Synthesis of ZrSiO, powders by a sol-gel method with varied calcination temperatures

G Elsandika, A D C Putri, M Musyarofah and S Pratapa

Department of Physics, Faculty of Science, Institute Technology Sepuluh Nopember, Surabaya 60111, Indonesia

Corresponding author: suminar_pratapa@physics.its.ac.id

Abstract. The effect of calcination temperature on phase formation of the powders prepared with starting materials ZrCl and TEOS (tetraethylorthosilicate) was studied. Stoichiometric Zr/Si (1:1 mol%) mixture of samples were prepared by a sol-gel method after 5 wt.% of PVA (polyvinyl alcohol) addition as a catalyst and mechanical activation via ball milling for 5 h. The mixtures were then calcined at 900, 1000, 1100, 1200, and 1300 °C for 10 h. The phase composition was determined by Rietveld analysis of X-ray diffraction (XRD) data using Rietica software. Results showed that at calcination temperatures of 900, 1000, and 1100 °C, only tetragonal zirconia was observed, but retained silica in an amorphous state. Both phases then completely reacted to form zircon at 1200 °C. At 1300 °C, a little amount of zircon decomposed into tetragonal zirconia and cristobalite.

Keywords: ZrSiO (zircon) powder, sol-gel method, ZrCl, TEOS, decomposition.

1. Introduction

Ceramics are used to support human daily activities. One of functional ceramic materials is ZrSiO (zircon or zirconium silicate) that has been found to exhibit physical properties appropriate as sensors, circuit applications, semiconductor hetero junctions, ceramic pigments, nuclear waste disposal, and high dielectric materials [1]. Zircon has a high dielectric constant (≈15), strong corrosion resistance, low thermal expansion coefficient and conductivity, as well as excellent phase and chemical stability [2], and relatively high refractive index (1.92), so it can be used as a light-dyeing material [3]. Zircon has a tetragonal with I_4/amd space group [4]. The unit cell parameters are a = 0.653 nm and c = 0.591 nm [5].

There were several ways to produce zircon powders: solid state reaction, low temperature hydrothermal, micro emulsion, co-precipitation, and sol-gel methods. Synthetic zircon was usually obtained from a high temperature process. Inspite of its effortlessness, the solid state reaction is difficult to provide high purity zircon at temperature lower than 1450 °C [6]. Pure zircon powder, can also be obtained at a lower calcination temperature 1300 °C but via a sol-gel method [7]. Itoh [8] began this method with mixing ZrOCI, with colloidal silica and heating at 500-1300 °C temperature. They got zircon and tetragonal zirconia phase at 1300 °C temperature. Du et al. [9] had 90% zircon at 1500 °C calcination temperature with addition 2.5 mol% Y2O3 and 3 wt.% zircon seeds to ZrOCI and TEOS mixture before the heating treatment. In 2014, Cu et al. [10] used zirconium (IV) nitrate and TEOS as the precursors to obtain tetragonal zirconia at 1173-1373 K, also zircon at 1473 K.

The main role of PVA is a binder between some substance [11]. In a previous study, PVA was used as a binder between zirconia and silica powder [12]. Feng et al. [13] successfully synthesis monophases LaFeO3 powders at low temperature by PVA addition.
In this research will be studied the effect of varied temperature in the zircon phase formation which is given by PVA as the additive material.

2. Experimental

The raw materials used in this study were zirconium chloride (ZrCl₄) powder from Merck and TEOS (tetraethylorthosilicate, Si(OC₂H₅)₄) solution from Sigma Aldrich. The precursors were mixed with 1:1 Si/Zr ratio. The mixing was done to obtain gel prior to washing with water. The washed gel was dried and then crushed to obtain powder. Two powders were prepared, i.e. the as-sol-gel route product, designated as ZS sample, and ZS sample with mechanical activation, named as ZSP sample. The ZSP powder were uniformly mixed with 3wt% polyvinyl alcohol (PVA) and then subjected to a mechanical activation process in a planetary ball-mill for 5 h and finally dried. These samples were calcined at various temperature following the DTA-TGA history of the samples.

The obtained zircon powders were characterized using a powder X-ray diffractometer (XRD). The XRD patterns of the samples were recorded using Cu-Kα (λ=1.54056 Å) radiation, at 2-theta range of 15-65° and step size of 0.017°. The patterns were analysed using a Rietveld refinement method embedded in the Rietica software package [14] for phase composition calculation.

3. Results and discussion

Figure 1 presents the diffraction patterns for the uncalcined ZS and ZSP samples. What stands out in the pattern is no peak identified. This result indicates that both samples were in an amorphous state. The synthesis resulted in amorphous zirconia and silica powders. After precursor mixing and before calcination, crystallization did not occur. To obtain the crystalline structure, a driving force in the form of heat can be applied. The required heat can be predicted using TGA and DTA measurement.

The results of the TGA and DTA are set out in figure 2. The results of TGA measurements in the temperature range between 29 and 600 °C indicate a loss of 27%, which can be attributed to the release of alcohols, ammonium hydroxide, adsorbed water and organic species decomposition from the samples [15]. Confirmation of the loss of alcohol and water absorbed by the sample was also obtained from the DTA results with the presence of endothermic peak around 100 °C. There are two other exothermic peaks observed in the DTA result, one around 350 °C as a result of surfactant and acetate elimination and another one at approximately 892 °C as a result of crystallization of tetragonal zirconia [16]. The latter result is in accordance with the work by Veytizou et al. [7] who reported that crystallization process of amorphous zirconia becomes tetragonal-zirconia phase took place above 800 °C. Meanwhile, Du et al. [9] stated that the formation of low cristobalite phase of silica occurred at temperature range 1000-1200 °C [9]. We conclude that, for studying the zircon synthesis in our case, the calcination should be carried out at temperature range of 900-1300 °C.
Figure 2. DTA-TGA analysis of ZSP powder

Figure 3. X-ray diffraction pattern (CuKα) of powders after calcination at 900-1300 °C for 10 hours (z=zircon, t=tetragonal zirconia, c=cristobalite)

Figure 3 compares the XRD patterns of the calcined samples. The patterns show that the samples have undergone crystallization as indicated by the appearance of some peaks. Three different groups of crystalline phases were obtained. The calcination temperature of 900-1100 °C gave only a tetragonal zirconia [No. PDF 079-1767], and that at 1200 °C produced only zircon [No. PDF 072-0402], while those at 1300 °C were zircon, t-zirconia, and low cristobalite [No. PDF 076-0940] phase. It appears that calcination below 1200 °C could not provide sufficient energy to allow zircon formation. The fact that only tetragonal was found at 1100 °C and only zircon at 1200 °C implies that below 1100 °C silica is in an amorphous state and unable to react with zirconia to form zircon. The reaction of zircon formation is shown in equation (1). The formation of a single-phase zircon at 1200 °C due to the formation Gibbs energy of the tetragonal zirconia and amorphous SiO₂ has been met, resulting in enough energy to obtain zircon crystal.

\[
\text{ZrO}_2 + \text{SiO}_2 \rightarrow \text{ZrSiO}_4
\]  (1)
Table 1. Result of quantitative analysis of X-Ray diffraction pattern of samples calcined at varied temperatures using Rietveld method

| Sample (°C) | Phase Composition (mole%) |
|------------|---------------------------|
|            | Zircon | t-Zirconia | Cristobalite |
| 900        | -      | 100.0 (0)  | -            |
| 1000       | -      | 100.0 (0)  | -            |
| 1100       | -      | 100.0 (0)  | -            |
| 1200       | 100.0 (0) | -      | -            |
| 1300       | 93.0 (16) | 3.0 (2) | 4.0 (4) |

As shown in figure 3, the sample decomposes to zirconia and silica at 1300 °C. The decomposition of zircon results in tetragonal zirconia and cristobalite. The result was confirmed by the Rietveld analysis of XRD patterns as shown in Table 1. Decomposition reaction is a chemical reaction on a single compound breaking down into two or more forms under a particular condition. This zircon decomposition is the result of thermal decomposition from high calcination temperature [17]. In this study, the amount of decomposed phase is 7%. Zircon phase usually form at 1600 °C, but in this study at 1200 °C has been done.

The role of PVA addition is an interesting aspect in our work. Basically, the purpose of PVA addition was to favor crystal growth [11]. However, we showed here that it can be used to accelerate the formation of high purity zircon at lower calcination temperature. Normally, the formation of zircon was at approximately 1350-1500 °C [6–10]. PVA melts at 228 °C [18]. When the ZSP mixture was calcined at 1200 °C, the PVA melted and then easily inserted through the samples to draw the zirconia and silica particles closer and allow them to react. Thus, in addition to its role as a crystal growth enhancer, PVA can also act as a catalyst.

On the other hand, the mechanical activation leads to formation of reactants with high surface energy [19]. As a result, the expected phase can be formed at the low calcination temperature. The formation of the phase is due to the increasing speed of diffusion and the higher particle homogeneity [20]. During the mechanical activation process, the sample exhibited plastic deformation to facilitate atomic mobility. Moreover, the milling time affects the number of collisions occurred between the particles in the sample. The collision led to a reduction of aggregate and grain size and hence improved the homogeneity of the mixture. The homogenization caused the reaction between amorphous zirconia and amorphous silica particles became easier. The surface area contact between zirconia and silica particles will be more widespread by reducing their grain size so that more particles react [19]. Therefore, another explanation for the formation of zircon at 1200 °C is because of the increasing speed of diffusion and the higher particles homogeneity [20].

4. Summary
Zircon (ZrSiO₄) powders has been successfully synthesized using ZrCl powders (zirconium chloride) and TEOS (tetraethoxyorthosilicate) solution by a sol-gel method followed by calcination. The application of mechanical activation by a planetary ball mill for 5 hours and the addition of 3 wt% PVA significantly influenced the formation of zircon. The varied calcination temperature affected the phase formation. At 900-1100 °C tetragonal zirconia and silica amorphous were formed, while at 1200 °C, the single-phase zircon was obtained. Moreover, the zircon powder decomposed into multiphase, i.e. 93% zircon, 3% tetragonal zirconia and 4% low cristobalite after calcination at 1300 °C.

Acknowledgements
The authors would like to thank Ministry of Research Technology and Higher Education of the Republic of Indonesia to support finance through program Penelitian PMDSU (Pendidikan Magister Menuju Doktor untuk Sarjana Unggul) Tahun Anggaran 2017 No. 491/PKS/ITS/2017.

References
[1] Huang S, Li Q, Wang Z, Cheng X and Wen H 2017 Ceram. Int. 43 875–9
[2] Hays D C, Gila B P, Pearton S J, Kim B J and Ren F 2016 Vacuum 125 113–7
[3] Focke W W, Manhique A and Carter R 2002 J. Am. Ceram. Soc. 85 1139–44
[4] Srikanth S, Devi V L and Kumar R 2016 Hydrometallurgy 165 125–36
[5] Puthenkovilakam R, Carter E A and Chang J P 2004 Phys. Rev. B 69 155329
[6] Wang F, Liu D W, Zhu J F and Li D 2011 Adv. Mater. Res. 295–297 1485–8
[7] Veytizou C, Quinson J F and Douy A 2000 J. Mater. Chem. 10 365–70
[8] Itoh T 1992 J. Cryst. Growth 125 223–8
[9] Du C, Yuan Q and Yang Z 1999 J. Mater. Sci. Lett. 18 965–6
[10] Cu H L, Hwang W S, Wang C L, Wang M C, Lee K C, Huang H H and Lee H E 2014 J. Alloys Compd. 616 413–9
[11] Peko C, Groth B and Nettleship I 2010 J. Am. Ceram. Soc. 95 115–20
[12] Musyarofah, Nurlaila R, Muwwaqor N F, Saukani M, Kuswoyo A, Triwikantoro and Pratapa S 2017 J. Phys.: Conf. Ser. 817 012033
[13] Feng J, Liu T, Xu Y, Zhao J and He Y 2011 Ceram. Int. 37 1203–7
[14] Pratapa S 2010 Makara J. Sci. 11 85–90
[15] Tartaj P and de Jonghe L C 2000 J. Mater. Chem. 10 2786–90
[16] Aguilar D H, Torres-Gonzales L C, Fuentes A F, Torres-Martinez L M, Lopez T and Quintana P 2000 J. Solid State Chem. 158 349–57
[17] Abdelkader A M, Duher A and El-Kashef E 2008 J. Alloys Compd. 460 577–80
[18] Tubbs R K 1965 J. Polym. Sci. A 3 4181–9
[19] Emadi R, Ashrafi H and Zamani Foroushani R 2015 Ceram. Int. 41 14400–5
[20] Ahmadzadeh M, Ataie A and Mostafavi E 2015 J. Alloys Compd. 622 548–56