

Hydrothermal Synthesis and Phase Stability of New Zircon- and Scheelite-Type ZrGeO_4

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Single-phase zircon- and scheelite-type ZrGeO_4 were selectively synthesized from the reaction of a ZrOCl_2 solution and GeO_2 under mild hydrothermal conditions at 120–240 °C by pH control of the solution via homogeneous generation of a hydroxide ion through the decomposition of urea. New phase zircon-type ZrGeO_4 octahedral-like particles that were assemblies of small crystals (10–80 nm in size) were directly formed under acid conditions, and the particle size was controlled (0.4–1.5 μm in size) by the absence or presence of urea as well as hydrothermal treatment temperature. Scheelite-type ZrGeO_4 particles (50–100 nm in size) that were a coagulation of nanometer-sized crystals were formed under moderate neutral to acid conditions ($6 \geq \text{pH} > 2$) in the presence of urea. The zircon-type ZrGeO_4 was stable below 1160 °C in air and transformed to the scheelite-type structure at 1180 °C. The dissociation of ZrGeO_4 to tetragonal ZrO_2 and GeO_2 occurred by heat treatment under conditions above 1350 °C for 5 h or 1450 °C for 1 h.

Introduction

Zirconium germanate with a composition of ZrGeO_4 has been known to have a scheelite (CaWO_4)-type structure in which large Zr is eight-coordinated and small Ge is in a tetrahedral site. MGeO_4 germanates of tetravalent elements ($\text{M} = \text{Zr}, \text{Hf}, \text{Ce}, \text{Th}$) have the same structure as scheelite. Actinide germanates, for instance ThGeO_4 , also exhibit the scheelite-type structure and a high-temperature form with zircon-type structure.^{1–5} The crystal structures of ZrGeO_4 ,^{6,7} HfGeO_4 , and ThGeO_4 ⁸ have been determined by X-ray diffraction (XRD) and infrared and Raman spectroscopic investigation. MSiO_4 silicates of tetravalent elements ($\text{M} = \text{Zr}, \text{Hf}, \text{Th}$) are well-known to show the zircon-type structure.¹ ThSiO_4 has two forms, the tetragonal ThSiO_4 (thorite) and the high-temperature monoclinic ThSiO_4 (huttonite). ZrSiO_4 zircon is converted to the scheelite type, with an 11% increase in density as compared with the original zircon form at 900 °C under high pressure (120 kbar), and there is no change in the coordination of Zr, Si, or O atoms in the zircon–scheelite transformation.⁹

In the ZrO_2 – GeO_2 system, the scheelite structure appears at two compositions as ZrGeO_4 (c/a ratio 2.168)

and Zr_3GeO_8 (c/a ratio 2.216).^{6,7} ZrGeO_4 single crystals have been reported to be grown from several flux systems.^{10,11} The scheelite-type ZrGeO_4 activated with Ti^{4+} yields blue luminescence when irradiated with X-rays.¹² The crystal structure of the scheelite-type ZrGeO_4 doped with Ti^{4+} was investigated by Raman spectroscopy.¹² The scheelite-type ZrGeO_4 was also crystallized by heat treatment at around 800 °C through a sol–gel route in the ZrO_2 – GeO_2 –(H_2O) system from zirconium tetraisopropoxide and germanium tetraisopropoxide.¹³ In the ZrO_2 – GeO_2 system, the existence of only the scheelite-type tetragonal ZrGeO_4 phase at >45 mol % GeO_2 has been shown by Raman spectroscopic investigation based on the solid-state reaction between GeO_2 and 2 mol % Y_2O_3 -doped ZrO_2 powder.¹⁴ There were no reports on the synthesis of zircon-type ZrGeO_4 as well as no crystal data (lattice parameters, crystal morphology, etc.) of the zircon-type structure of ZrGeO_4 . We have directly synthesized fine particles of crystalline inorganic materials through soft solution routes^{15–21} and reported on the hydrothermal synthesis, XRD data, and morphology of the zircon-type ZrGeO_4 particles and zircon-type solid solutions over the whole

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composition range in the ZrGeO_4 – ZrSiO_4 system.²²

In the present study, the effect of the solution pH on the crystal structure of synthesized ZrGeO_4 was investigated by controlling the pH using the homogeneous generation of a hydroxide ion through decomposition of urea. Synthesis conditions of the scheelite- and zircon-type ZrGeO_4 were clarified. Phase transformation from the zircon- to scheelite-type structure and the decomposition behavior of ZrGeO_4 via heat treatment in air were investigated.

Experimental Section

Reagent-grade germanium oxide (GeO_2 ; High Purity Chemical Laboratory, Japan) and zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$; Kishida Chemical, Japan) were used as the starting materials. A given quantity (18 cm³) of a mixed solution of germanium oxide and zirconium oxychloride with a cation (Ge and Zr) concentration of 0.2 and 0.3 mol/dm³, with or without the addition of 0.1–0.2 mol/dm³ urea [$\text{CO}(\text{NH}_2)_2$] was taken into a 25 cm³ Teflon container held in a stainless steel vessel. The vessel, after being tightly sealed, was heated at 100–240 °C for 10 h under rotation at 15 rpm. After hydrothermal treatment, the precipitates were washed with distilled water until the pH value of the rinsed water was 7.0, separated from the solution by either centrifuging or ultrafiltration, and dried in an oven at 60 °C. The powders thus prepared were heat treated in an alumina crucible at a temperature ranging from 500 to 1600 °C for 1 h in air.

Phase identification of as-prepared and heat-treated powders was performed with powder X-ray diffractometry (XRD; RINT-2000, Rigaku, Tokyo, Japan) using $\text{Cu K}\alpha$ radiation. The crystallite size of zircon was estimated from line broadening of the (200) diffraction peak according to the Scherrer equation: $D_{\text{XRD}} = K\lambda/\beta \cos \theta$, where θ is the Bragg angle of diffraction lines, K is a shape factor ($K = 0.9$ in this work), λ is the wavelength of incident X-rays, and β is the corrected half-width given by $\beta^2 = \beta_m^2 - \beta_s^2$, where β_m is the measured half-width and β_s is the half-width of a standard sample with a known crystallite size of larger than 200 nm. The lattice parameters a_0 and c_0 of the zircon-type structure were measured using silicon as the internal standard. The volume fraction of the ZrO_2 phase dissociated from the scheelite-type ZrGeO_4 was determined from integrated diffraction intensities (I) of corresponding lines being around 30° in 2θ by using the following equation: $\text{ZrO}_2 \text{ phase (\%)} = [I \text{ of tetragonal } \text{ZrO}_2 (111) / \{I \text{ of scheelite } \text{ZrGeO}_4 (112) + I \text{ of tetragonal } \text{ZrO}_2 (111)\}] \times 100$. The volume fraction of monoclinic ZrO_2 transformed from the tetragonal phase was determined from integrated diffraction intensities of corresponding lines by using the following equation: $\text{monoclinic } \text{ZrO}_2 \text{ (\%)} = [\{I \text{ of monoclinic } \text{ZrO}_2 (111) + I \text{ of monoclinic } \text{ZrO}_2 (1,1,-1)\} / \{I \text{ of tetragonal } \text{ZrO}_2 (111) + I \text{ of monoclinic } \text{ZrO}_2 (111) + I \text{ of monoclinic } \text{ZrO}_2 (1,1,-1)\}] \times 100$. Raman spectra were obtained from a Raman spectrometer (NRS-1000, Nihon Bunko, Tokyo, Japan) with the 532 nm line of a 10 mW green laser. The morphology of the particles was examined using transmission electron microscopy (TEM; JEM-2010, JEOL, Tokyo, Japan). Elemental analysis for the samples was done by analysis using an inductively coupled plasma (ICP; ICP575II, Nippon Jarrell-Ash, Japan) emission spectrometer.

Results and Discussion

Influence of the Solution pH on the Crystal Structure of ZrGeO_4 . After the reaction of GeO_2 and a ZrOCl_2 solution via hydrothermal treatment in a vessel tightly sealed at a temperature above 100 °C, the solution becomes more acidic than the starting ZrOCl_2

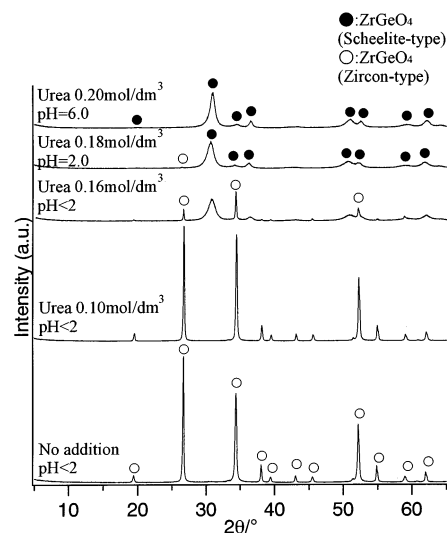


Figure 1. XRD patterns of ZrGeO_4 precipitates obtained by hydrothermal treatment at 240 °C for 10 h from the reaction of a 0.2 mol/dm³ ZrOCl_2 solution and 0.2 mol/dm³ GeO_2 in the presence of different concentrations of urea.

solution by the formation of HCl through thermal hydrolysis of ZrOCl_2 . The pH of the acid solution could be well controlled by the homogeneous generation of a hydroxide ion, i.e., by the decomposition of urea, through the adjustment of the urea concentration under hydrothermal conditions.

The effect of the solution pH on the crystal phase of the solid precipitates formed under hydrothermal conditions at 240 °C for 10 h from the reaction of GeO_2 and a ZrOCl_2 solution in the presence or absence of urea is shown as the XRD patterns in Figure 1. As-prepared samples from the aqueous solutions in the presence of 0.2 mol/dm³ urea showed very broad peaks, whose diffraction angles corresponded to those of the scheelite-type ZrGeO_4 . The solution pH after synthesis of the scheelite-type ZrGeO_4 was 6.0. Under the condition in the presence of 0.18 mol/dm³ urea (solution pH = 2.0), precipitation of a very small amount of zircon-type ZrGeO_4 as well as the scheelite-type ZrGeO_4 was observed. The zircon-type ZrGeO_4 and scheelite-type ZrGeO_4 coexisted in the precipitates obtained from the solution (pH < 2.0) in the presence of 0.16 mol/dm³ urea, while single-phase zircon-type ZrGeO_4 was formed under the condition of less than 0.1 mol/dm³ urea.

The X-ray powder pattern of the solid precipitate formed from an aqueous acid solution in the absence of urea showed relatively sharp peaks, which could be perfectly indexed by the zircon-type tetragonal structure, having $a = 0.6694$ and $c = 0.6266$ nm, a c/a ratio of 0.9360. The chemical composition of the single-phase zircon-type ZrGeO_4 formed from the solution in the absence of urea, which was determined by the elemental analysis using an ICP emission spectrometer, is shown in Table 1. The synthesized zircon-type ZrGeO_4 was clarified to have an approximately stoichiometric composition. Investigation of the crystallization of amorphous gel over a wide composition range in the ZrO_2 – GeO_2 (– H_2O) system prepared through a sol–gel route from zirconium tetraisopropoxide and germanium tetraisopropoxide showed that the gel with a stoichiometric ZrGeO_4 composition crystallized into the scheelite-type ZrGeO_4 at a temperature above 800 °C.¹³ Thermody-

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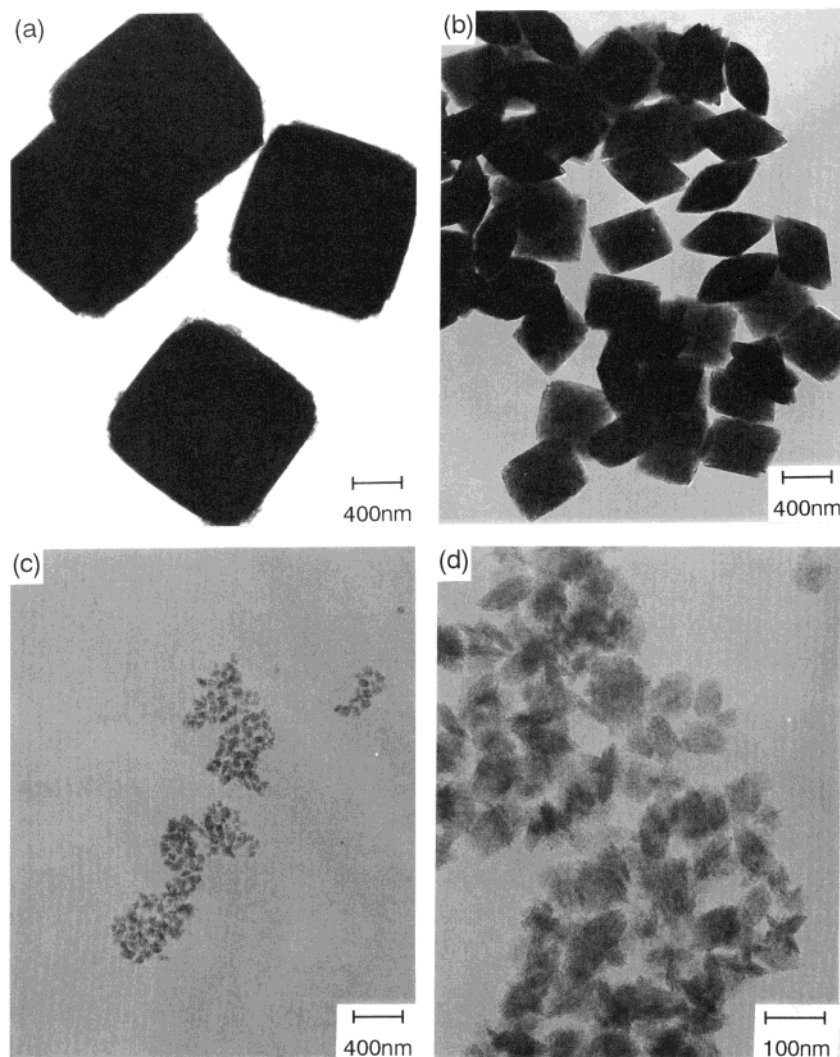


Figure 2. TEM micrographs of ZrGeO_4 precipitates [(a and b) zircon-type ZrGeO_4 ; (c) scheelite-type ZrGeO_4] obtained by hydrothermal treatment at 240 °C for 10 h from the reaction of a 0.2 mol/dm³ ZrOCl_2 solution and 0.2 mol/dm³ GeO_2 (a) in the absence of urea, (b) in the presence of 0.1 mol/dm³ urea, and (c) in the presence of 0.2 mol/dm³ urea; (d) magnified view of part c.

Table 1. Elemental Analysis of Zircon-Type ZrGeO_4 ^a

	ZrO_2	HfO_2	GeO_2
wt %	50.3	1.09	38.5
molar fraction (%)	52.2	0.7	47.1

^a Sample: preparation by hydrothermal treatment at 240 °C for 10 h from the reaction of a 0.2 mol/dm³ ZrOCl_2 solution and 0.2 mol/dm³ GeO_2 in the absence of urea.

namically stable phase of the ZrGeO_4 compound is tetragonal scheelite-type, and there was no finding of reports on the direct formation of the zircon-type ZrGeO_4 except for our study through the soft solutions routes.²² The d/a ratio of the zircon-type ZrGeO_4 was larger than that of ZrSiO_4 (0.9054). The zircon-type ZrGeO_4 is supposed to be a metastable phase and to be synthesized under highly acidic conditions ($\text{pH} < 2$) in the presence of less than 0.18 mol/dm³ urea. Thermodynamically stable scheelite-type ZrGeO_4 was formed under milder pH conditions than those of the metastable zircon-type. Thus, selective and direct synthesis of the scheelite- and zircon-type ZrGeO_4 was shown to be possible under mild hydrothermal conditions by controlling the solution pH.

TEM photographs of the as-prepared powders are presented in Figure 2. The as-prepared scheelite-type ZrGeO_4 (Figure 2c,d) was agglomerated particles of 50–100 nm in size consisting of nanometer-sized (primary) particles. The zircon-type ZrGeO_4 (Figure 2a) prepared under highly acidic conditions without urea appeared to be larger micron-sized octahedral-shape particles, i.e., with secondary particles being assemblies of small (primary) crystals. The (secondary) particle size of the zircon-type ZrGeO_4 was decreased via a decrease in the solution acidity by the supply of hydroxide ions through the decomposition of urea added in the starting solution (Figure 2b).

The Raman spectra observed for both zircon- and scheelite-type ZrGeO_4 are shown in Figure 3. The assignments of Raman bands of the zircon- and scheelite-type ZrGeO_4 are also indicated in Figure 3 based on the data of the zircon- and scheelite-type structure reported previously.^{6,12,23,24} ZrSiO_4 zircon and the zircon-type ZrGeO_4 are confirmed isomorphic crystals, and the unit

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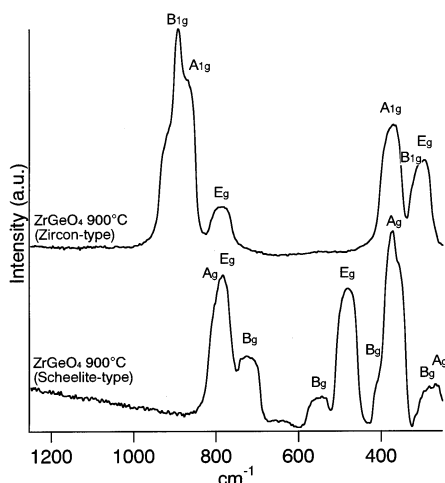


Figure 3. Raman spectra of zircon- and scheelite-type ZrGeO_4 after heat treatment at 900 °C for 1 h in air.

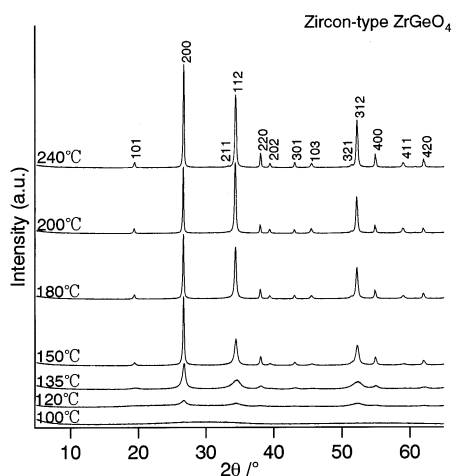


Figure 4. XRD patterns of zircon-type ZrGeO_4 precipitates obtained by hydrothermal treatment at different temperatures for 10 h from the reaction of a 0.3 mol/dm³ ZrOCl_2 solution and 0.3 mol/dm³ GeO_2 .

cell (tetragonal) contains four molecules. For zircon-type ZrGeO_4 , we have no symmetry information and must rely on frequency and intensity in the comparison with ZrSiO_4 zircon. The peak of the A_{1g} band overlaps with that of the B_{1g} band at 870–920 cm^{-1} in the Raman spectra of the zircon-type ZrGeO_4 . In the Raman spectra of the scheelite-type ZrGeO_4 , the peak E_g overlaps with that of A_g at 780–800 cm^{-1} and the peak A_g overlaps with that of B_g at 380–400 cm^{-1} , which were due to a low-resolution broad Raman powder spectrum. The $E_g(\nu_3)$ band²³ of the zircon-type structure around 800 cm^{-1} in Figure 3 was much stronger in ZrGeO_4 than that in ZrSiO_4 , in which the $E_g(\nu_3)$ band was hardly detected in the ZrSiO_4 zircon synthesized under the same hydrothermal conditions from ZrOCl_2 and tetraethoxysilane.²² The Raman spectra observed for the scheelite-type ZrGeO_4 agreed with the data reported.¹²

Influence of the Treatment Temperature on the Crystallite Growth and Morphology of ZrGeO_4 . The effect of the hydrothermal treatment temperature on the crystallite growth of the zircon-type ZrGeO_4 is shown in XRD profiles (Figure 4). With increasing treatment temperature, (200) and (112) diffraction lines of the zircon-type ZrGeO_4 gradually became sharp.

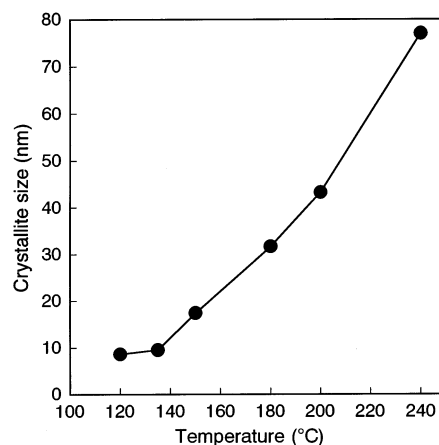


Figure 5. Influence of the hydrothermal treatment temperature on the crystallite size of zircon-type ZrGeO_4 obtained by hydrothermal treatment for 10 h from the reaction of a 0.3 mol/dm³ ZrOCl_2 solution and 0.3 mol/dm³ GeO_2 .

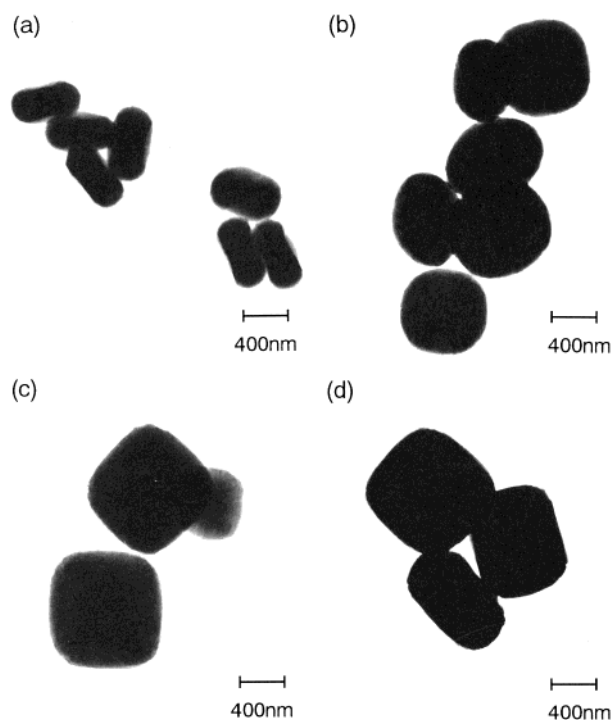


Figure 6. TEM micrographs of zircon-type ZrGeO_4 particles obtained by hydrothermal treatment at (a) 120 °C, (b) 150 °C, (c) 180 °C, and (d) 200 °C for 10 h from the reaction of a 0.3 mol/dm³ ZrOCl_2 solution and 0.3 mol/dm³ GeO_2 .

There was no trace of any other diffraction peaks, besides that of zircon in the XRD patterns. From the XRD results, it appears that the zircon-type ZrGeO_4 is directly precipitated from the reaction of GeO_2 and a ZrOCl_2 solution at low temperature above 120 °C. The change in the crystallite size of the zircon-type ZrGeO_4 estimated from the XRD line broadening of the (200) peak is shown in Figure 5. The crystallite size of the zircon-type ZrGeO_4 particles increased from 10 to 80 nm with increasing treatment temperature from 120 to 240 °C.

The change in the secondary particle size and morphology of the zircon-type ZrGeO_4 formed at different temperatures is shown in TEM photographs (Figure 6). The synthesized zircon-type particles were relatively

regular in size. Yield of the zircon-type ZrGeO_4 increased with increasing treatment temperature at a temperature range of less than 180 °C. It is clearly observed that the secondary particle size increases with increasing treatment temperature. The particle size observed by TEM did not agree with the crystallite size determined by the XRD line broadening. The individual particles were not single crystals but polycrystals consisting of small crystallites. The zircon-type ZrGeO_4 particles synthesized at 240 °C were octahedral in shape and appeared to be compressed in one direction,²² while the morphology of the zircon-type ZrGeO_4 particles grew insufficiently such that those obtained at 120 °C (Figure 6a) appeared to be red blood cell like, which was similar to ZrSiO_4 zircon hydrothermally synthesized at 150–200 °C²⁵ and 240 °C.²² Kido and Komarneni suggested that the hydrothermal ZrSiO_4 zircon particles were assemblies of small crystals with the same crystallographic orientation.²⁵ Valero et al. showed that hydrothermal ZrSiO_4 zircon particles prepared in a fluoride medium were porous and characterized by a very peculiar morphology in the form of ellipsoidal layered agglomerates [layers with the main face (200)].²⁶ They explained that the surface heterogeneity in polymeric species of zirconium could be the starting point for the growth of another layer with a different orientation, leading finally to formation of the ellipsoidal agglomerates. The red blood cell like ZrGeO_4 particles formed at low temperature apparently grow in size and change in shape to the octahedral morphology with increasing hydrothermal treatment temperature, as shown in Figures 2a and 6. Because the crystallite size and secondary particle size (agglomerate size) of the zircon-type ZrGeO_4 were much larger than those of ZrSiO_4 zircon formed under the same hydrothermal condition, i.e., 240 °C for 10 h,²² the growth rate for the ZrGeO_4 crystallite was suggested to be much higher than that for the ZrSiO_4 zircon crystallite. With increasing hydrothermal treatment temperature, the zircon-type ZrGeO_4 with the morphology like that of red blood cells (Figure 6a) is considered to have gradually changed to dense octahedral agglomerates via crystallite growth according to the solution and precipitation mechanism.

HCl formed in the aqueous solution through thermal hydrolysis of ZrOCl_2 is supposed to lead to an increase the solubility of GeO_2 . The principal species in Zr(IV) aqueous solutions, i.e., $[\text{Zr}_4(\text{OH})_8]^{8+}$, which has a square-planar structure,²⁷ is the tetramer $[\text{Zr}(\text{OH})_2 \cdot 4\text{H}_2\text{O}]_4^{8+}$.²⁸ The four water molecules are part of the coordination sphere of Zr. In solution, hydrolysis occurs by split out of protons from the water to reduce the charge on the tetramer and increase the acidity of the solution. The exact form of the species depends on the pH. At higher pH, the tetramer is certainly in equilibrium with more highly polymerized species.²⁸ Those species of Zr(IV) and Ge(IV), i.e., $\text{Ge}(\text{OH})_4$, may react to produce polymeric species under hydrothermal conditions. When the concentration of the polymeric species reaches a supersaturation level, nuclei for zirconium germanate are gener-

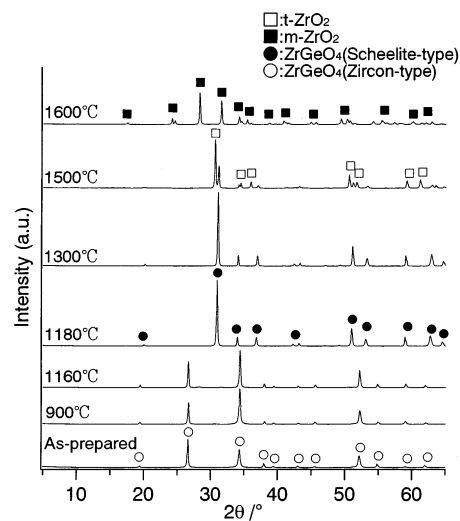


Figure 7. XRD patterns of as-prepared zircon-type ZrGeO_4 and the samples after heat treatment at different temperatures for 1 h.

ated, and their primary particles are formed by their crystal growth. It was confirmed that metastable zircon-type ZrGeO_4 was crystallized under highly acidic conditions ($\text{pH} < 2$) as compared with thermodynamically stable scheelite-type ZrGeO_4 formed under milder acid conditions ($6 \geq \text{pH} > 2$). The clue as to why different phases form at different pH values must lie in the state of the species in solution at the higher and lower pH levels of preparation.

Phase Transformation and Decomposition of ZrGeO_4 . The phase stability of the zircon-type ZrGeO_4 has been confirmed by heating to 900 °C in air.²² The phase stability above 900 °C has been investigated in the present study. Figure 7 shows XRD patterns for the zircon-type ZrGeO_4 heat-treated in air at different temperatures. The as-prepared zircon-type ZrGeO_4 was certified to exist stable up to the temperature of 1160 °C in air. The lattice parameters of the zircon-type ZrGeO_4 after heat treatment at 900 °C in air were $a_0 = 0.6685$ and $c_0 = 0.6260$ nm. The lattice parameters for the as-prepared zircon-type ZrGeO_4 were a little larger compared to those after heat treatment. The reason for this difference may be ascribed to a very small amount of residual OH remaining in the structure of the zircon-type ZrGeO_4 hydrothermally prepared. The zircon-type ZrGeO_4 transformed to the scheelite-type structure at 1180 °C. It is presumed that the decomposition from the scheelite-type ZrGeO_4 to tetragonal ZrO_2 and melted GeO_2 was done in a portion of the scheelite-type ZrGeO_4 by heat treatment at 1500 °C, as shown in Figure 7, and the melted GeO_2 forms an amorphous phase via cooling. Only monoclinic ZrO_2 was detected for the sample after heat treatment at 1600 °C for 1 h.

Based on the XRD data, the decomposition behavior of the scheelite-type ZrGeO_4 that was transformed from the zircon-type structure is shown in Figure 8. The decomposition of ZrGeO_4 seriously depended on a period of heat treatment. The dissociation originated at 1425 °C and concluded at 1525 °C in the case of a heat-treatment period of 1 h. The dissociation occurred at a

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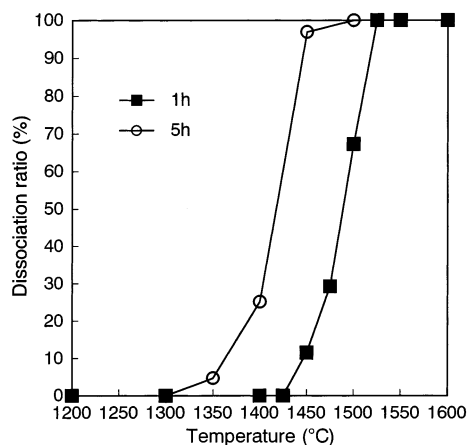


Figure 8. Dissociation of ZrO_2 caused by decomposition of ZrGeO_4 via heat treatment at different temperatures for 1 or 5 h.

lower temperature than that of ZrSiO_4 zircon²⁹ by more than 250 °C.

In Figure 9, the monoclinic ZrO_2 fraction that was transformed from the tetragonal ZrO_2 produced by dissociation from ZrGeO_4 is plotted as a function of the treatment temperature. The existence of a tetragonal phase of ZrO_2 solid solutions that contain GeO_2 has been reported, and the solubility limit of GeO_2 determined from the ZrO_2 – GeO_2 binary system has been shown to be 8 mol %, ³⁰ which is higher than the solubility limit (=3–4 mol %) of GeO_2 into 2 mol % Y_2O_3 -doped ZrO_2 (2Y-TZP).¹⁴ ZrO_2 , which is formed by dissociation of ZrGeO_4 at relatively low temperature such as 1350–1500 °C, may make solid solutions with a small amount of GeO_2 , and by this means the metastable tetragonal ZrO_2 phase, it is thought to be able to exist. An increase in the particle size of the tetragonal ZrO_2 is supposed to have occurred by high-temperature heat treatment

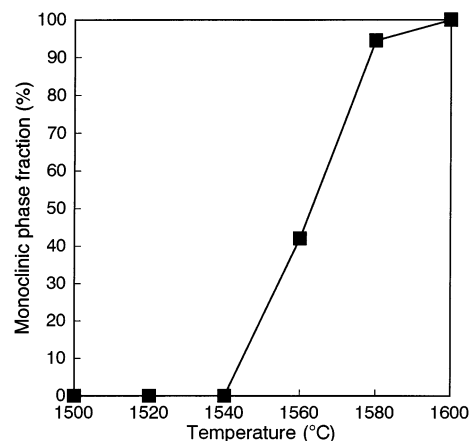


Figure 9. Monoclinic phase fraction transformed from tetragonal ZrO_2 that was dissociated from ZrGeO_4 by heat treatment at different temperatures for 1 h.

above 1540 °C, which is likely to have led to the phase transformation from the tetragonal to monoclinic structure in the process of cooling.

Summary

Zircon- and scheelite-type ZrGeO_4 were synthesized by controlling the solution pH using the homogeneous generation of a hydroxide ion through the decomposition of urea. Metastable zircon-type ZrGeO_4 was crystallized under highly acidic conditions as compared with the scheelite-type ZrGeO_4 formed under milder acid conditions. ZrGeO_4 with the zircon-type structure was stable up to the temperature of 1160 °C in air. The phase transformation from the zircon- to scheelite-type structure occurred at 1180 °C, and the decomposition from the scheelite-type ZrGeO_4 to tetragonal ZrO_2 and GeO_2 originated by heat treatment above 1350 °C for 5 h.

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