with high surface area in the final products [42].

Morphology and microstructure of the ASZ nanoparticles

Nanoparticles with their high surface areas often agglomerate in order to minimize the interfacial energy of the system. This agglomeration phenomenon could be found in the nanoparticles ASZ after thermal treatment at 600 °C, as shown by TEM bright field images in Fig. 3 [28]. The phenomenon is due to adhesion of the particles to each other because of *van der Waals* forces of attraction, which dominates at the nanoscale due to the enlarged surface area to volume ratio [16, 43]. Nevertheless, the sizes of ZrO_2 powders are found to be less than 20 nm at the calcination temperature of 600 °C. Besides, the electron diffraction (ED) patterns of the ASZ sample is indexed to the tetragonal zirconia phase with the crystal plane orientations of (101), (002), (102), (112) and (103). This ED result corroborates the XRD result for the ASZ sample, not only showing the formation of the t-

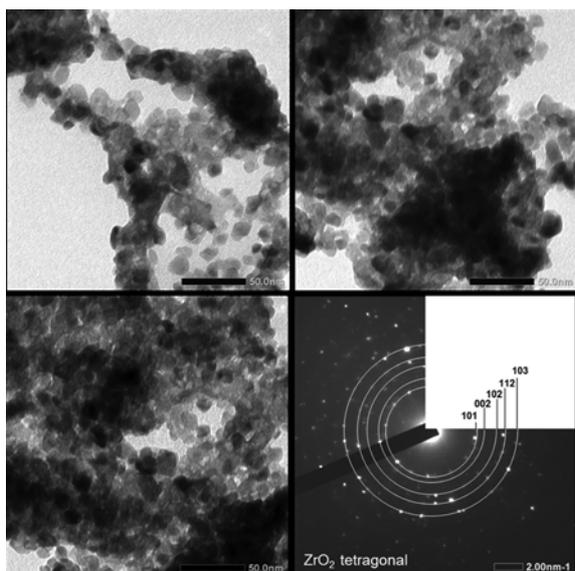


Fig. 3. TEM bright field images and an ED result of the nanoparticles ASZ calcined at 600 °C for 5 hours [28].

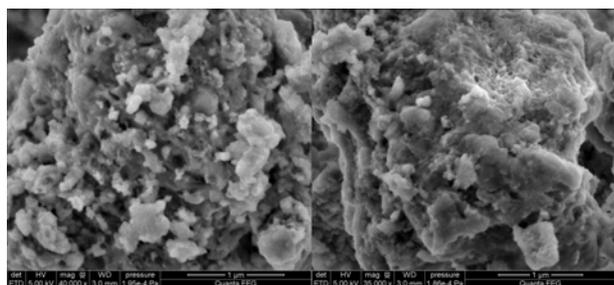


Fig. 4. Typical SEM images of the nanoparticles ASZ calcined at 800 °C for 5 hours.

ZrO₂ phase in the sample but also no transition aluminas identified.

In addition, the morphology of zirconia particles in ASZ can be seen more clearly when using a more sophisticated SEM such as a Quanta FEG SEM, which can observe and investigate material microstructure in a very high resolution until 50 nm magnification. Therefore, a Quanta FEG SEM was used to observe the morphology of ASZ sample calcined at 800 °C to get clearer images as can be seen in Fig. 4. However, the images show high agglomeration at most region of the ASZ powder, as shown in Fig. 4. Many aggregates or lumps (secondary particles) consisting of very fine particles can be observed in the ASZ powder.

Conclusions

Nanoparticles of ASZ were prepared from zirconium salt and approximately 23 wt % of alumina stabilizer with ammonia as a base catalyst and sucrose as a gelling agent at the temperatures of 500 °, 600 °, 700 °, and 800 °C. Crystallization of the as-synthesized ASZ produced the tetragonal phase of ZrO₂ at a low

temperature of 500 °C. A further phase transformation of the ASZ maintained the tetragonal ZrO₂ less than 20 nm in size at 600 °C. The tetragonal phase of ZrO₂ was stable and no transition alumina was identified at 800 °C; however, high agglomeration was found in the ASZ particles at that temperature. The addition of 23 weight % of Al₂O₃ has stabilized zirconia into the tetragonal form by means of forming a solid solution in the tetragonal zirconia polymorph at the elevated temperatures of 600, 700, and 800 °C.

References

- O. Vasylykiv, Y. Sakka, and V. V. Skorokhod, *J. Am. Ceram. Soc.*, 86 [2] (2003) 299-304.
- K.C. Patil, M.S. Hedge, T. Rattan, S T Aruna, in *Chemistry of Nanocrystalline Oxide Materials*, Combustion Synthesis, Properties and Applications, (World Scientific, 2008).
- N.Q. Minh. *J Am. Ceram. Soc.* 76 [3] (1993) 563-588.
- C. J. Mogab, the Review of Scientific Instruments, 43 [11] (1972) 1605-1610.
- F. M. L. Figueiredo and F. M. B. Marques. *WIREs Energy Environ.* 2012. doi: 10.1002/wene.23.
- Z. Li, W. E. Lee, and S. Zhang, *J. Am. Ceram. Soc.*, 90 [2] (2007) 364-368.
- R. Muccillo, R.C. Buissa Netto, and E.N.S. Muccillo, *Matter. Lett.*, 49 (2001) 197-201.
- G. C. C. Costa and R. Muccillo, *Solid State Ionics*, 179 (2008) 1219-1222.
- A. K. Nikumbh and P. V. Adhyapak, *Natural Science*, 2 [7] (2010) 694-706: doi:10.4236/ns.2010.27086 at <http://www.scirp.org/journal/NS/>
- Jong-Heun Lee, Je Hun Lee, Young-Soo Jung, and Doh-Yeon Kim, *J. Am. Ceram. Soc.* 86 [9] (2003) 1518-1521.
- P. K. Schelling, S. R. Phillpot, and D. Wolf, *J. Am. Ceram. Soc.*, 84 [7] (2001) 1609-1619.
- G. Xu, Ya-Wen Zhang, Chun-Sheng Liao, and Chun-Hua Yan, *J. Am. Ceram. Soc.*, 87 [12] (2004) 2275-2281.
- K. Boobalan, R. Vijayaraghavan, K. Chidambaram, U. Mudali, K. Mudali, and B. Raj, *J. Am. Ceram. Soc.*, 93 [11] (2010) 3651-3656.
- F. Namavar, G. Wang, C.L. Cheung, R.F. Sabirianov, X.C. Zeng, W.N. Mei, J. Bai, J.R. Brewer, H. Haider, and K.L. Garvin, *Nanotechnology*, 18 (2007) 415702 (6 pp); doi:10.1088/0957-4484/18/41/415702, Online at <http://stacks.iop.org/Nano/18/415702>.
- A. S. Gandhi, V. Jayaram, and A. H. Chokshi, *J. Am. Ceram. Soc.*, 82 [10] (1999) 2613-2618.
- V. Santos, M. Zeni, C.P. Bergmann and J.M. Hohemberger, *Rev. Adv. Mater. Sci.*, 17(2008) 62-70.
- S. Fabris, A. T. Paxton and M. W. Finnis, *A Stabilization Mechanism of Zirconia Based on Oxygen Vacancies Only*, 2008, http://cnr-it.academia.edu/StefanoFabris/Papers/446049/A_Stabilization_Mechanism_of_Zirconia_Based_on_Oxygen_Vacancies_Only, downloaded 18 January 2012.
- M. A. Stough, and J. R. Hellmann Jr., *J. Am. Ceram. Soc.*, 85 [12] (2002) 2895-2902.
- M.K. Loudjani and R. Cortès, *J. Eur. Ceram. Soc.* 20 [10] (2000) 1483-1491.
- D.A. Jerebtsov, G.G. Mikhailov, and S.V. Sverdina, *Ceram. Int.* 26 [8] (2000) 821-823.
- V.V. Srdiæ, M. Winterer, and H. Hahn. *J. Am. Ceram. Soc.*, 83 [8] (2000) 1853-1860.

22. R.H.L. Garcia, V. Ussui, N.B. de Lima, E.N.S. Muccillo, and D.R.R. Lazar, *Journal of Alloys and Compounds*, 486 (2009) 747-753.
23. A.K. Shukla, V. Sharma, N.A. Dhas, and K.C. Patil, *Mater. Sci. Eng. B40* (1996) 153-157.
24. P. Manivasakan, V. Rajendran, P. R. Rauta, B. B. Sahu, and B. K. Panda, *J. Am. Ceram. Soc.*, 94 [5] (2011) 1410-1420.
25. R. Septawendar, A. Setiati, and S. Sutardi, *Ceramics International*, 37 [8] (2011) 3747-3754.
26. R. Septawendar, B. S. Purwasasmita, and S. Sutardi, *Journal of the Australian Ceramic Society*, 49 [1] (2013) 101- 108.
27. Y. J. Kwon, K.H. Kim, C.S. Lim, and K.B. Shim, *Journal of Ceramic Processing Research*, 3 [3] (2002) 146-149.
28. R. Septawendar, S.Sutardi, Soesilowati, and B.S. Purwasasmita, in the *Proceeding of the 1st Workshop of Research and Development on Nanotechnology in Indonesia*, 12 December 2013, (Center for Advance Sciences at Institute of Technology Bandung, 2014), pp. 15-19.
29. S. Sakka, in *"Handbook of Sol-Gel Science and Technology: processing, characterization and applications"*, Volume I *Sol-gel processing*, (Kluwer Academic Publishers, 2004) p. 116.
30. R. Go´mez, T. Lo´pez, X. Bokhimi, E. Muqnoz, J.L. Bold´u and O. Novaro, *J. Sol-Gel Sci. Tech.*, 11 (1998) 309-319.
31. G. Shevla, in *"Vogel's textbook of macro and semimicro qualitative inorganic analysis"*, 5th edition, (Longman Inc., 1979) pp. 39-48, 283, 535.
32. C. R. Foschini, O. Treu filho, S. A. Juiz, A. G. Souza, J. B. L. Oliveira, E. Longo, E. R. Leite, C. A. Paskocimas, and J. A. Varela, *J. Mater. Sci.* 39 (2004) 1935-1941.
33. H.A. Abbas, F.F. Hamad, A.K. Mohamad, Z.M. Hanafi, and M. Kilo, 8 (2008) 7.1-7.8.
34. X. Lu, K. Liang, S. Gu, Y. Zheng, H. Fang, *J. Mater. Sci.*, 32 (1997) 6653-6656.
35. P. Souza Santos, H. Souza Santos, S.P. Toledo, *Materials Research*, 3 [4] (2000) 104-114.
36. S. Shukla and S. Seal, *International Materials Reviews*, 50 [1] (2005) 1-20.
37. R. Septawendar, Suhanda, and F. Edwin. *Journal of Ceramic Processing Research*, 12 [4] (2011) 365-370.
38. R. Septawendar, B. S. Purwasasmita, S. Sutardi, N. Sofyaningsih and W. Kristanto, *Journal of Ceramic Processing Research*, 13 [3] (2012) 338-343.
39. Anonymous. *The Chemistry of Caramel*. <http://sciencegeist.net/the-chemistry-of-caramel/>. Posted on 12 January 2011. Accessed on 5 August 2014.
40. S. M. M. Zawawi, R. Yahya, A. Hassan, H. N. M. E. Mahmud and M. N. Daud, *Chemistry Central Journal*, 7 (2013) 1-10. doi:10.1186/1752-153X-7-80. <http://journal.chemistrycentral.com/content/7/1/80>.
41. K. Prabhakaran, A. Melkeri, N.M. Gokhale, and S.C. Sharma, *Ceramics International*, 33 (2007) 1551-1555.
42. Y. Wu, A. Bandyopadhyay, and S. Bose, *Materials Science and Engineering, A* 380 (2004) 349-355.
43. A. Dhawan and V. Sharma, *Anal Bioanal Chem.* 398 (2010) 589-605.