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Synthesis of zircon powder by polyvinyl alcohol addition

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Abstract. The effect of polyvinyl alcohol (PVA) addition on the formation of zircon ($ZrSiO_4$) powders was studied. The powders were prepared with a stoichiometric Zr/Si (1:1 mol%) mixture of zirconium oxychloride aqueous solution ($ZrOCl_2.H_2O$) and tetraethoxysilane (TEOS) ($Si(OC_2H_5)_4$) by a sol-gel method after PVA addition. The amount of added PVA varied between 1, 2, 3, and 4% by weight. The addition of PVA was aimed to be a catalyst which can accelerate the formation of zircon. The sol-gel process was followed by a mechanical activation via ball-milling and by calcination at 1000-1200 °C for 10 h. The phase composition of the resulted powders was determined through Rietveld analysis of X-ray diffraction (XRD) data using *Rietica* software. Results showed that amorphous zirconia transformed to a transient tetragonal zirconia phase at a calcination temperature of 1100 °C for all added PVA compositions, then reacted with silica to form zircon at 1200 °C. The 1, 2, and 4 wt% PVA-added samples crystallized to form zircon with the secondary phases of *t*-zirconia, *m*-zirconia, and cristobalite. The single phase of zircon was obtained in the 3 wt% PVA added-powder calcined at 1200 °C.

1. Introduction

The thermo-mechanical properties of zircon ($ZrSiO_4$) are excellent i.e. its heat conductivity coefficient at room and high temperature is very low, its mechanical strength is good and its thermal expansion coefficient is low [1–3], which do not even alter at high temperature above 1400 °C [4,5]. Zircon has the potential to be used in refractory applications because of its durability, stability, and resistance to thermal shock. Ferry *et al.* [6] reported the Gibbs energy ΔG_f of formation of zircon from the oxides at a value of -18.44 kJ/mol which was derived from a phase-equilibrium study. The high yield of pure zircon synthesis is quite difficult to obtain because the formation energy is relatively small [7], the diffusion kinetics are slow and the kinetic activation energy required for the combination reaction between the oxide components of zirconium and silica [8]. In addition, large changes in the crystal structure of zirconium between the structure of zirconia (ZrO_2) and zircon ($ZrSiO_4$) and the very low solubility of the solids of SiO_2 in ZrO_2 increase the difficulty of obtaining such high yield synthesis [8].

Curtis and Sowman [9] found that zircon formation occurs minimum at temperature around 1320 °C. They obtained these results based on their research for zircon formation from a mixture of zirconia and tridimite, zirconia and quartz and zirconia and cristobalite. Furthermore, in our previous work [10,11], we have synthesized the stoichiometric SiO_2-ZrO_2 polymorphic combination powders by mechanical activation using ball mill followed by a calcination at the varied temperatures, as the four reactions, i.e. *a*-SiO_2 + *a*-ZrO_2, *a*-SiO_2 + *t*-ZrO_2, *c*-SiO_2 + *a*-ZrO_2, *c*-SiO_2 + *t*-ZrO_2 (with *a* amorphous, *t* tetragonal, and *c* cristobalite). The results revealed that the mixture of amorphous oxides of silica and zirconia (SiO_2-ZrO_2) would be crystallized to form zircon at a lower calcination temperature if the fraction of one component in the composition was greater than the other components, c.a. 82.9 mol%. However, the method based on the solid-state reaction of a mixture of amorphous powder of oxide

zirconium and silica (ZrO$_2$-SiO$_2$) reveals that the crystallization that occurs in the powder is incomplete with the heat treatment.

Several studies to obtain pure zircon powder have been attempted through micro-emulsion process, reverse micelle process, chemical reaction like aerosols, sol-gel routes and hydrothermal. Seeding of the oxide precursor powders with zircon powder to initiate zircon phase formation from the reaction between precursors has been reported [4,12,13]. Very high results have been achieved when using such seeding, which is carried out through the synthesis of sol-gel and hydrothermal methods. On the other hand, efforts to produce zircon previously involving only the sintering process of zirconia and silica powder require very long calcination time and relatively low yield (<50%) [8,13].

The addition of polyvinyl alcohol (PVA) was used in several works to synthesize some oxides by a sol-gel method such as LaFeO$_3$ [14], BiFeO$_3$ [15], and LiMn$_2$O$_4$ [16] etc. The function of PVA is as a binder in solid-state reactions of magnesium and silica [17,18]. In our previous works [10,11], we also used the addition of PVA with a fixed amount in the SiO$_2$-ZrO$_2$ mixture with solid-state reaction method. There is no literature that reports the work in examining the effect of the amount of PVA on the zircon formation. In the present paper, the synthesis of zircon powder with sol-gel method followed by the addition of PVA through mechanical activation using ball mills is reported. The effect of calcination temperature and PVA content on zircon formation were investigated.

2. Experimental
Zircon powders were synthesized from zirconium oxychloride aqueous solution (ZrOCl$_2$.H$_2$O) and tetraethoxysilane (TEOS) (Si(OC$_2$H$_5$)$_4$) in a Zr/Si stoichiometric ratio. The precursors were mixed under stirring at a temperature of 100 °C for 24 hours. Then an amount of 3 M ammonia solution was added into the mixture until pH 11 and form gel, then followed by washing and drying to obtain the powder. A variation content of polyvinyl alcohol (PVA), i.e., 1, 2, 3, and 4 wt%, was added to the powders followed by the mechanical activation using ball milling. The resulting powder is then calcined for three temperature variations of 1100, 1200, and 1300 ° C for 10 hours. The Diffractometer of Philips XPert Powder (CuKα λ = 1.54060 Å and step size 0.0170 °) was used to obtain phases from X-ray diffraction data (XRD) for all samples. Analysis of the XRD patterns is done by Match! 2 for the phases identification and the accurate powder phase composition can be obtained by using Rietica [19] and Rietveld refinement.

3. Results and discussion
Figure 1 presents the X-ray diffraction patterns of the PVA-added powders prepared by the sol-gel method followed by mechanical activation and calcination at 1100, 1200, and 1300 °C. All calcined powder shows phases which are a combination of zircon (PDF No. 9-582), cristobalite (SiO$_2$) (COD No. 1-010-938), tetragonal-zirconia (COD No. 1-525-706) and monoclinic-zirconia (PDF No. 89-426). There is no zircon phase identified for all PVA-added powders calcined at 1100 °C, only the tetragonal zirconia is identified. The zircon phase is identified for all PVA-added powders calcined at 1200 °C but accompanied by the presence of the other phases from oxide components, i.e., SiO$_2$ (cristobalite) and ZrO$_2$ (tetragonal and monoclinic), except for 3 wt. % PVA-added powders. The addition of 3 wt.% PVA presents only the zircon phase without the presence of the other phases. Itoh [20] has explained the mechanism of amorphous zirconia and amorphous silica powder in forming zircon. Zircon formation is occurs as a result of the reaction between tetragonal zirconia and amorphous silica. At the calcination temperature of 1100 °C, the thermal energy is not sufficient for zircon formation but rather used for the crystallization process of tetragonal zirconia. The onset of zircon formation is detected at 1200 °C. The remaining amorphous silica will change to cristobalite silica. During the cooling process, unreacted zirconia will transform from tetragonal to monoclinic [20].

In a previous study, Du *et al.* [21] worked on the synthesis of zircon powder by yttria and zircon seed addition without the addition of PVA. The almost complete reaction was found when the powder was calcined at 1500 °C. In our work, the pure zircon can be achieved at a lower calcination temperature of 1200 °C by adding 3 wt% of PVA. Therefore, the addition of PVA is effective to lower the temperature of zircon formation. However, zircon can dissociate into silica and zirconia at temperatures more than 1500 °C (determined by the condition of the system) [3,9,22,23] by following the reaction:

$$ZrSiO_4 \rightarrow ZrO_2 + SiO_2 \qquad (1)$$

Table 1. Results of quantitative analysis of X-ray diffraction patterns of PVA-added powders calcined at varied temperatures using *Rietica* [19].

Samples		Zircon	*t*-Zirconia	*m*-Zirconia	Cristobalite
1 wt%	1100	-	100	-	-
	1200	16.3 ± 1	1.5 ± 0	77.3 ± 2	4.9 ± 1
	1300	95.3 ± 1	0.1 ± 0	3.0 ± 4	1.6 ± 5
2 wt%	1100	-	100	-	-
	1200	11.1 ± 2	2.7 ± 1	71.6 ± 3	14.5 ± 3
	1300	86.3 ± 8	0.1 ± 0	4.5 ± 3	9.1 ± 5
3 wt%	1100	-	100	-	-
	1200	100	-	-	-
	1300	87.6 ± 2	0.1 ± 0	2.5 ± 7	9.7 ± 9
4 wt%	1100	-	100	-	-
	1200	9.3 ± 2	2.2 ± 1	80.7 ± 3	7.8 ± 2
	1300	91.1 ± 9	0.1 ± 0	0.3 ± 4	8.6 ± 5

(a)

(b)

(c)

(d)
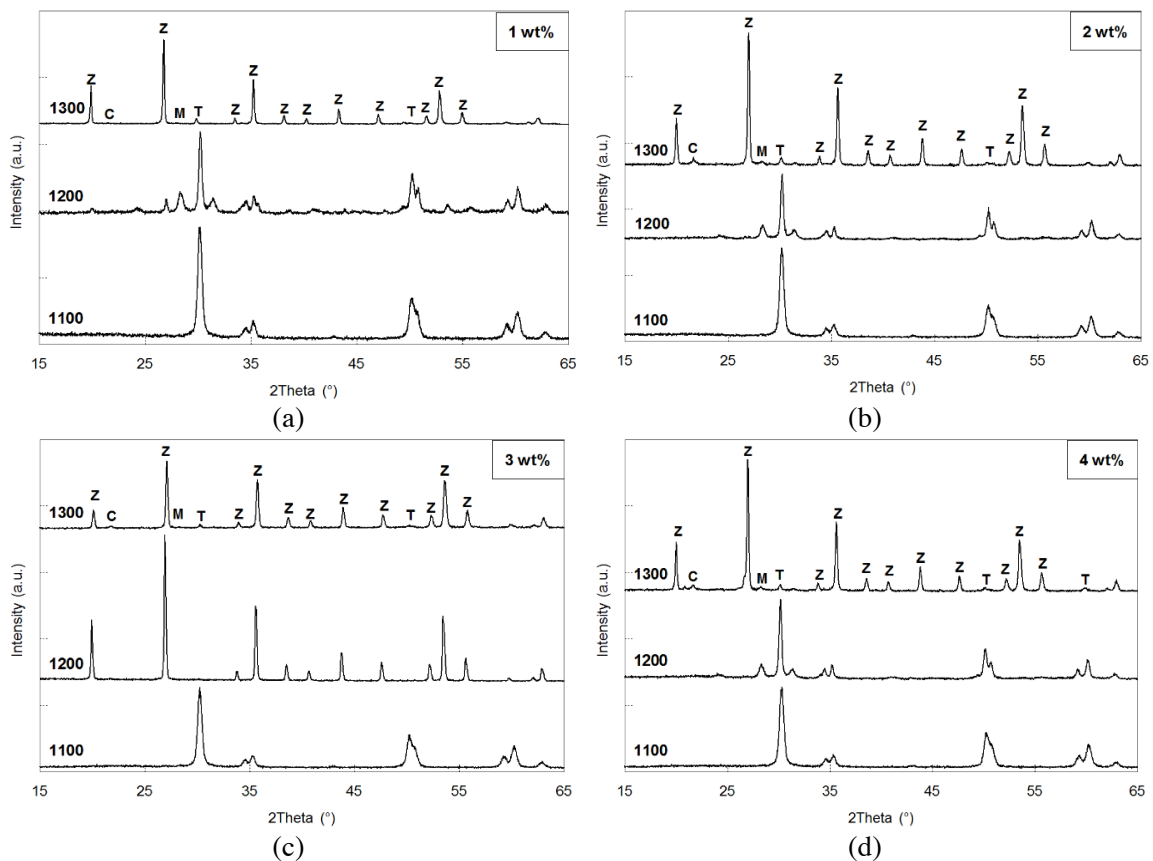
Figure 1. X-ray diffraction patterns (CuKα) of PVA-added powders calcined at varied temperatures with *z* zircon, *m* monoclinic zirconia, *t* tetragonal zirconia, and *c* cristobalite.

The silica can be present in a glassy phase that is not detected by XRD. The glassy phase of silica can be crystallized into quartz or cristobalite phases, both of which can be observed with XRD [2]. Zirconia, can also be identified by XRD. At room temperature, zirconia is generally stable in

monoclinic phase (m-ZrO_2). However, if the size of the particles is small enough, zirconia may present in tetragonal phase (t-ZrO_2) that has higher energy state, at room temperature [2]. In this work, with the 3 wt.% PVA-added powder that calcined at 1300 °C, there is a dissociation of zircon which produces silica in a cristobalite phase and zirconia in tetragonal and monoclinic phases, in addition to zircon crystal formation. The zircon dissociation temperature is obtained lower than 1500 °C with the addition of PVA.

Table 1 presents the relative mole fraction of each phase as a result of quantitative analysis of X-ray diffraction patterns based on the Rietveld method for all samples. For each addition of PVA, zircon content shows an increase with increasing temperature during the calcination process, i.e., up to 95.3 mol%, except for the 3 wt.% PVA addition. For this PVA addition, the reaction straightly completed to yield a single-phase of zircon at 1200 °C, but calcination at 1300 °C makes zircon dissociate into silica and zirconia so that the final zircon content is only 84.6 wt.% mol.

The main function of PVA is to provide polymer networks that can inhibit cation mobility so that local stoichiometry allows to be maintained and it also helps minimizing precipitation of unexpected phases [24]. PVA may also act as a binder [25] so that the wet ability between the powders can be increased during sintering [10–11]. It is therefore argued that these roles of PVA which have enhanced the reaction between raw powders and hence produces a higher zircon content. The PVA content that can optimize the reaction is 3 wt.%. However, the higher PVA content produces smaller zircon content. It is estimated that increasing the PVA addition cause the raw material particles to become entrapped in entangled network from organic polymers so that it will hinder the reaction.

4. Summary
Zircon ($ZrSiO_4$) powders were synthesized by a sol-gel method with polyvinyl alcohol (PVA) addition followed by a mechanical activation via ball-milling and by calcination at 1100-1300 °C for 10 h. In the 1100 °C of all calcined PVA-added powders, only t-zirconia was identified, but zircon was not. Amorphous zirconia transformed to a transient tetragonal zirconia phase at a calcination temperature of 1100 °C for all added PVA compositions. Tetragonal zirconia started to react with silica to form zircon at 1200 °C. The 1, 2, and 4 wt% PVA-added samples in particular crystallized to form zircon with the secondary phases, i.e. t-zirconia, m-zirconia, and cristobalite. The addition of 3 wt% PVA was able to optimize the reaction until the single phase of zircon was formed at 1200 °C.

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