

# Hydrothermal Synthesis and Phase Stability of New Zircon- and Scheelite-Type $\text{ZrGeO}_4$

Masanori Hirano\* and Hiroshi Morikawa

Department of Applied Chemistry, Faculty of Engineering, Aichi Institute of Technology, Yakusa, Toyota 470-0392, Japan

Received June 11, 2002. Revised Manuscript Received February 27, 2003

Single-phase zircon- and sheelite-type  $\text{ZrGeO}_4$  were selectively synthesized from the reaction of a  $\text{ZrOCl}_2$  solution and  $\text{GeO}_2$  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  $\text{ZrGeO}_4$  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  $\mu\text{m}$  in size) by the absence or presence of urea as well as hydrothermal treatment temperature. Scheelite-type  $\text{ZrGeO}_4$  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  $\text{ZrGeO}_4$  was stable below 1160 °C in air and transformed to the scheelite-type structure at 1180 °C. The dissociation of  $\text{ZrGeO}_4$  to tetragonal  $\text{ZrO}_2$  and  $\text{GeO}_2$  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  $\text{ZrGeO}_4$  has been known to have a scheelite ( $\text{CaWO}_4$ )-type structure in which large Zr is eight-coordinated and small Ge is in a tetrahedral site. M $\text{GeO}_4$  germanates of tetravalent elements (M = Zr, Hf, Ce, Th) have the same structure as scheelite. Actinide germanates, for instance  $\text{ThGeO}_4$ , also exhibit the scheelite-type structure and a high-temperature form with zircon-type structure.<sup>1–5</sup> The crystal structures of  $\text{ZrGeO}_4$ ,<sup>6,7</sup>  $\text{HfGeO}_4$ , and  $\text{ThGeO}_4$ <sup>8</sup> have been determined by X-ray diffraction (XRD) and infrared and Raman spectroscopic investigation. MSiO<sub>4</sub> silicates of tetravalent elements (M = Zr, Hf, Th) are well-known to show the zircon-type structure.<sup>1</sup>  $\text{ThSiO}_4$  has two forms, the tetragonal  $\text{ThSiO}_4$  (thorite) and the high-temperature monoclinic  $\text{ThSiO}_4$  (huttonite).  $\text{ZrSiO}_4$  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.<sup>9</sup>

In the  $\text{ZrO}_2$ – $\text{GeO}_2$  system, the scheelite structure appears at two compositions as  $\text{ZrGeO}_4$  (*c/a* ratio 2.168)

and  $\text{Zr}_3\text{GeO}_8$  (*c/a* ratio 2.216).<sup>6,7</sup>  $\text{ZrGeO}_4$  single crystals have been reported to be grown from several flux systems.<sup>10,11</sup> The scheelite-type  $\text{ZrGeO}_4$  activated with  $\text{Ti}^{4+}$  yields blue luminescence when irradiated with X-rays.<sup>12</sup> The crystal structure of the scheelite-type  $\text{ZrGeO}_4$  doped with  $\text{Ti}^{4+}$  was investigated by Raman spectroscopy.<sup>12</sup> The scheelite-type  $\text{ZrGeO}_4$  was also crystallized by heat treatment at around 800 °C through a sol–gel route in the  $\text{ZrO}_2$ – $\text{GeO}_2$ – $(\text{H}_2\text{O})$  system from zirconium tetraisopropoxide and germanium tetraisopropoxide.<sup>13</sup> In the  $\text{ZrO}_2$ – $\text{GeO}_2$  system, the existence of only the scheelite-type tetragonal  $\text{ZrGeO}_4$  phase at >45 mol %  $\text{GeO}_2$  has been shown by Raman spectroscopic investigation based on the solid-state reaction between  $\text{GeO}_2$  and 2 mol %  $\text{Y}_2\text{O}_3$ -doped  $\text{ZrO}_2$  powder.<sup>14</sup> There were no reports on the synthesis of zircon-type  $\text{ZrGeO}_4$  as well as no crystal data (lattice parameters, crystal morphology, etc.) of the zircon-type structure of  $\text{ZrGeO}_4$ . We have directly synthesized fine particles of crystalline inorganic materials through soft solution routes<sup>15–21</sup> and reported on the hydrothermal synthesis, XRD data, and morphology of the zircon-type  $\text{ZrGeO}_4$  particles and zircon-type solid solutions over the whole

\* Corresponding author. Tel.: +81-565-48-8121. Fax: +81-565-48-0076. E-mail: hirano@ac.aitech.ac.jp.

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composition range in the  $\text{ZrGeO}_4$ – $\text{ZrSiO}_4$  system.<sup>22</sup>

In the present study, the effect of the solution pH on the crystal structure of synthesized  $\text{ZrGeO}_4$  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  $\text{ZrGeO}_4$  were clarified. Phase transformation from the zircon- to scheelite-type structure and the decomposition behavior of  $\text{ZrGeO}_4$  via heat treatment in air were investigated.

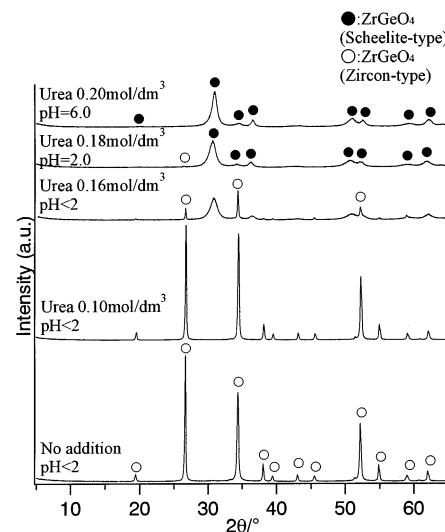
## Experimental Section

Reagent-grade germanium oxide ( $\text{GeO}_2$ ; 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 ( $18\text{ cm}^3$ ) of a mixed solution of germanium oxide and zirconium oxychloride with a cation (Ge and Zr) concentration of 0.2 and  $0.3\text{ mol}/\text{dm}^3$ , with or without the addition of  $0.1$ – $0.2\text{ mol}/\text{dm}^3$  urea [ $\text{CO}(\text{NH}_2)_2$ ] was taken into a  $25\text{ cm}^3$  Teflon container held in a stainless steel vessel. The vessel, after being tightly sealed, was heated at  $100$ – $240\text{ }^\circ\text{C}$  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  $60\text{ }^\circ\text{C}$ . The powders thus prepared were heat treated in an alumina crucible at a temperature ranging from 500 to  $1600\text{ }^\circ\text{C}$  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  $\theta$  is the Bragg angle of diffraction lines,  $K$  is a shape factor ( $K = 0.9$  in this work),  $\lambda$  is the wavelength of incident X-rays, and  $\beta$  is the corrected half-width given by  $\beta^2 = \beta_m^2 - \beta_s^2$ , where  $\beta_m$  is the measured half-width and  $\beta_s$  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  $\text{ZrO}_2$  phase dissociated from the scheelite-type  $\text{ZrGeO}_4$  was determined from integrated diffraction intensities ( $I$ ) of corresponding lines being around  $30^\circ$  in  $2\theta$  by using the following equation:  $\text{ZrO}_2$  phase (%) by dissociation =  $[I \text{ of tetragonal } \text{ZrO}_2(111)/\{I \text{ of scheelite } \text{ZrGeO}_4(112) + I \text{ of tetragonal } \text{ZrO}_2(111)\}] \times 100$ . The volume fraction of monoclinic  $\text{ZrO}_2$  transformed from the tetragonal phase was determined from integrated diffraction intensities of corresponding lines by using the following equation: monoclinic  $\text{ZrO}_2$  (%) =  $[I \text{ of monoclinic } \text{ZrO}_2(111) + I \text{ of monoclinic } \text{ZrO}_2(1,1,-1)]/I \text{ of tetragonal } \text{ZrO}_2(111) + I \text{ of monoclinic } \text{ZrO}_2(111) + I \text{ of monoclinic } \text{ZrO}_2(1,1,-1)] \times 100$ . Raman spectra were obtained from a Raman spectrometer (NRS-1000, Nihon Bunko, Tokyo, Japan) with the  $532\text{ nm}$  line of a  $10\text{ mW}$  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  $\text{ZrGeO}_4$ .** After the reaction of  $\text{GeO}_2$  and a  $\text{ZrOCl}_2$  solution via hydrothermal treatment in a vessel tightly sealed at a temperature above  $100\text{ }^\circ\text{C}$ , the solution becomes more acidic than the starting  $\text{ZrOCl}_2$

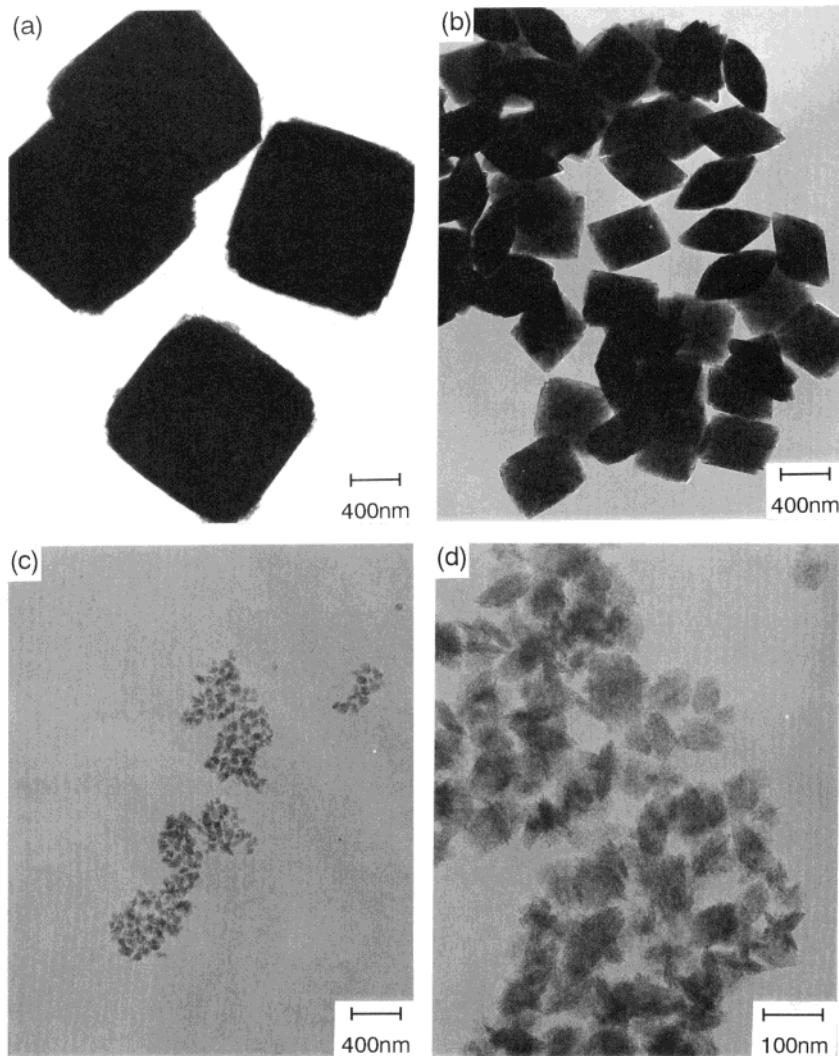


**Figure 1.** XRD patterns of  $\text{ZrGeO}_4$  precipitates obtained by hydrothermal treatment at  $240\text{ }^\circ\text{C}$  for 10 h from the reaction of  $0.2\text{ mol}/\text{dm}^3$   $\text{ZrOCl}_2$  solution and  $0.2\text{ mol}/\text{dm}^3$   $\text{GeO}_2$  in the presence of different concentrations of urea.

solution by the formation of  $\text{HCl}$  through thermal hydrolysis of  $\text{ZrOCl}_2$ . 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  $240\text{ }^\circ\text{C}$  for 10 h from the reaction of  $\text{GeO}_2$  and a  $\text{ZrOCl}_2$  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  $0.2\text{ mol}/\text{dm}^3$  urea showed very broad peaks, whose diffraction angles corresponded to those of the scheelite-type  $\text{ZrGeO}_4$ . The solution pH after synthesis of the scheelite-type  $\text{ZrGeO}_4$  was 6.0. Under the condition in the presence of  $0.18\text{ mol}/\text{dm}^3$  urea (solution pH = 2.0), precipitation of a very small amount of zircon-type  $\text{ZrGeO}_4$  as well as the scheelite-type  $\text{ZrGeO}_4$  was observed. The zircon-type  $\text{ZrGeO}_4$  and scheelite-type  $\text{ZrGeO}_4$  coexisted in the precipitates obtained from the solution (pH < 2.0) in the presence of  $0.16\text{ mol}/\text{dm}^3$  urea, while single-phase zircon-type  $\text{ZrGeO}_4$  was formed under the condition of less than  $0.1\text{ mol}/\text{dm}^3$  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  $c = 0.6266\text{ nm}$ , a  $c/a$  ratio of 0.9360. The chemical composition of the single-phase zircon-type  $\text{ZrGeO}_4$  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  $\text{ZrGeO}_4$  was clarified to have an approximately stoichiometric composition. Investigation of the crystallization of amorphous gel over a wide composition range in the  $\text{ZrO}_2$ – $\text{GeO}_2$ – $\text{H}_2\text{O}$  system prepared through a sol–gel route from zirconium tetrakisopropoxide and germanium tetrakisopropoxide showed that the gel with a stoichiometric  $\text{ZrGeO}_4$  composition crystallized into the scheelite-type  $\text{ZrGeO}_4$  at a temperature above  $800\text{ }^\circ\text{C}$ .<sup>13</sup> Thermody-



**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/dm<sup>3</sup>  $ZrOCl_2$  solution and 0.2 mol/dm<sup>3</sup>  $GeO_2$  (a) in the absence of urea, (b) in the presence of 0.1 mol/dm<sup>3</sup> urea, and (c) in the presence of 0.2 mol/dm<sup>3</sup> 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

<sup>a</sup> Sample: preparation by hydrothermal treatment at 240 °C for 10 h from the reaction of a 0.2 mol/dm<sup>3</sup>  $ZrOCl_2$  solution and 0.2 mol/dm<sup>3</sup>  $GeO_2$  in the absence of urea.

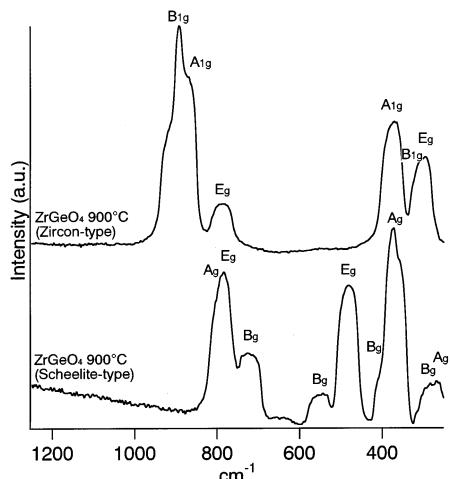
namically stable phase of the  $ZrGeO_4$  compound is tetragonal scheelite-type, and there was no finding of reports on the direct formation of the zircon-type  $ZrGeO_4$  except for our study through the soft solutions routes.<sup>22</sup> The  $c/a$  ratio of the zircon-type  $ZrGeO_4$  was larger 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 ( $pH < 2$ ) in the presence of less than 0.18 mol/dm<sup>3</sup> 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).

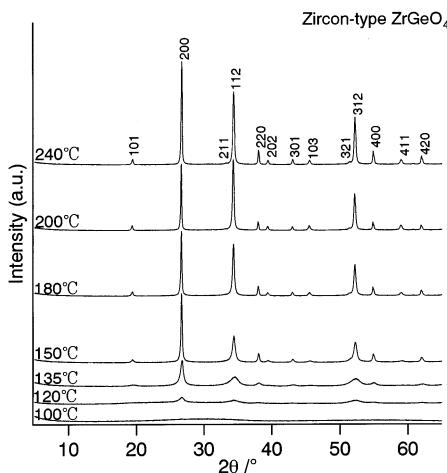
The Raman spectra observed for both zircon- and scheelite-type  $ZrGeO_4$  are shown in Figure 3. The assignments of Raman bands of the zircon- and scheelite-type  $ZrGeO_4$  are also indicated in Figure 3 based on the data of the zircon- and scheelite-type structure reported previously.<sup>6,12,23,24</sup>  $ZrSiO_4$  zircon and the zircon-type  $ZrGeO_4$  are confirmed isomorphous crystals, and the unit

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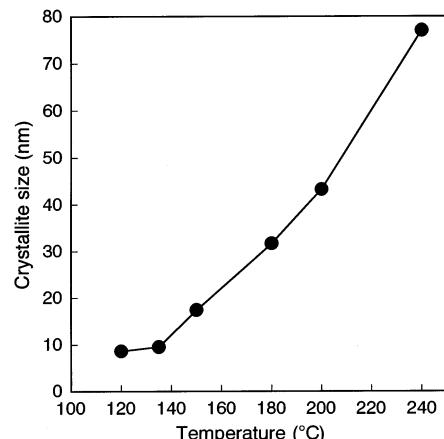
**Figure 3.** Raman spectra of zircon- and scheelite-type  $\text{ZrGeO}_4$  after heat treatment at 900  $^{\circ}\text{C}$  for 1 h in air.



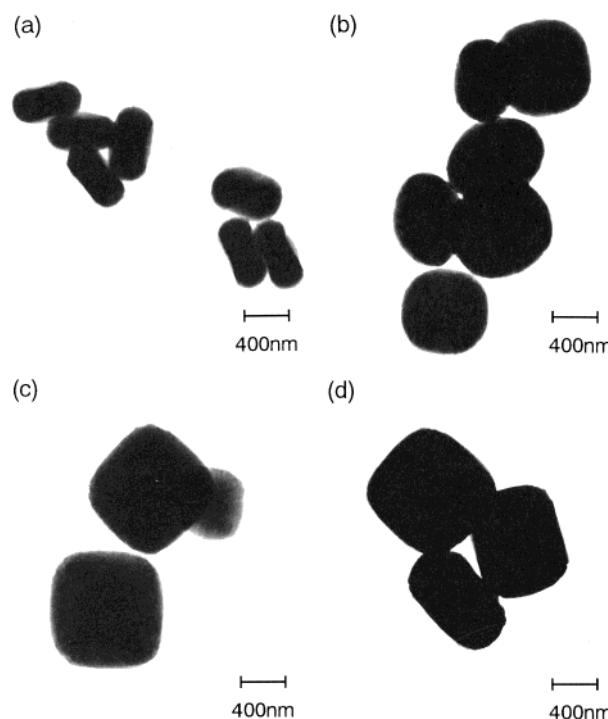
**Figure 4.** XRD patterns of zircon-type  $\text{ZrGeO}_4$  precipitates obtained by hydrothermal treatment at different temperatures for 10 h from the reaction of a 0.3 mol/dm<sup>3</sup>  $\text{ZrOCl}_2$  solution and 0.3 mol/dm<sup>3</sup>  $\text{GeO}_2$ .

cell (tetragonal) contains four molecules. For zircon-type  $\text{ZrGeO}_4$ , we have no symmetry information and must rely on frequency and intensity in the comparison with  $\text{ZrSiO}_4$  zircon. The peak of the  $\text{A}_{1g}$  band overlaps with that of the  $\text{B}_{1g}$  band at 870–920  $\text{cm}^{-1}$  in the Raman spectra of the zircon-type  $\text{ZrGeO}_4$ . In the Raman spectra of the scheelite-type  $\text{ZrGeO}_4$ , the peak  $\text{E}_g$  overlaps with that of  $\text{A}_g$  at 780–800  $\text{cm}^{-1}$  and the peak  $\text{A}_g$  overlaps with that of  $\text{B}_g$  at 380–400  $\text{cm}^{-1}$ , which were due to a low-resolution broad Raman powder spectrum. The  $\text{E}_g$  ( $\nu_3$ ) band<sup>23</sup> of the zircon-type structure around 800  $\text{cm}^{-1}$  in Figure 3 was much stronger in  $\text{ZrGeO}_4$  than that in  $\text{ZrSiO}_4$ , in which the  $\text{E}_g$  ( $\nu_3$ ) band was hardly detected in the  $\text{ZrSiO}_4$  zircon synthesized under the same hydrothermal conditions from  $\text{ZrOCl}_2$  and tetraethoxysilane.<sup>22</sup> The Raman spectra observed for the scheelite-type  $\text{ZrGeO}_4$  agreed with the data reported.<sup>12</sup>

**Influence of the Treatment Temperature on the Crystallite Growth and Morphology of  $\text{ZrGeO}_4$ .** The effect of the hydrothermal treatment temperature on the crystallite growth of the zircon-type  $\text{ZrGeO}_4$  is shown in XRD profiles (Figure 4). With increasing treatment temperature, (200) and (112) diffraction lines of the zircon-type  $\text{ZrGeO}_4$  gradually became sharp.



**Figure 5.** Influence of the hydrothermal treatment temperature on the crystallite size of zircon-type  $\text{ZrGeO}_4$  obtained by hydrothermal treatment for 10 h from the reaction of a 0.3 mol/dm<sup>3</sup>  $\text{ZrOCl}_2$  solution and 0.3 mol/dm<sup>3</sup>  $\text{GeO}_2$ .



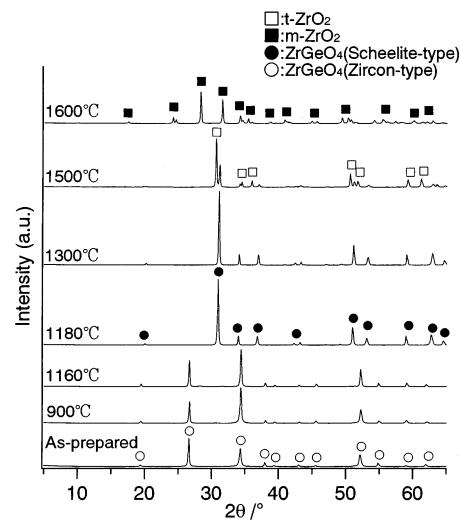
**Figure 6.** TEM micrographs of zircon-type  $\text{ZrGeO}_4$  particles obtained by hydrothermal treatment at (a) 120  $^{\circ}\text{C}$ , (b) 150  $^{\circ}\text{C}$ , (c) 180  $^{\circ}\text{C}$ , and (d) 200  $^{\circ}\text{C}$  for 10 h from the reaction of a 0.3 mol/dm<sup>3</sup>  $\text{ZrOCl}_2$  solution and 0.3 mol/dm<sup>3</sup>  $\text{GeO}_2$ .

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  $\text{ZrGeO}_4$  is directly precipitated from the reaction of  $\text{GeO}_2$  and a  $\text{ZrOCl}_2$  solution at low temperature above 120  $^{\circ}\text{C}$ . The change in the crystallite size of the zircon-type  $\text{ZrGeO}_4$  estimated from the XRD line broadening of the (200) peak is shown in Figure 5. The crystallite size of the zircon-type  $\text{ZrGeO}_4$  particles increased from 10 to 80 nm with increasing treatment temperature from 120 to 240  $^{\circ}\text{C}$ .

The change in the secondary particle size and morphology of the zircon-type  $\text{ZrGeO}_4$  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,<sup>22</sup> 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<sup>25</sup> and 240 °C.<sup>22</sup> Kido and Komarneni suggested that the hydrothermal  $ZrSiO_4$  zircon particles were assemblies of small crystals with the same crystallographic orientation.<sup>25</sup> 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)].<sup>26</sup> 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,<sup>22</sup> 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 in the solubility of  $GeO_2$ . The principal species in Zr(IV) aqueous solutions, i.e.,  $[Zr_4(OH)_8]^{8+}$ , which has a square-planar structure,<sup>27</sup> is the tetramer  $[Zr(OH)_2 \cdot 4H_2O]^{8+}$ .<sup>28</sup> The four water molecules are part of the coordination sphere of Zr. In solution, hydrolysis occurs by splitting 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.<sup>28</sup> Those species of Zr(IV) and Ge(IV), i.e.,  $Ge(OH)_4$ , 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 ( $pH < 2$ ) as compared with thermodynamically stable scheelite-type  $ZrGeO_4$  formed under milder acid conditions ( $6 \geq pH > 2$ ). 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.<sup>22</sup> 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.

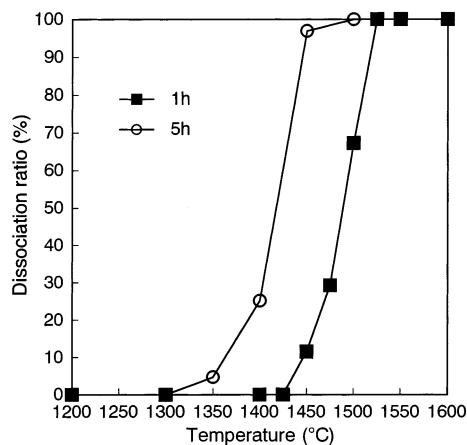
Based on the XRD data, the decomposition behavior of the scheelite-type  $ZrGeO_4$  that was transformed from the zircon-type structure is shown in Figure 8. The decomposition of  $ZrGeO_4$  seriously depended on a period of heat treatment. The dissociation originated at 1425 °C and concluded at 1525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

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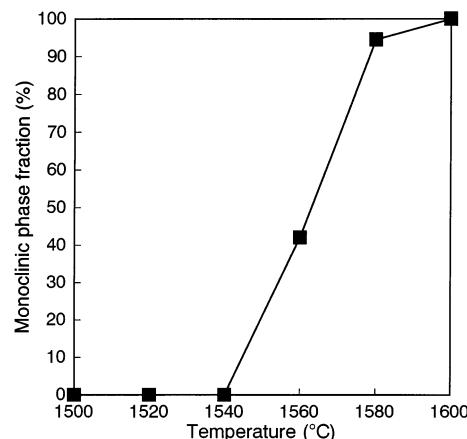
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**Figure 8.** Dissociation of  $\text{ZrO}_2$  caused by decomposition of  $\text{ZrGeO}_4$  via heat treatment at different temperatures for 1 or 5 h.

lower temperature than that of  $\text{ZrSiO}_4$  zircon<sup>29</sup> by more than 250 °C.

In Figure 9, the monoclinic  $\text{ZrO}_2$  fraction that was transformed from the tetragonal  $\text{ZrO}_2$  produced by dissociation from  $\text{ZrGeO}_4$  is plotted as a function of the treatment temperature. The existence of a tetragonal phase of  $\text{ZrO}_2$  solid solutions that contain  $\text{GeO}_2$  has been reported, and the solubility limit of  $\text{GeO}_2$  determined from the  $\text{ZrO}_2$ – $\text{GeO}_2$  binary system has been shown to be 8 mol %,<sup>30</sup> which is higher than the solubility limit (=3–4 mol %) of  $\text{GeO}_2$  into 2 mol %  $\text{Y}_2\text{O}_3$ -doped  $\text{ZrO}_2$  (2Y-TZP).<sup>14</sup>  $\text{ZrO}_2$ , which is formed by dissociation of  $\text{ZrGeO}_4$  at relatively low temperature such as 1350–1500 °C, may make solid solutions with a small amount of  $\text{GeO}_2$ , and by this means the metastable tetragonal  $\text{ZrO}_2$  phase, it is thought to be able to exist. An increase in the particle size of the tetragonal  $\text{ZrO}_2$  is supposed to have occurred by high-temperature heat treatment



**Figure 9.** Monoclinic phase fraction transformed from tetragonal  $\text{ZrO}_2$  that was dissociated from  $\text{ZrGeO}_4$  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  $\text{ZrGeO}_4$  were synthesized by controlling the solution pH using the homogeneous generation of a hydroxide ion through the decomposition of urea. Metastable zircon-type  $\text{ZrGeO}_4$  was crystallized under highly acidic conditions as compared with the scheelite-type  $\text{ZrGeO}_4$  formed under milder acid conditions.  $\text{ZrGeO}_4$  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  $\text{ZrGeO}_4$  to tetragonal  $\text{ZrO}_2$  and  $\text{GeO}_2$  originated by heat treatment above 1350 °C for 5 h.

**Acknowledgment.** The authors thank Professor Michio Inagaki (Aichi Institute of Technology) for useful discussions.

CM020661Q

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